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Russell A. Bonham

Jerry Peacher
Missouri University of Science and Technology, peacher@mst.edu

Henry L. Cox

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On the Calculation of Multicenter Two-Electron Repulsion Integrals Involving Slater Functions*†

R. A. BONHAM, J. L. PEACHER, AND H. L. COX, JR.

Departments of Chemistry and Physics, Indiana University, Bloomington, Indiana

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Integral transforms are used to evaluate many-center two-electron repulsion integrals involving Slater s-type functions. The reduction of a general four-center integral of this type to a form convenient for computational purposes is presented. The technique described has the important advantage that all lesser many-center and one-center integrals can be obtained from the four-center case by proper choice of constants. The form of the result is such that simple single-precision numerical techniques yield rapid and accurate evaluations of many-center integrals. Several numerical examples are presented.

I. INTRODUCTION

THERE are a number of integral transforms which have proved useful in solving scattering problems.[1-3] It is the central purpose of this paper to show the utility of applying these same techniques to the evaluation of certain multicenter integrals found in molecular quantum mechanics. The main integral transform which is used is the momentum space representation of the Green's function for an outgoing scattered wave

$$\frac{\exp[ik \mid \mathbf{r}_1 - \mathbf{r}_2 \mid]}{\mid \mathbf{r}_1 - \mathbf{r}_2 \mid} = (2\pi^2)^{-1} \int \frac{d\mathbf{K} \exp[i\mathbf{K} \cdot (\mathbf{r}_1 - \mathbf{r}_2)]}{(K^2 - k^2)}.$$
(1.0)

We can obtain two very useful relations from (1.0) by first setting $k=0$ to obtain the relation

$$\mid \mathbf{r}_1 - \mathbf{r}_2 \mid^{-1} = (2\pi^2)^{-1} \int \frac{d\mathbf{K} \exp[i\mathbf{K} \cdot (\mathbf{r}_1 - \mathbf{r}_2)]}{K^2}, \quad (1.1)$$

and secondly by letting $k=iZ$ and by making use of Leibnitz's rule to get

$$\mid \mathbf{r}_1 - \mathbf{r}_2 \mid^N \exp[-Z \mid \mathbf{r}_1 - \mathbf{r}_2 \mid]$$

$$= (2\pi^2)^{-1}(-d/dZ)^{N+1} \int \frac{d\mathbf{K} \exp[i\mathbf{K} \cdot (\mathbf{r}_1 - \mathbf{r}_2)]}{(K^2 + Z^2)}. \quad (1.2)$$

Equation (1.1) is used to separate the $1/\mid \mathbf{r}_1 - \mathbf{r}_2 \mid$ term in electron repulsion integrals while Eq. (1.2) serves as a means of transforming s-type Slater functions from one center to another.

It should be pointed out that the Fourier transform

¹ P. M. Morse and H. Fechbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, p. 1076.
² R. A. Mapleton, Phys. Rev. **112**, 479 (1960); K. Ruedenberg (private communication).
³ A closely related approach has been given for certain cases which utilize the convolution theorem. F. P. Prosser and C. H. Blanchard, J. Chem. Phys. **36**, 1112 (1962) and M. Geller, J. Chem. Phys. **39**, 84 (1963).

of Eq. (1.1) yields the familiar Bethe relation[4]

$$\int \frac{d\mathbf{r}_1 \exp[i\mathbf{K} \cdot \mathbf{r}_1]}{\mid \mathbf{r}_1 - \mathbf{r}_2 \mid} = \frac{4\pi \exp[i\mathbf{K} \cdot \mathbf{r}_2]}{K^2}. \quad (1.3)$$

II. FOUR-CENTER ELECTRON REPULSION INTEGRAL

Application of the techniques outlined above will be applied to the most difficult and general electron repulsion integral first as it will be shown later that all the other electron repulsion integrals can be obtained from this result. A general four-center integral can be reduced to the calculation of two one-electron two-center integrals by application of (1.1)

$$\langle \phi_a(1)\phi_b(2) \mid (\mid \mathbf{r}_1 - \mathbf{r}_2 \mid)^{-1} \mid \phi_c(1)\phi_d(2) \rangle$$

$$= (2\pi^2)^{-1} \int \frac{d\mathbf{K}}{K^2} \exp[i\mathbf{K} \cdot \mathbf{r}_{ab}]$$

$$\langle \phi_a(1) \mid \exp[i\mathbf{K} \cdot \mathbf{r}_1] \mid \phi_c(1) \rangle$$

$$\cdot \langle \phi_b(2) \mid \exp[-i\mathbf{K} \cdot \mathbf{r}_2] \mid \phi_d(2) \rangle, \quad (2.0)$$

where the term $\exp[i\mathbf{K} \cdot \mathbf{r}_{ab}]$ must be introduced to translate $\exp[-i\mathbf{K} \cdot \mathbf{r}_2]$ from Center a to Center b.

Equation (1.2) is used to simplify the remaining one-electron integrals so that

$$\langle \phi_a(1) \mid \exp[i\mathbf{K} \cdot \mathbf{r}_1] \mid \phi_c(1) \rangle$$

$$= (1/2\pi^3)(Z_a Z_c)^{\frac{3}{2}}(-d/dZ_c)$$

$$\times \int \frac{d\mathbf{q} \exp[i\mathbf{q} \cdot \mathbf{r}_{ac}]}{(q^2 + Z_c^2)} \cdot \int d\mathbf{r}_1 \exp[-Z_a r_1 + i(\mathbf{q} + \mathbf{K}) \cdot \mathbf{r}_1],$$
(2.1)

where $\phi_a(1) = (Z_a^3/\pi^{\frac{1}{2}}) \exp[-Z_a r_1]$, and $\phi_c(1) = (Z_c^3/\pi^{\frac{1}{2}}) \exp[-Z_c r_1]$. Slater $1=s$ functions have been used to simplify the algebra. The integration over $\mathbf{r}_1$ can be carried out resulting in

$$\langle \phi_a(1) \mid \exp[i\mathbf{K} \cdot \mathbf{r}_1] \mid \phi_c(1) \rangle = \frac{2}{\pi^2}(Z_a Z_c)^{\frac{3}{2}} \frac{d^2}{dZ_a dZ_c}$$

$$\times \int \frac{d\mathbf{q} \exp[i\mathbf{q} \cdot \mathbf{r}_{ac}]}{(q^2 + Z_c^2)(\mid \mathbf{q} + \mathbf{k} \mid^2 + Z_a^2)}. \quad (2.2)$$

⁴ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), p. 226.

The **q** integration can also be carried out by making use of the Feynman identity

$$(ab)^{-1} = \int_0^1 \frac{d\alpha}{[a+(b-a)\alpha]^2} \tag{2.3}$$

and the substitution $\mathbf{p}=\mathbf{q}+\alpha\mathbf{k}$. This reduces Eq. (2.2) to

$$\langle\phi_a(1) \mid \exp[i\mathbf{k}\cdot\mathbf{r}_1] \mid \phi_c(1)\rangle = \frac{2}{\pi^2}(Z_aZ_c)^{\frac{3}{2}}\frac{d^2}{dZ_adZ_c}$$

$$\times\int_0^1 d\alpha \exp[-i\alpha\mathbf{k}\cdot\mathbf{r}_{ac}]\int\frac{d\mathbf{p} \exp[i\mathbf{p}\cdot\mathbf{r}_{ac}]}{[p^2+M]^2}, \tag{2.4}$$

where M is given by

$$M = k^2\alpha(1-\alpha)+(Z_a^2-Z_c^2)\alpha+Z_c^2. \tag{2.5}$$

The integral over **q** has thus been reduced to a simple form in terms of the variable **p** and can be integrated and differentiated with respect to the Z's to yield

$$\langle\phi_a(1) \mid \exp[i\mathbf{K}\cdot\mathbf{r}_1] \mid \phi_c(1)\rangle = 2(Z_aZ_c)^{\frac{3}{2}}\int_0^1 d\alpha \; \alpha(1-\alpha)$$

$$\times\left(\frac{\exp[-i\alpha\mathbf{k}\cdot\mathbf{r}_{ac}-r_{ac}M]}{M^{\frac{5}{2}}}\right)\left(r_{ac}^2+\frac{3r_{ac}}{M^{\frac{1}{2}}}+\frac{3}{M}\right). \tag{2.6}$$

In like manner the remaining one-electron integral can be written as

$$\langle\phi_b(2) \mid \exp[-i\mathbf{K}\cdot\mathbf{r}_2] \mid \phi_d(2)\rangle = 2(Z_bZ_d)^{\frac{3}{2}}\int_0^1 d\beta \; \beta(1-\beta)$$

$$\times\left(\frac{\exp[i\beta\mathbf{k}\cdot\mathbf{r}_{bd}-r_{bd}N]}{N^{\frac{5}{2}}}\right)\left(r_{bd}^2+\frac{3r_{bd}}{N^{\frac{1}{2}}}+\frac{3}{M}\right), \tag{2.7}$$

where

$$N = k^2\beta(1-\beta)+(Z_b^2-Z_d^2)\beta+Z_d^2. \tag{2.8}$$

Putting Eqs. (2.6) and (2.7) into Eq. (2.0) and performing the angular integrations yields the final formula for the four-center case as

$$\langle\phi_a(1)\phi_b(2) \mid 1/\mid \mathbf{r}_1-\mathbf{r}_2 \mid\mid \phi_c(1)\phi_d(2)\rangle$$

$$= (8/\pi)(Z_aZ_bZ_cZ_d)^{\frac{3}{2}}$$

$$\times\int_0^1 d\alpha\alpha(1-\alpha)\int_0^1 d\beta\beta(1-\beta)\int_0^\infty dk$$

$$\times j_0(k \mid \mathbf{r}_{ab}-\alpha\mathbf{r}_{ac}+\beta\mathbf{r}_{bd} \mid)$$

$$\times\left\{\left(\frac{\exp[-r_{ac}M-r_{bd}N]}{(MN)^{\frac{5}{2}}}\right)\left(r_{ac}^2+\frac{3r_{ac}}{M^{\frac{1}{2}}}+\frac{3}{M}\right)\right.$$

$$\left.\times\left(r_{bd}^2+\frac{3r_{bd}}{N^{\frac{1}{2}}}+\frac{3}{N}\right)\right\}. \tag{2.9}$$

It is of interest to note that all the Z dependence is contained in that part of the integral in (2.9) which is in the { } brackets and all the angular dependence of the geometry of the four centers is contained in the argument of the zero-order spherical Bessel function.

These facts can be useful in economizing on computing time.

Equation (2.9) can be also readily modified for the cases of high-order s-type Slater functions (i.e., $2s$, $3s$, etc.) simply by differentiation with respect to the appropriate Z value. Also of importance is the fact that Eq. (2.9) is valid for the case where the term $1/\mid \mathbf{r}_1-\mathbf{r}_2 \mid$ is placed on a fifth center, say Center e, if the argument of the spherical Bessel function is replaced by the expression $(k \mid \mathbf{r}_{ae}+\mathbf{r}_{be}-\alpha\mathbf{r}_{ac}+\beta\mathbf{r}_{bd} \mid)$. All the three-center, two-center, and one-center cases can be obtained from Eq. (2.9) by proper choices of the Z and r parameters. The details are given in Table I. It should be noted that only the main types of integrals have been listed and that additional permutations within a given type may take place requiring certain redefinitions of r and Z parameters.

As a check of the foregoing results it is worthwhile to consider the one-center case which can be obtained from Eq. (2.9) by allowing $Z=Z_a=Z_b=Z_c=Z_d$ and $r_{ab}=r_{ac}=r_{bd}=0$. Equation (2.6) can then be written as

$$\langle\phi_a(1) \mid \exp[i\mathbf{K}\cdot\mathbf{r}_1] \mid \phi_c(1)\rangle$$

$$= 6Z^5\int_0^1 \frac{d\alpha\alpha(1-\alpha)}{[k^2\alpha(1-\alpha)+Z^2]^{\frac{5}{2}}} \tag{2.10}$$

which upon integration reduces to

$$\langle\phi_a(1) \mid \exp[i\mathbf{K}\cdot\mathbf{r}_1] \mid \phi_c(1)\rangle = 8Z^4/(k^2+4Z^2)^2. \tag{2.11}$$

Substituting the square of Eq. (2.11) into Eq. (2.0) and performing the integration over k yields the familiar result

$$\langle\phi_a(1)\phi_b(2) \mid 1/\mid \mathbf{r}_1-\mathbf{r}_2 \mid\mid \phi_c(1)\phi_d(2)\rangle = 5Z/8. \tag{2.12}$$

An attempt has also been made to include higher spherical harmonics in the Slater-type one-electron functions but so far we have been unable to evaluate the integrals.

$$\int d\mathbf{q}\frac{\exp[i\mathbf{q}\cdot\mathbf{r}_{ac}] \mid \mathbf{q}+\mathbf{k} \mid}{(q^2+Z_c^2)(\mid \mathbf{q}+\mathbf{k} \mid^2+Z_a^2)} = \int_0^1 d\alpha \exp[i\alpha\mathbf{k}\cdot\mathbf{r}_{ac}]$$

$$\cdot\int d\mathbf{p}\frac{\exp[i\mathbf{p}\cdot\mathbf{r}_{ac}] \mid \mathbf{p}+(1-\alpha)\mathbf{k} \mid}{(p^2+M)^2}. \tag{2.13}$$

These integrals are the only ones which arise from the introduction of functions of p-type symmetry which we have not been able to reduce to a form as simple as the one presented in Eq. (2.9).

III. NUMERICAL EXAMPLES

As the main purpose of this paper is to present a new approach to evaluating multicenter integrals no attempt has been made to construct an optimum computer program for the calculation of Eq. (2.9). Rather a seven-point Gauss quadrature scheme[5] was

[5] J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, Maryland, 1930), pp. 131–139.

TABLE I. Multicenter $1s$ electron repulsion integrals obtainable from Eq. (2.9) by redefinition of the r and Z parameters.

Number of centers	Integral type	Choice of Z parameters	Choice of r parameters
5	$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_c(1)\phi_d(2)\rangle$[a]		$\mathbf{r}_{ab}=\mathbf{r}_{ae}+\mathbf{r}_{be}$
4	$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_c(1)\phi_d(2)\rangle$		
	$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_a(1)\phi_d(2)\rangle$[a]	$Z_a=Z_c$	$r_{ac}=0,\ \mathbf{r}_{ab}=\mathbf{r}_{ae}+\mathbf{r}_{be}$
	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_b(1)\phi_d(2)\rangle$[a]	$Z_c=Z_a$	$\mathbf{r}_{ab}=2\mathbf{r}_{ae}$
3	$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_a(1)\phi_d(2)\rangle$	$Z_a=Z_c$	$r_{ac}=0$
	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_b(1)\phi_d(2)\rangle$	$Z_c=Z_a$	$r_{ab}=0$
	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_a(1)\phi_b(2)\rangle$[a]	$Z_b=Z_c=Z_a,\ Z_d=Z_b$	$r_{ac}=0,\ \mathbf{r}_{ab}=2\mathbf{r}_{ae},\ \mathbf{r}_{bd}=\mathbf{r}_{ab}$
	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_b(1)\phi_b(2)\rangle$[a]	$Z_b=Z_a,\ Z_c=Z_b,\ Z_d=Z_b$	$\mathbf{r}_{ac}=\mathbf{r}_{bd}=\mathbf{r}_{ab},\ \mathbf{r}_{ab}=2\mathbf{r}_{ae}$
	$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_a(1)\phi_b(2)\rangle$[a]	$Z_c=Z_a,\ Z_d=Z_b$	$\mathbf{r}_{ac}=\mathbf{r}_{bd}=\mathbf{r}_{ab},\ \mathbf{r}_{ab}=2\mathbf{r}_{ae}$
2	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_a(1)\phi_b(2)\rangle$	$Z_b=Z_c=Z_a,\ Z_d=Z_b$	$r_{ab}=r_{ac}=0,\ \mathbf{r}_{bd}=\mathbf{r}_{ab}$
	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_b(1)\phi_b(2)\rangle$	$Z_b=Z_a,\ Z_c=Z_b,\ Z_d=Z_b$	$r_{ab}=0,\ \mathbf{r}_{ac}=\mathbf{r}_{bd}=\mathbf{r}_{ab}$
	$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_a(1)\phi_b(2)\rangle$	$Z_c=Z_a,\ Z_d=Z_b$	$r_{ac}=r_{bd}=0$
	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_a(1)\phi_a(2)\rangle$[a]	$Z_b=Z_c=Z_d=Z_a$	$r_{ac}=r_{ba}=0,\ \mathbf{r}_{ab}=2\mathbf{r}_{ae}$
1	$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_a(1)\phi_a(2)\rangle$	$Z_t=Z_c=Z_d=Z_a$	$r_{ab}=r_{ac}=r_{td}=0$

[a] In these cases the term $1/r_{12}$ is on a different center which has been designated Center e.

TABLE II. Values of various electron repulsion integrals calculated from Eq. (2.9).

Integral	Value from Eq. (2.9)	Comparison value	Computing time	Parameters
$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_c(1)\phi_d(2)\rangle$	0.0127424	0.0127405[a]	8 min	$r_{ab}=r_{ac}=r_{ad}=2.0,\ Z_a=5.7,\ Z_b=Z_c=Z_d=1.0$ $\theta(\hat{r}_{ab}\cdot\hat{r}_{ac})=\theta(\hat{r}_{ab}\cdot\hat{r}_{ad})=109.4712$ deg $\Phi=120.000$ deg
$\langle\phi_a(1)\phi_b(2)\mid 1/r_{12}\mid\phi_a(1)\phi_d(2)\rangle$	0.28477401	0.28477434[b]	7 sec	$r_{ab}=r_{ad}=1.66,\ Z_a=Z_b=Z_c=Z_d=1.4$ $r_{ac}=0$ $\theta(\hat{r}_{ab}\cdot\hat{r}_{ad})=60.00$ deg
$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_b(1)\phi_d(2)\rangle$	0.1644556	0.1644528[b]	7 sec	$r_{ab}=r_{ad}=1.66,\ r_{ac}=0,\ Z_a=Z_b=Z_c=Z_d=1.4$ $\theta(\hat{r}_{ab}\cdot\hat{r}_{ad})=60.00$ deg
$\langle\phi_a(1)\phi_a(2)\mid 1/r_{12}\mid\phi_a(1)\phi_a(2)\rangle$	0.624995	0.625000[c]	3 min	$r_{ab}=r_{ac}=r_{ad}=0$ $Z_a=Z_b=Z_c=Z_d=1.0$

[a] Calculated using the program discussed by Ref. 7.
[b] Calculated by R. Christoffersen using programs based on Barnett and Coulson Reiman zeta-function technique.
[c] Exact value.

TABLE III. Survey of four-center homonuclear electron repulsion integrals for a tetrahedron as a function of internuclear distance r and screening constant Z.

r	Z						
	0.8	1.0	1.2	1.4	1.8	2.2	2.8
1.0	0.475152	0.413102	0.351481	0.293494	0.195255	0.123506	5.78498×10^{-2}
1.5	0.527222	0.399780	0.292882	0.208582	9.89604×10^{-2}	4.38856×10^{-2}	1.18489×10^{-2}
2.0	0.482206	0.312306	0.193460	0.115700	3.82124×10^{-2}	1.16772×10^{-2}	1.78555×10^{-3}
3.0	0.290190	0.132750	5.73186×10^{-2}	2.36977×10^{-2}	3.68697×10^{-3}	5.25019×10^{-4}	2.52514×10^{-5}
4.0	0.134530[a]	4.25902×10^{-2a}	1.263117×10^{-2b}	3.57111×10^{-3b}	2.57795×10^{-4b}	1.69213×10^{-5b}	2.52601×10^{-7b}

[a] These values are accurate to at least four significant figures.
[b] These values are accurate to at least five significant figures.

employed to evaluate the integrals and the programs and computations were carried out in Fortran using an IBM 709 computer. The accuracy of the computations was checked by comparison with known values and values obtained from other multicenter integral routines.[6] In Table II some actual comparisons are presented along with the computation times involved.

In order to further illustrate the utility of the method an investigation of a four-center integral for a tetrahedral arrangement of the four centers was carried out with respect to variation of r and Z. The results are presented in Table III. The computing time per integral was 7 sec.

With the crude techniques that were employed to integrate (2.9) it was found that for small values of Z ($Z<2$) all the integrals could be obtained to six-place accuracy in from 7 to 30 sec. The introduction of large Z ($Z>4$) values, however, caused a substantial increase of computing time since more than seven points were needed to evaluate the α and β integrals. For symmetrical cases (i.e., homonuclear diatomics, three-

center homonuclear equilateral triangles, and four-center homonuclear tetrahedrons), it can be shown that the α and β integrals need only be evaluated from 0 to $\frac{1}{2}$, thus reducing the computation time for these special cases by a factor of 4.

It would appear that a substantial improvement in accuracy and computing time can be gained by using integration schemes which made use of the functional forms contained in the integrand function in Eq. (2.9) as weighting functions. Another advantage of the approach used here which became apparent during the course of the numerical investigations was the fact that rounding errors are not serious and in one example it appeared that only two significant figures were lost because of rounding errors when more than 60 000 Gaussian points were used in the evaluation of Eq. (2.9).

ACKNOWLEDGMENTS

[6] R. M. Pitzer, J. P. Wright, and M. P. Barnett, Technical Note No. 23, Cooperative Computing Laboratory, Massachusetts Institute of Technology.