

Unified Treatment of Two-Center Overlap, Coulomb, and Kinetic-Energy Integrals*

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(Received 8 January 1970)

A single analytical formula is derived which gives the two-center overlap, Coulomb, nuclear-attraction, and kinetic-energy integrals as special cases. There are no difficulties when orbital exponents are nearly equal. Simplification of the derivative operators, which are characteristic of the approach, is discussed in detail. A computational scheme is outlined, and computing times are given.

I. INTRODUCTION

Despite the extensive literature on two-center integrals with Slater-type atomic orbitals (STO's), room remains for further simplification, unification, and computational economy. In this paper, two-center overlap, Coulomb, nuclear-attraction, and kinetic-energy integrals are re-examined with the Fourier transform technique, and a *single* analytical formula for all these integrals is derived. The formula is simple. It is valid for general $nlm\zeta$ and R values, presents no difficulties when ζ 's are nearly equal, and is computationally efficient.

Past analytical work on overlap-related two-center integrals can be characterized a number of ways.¹ There are formulas involving specific orbitals,²⁻⁶ schemes⁷⁻¹² or formulas¹²⁻¹⁸ for STO's with arbitrary quantum numbers, formulas with^{3,6,11,15,17,18} or without^{2,4,5,7-10,12-14,16} singularities when ζ 's are equal, and formulas derived via elliptical coordinates,^{2-5,7,8,11,13,14,16} Fourier transforms,^{6,11,12,15,17,18} or the expansion of an STO "about another center."^{9,10} In general, the formulas (for arbitrary STO's) with canceling singularities are simpler in form than those without singularities. Except in the Fourier-transform method, the overlap and Coulomb integrals require distinct derivations. The kinetic-energy integral is usually given as a sum of three overlap integrals.

In this paper, the overlap, Coulomb, and kinetic-energy integrals are evaluated as special cases of a more general, single integral in Fourier-transform space.^{6,15} As a result, one final formula gives all three integrals, and all three integrals are equally easy to calculate.¹⁹ The formula derived here contains derivative operators, modified spherical Bessel functions, and exponential-type integrals, similar to those occurring in analytical formulas^{17,20-23} for multicenter integrals of $1/r_{12}$. The computational techniques developed here are basic to the use of these analytical multicenter-integral formulas. Moreover, basic components of the two-center integrals can be stored and reused in the computation of the multicenter integrals.

We note in passing that the singularity-free formula for the overlap integral given here can be incorporated into the Taylor-series approach to four-center integrals¹⁷ to eliminate the most troublesome of the canceling singularities for equal ζ 's.

The single formula for the two-center integrals is contained in Eqs. (16) and (21). The computational adaptation is Eqs. (39), (44), and (46). The translation of the single formula to the individual types of integrals is given by Eqs. (11)-(13). Computational details with computing times are given in Sec. III.

II. THE UNIFIED FORMULA

A. Derivation

This section contains basic definitions and the formulation of the integrals via the Fourier-transform convolution theorem. Equations (1)-(17) essentially are explicit and/or implicit in earlier work^{6,15} but are included here for completeness and clarity.

The overlap, Coulomb, and kinetic energy integrals are defined by

$$S_{n_a l_a m_a \zeta_a; n_b l_b m_b \zeta_b}(\mathbf{R}) = \int dV \Psi_{n_a l_a m_a \zeta_a}^*(\mathbf{r}) \times \Psi_{n_b l_b m_b \zeta_b}(\mathbf{r}-\mathbf{R}) \quad (1)$$

$$= S_{ab}(\mathbf{R}), \quad (2)$$

$$C_{ab}(\mathbf{R}) = \int dV_1 \int dV_2 r_{12}^{-1} \Psi_a^*(\mathbf{r}_1) \Psi_b(\mathbf{r}_2-\mathbf{R}), \quad (3)$$

$$T_{ab}(\mathbf{R}) = \int dV \Psi_a^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \Psi_b(\mathbf{r}-\mathbf{R}). \quad (4)$$

The nuclear attraction integrals are equivalent to overlap integrals,

$$V_{ab}^{(a)}(\mathbf{R}) = \int dV r^{-1} \Psi_a^*(\mathbf{r}) \Psi_b(\mathbf{r}-\mathbf{R}) \quad (5)$$

$$= S_{n_a-1, l_a, m_a, \zeta_a; n_b l_b m_b \zeta_b}(\mathbf{R}), \quad (6)$$

$$V_{ab}^{(b)}(\mathbf{R}) = S_{n_a l_a m_a \zeta_a; n_b-1, l_b, m_b, \zeta_b}(\mathbf{R}). \quad (7)$$

The Ψ denotes an unnormalized STO,

$$\Psi_{nlm\zeta}(\mathbf{r}) = r^{n-1} \exp(-\zeta r) Y_l^m(\theta, \phi), \quad (8)$$

where the Y_l^m is a spherical harmonic, and n and l are integers satisfying

$$n \geq l+1. \quad (9)$$

We note, however, that the overlap formula will be valid when $n=l$, so that there is no difficulty evalu-

ating the nuclear-attraction integrals with Eqs. (6) and (7). Note also that the Coulomb integral [Eq. (3)] is defined in terms of STO *charge distributions*.

We recast the T , S , and C integrals simultaneously via the Fourier-transform convolution theorem^{6,15} as the following integral in transform variables²⁴:

$$I_{n_a l_a m_a \zeta_a; n_b l_b m_b \zeta_b}^{(N)}(\mathbf{R}) = (2\pi)^{-3} \int d^3\mathbf{k} k^{2N} \times \exp(i\mathbf{k}\cdot\mathbf{R}) f_{n_a l_a \zeta_a}^*(k) f_{n_b l_b \zeta_b}(k) \times Y_{l_a m_a}^*(\theta_k, \phi_k) Y_{l_b m_b}(\theta_k, \phi_k), \quad (10)$$

where

$$T = \frac{1}{2} I^{(1)}, \quad (11)$$

$$S = I^{(0)}, \quad (12)$$

$$C = 4\pi I^{(-1)}, \quad (13)$$

and use has been made of the Fourier-transform of an STO^{6,15}

$$\int dV \exp(i\mathbf{k}\cdot\mathbf{r}) \Psi_{nlm\zeta}(\mathbf{r}) = f_{nl\zeta}(k) Y_l^m(\theta_k, \phi_k), \quad (14)$$

$$f_{nl\zeta}(k) = 2\pi i^{l-1} (-d/d\zeta)^{n-l} (-k)^l (k^{-1}d/dk)^l k^{-1} \times [(\zeta - ik)^{-1} - (\zeta + ik)^{-1}]. \quad (15)$$

We use Eq. (15), which keeps the derivatives explicit and which was first given in Ref. 15, Eq. (13), rather than the expanded version given by Geller,¹⁵ because Eq. (15) (i) leads directly to singularity-free formulas, (ii) readily permits $(-d/d\zeta_a)^{n_a-l_a}$ to be treated differently from $(-d/d\zeta_b)^{n_b-l_b}$, and (iii) allows the derivatives in the similar functions $A_{ln}(x, y)$ and $\hat{A}_{ln}(x, y)$ to be treated differently [Eqs. (37), (38), (44), and (46) below].

The angular integrations in Eq. (10) are readily evaluated with the aid of the well-known expansion²⁵ of $\exp(i\mathbf{k}\cdot\mathbf{R})$ in terms of spherical Bessel functions [$j_\lambda(kR)$] and spherical harmonics, and with the aid

of Condon-Shortley coefficients²⁶ [$c^\lambda(l_b m_b; l_a m_a)$]:

$$I^{(N)} = (-1)^{l_a} \sum_{\lambda=|l_a-l_b|}^{l_a+l_b} [(2\lambda+1)/4\pi]^{1/2} \times c^\lambda(l_b, m_b; l_a, m_a) Y_\lambda^{m_b-m_a}(\theta_R, \phi_R) J_{ob\lambda}^{(N)}(R), \quad (16)$$

$$J_{ab\lambda}^{(N)}(R) = \frac{1}{2} \pi^{-2} \lambda^N \int_0^\infty dk k^{2N+2} f_{n_a l_a \zeta_a}(k) \times f_{n_b l_b \zeta_b}(k) j_\lambda(kR). \quad (17)$$

The integration over k in Eq. (17) is carried out with complex variable theory techniques via the following steps^{24a}:

(1) Replace

$$\int_0^\infty dk \text{ by } \frac{1}{2} \int_{-\infty}^\infty dk$$

since the integrand is even.

(2) For $(\zeta_a \pm ik)^{-1}$ in $f_{n_a l_a \zeta_a}(k)$, use

$$(\zeta_a \pm ik)^{-1} = R\alpha_0[(\zeta_a \pm ik)R] - R\hat{\alpha}_0[(\zeta_a \pm ik)R], \quad (18)$$

where the exponential-type integral²⁷ $\alpha_n(x)$ is

$$\alpha_n(x) = (-d/dx)^n x^{-1} \exp(-x), \quad (19)$$

and where

$$\hat{\alpha}_n(x) = \alpha_n(x) - n! x^{-n-1}. \quad (20)$$

(3) For the $\hat{\alpha}$ terms, “close” the contour for the $\exp(ikR)$ [$\exp(-ikR)$] part of the $j_\lambda(kR)$ in the upper [lower] half-plane, and evaluate the integral (after integration by parts l_b times) as $2\pi i$ [$-2\pi i$] times the residue at $k = i\zeta_b$ [$-i\zeta_b$].

(4) For the $\alpha_0[(\zeta_a + ik)R]$ [$\alpha_0[(\zeta_a - ik)R]$] terms, “close” the contour in the lower [upper] half-plane, and obtain (after integration by parts l_b times) $-2\pi i$ [$2\pi i$] times the residue at $k = -i\zeta_b$ [$+i\zeta_b$].

(5) Steps (1)–(4) above generate a simple pole at the origin when $N = -1$ (Coulomb case) and $\lambda = l_a \pm l_b$, yielding additional residues at $k = 0$. The final result is

$$J_{ab\lambda}^{(N)}(R) = (-1)^{N+n_b-l_b} 2\pi R^{n_a+n_b+1-2N} (d/d\rho_b)^{n_b-l_b} \{ (-1)^{l_a} (\rho_b^{-1}d/d\rho_b)^{l_b} \rho_b^{l_a+l_b+2N+1} \mathfrak{K}_\lambda(\rho_b) (\rho_b^{-1}d/d\rho_b)^{l_a} \rho_b^{-1} \times [\hat{\alpha}_{n_a-l_a}(\rho_a+\rho_b) - \hat{\alpha}_{n_a-l_a}(\rho_a-\rho_b)] + 2(-1)^{l_b} (\rho_b^{-1}d/d\rho_b)^{l_b} \rho_b^{l_a+l_b+2N+1} \mathfrak{G}_\lambda(\rho_b) (\rho_b^{-1}d/d\rho_b)^{l_a} \rho_b^{-1} \alpha_{n_a-l_a}(\rho_a+\rho_b) + \delta_{N,-1} \delta_{\lambda, l_a+l_b} 2(-1)^\lambda \rho_b^{-2l_b-2} [(2l_b)!!(2\lambda-1)!!/(2l_a+1)!!] \hat{\alpha}_{n_a+l_a+1}(\rho_a) - \delta_{N,-1} \delta_{\lambda, l_a-l_b} 2(-1)^{l_a} \rho_b^{-2l_b-2} \times [(2l_b)!!(2l_a-1)!!/(2\lambda+1)!!] \alpha_{n_a-l_a}(\rho_a) \} \quad (21)$$

where^{24b}

$$\rho_a = \zeta_a R, \quad (22)$$

$$\rho_b = \zeta_b R, \quad (23)$$

$$\mathfrak{K}_\lambda(x) = (-x)^\lambda (x^{-1}d/dx)^\lambda x^{-1} \exp(-x), \quad (24)$$

$$\mathfrak{G}_\lambda(x) = x^\lambda (x^{-1}d/dx)^\lambda x^{-1} \sinh(x). \quad (25)$$

B. Remarks

Equations (16) and (21), through Eqs. (11)–(13), constitute a single, unified formula for $SC T$ (and V) integrals. Moreover, since $\zeta_a - \zeta_b$ (in the form $\rho_a - \rho_b$) appears as an argument only in the singularity-free $\hat{\alpha}_{n_a-l_a}$, there are no difficulties when $\zeta_a - \zeta_b \sim 0$.

From Eqs. (10)–(13) one can immediately deduce the Poisson equations,¹⁴

$$\nabla_R^2 C(\mathbf{R}) = -4\pi S(\mathbf{R}), \tag{26}$$

$$\nabla_R^2 S(\mathbf{R}) = -2T(\mathbf{R}). \tag{27}$$

III. COMPUTATIONAL DISCUSSION

A. Expansion of Derivatives

We discuss the simplification of the derivatives in Eq. (21) in detail, because the usefulness of the present formulas and of analytical formulas for multicenter integrals given previously^{17,20–23} hangs on this simplification.

The first step is the identity,

$$(d/d\rho_b)^{n_b-l_b} = \sum_{j=0}^{\lfloor (n_b-l_b)/2 \rfloor} \frac{(n_b-l_b)!}{(n_b-l_b-2j)!(2j)!!} \rho_b^{n_b-l_b-2j} (\rho_b^{-1}d/d\rho_b)^{n_b-l_b-j}, \tag{28}$$

which casts all the derivatives appearing in Eq. (21) in the form $(\rho_b^{-1}d/d\rho_b)$. The $\lfloor (n_b-l_b)/2 \rfloor$ denotes the largest integer $\leq (n_b-l_b)/2$.

The second step [after substituting Eq. (28) into Eq. (21)] is to regard the *non- $\delta_{N,-1}$* terms as $(\rho_b^{-1}d/d\rho_b)^{n_b-j}$ operating on the product of three factors. The first factor is

$$\rho_b^{l_a+l_b+\lambda+2N+1}. \tag{29}$$

The second factor is either

$$\rho_b^{-\lambda} \mathcal{K}_\lambda(\rho_b) \quad \text{or} \quad \rho_b^{-\lambda} \mathcal{G}_\lambda(\rho_b). \tag{30}$$

The third factor is either

$$(\rho_b^{-1}d/d\rho_b)^{l_a} \rho_b^{-1} [\hat{\alpha}_{n_a-l_a}(\rho_a+\rho_b) - \hat{\alpha}_{n_a-l_a}(\rho_a-\rho_b)] \tag{31}$$

or

$$(\rho_b^{-1}d/d\rho_b)^{l_a} \rho_b^{-1} \alpha_{n_a-l_a}(\rho_a+\rho_b). \tag{32}$$

This decomposition is motivated by Leibniz’s theorem for the differentiation of a product, which is adapted here in the form

$$(\rho_b^{-1}d/d\rho_b)^{n_b-j} [F(\rho_b)G(\rho_b)H(\rho_b)] = \sum_{s+t+u=n_b-j} \frac{(n_b-j)!}{s!t!u!} [(\rho_b^{-1}d/d\rho_b)^s F][(\rho_b^{-1}d/d\rho_b)^t G][(\rho_b^{-1}d/d\rho_b)^u H], \tag{33}$$

and the simple rules,

$$(\rho_b^{-1}d/d\rho_b)^s \rho_b^{l_a+l_b+\lambda+2N+1} = \frac{(l_a+l_b+\lambda+2N+1)!!}{(l_a+l_b+\lambda+2N+1-2s)!!} \rho_b^{l_a+l_b+\lambda+2N+1-2s}, \tag{34}$$

$$(\rho_b^{-1}d/d\rho_b)^t \rho_b^{-\lambda} \mathcal{K}_\lambda(\rho_b) = (-1)^t \rho_b^{-\lambda-t} \mathcal{K}_{\lambda+t}(\rho_b), \tag{35}$$

and

$$(\rho_b^{-1}d/d\rho_b)^t \rho_b^{-\lambda} \mathcal{G}_\lambda(\rho_b) = \rho_b^{-\lambda-t} \mathcal{G}_{\lambda+t}(\rho_b). \tag{36}$$

The third step is to regard the repeated derivatives of the third factors [Eqs. (31) and (32)] as special, auxiliary functions:

$$A_{ln}(x, y) = (-x)^l (x^{-1}d/dx)^l x^{-1} \alpha_n(x+y), \tag{37}$$

$$\hat{A}_{ln}(x, y) = \frac{1}{2} x^l (x^{-1}d/dx)^l x^{-1} [\hat{\alpha}_n(y+x) - \hat{\alpha}_n(y-x)]. \tag{38}$$

The expanded expression for $J_{ab\lambda}^{(N)}$ then becomes²⁸

$$\begin{aligned} J_{ab\lambda}^{(N)} = & \delta_{N,-1} 4\pi R^{n_a+n_b+3} \rho_b^{-n_b-l_b-2} (n_b+l_b+1)! \{ -\delta_{\lambda, l_a+l_b} (-1)^\lambda \frac{(2\lambda-1)!!}{(2l_a+1)!!(2l_b+1)!!} \hat{\alpha}_{n_a+l_a+1}(\rho_a) \\ & + \delta_{\lambda, l_a-l_b} (-1)^{l_a} \frac{(2l_a-1)!!}{(2l_b+1)!!(2\lambda+1)!!} \alpha_{n_a-l_a}(\rho_a) \} + (-1)^{N+n_b-l_b} 4\pi R^{n_a+n_b+1-2N} \sum_{j=0}^{\lfloor (n_b-l_b)/2 \rfloor} \frac{(n_b-l_b)!}{(n_b-l_b-2j)!(2j)!!} \\ & \times \sum_{s+t+u=n_b-j} \frac{(n_b-j)!(l_a+l_b+\lambda+1+2N)!!}{s!t!u!(l_a+l_b+\lambda+1+2N-2s)!!} \rho_b^{2N+1-s-j} [(-1)^{t+l_a} \mathcal{K}_{\lambda+t}(\rho_b) \hat{A}_{l_a+u, n_a-l_a}(\rho_b, \rho_a) \\ & + (-1)^{u+l_a+l_b} \mathcal{G}_{\lambda+t}(\rho_b) A_{l_a+u, n_a-l_a}(\rho_b, \rho_a)]. \tag{39} \end{aligned}$$

B. The Auxilliary Functions A and \hat{A}

The A and \hat{A} are related to the S and P functions of Barnett and Coulson⁹⁻¹⁰:

$$A_{ln}(x, y) = (2/\pi)^{1/2} x^{-n-l-2} S_{n+l+1/2, l+1/2}(y/x, x), \quad (40)$$

$$\hat{A}_{ln}(x, y) = (\pi/2)^{1/2} x^{-n-l-2} P_{n+l+1/2, l+1/2}(y/x, x). \quad (41)$$

The A and \hat{A} are actually definite integrals of (spherical) Bessel functions,

$$A_{ln}(x, y) = \int_1^\infty dt t^{n+l+1} \exp(-yt) \mathcal{K}_l(xt), \quad (42)$$

$$\hat{A}_{ln}(x, y) = \int_0^1 dt t^{n+l+1} \exp(-yt) \mathcal{J}_l(xt), \quad (43)$$

which are discussed in standard reference works.^{29,30a} A complete set of recursion formulas^{29,30} can easily be derived from Eqs. (42) and (43) and the well-known recursion formulas for Bessel functions. After some exploratory work with recursion schemes, we concluded that the simplest, most reliable ways to calculate the A and \hat{A} were the explicit, finite sum for the former,

$$A_{ln}(x, y) = \sum_{m=0}^l (l+m)! [(l-m)! (2m)!]^{-1} \times x^{-m-1} \alpha_{n+l-m}(x+y), \quad (44)$$

which follows from Eq. (37) and the identity,

$$(-x)^l (x^{-1} d/dx)^l x^{-1} = \sum_{m=0}^l (l+m)! [(l-m)! (2m)!]^{-1} \times x^{-m-1} (-d/dx)^{l-m}, \quad (45)$$

and the Taylor series for the latter,^{30b}

$$\hat{A}_{ln}(x, y) = - \sum_{s=0}^\infty x^{l+2s} \times \hat{\alpha}_{n+2l+1+2s}(y) / [(2l+2s+1)! (2s)!] \quad (46)$$

which follows from Eq. (38) and the series,

$$\hat{\alpha}_n(y \pm x) = \sum_{m=0}^\infty (\mp x)^m \hat{\alpha}_{n+m}(y) / m!. \quad (47)$$

Equations (44) and (46) are useful primarily because all the terms are positive. The equivalent of Eqs. (44) and (46) were used by Barnett and Coulson.^{9,10} [Indeed, most of the special function used here were used by Barnett and Coulson. Despite the use of similar functions, however, the final schemes are very different, as is illustrated in the Appendix. The present scheme appears much more efficient, especially as n and l increase.]

C. The Special Functions α_n , $\hat{\alpha}_n$, \mathcal{K}_n , and \mathcal{J}_n

These function have been studied by numerous workers.^{9,10,31,32} The methods we found most useful are summarized here. Insofar as we can determine, the scheme for computing $\hat{\alpha}_n$ has not been used before.

The $\alpha_n(x)$ are accurately computed recursively from

$$\alpha_0(x) = x^{-1} \exp(-x), \quad (48)$$

$$\alpha_n(x) = x^{-1} [\exp(-x) + n\alpha_{n-1}(x)]. \quad (49)$$

The $\mathcal{K}_n(x)$ are accurately computed recursively from

$$\mathcal{K}_0(x) = x^{-1} \exp(-x), \quad (50)$$

$$\mathcal{K}_1(x) = (x^{-1} + x^{-2}) \exp(-x), \quad (51)$$

$$\mathcal{K}_n(x) = [(2n-1)/x] \mathcal{K}_{n-1}(x) + \mathcal{K}_{n-2}(x). \quad (52)$$

The \mathcal{J}_n are calculated by a slight modification of a method used by Corbato.³² One calculates by *downward* recursion the ratio

$$r_n(x) = \mathcal{J}_n(x) / \mathcal{J}_{n-1}(x), \quad (53)$$

via

$$r_n(x) = x / (2n+1+x r_{n+1}). \quad (54)$$

Then one computes $\mathcal{J}_n(x)$ by upwards recursion from

$$\mathcal{J}_0(x) = x^{-1} \sinh(x), \quad (55)$$

$$\mathcal{J}_n(x) = r_n(x) \times \mathcal{J}_{n-1}(x). \quad (56)$$

The highest $r_N(x)$, which is required to start the downwards recursion, is obtained (unlike Corbato³²) from the continued fraction,³³

$$r_n^{-1} = \frac{2n+1}{x} + \frac{1}{(2n+3)/x} + \frac{1}{(2n+5)/x} + \dots \quad (57)$$

The $\hat{\alpha}_n$ satisfy the same recursion formulas as α_n ,

$$\hat{\alpha}_n(x) = x^{-1} [\exp(-x) + n\hat{\alpha}_{n-1}(x)], \quad (58)$$

except that

$$\hat{\alpha}_0(x) = x^{-1} [\exp(-x) - 1]. \quad (59)$$

However, upwards recursion loses accuracy when $n \gg x$, and downwards recursion loses accuracy when $n \ll x$.³⁴ The method we used involves both upwards and downwards recursion to an intermediate value of n (determined empirically). The downwards recursion is via the ratio method. Let

$$\tau_n(x) = \hat{\alpha}_n(x) / \hat{\alpha}_{n-1}(x). \quad (60)$$

Then

$$\tau_{n-1}(x) = (n-1) / [(n+x) - x \tau_n]. \quad (61)$$

The highest τ_n is obtained from the continued fraction,

$$\tau_n = \frac{n/(n+x+1)}{1 + \frac{-x(n+1)/[(n+1+x)(n+2+x)]}{1 + \frac{-x(n+j)/[(n+j+x)(n+j+1+x)]}{1 + \dots}} \dots \quad (62)$$

The downwards recursion is stopped at

$$m = \max\{0, [4+0.367(x-10)]\}, \quad (63)$$

where, again, $[]$ denotes the "integer part." Then

the value of $\hat{\alpha}_{n-1}(x)$, obtained from upwards recursion with Eqs. (58) and (59) is used, along with

$$\hat{\alpha}_n(x) = \tau_n(x) \times \hat{\alpha}_{n-1}(x), \quad (64)$$

to convert the τ 's into $\hat{\alpha}$'s. Accuracy is usually seven decimal digits on a 36-bit IBM machine.

D. Computational Scheme and Times

The basic computational scheme we use is as follows:

- (1) Determine maximum indices on special functions.
- (2) Calculate and store tables of $\hat{\alpha}_n(\rho_a)$, $\alpha_n(\rho_a)$, $\alpha_n(\rho_a + \rho_b)$, $\mathcal{K}_n(\rho_b)$, $\mathcal{G}_n(\rho_b)$.
- (3) Calculate and store tables of $A_{ln}(\rho_b, \rho_a)$ and $\hat{A}_{ln}(\rho_b, \rho_a)$ from the $\alpha_n(\rho_a + \rho_b)$ and $\hat{\alpha}_n(\rho_a)$.
- (4) Calculate and store $J_{ab\lambda}^{(N)}$.
- (5) Calculate and store $Y_{\lambda}^{mb-ma}(\theta_R, \phi_R)$.
- (6) Perform multiplications and summations in Eq. (16). The $c^\lambda(l_b, m_b; l_a, m_a)$ are calculated as needed, and are not stored.

The Condon-Shortley coefficients were calculated with a program written by Dr. Edward F. Hayes. Since our primary interest was the method for the "radial" functions, no special attention was given to the optimal incorporation of the Condon-Shortley routine. An improvement in efficiency would result from storing a table of the Condon-Shortley coefficients and retrieving them (rather than calculating them) as needed.

Two "driver" routines were written, one to calculate all nonzero S , T , $V^{(a)}$, and $V^{(b)}$ integrals, the second to calculate all nonzero Coulomb integrals. To test the method, calculations³⁵ were carried out with a basis consisting of all STO's with $n \leq 3$, $l \leq n-1$, with a different value of ζ for each (nl) set on each atom. (There were fourteen basis functions on each atom.) The Coulomb integrals calculated by the routine were for charge distributions arising from the products of STO's, and the program expressed these products as linear combinations of STO charge distributions at an intermediate stage of the calculation, as required by Eq. (3).

There are $14 \times 14 \times 4 = 784$ $STV^{(a)}V^{(b)}$ integrals, but only 184 are distinct and nonzero.

There are $14^4 = 38\,416$ Coulomb integrals, but clearly one need consider only $(14 \times 15/2)^2 = 11\,025$ integrals. Only 1,338 are distinct and nonzero. The total computing time on an IBM 7094/I for the $STV^{(a)}V^{(b)}$ integrals was typically 1.8 sec, i.e., 10 msec, per distinct nonzero integral. Approximately one-fourth of this time was used to "set up" the calculation and to compute the Condon-Shortley coefficients. The total computing time for the Coulomb integrals was typically 60 sec, i.e., 45 msec per distinct nonzero integral. Approximately half of this time was required to "set up" and to calculate Condon-Shortley coeffi-

icients. "Set up" time means the time to determine which integrals to calculate and also includes the output time. These computing times seem to compare favorably, especially in the Coulomb case, with recent quotations,¹⁶ but seem slower than some numerical integration schemes.^{11,36} We emphasize, however, that in our scheme there is no difficulty either with large (ζR) values or with equal ζ 's. We also emphasize that the times quoted here are not based on an optimum computer program. Clever programming, the use of prestored coefficients in Eq. (39) (cf. Ref. 16), and recursion formulas for the A_n^l and \hat{A}_n^l functions^{29,30} would reduce computing times significantly.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors also wish to thank Dr. Edward F. Hayes for graciously permitting the use of his Condon-Shortley-coefficient subroutine, and Mr. Akiva M. Eisenberg for assistance in programming the \mathcal{G}_n subroutine.

APPENDIX

This Appendix, stimulated by referees' comments, is to demonstrate by example some differences between the present scheme and the Barnett-Coulson scheme.^{9,10}

Superficially, the results of both schemes appear similar, like two houses built from bricks. The arrangement of the bricks and, in some cases, the nature of the bricks, however, are quite different. For instance, if one examines the overlap integral between two 1s orbitals, the formulas of the two methods are not just nonidentical, but considerable effort is necessary to show their equivalence. We have chosen the example of the Coulomb integral between $2p_z$ and 1s charge distributions, $C_{2p_z,1s} \equiv C_{210\zeta_a, 100\zeta_b}$, to exemplify the difference between the two methods, because for this integral the Barnett-Coulson scheme makes use of distinctly different mathematical functions. [The z axis is taken parallel to \mathbf{R} .]

In the Barnett-Coulson scheme, $C_{2p_z,1s}$ would be evaluated via the following equations and tables of Ref. 9: Eq. (56); Table 9, the entry ($1s\ 2p_z, 1s, 1s$); Table 11, the entry ($n=4$); and Eq. (17). With the aid of Eq. (41) of Ref. 10, the result is

$$\begin{aligned} C_{2p_z,1s} = N_e \{ & 8[Z_{0,0,1/2}(0, \rho_b) - Z_{0,2,1/2}(0, \rho_b)] \\ & - 8[Z_{0,0,1/2}(\zeta_a/\zeta_b, \rho_b) - Z_{0,2,1/2}(\zeta_a/\zeta_b, \rho_b)] \\ & - 8(\zeta_a/\zeta_b)[Z_{0,0,3/2}(\zeta_a/\zeta_b, \rho_b) - Z_{0,2,3/2}(\zeta_a/\zeta_b, \rho_b)] \\ & - 4(\zeta_a/\zeta_b)^2[Z_{0,0,5/2}(\zeta_a/\zeta_b, \rho_b) - Z_{0,2,5/2}(\zeta_a/\zeta_b, \rho_b)] \\ & - (\zeta_a/\zeta_b)^3[Z_{0,0,7/2}(\zeta_a/\zeta_b, \rho_b) - Z_{0,2,7/2}(\zeta_a/\zeta_b, \rho_b)] \}, \quad (A1) \end{aligned}$$

where N_e is a normalization constant. Analytical formulas for the Z 's are given in Eqs. (47)-(48) of

Ref. 10. The basic result is

$$Z_{0,n,l+1/2}(\kappa, \tau) = K_{n+1/2}(\tau) P_{l+1/2, n+1/2}(\kappa, \tau) \\ + I_{n+1/2}(\tau) S_{l+1/2, n+1/2}(\kappa, \tau), \quad (\text{A2})$$

where $I_{n+1/2}$ and $K_{n+1/2}$ differ only slightly from \mathcal{I}_n and \mathcal{K}_n , and where S and P are related to A and \hat{A} via Eqs. (40) and (41) above.

Our formula for $C_{2p_a, 1s}$ [Eqs. (3), (13), (16), and (39)] is

$$C_{2p_a, 1s} = N \{ (2/3) \rho_b^{-2} [\alpha_1(\rho_a) - \hat{\alpha}_1(\rho_a)] \\ + \rho_b^{-1} [\mathcal{K}_1(\rho_b) \hat{A}_{11}(\rho_b, \rho_a) + \mathcal{I}_1(\rho_b) A_{11}(\rho_b, \rho_a)] \\ - [\mathcal{K}_2(\rho_b) \hat{A}_{11}(\rho_b, \rho_a) - \mathcal{I}_2(\rho_b) A_{11}(\rho_b, \rho_a)] \\ + [\mathcal{K}_1(\rho_b) \hat{A}_{21}(\rho_b, \rho_a) - \mathcal{I}_1(\rho_b) A_{21}(\rho_b, \rho_a)] \}, \quad (\text{A3})$$

where N contains normalization constants and powers of R .

Despite the superficial resemblance between Eq. (A3) and Eqs. (A1) and (A2), the significant differences are in the nature of the functions that appear. The A_{ln} and \hat{A}_{ln} that appear in Eq. (A3) [and Eq. (39)] can be expressed entirely in terms of α_m and $\hat{\alpha}_m$ functions. In contrast, some of the Z functions in Eq. (A1) require additional functions. For instance, $Z_{0,2,1/2}$ involves [Eq. (A2)] $S_{1/2,5/2}$, which according to Eqs. (47), (48), and (51) of Ref. 10 is

$$S_{1/2,5/2}(\zeta_a/\zeta_b, \rho_b) = (\pi/2)^{1/2} [\rho_b \alpha_0(\rho_a + \rho_b) + 3 E_1(\rho_a + \rho_b) \\ + 3 \rho_b^{-1} E_2(\rho_a + \rho_b)]. \quad (\text{A4})$$

The exponential-type integral,

$$E_n(x) = \int_1^\infty dt t^{-n} \exp(-xt), \quad (\text{A5})$$

is a more complicated function than the α_n or $\hat{\alpha}_n$, and it is a specific part of the Barnett-Coulson scheme not present in the scheme described in this paper.

To summarize, in general the Barnett-Coulson formulas can involve the exponential-type integral $E_n(x)$, which does not enter our formulas. When reduced to basic functions, our formula seems to have fewer terms. It is to be emphasized that our formula is explicit, transparent, and general, whereas the Barnett-Coulson method is a scheme based on recursion relations (which are not always simple or stable); it is not particularly transparent, and the formulas given are for specific values of n and l .

* Supported in part by a National Science Foundation Grant. † American Chemical Society—Petroleum Research Fund Fellow.

‡ Alfred P. Sloan Research Fellow.

¹ The references given here to past work on two-center integrals are meant more to be representative than exhaustive.

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¹⁹ In Ref. 12, a general recursion scheme is used to derive formulas for Coulomb integrals with specific charge distributions. The results are expressed as a sum of several two-center overlap integrals and a nuclear attraction integral. The latter integrals are to be evaluated by some independent method. The present work expresses the overlap, kinetic energy, nuclear attraction, and Coulomb integrals as specific cases of one general formula, so that the Coulomb integral is of the same order of difficulty as a single overlap plus a nuclear attraction integral.

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²⁵ M. Abramowitz and I. A. Stegun (Eds.), *Natl. Bur. Std., (U.S.) Appl. Math. Ser.* **55**, 440 (1964); see Eq. (10.1.47).

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²⁷ Reference 25, p. 228.

²⁸ Note that $[(-2N-1)!!]^{-1} = (-1)^N (2N-1)!!$. It is also possible to expand Eq. (21) so that the subscripts in \mathcal{I} and \mathcal{K} decrease, rather than increase.

²⁹ Reference 25, p. 483.

³⁰ (a) Y. L. Luke, *Integrals of Bessel Functions* (McGraw-Hill, New York, 1962). (b) Equation (46) also follows immediately from Eq. (43), the power series for $\mathcal{I}_l(xt)$, and the integral representation,

$$\hat{\alpha}_n(x) = - \int_0^1 dt t^n \exp(-xt).$$

³¹ Reference 25, pp. 235 and 455.

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³⁴ Strictly speaking, Eq. (58) is stable for recursion in the downward direction. The loss in accuracy is due to round-off error.

³⁵ An accuracy of seven significant figures was aimed for. For all integrals that could be obtained from other sources that were accurate to seven digits, the first seven nonzero digits from the present program were identical. We estimate that the usual accuracy of the program is one part in 10^7 , but exceedingly small integrals may be accurate only to one part in 10^6 .

³⁶ S. A. Hagstrom (private communication).