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Note

# Reduction of Hybrid Electron-repulsion Integrals to Overlap Integrals*

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It is shown how two-center electron-repulsion integrals of hybrid type can be reduced to linear combinations of overlap integrals. In certain cases the overlap integrals involve orbitals whose principal quantum numbers are less than their azimuthal quantum numbers. Explicit formulas are presented for the reduction of all hybrid integrals containing only orbitals of principal quantum numbers 1 or 2.

## INTRODUCTION

Much of the recent work on the evaluation of molecular integrals for Slater-type orbitals (STO's) has been directed toward the development of unified computational schemes for handling all the integrals arising in a molecular energy calculation[1]. Such approaches have the advantage of minimizing the computational effort for complete ab initio studies, but are of no particular advantage when only one, or a few integrals are required. Since many of the procedures for approximate molecular-orbital calculation use only a limited group of integrals, there remains a real need for rapid evaluation of integrals of specific types.

The earlier work on molecular integrals has provided separate discussions for several types of integrals, e. g. overlap, diatomic nuclear attraction, two--center electron-repulsion integrals of coulomb, hybrid, and exchange type, etc.[2]. However, some of the standard formulations yield expressions with numerical difficulties, while others are more complex than might be desired. One approach which we believe has been insufficiently exploited is the development of relations between integrals, thereby permitting some integrals to be expressed in terms of others whose structure is more easily understood. This point of view is illustrated by a previous study of the authors[3], in which it was shown how two-center Coulomb integrals could be reduced to simple linear combinations of overlap integrals. In another previous study[4], it was pointed out than the Z-functions, first introduced by Barnett and Coulson[5] to reduce molecular integrals, could themselves be expressed as overlap integrals thereby indicating that additional electron repulsion integrals could be reduced to overlaps.

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The reduction of other integrals to overlaps has several advantages. One virtue is that it separates the long-range (or longer-range) and short(er)-range contributions to integrals, thereby avoiding much of the numerical difficulty inherent in other formulations. This numerical difficulty is transferred to the evaluation of overlap integrals, where it has been more fully analyzed and understood. Moreover, there exist a number of satisfactory procedures for evaluating overlap integrals, so that the reduction leads to expressions whose evaluation can easily be completed.

The present paper provides an explicit formulation of two-center hybrid integrals as simple linear combinations of overlaps, and thus completes the task of providing simple and rapid evaluations for the electron-repulsion integrals most likely to be used in approximate molecular calculations. In developing the material here presented, we found it convenient to focus attention on various relations connecting two-center charge distributions. These relations, though clearly not newly discovered, have seen less application than is warranted by their utility. We also found it useful to express the potential of an STO distribution in terms of STO's. This device, though long known, could have been used to simplify much previous work, including that of one the present authors.

When the above-described reduction is carried out, we find that we encounter overlap integrals of orbitals whose principal quantum numbers are smaller than their azimuthal quantum numbers, or possibly even negative. Such overlap integrals cannot be written as simple linear combinations of the well-known[6] auxiliary functions $A_n$ and $B_n$. However, these unusual overlap integrals are well-defined functions related to the exponential-integral function, and they present no serious evaluation problem. On the contrary, their use permits a greater degree of systematization to the integral evaluation than would be possible if their introduction were circumvented.

## DEFINITIONS AND BASIC FORMULAS

We shall be concerned with STO's

$$\psi_{nlm} = A r^{n-1} e^{-\zeta r} Y_{lm}(\vartheta, \varphi), \tag{1}$$

where $Y_{lm}$ is a normalized spherical harmonic in complex form,

$$Y_{lm}(\vartheta, \varphi) = \left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^m(\cos\vartheta) e^{im\varphi}. \tag{2}$$

The factor A is a normalization constant

$$A = \left[\frac{(2\zeta)^{2n+1}}{(2n)!}\right]^{1/2} \tag{3}$$

When convenient, $\psi_{nlm}$ will be represented by the conventional symbols 1s, 2pσ, etc., with negative $m$ values indicated by a superscript bar, e. g. $2p\bar{\pi}$. When different STO's must be distinguished, we shall use primes or superscripts on the quantum numbers, the normalization constant, and the $\zeta$ value, or on the orbital symbol, e. g. 1s′.

This paper deals with hybrid electron-repulsion integrals of the general form

$$[a'a'' \mid ab] \equiv \int d\mathbf{r}_1\, d\mathbf{r}_2\, a'(\mathbf{r}_1)\, a''^*(\mathbf{r}_1)\, r_{12}^{-1}\, a^*(\mathbf{r}_2)\, b(\mathbf{r}_2) \tag{4}$$

where $a$, $a'$, and $a''$ represent STO's on Center A and $b$ represents a STO on Center B. Centers A and B are separated by a distance $R$, and the coordinate systems for all orbitals have a common polar axis indicated by the directed line $A \rightarrow B$. Note that this coordinate system is the same as that used in our earlier paper on Coulomb integrals but is at Center B the reverse of that used in some previous studies by other investigators. In this paper, the bracket notation introduced in Eq. (4) will be understood to refer to orbitals at Centers A and B as there specified, so that the orbital location can be suppressed. For example, in $[1s2s \mid 1s'2p\sigma]$, the orbitals 1s, 2s, and 1s′ are on Center A, and $2p\sigma$ is on Center B. We shall also have occasion to discuss the charge distributions of which the integrals are composed. We shall use square half-brackets for this purpose, with the understanding that in a left half-bracket both orbitals are on Center A, while in a right half-bracket the first orbital is on Center A and the second orbital is on Center B. Taking note of the conventional complex conjugation in the left half-bracket,

$$|\, ab] = a^*(\mathbf{r})\, b(\mathbf{r}) \tag{5a}$$

$$[a'a''\,| = a'(\mathbf{r})\, a''^*(\mathbf{r}) \tag{5b}$$

## RELATIONS BETWEEN CHARGE DISTRIBUTIONS

The number of formulas needed to present all hybrid integrals of low quantum numbers can be greatly reduced by use of relations connecting charge distributions. Using the equations $z_a = z_b + R$, $x_a = x_b$, and $y_a = y_b$, we may manipulate each charge distribution $|\, ab\,]$ so that STO $a$ is of s symmetry. This will turn out to minimize the complexity of the formulas to be obtained later. The specific relations needed for hybrid integrals of principal quantum numbers 1 and 2 are presented in Table I. We assume that a first step in the evaluation

TABLE I

*Relations connecting charge distributions**

$$|\, 2p\sigma\ 1s] = \zeta_b R\, |\, 1s\ 1s] + \frac{\zeta_b}{\zeta_a}\, |\, 1s\ 2p\sigma]$$

$$|\, 2p\sigma\ 2s] = \zeta_b R\, |\, 1s\ 2s] + \frac{\zeta_b}{\zeta_a}\, \frac{\sqrt{10}}{2}\, |\, 1s\ 3p\sigma]$$

$$|\, 2p\sigma\ 2p\sigma] = \zeta_b R\, |\, 1s\ 2p\sigma] + \frac{\zeta_b}{\zeta_a} \left(\sqrt{2}\, |\, 1s\ 3d\sigma] + \frac{\sqrt{10}}{2}\, |\, 1s\ 3s]\right)$$

$$|\, 2p\sigma\ 2p\pi] = \zeta_b R\, |\, 1s\ 2p\pi] + \frac{\zeta_b}{\zeta_a}\, \frac{\sqrt{6}}{2}\, |\, 1s\ 3d\pi]$$

$$|\, 2p\pi\ 2p\pi] = |\, 2p\bar{\pi}\ 2p\bar{\pi}] = \frac{\zeta_b}{\zeta_a} \left(\frac{\sqrt{10}}{2}\, |\, 1s\ 3s] - \frac{\sqrt{2}}{2}\, |\, 1s\ 3d\sigma]\right)$$

* Notation is defined in Eqs. (5). STO's on Centers A and B have respective screening parameters $\zeta_a$ and $\zeta_b$.

$$|\,2p\pi\ 1s] = \frac{\zeta_b}{\zeta_a}\,|\,1s\ 2p\overline{\pi}]$$

$$|2p\pi\ 2s] = \frac{\zeta_b}{\zeta_a}\,\frac{\sqrt{10}}{2}\,|\,1s\ 3p\overline{\pi}]$$

$$|\,2p\pi\ 2p\sigma] = \frac{\zeta_b}{\zeta_a}\,\frac{\sqrt{6}}{2}\,|\,1s\ 3d\overline{\pi}]$$

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of a hybrid integral will be the use of Table I to remove any quantities listed on the left hand sides of its equations.

### POTENTIALS OF ONE-CENTER CHARGE DISTRIBUTIONS

The next step in hybrid integral evaluation is the integration over the coordinates of Electron 1. For an integral $[a'a''\,|\,ab]$, this integration amounts to obtaining the electrostatic potential of the one-center charge distribution $[a'a''\,|$. Since $a'^*a''$ can be written as a linear combination of STO's, we require the potentials associated with charge distributions of the general form $r^{N-1}\exp(-\zeta r)Y_{LM}$, where $\zeta = \zeta' + \zeta''$. One may find

$$V\{r^{N-1}\ e^{-\zeta r}\ Y_{LM}\} = \frac{4\pi\,(N+L+1)!}{(2L+1)\,\zeta^{N+L+2}\,r^{L+1}}\left[1 - e^{-\zeta r}\sum_{j=0}^{N+L}(\zeta r)^j \times \right.$$

$$\left. \times\left(\frac{1}{j!} - \frac{(N-L)!}{(N+L+1)!\,(j-2L-1)!}\right)\right] Y_{LM} \tag{6}$$

In the summation in Eq. (6), note that values $j \leq 2L$ cause the factorial ratio to vanish. It is clear from Eq. (6) that these potentials can themselves be written as STO's, providing we permit the assignment of quantum numbers $n \leq l$. Material equivalent to various cases of Eq. (6) is tabulated in the paper of Barnett and Coulson[5].

### REDUCTION TO OVERLAP INTEGRALS

We are now ready to complete the reduction of hybrid integrals to overlap form by the introduction of Eq. (6). We use the general relation

$$[a'a''\,|\,ab] = \langle V\{a'^*a''\}\,a\,|\,b\rangle \tag{7}$$

Since we have previously arranged for $a$ to be an s orbital, its effect on the STO's comprising $V\{a'^*a''\}$ is merely to increase the principal quantum number and to alter the normalization.

Carrying out the steps represented by Eq. (7), we obtain for hybrid integrals originally containing principal quantum numbers 1 and 2 the formulas listed in Table II. The overlap integrals appearing on the right hand sides of the equations in Table II are defined in unnormalized form, as follows:

$$(nl\zeta\,|\,n'\,l'\,\zeta')_m = \int r_a^{n-1}\exp(-\zeta r_a)\,Y^*_{l,m}(\vartheta_a,\varphi_a)\,r_b^{n'-1}\exp(-\zeta' r_b)\cdot Y_{l',m}(\vartheta_b\varphi_b)\,d\mathbf{r} \tag{8}$$

For $n \geq l$ and $n' \geq l'$, these overlap integrals are expressible as well known linear combinations of the auxiliary functions $A_n$ and $B_n$[6]. We note, however, that some of the overlap integrals in Table II may involve $n$ values such that $n < l$. These »unconventional« overlap integrals are discussed below.

TABLE II

*Reduction of Hybrid Integrals [a′ a″ | ab] to Overlap Integrals, as Defined in Eq. (8)**

$$[1s'\,1s'' \mid nsb] = 8\left(\frac{\zeta'\,\zeta''}{\zeta^2}\right)^{3/2} A_a\,A_b\,\delta_{m_b,0}\;[(n-1,0,\zeta_a \mid n_b\,l_b\,\zeta_b)_0 - (n-1,0,Z \mid n_b\,l_b\,\zeta_b)_0 - \frac{1}{2}(n,0,Z \mid n_b\,l_b\,\zeta_b)_0]$$

$$[1s'\,2s'' \mid nsb] = 24\left(\frac{\zeta'^3\,\zeta''^5}{3\zeta^8}\right)^{1/2} A_a\,A_b\,\delta_{m_b,0}\;[(n-1,0,\zeta_a \mid n_b\,l_b\,\zeta_b)_0 - (n-1,0,Z \mid n_b\,l_b\,\zeta_b)_0 - \frac{2}{3}\zeta\,(n,0,Z \mid n_b\,l_b\,\zeta_b)_0 - \frac{1}{6}\zeta^2\,(n+1,0,Z \mid n_b\,l_b\,\zeta_b)_0]$$

$$[2s'\,2s'' \mid nsb] = 32\left(\frac{\zeta'\,\zeta''}{\zeta^2}\right)^{5/2} A_a\,A_b\,\delta_{m_b,0}\;[(n-1,0,\zeta_a \mid n_b\,l_b\,\zeta_b)_0 - (n-1,0,Z \mid n_b\,l_b\,\zeta_b)_0 - \frac{3}{4}\zeta\,(n,0,Z \mid n_b\,l_b\,\zeta_b)_0 - \frac{1}{4}\zeta^2\,(n+1,0,Z \mid n_b\,l_b\,\zeta_b)_0 - \frac{1}{24}\zeta^3\,(n+2,0,Z \mid n_b\,l_b\,\zeta_b)_0]$$

$$[2p'\,1s'' \mid nsb] = 32\left(\frac{\zeta'^5\,\zeta''^3}{3\zeta^{10}}\right)^{1/2} A_a\,A_b\,\delta_{n_b,m'}[(n-2,1,\zeta_a \mid n_b\,l_b\,\zeta_b)_{m'} - (n-2,1,Z \mid n_b\,l_b\,\zeta_b)_{m'} - \zeta\,(n-1,1,Z \mid n_b\,l_b\,\zeta_b)_{m'} - \frac{1}{2}\zeta^2\,(n,1,Z \mid n_b\,l_b\,\zeta_b)_{m'} - \frac{1}{8}\zeta^3\,(n+1,1,Z \mid n_b\,l_b\,\zeta_b)_{m'}]$$

$$[2p'\,2s'' \mid nsb] = \frac{160}{3}\left(\frac{\zeta'^5\,\zeta''^5}{\zeta^{12}}\right)^{1/2} A_a\,A_b\,\delta_{m_b,m'}\;[(n-2,1,\zeta_a \mid n_b\,l_b\,\zeta_b)_{m'} - (n-2,1,Z \mid n_b\,l_b\,\zeta_b)_{m'} - \zeta\,(n-1,1,Z \mid n_b\,l_b\,\zeta_b)_{m'} - \frac{1}{2}\zeta^2\,(n,1,Z \mid n_b\,l_b\,\zeta_b)_{m'} - \frac{3}{20}\zeta^3\,(n+1,1,Z \mid n_b\,l_b\,\zeta_b)_m - \frac{1}{40}\zeta^4\,(n+2,1,Z \mid n_b\,l_b\,\zeta_b)_{m'}]$$

$$[2p\sigma'\,2p\sigma'' \mid nsb] = [2s'\,2s'' \mid nsb] + \sqrt{\frac{4}{5}}\,\delta_{m_b,0}\,W_0$$

$$[2p\pi'\,2p\sigma'' \mid nsb] = \sqrt{\frac{3}{5}}\,\delta_{m_b,1}\,W_1$$

$$[2p\pi'\,2p\pi'' \mid nsb] = [2s'\,2s'' \mid nsb] - \sqrt{\frac{1}{5}}\,\delta_{m_b,0}\,W_0$$

$$[2p\bar{\pi}'\,2p\pi'' \mid nsb] = \sqrt{\frac{6}{5}}\,\delta_{m_b,2}\,W_2$$

*In this table, $\zeta = \zeta' + \zeta''$, $Z = \zeta + \zeta_a$, $\delta_{ii} = 1$, and $\delta_{ij} = 0$ $(i \neq j)$. The normalization constants $A_a$, $A_b$ are defined in Eq. (3). Where the symbol 2p′ appears without an $m$ value, the formula is valid for all $m'$**.

** $W_m = 192\left(\frac{\zeta'^5\,\zeta''^5}{\zeta^{14}}\right) A_a A_b\,[(n-3,2,\zeta_a \mid n_b\,l_b\,\zeta_b)_m - (n-3,2,Z \mid n_b\,l_b\,\zeta_b)_m - (n-2,2,Z \mid n_b\,l_b\,\zeta_b)_m - \frac{1}{2}\zeta^2\,(n-1,2,Z \mid n_b\,l_b\,\zeta_b)_m - \frac{1}{6}\zeta^3\,(n,2,Z \mid n_b\,l_b\,\zeta_b)_m - \frac{1}{24}\zeta^4\,(n+1,2,Z \mid n_b\,l_b\,\zeta_b)_m - \frac{1}{144}\zeta^5\,(n+2,2,Z \mid n_b\,l_b\,\zeta_b)_m]$

When the expansion for $V\{a'^*a''\}$ is inserted into Eq. (7), its individual terms may under certain conditions produce conditionally convergent overlap integrals. Since $V\{a'^*a''\}$, as a whole, leads to absolutely convergent results, it is clear that the conditional convergence should produce no ambiguity in the final results. One way to avoid difficulty is to exclude the same small volume about Center A from the integration of all terms resulting from the expansion. For principal quantum numbers 1 and 2, the problem only arises for the overlap integrals involving the unconventional orbital — 2d.

## UNCONVENTIONAL OVERLAP INTEGRALS

Overlap integrals of the form given in Eq. (8) with $n < l$ may be evaluated in several different ways. We plan to present elsewhere a fuller discussion of various evaluation methods[7]. One possibility is to use the Barnett-Coulson expansion of $\psi_{n'l'm}(r_b)$ about Center A. The result will be a sum of integrals over the ranges $(0, R)$ and $(R, \infty)$ with, at least in some terms, integrands of the general form $r^{-p}\exp(-\zeta r)$ with $p > 0$. These terms will yield exponential functions which can be evaluated by standard means[8].

A second possibility is to write the unconventional overlap integral in ellipsoidal coordinates, then manipulating the resulting expressions into forms identifiable as previously characterized auxiliary functions, such as the $F_{k,m,n}(\alpha, \beta)$ of Kotani et al.[6].

A third alternative is to use Fourier representation methods to evaluate these integrals. This approach leads to integrals of forms such as

$$\int_0^\infty \frac{\mathrm{d}k\, k^p j_\mu(\mathrm{KR})}{(k^2+\zeta^2)\, q} \tan^{-1}\left(\frac{k}{\zeta'}\right)$$

which can be evaluated by contour integrals methods.

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## SAŽETAK

### Redukcija hibridnih integrala elektronskog odbijanja na integrale prekrivanja

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Pokazano je kako se hibridni integrali međuelektronskog odbijanja na dva središta mogu reducirati na linearnu kombinaciju integrala prekrivanja. Prikazane su eksplicitne formule za redukciju svih hibridnih integrala koji sadržavaju samo orbitale kvantnih brojeva 1 i 2.

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