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ENERGY INTEGRALS INVOLVING BOTH SLATER-TYPE AND GAUSSIAN ATOMIC ORBITALS

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Résumé. — On développe des formules explicites pour évaluer toutes les intégrales d'énergie cinétique et potentielle, pour un seul centre, et pour un ou deux électrons. Ces intégrales se présentent quand on utilise comme fonctions de base à la fois des orbitales du type de Slater et du type Gaussien.

Abstract. — Explicit formulas are developed for the evaluation of all single-center, one and two-electron kinetic and potential energy integrals arising with the use of a basis set consisting of both Slater-type and Gaussian atomic orbitals.

Introduction. — Slater-type and Gaussian atomic orbitals each have certain features that make their use in molecular basis sets advantageous. Slater-type orbitals (STO), whose radially nodeless forms are derived [1] from associated Laguerre functions which in turn are solutions to the Schrödinger equation for the hydrogen atom, are well suited to describe the atomic-like structure of atoms in molecules but give rise to rather difficult multi-center, electron-repulsion integrals. The Gaussian-type orbital (GTO) presents no major obstacle in terms of integral evaluation [2, 3] but is somewhat less suitable for describing molecular electronic structure [4]. The use of both types of orbital combined into a single basis set [5, 6] offers the possibility of incorporating the better features of each scheme into a single calculation.

For the general multi-center energy integrals, each involving both STO's and GTO's in various combinations, the Gaussian transform technique [7] is particularly appropriate. A transformation of the kind,

\[ e^{-\beta r} = \frac{1}{2} \beta \pi^{-1/2} \int_0^\infty ds s^{-3/2} e^{-\beta^{1/4}s^2} e^{-s^2}, \]  

reduces the exponential radial dependence of each of the STO's to Gaussian form so that the configuration space integrations can be easily evaluated. As an example, an exchange integral over four STO's involves four such integral transforms but for each GTO replacing an STO in the original integrand, one of these integrations is eliminated. Thus, augmenting an STO basis set by adding a collection of GTO's, adds various types of mixed STO-GTO and pure GTO integrals which are of increasingly more tractable form.

More direct procedures can be employed to handle the one-center, mixed STO-GTO integrals. An auxiliary function defined to enable the evaluation of overlap integrals provides a key to developing methods of treating the various two-electron integrals. In the following, the one-electron integrals are first examined and then the two-electron integrals are treated.

I. One-electron integrals. — A. DÉFINITIONS.

The normalized Slater-type atomic orbital, \( \chi \), is taken to have the form,

\[ \chi(nlm`\zeta) = N r^{n-1} e^{-\nu} Y_{lm}(\theta \phi), \]  

where \( Y_{lm} \) is a normalized, real spherical harmonic and the radial normalization constant, \( N \), is given by:

\[ N = (2 \zeta)^{n+1/2} [(2 n)!]^{-1/2}. \]  

The normalized Gaussian-type orbital, \( \phi \), is to be written as

\[ \phi(nlm`\zeta) = M r^{n-1} e^{-\beta^2} Y_{lm}(\theta \phi), \]  

where the radial normalization constant, \( M \), is expressed by

\[ M = [2(2 \zeta)^{n+1/2}/\Gamma(n + \frac{1}{2})]^{1/2} \]  

and \( \Gamma \) is the standard Gamma function.

The overlap integral,

\[ S = <\phi(n_1 l_1 m_1 \zeta_1) | \chi(n_2 l_2 m_2 \zeta_2)>, \]  

between a GTO and an STO is to be evaluated from the expression,

\[ S = \delta_{l_1 l_2} \delta_{m_1 m_2} M_1 N_2 F_{l_1 + l_2}(\zeta_1, \zeta_2), \]  

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where in the auxiliary function $F$ is defined:

$$F_k(\alpha, \beta) = \int_0^\infty dr \, r^k \, e^{-\alpha^2 - \beta r}.$$  \hspace{1cm} (8)

In terms of this function, the nuclear attraction integral,

$$V = \chi(n_1 l_1 m_1 \xi_1) - Z/r \, \psi(n_2 l_2 m_2 \xi_2),$$  \hspace{1cm} (9)

can be equated to

$$V = -Z \delta_{l_1 l_2} \delta_{m_1 m_2} N_1 N_2 F_{n_1 + n_2 - 1}(\xi_1, \xi_2).$$  \hspace{1cm} (10)

Of the two equivalent forms possible for the kinetic energy integral, the following is to be preferred:

$$T = \chi(n_1 l_1 m_1 \xi_1) - \frac{1}{2} \nabla^2 \chi(n_2 l_2 m_2 \xi_2) = \frac{1}{2} \xi_2 \xi_2 F_{n_1 + n_2}(\xi_1, \xi_2) - \frac{1}{2} (n_2 + l_2)(n_2 - l_2 - 1) F_{n_1 + n_2 - 2}(\xi_1, \xi_2).$$  \hspace{1cm} (11)

**B. AUXILIARY FUNCTION F.** — The auxiliary function $F$ can be computed from the recursion relation,

$$F_k(\alpha, \beta) = [(k - 1) F_{k-1}(\alpha, \beta) - \beta F_{k-2}(\alpha, \beta)]/2 \alpha,$$  \hspace{1cm} (12)

using the starting values:

$$F_0(\alpha, \beta) = \frac{\pi}{4 \alpha} \frac{e^{\beta^4/4 \alpha}}{\text{erfc} \left(\frac{\beta \alpha}{\sqrt{2}}\right)},$$  \hspace{1cm} (13)

$$F_1(\alpha, \beta) = \left[1 - \beta F_0(\alpha, \beta)\right]/2 \alpha,$$  \hspace{1cm} (14)

where erfc denotes the standard complimentary error function. Since the recursion procedure of eq. (12) involves differencing, a check has been made to determine that region of the parameter space of $\alpha$ and $\beta$ where the function with the highest needed parameter $k$ can be computed with a certain level of accuracy. This has been accomplished through use of a computer program designed to examine the number of significant places that are lost in each step in the recursive procedure for a range of $\alpha$ and $\beta$ from 0.15 to 28.0 and values of $k$ as high as 12. Using double precision arithmetic on an IBM 360/75, it was found that if $\beta^2/4 \alpha$ has a value less than about 13.0, one would lose no more than six significant figures out of the sixteen digit word. Of course, as $\beta^2/4 \alpha$ becomes larger, the differencing errors continue to increase.

Variants of the differential formulas,

$$F_k(\alpha, \beta) = -\frac{\partial}{\partial \alpha} F_{k-1}(\alpha, \beta),$$  \hspace{1cm} (15a)

$$F_k(\alpha, \beta) = -\frac{\partial}{\partial \beta} F_{k-1}(\alpha, \beta),$$  \hspace{1cm} (15b)

have proven to be useful within the context of two-electron integral formulations.

**II. Two-electron integrals.** — **A. PRELIMINARY.** — The electron repulsion integral, $E$, between electrons $p$ and $q$,

$$E = \psi_1(p) \psi_2(p) | \rho^{-1} \psi_1(q) \psi_2(q) >,$$  \hspace{1cm} (16)

where $\psi_i$ denotes either a GTO ($\phi$) or an STO ($\chi$) with corresponding orbital parameters having subscripts $i$, allows immediate integration over the four angular variables leaving the form:

$$E = \left\{ \prod_{i=1}^{4} K_i \right\} \sum_{\ell_A \ell_B} \sum_{m_{\ell_A m_B}} \delta_{\ell_A \ell_B} \delta_{m_{\ell_A m_B}} \left[ \sum_{j=1}^{4} (2 \ell_j + 1)^{\frac{1}{2}} \times \right.\left. q_{\ell_A m_A} (l_1 m_1 l_2 m_2) q_{\ell_B m_B} (l_3 m_3 l_4 m_4) R_{\ell_A \ell_B} \right],$$  \hspace{1cm} (17)

where $K_i$ is the appropriate normalization constant of eq. (3) or (5), the functions $q_{\ell A m_A}$ and the restrictions on the summation indices $l_A m_A$ and $l_B m_B$ and their relationships to $l_1 m_1 l_2 m_2$ and $l_3 m_3 l_4 m_4$ have been discussed previously [8] and the two radial integrals are embodied in the function $R_{\ell A \ell B}$, which is to be treated in detail below. $R_{\ell A \ell B}$ has the following six major designations corresponding to the six integral types shown:

$$R_1 \sim \psi_1 \psi_2 \| x_3 x_4 >,$$  \hspace{1cm} (R_1)

$$R_2 \sim \psi_1 \psi_2 \| x_3 x_4 >,$$  \hspace{1cm} (R_2)

$$R_3 \sim \psi_1 \psi_2 \| x_3 x_4 >,$$  \hspace{1cm} (R_3)

$$R_4 \sim \psi_1 \psi_2 \| x_3 x_4 >,$$  \hspace{1cm} (R_4)

$$R_5 \sim \psi_1 \psi_2 \| x_3 x_4 >,$$  \hspace{1cm} (R_5)

$$R_6 \sim \psi_1 \psi_2 \| x_3 x_4 >,$$  \hspace{1cm} (R_6)

where $\phi$ and $\chi$ correspond to GTO's and STO's, respectively. Hereafter, the following symbols shall be used:

$$L = l_A = l_B, \quad M = m_A = m_B,$$  \hspace{1cm} (18)

$$n_A = n_1 + n_2, \quad n_B = n_3 + n_4, \quad n = n_A + n_B,$$  \hspace{1cm} (19)

$$\zeta_A = \zeta_1 + \zeta_2, \quad \zeta_B = \zeta_3 + \zeta_4, \quad \zeta = \zeta_A + \zeta_B.$$  \hspace{1cm} (20)

**B. INTEGRAL TYPE 1.** — The radial integrations corresponding to $R_1$,

$$R_1 = \int_0^\infty dr \, r^\alpha \exp(-\zeta_A r) \int_1^\infty dt \, t^{\zeta_A - L - 1} \exp(-\zeta_B r) \times \int_1^\infty dt \, t^{\zeta_B - L - 1} \exp(-\zeta_A r),$$  \hspace{1cm} (21)

are easily performed analytically and the results appear here only for completeness:

$$R_1 = (n_A - L - 1)! \frac{\zeta_A^{n_A - L - 1} \zeta_B^{n_B - n_A}}{n_A - L + 1} \times \sum_{i=0}^{n_A - L - 1} (n_B + L + i)! \frac{(\zeta_A (\zeta_A)^{L + i})}{i!} + (n_B - L - 1)! \frac{\zeta_B^{n_B - n_A}}{n_B - L + 1} \times \sum_{j=0}^{n_A - L - 1} (n_A + L + j)! \frac{(\zeta_B (\zeta_B)^{L + j})}{j!}.$$  \hspace{1cm} (22)
C. INTEGRAL TYPE 2. — The procedure required to analytically integrate type 2, 
\[ R_2 = \int_0^1 dt t^{n_A + L} F_n(\zeta_1, \zeta_2 + \zeta_B t) + \]
\[ + \int_1^\infty dt t^{n_A - 1} F_n(\zeta_1, \zeta_2 + \zeta_B t), \]  
consists of repeated partial integration using eq. (15b) for the first term and inversion of the order of the \( t \)-integration with that embedded in the function \( F \) for the second term. After grouping the various summations, one has the result:  
\[ R_2 = (n_B + L)! \zeta_B^{-n_B - L - 1} F_{n_B - L - 1}(\zeta_1, \zeta_2) - \]
\[ - \sum_{i=1}^{n_B - L - 1} \frac{(n_B + L)!}{(n_B + L - i)!} \frac{(n_B - L - 1)!}{(n_B - L - 1 - i)!} \]
\[ \times F_{n_B - i}(\zeta_1, \zeta_2 + \zeta_B) \]
\[ \times \frac{\sum_{j=n_B - L}^n \left( (n_B + L)! \right) / (n_B + L - j)! F_{n_B - j}(\zeta_1, \zeta_2 + \zeta_B) }{r_B^{n_B + L + j}}. \]  
(D) INTEGRAL TYPE 3. — The third type of integral, 
\[ R_3 = \int_0^1 dt t^{n_A + L} F_n(\zeta_1 + \zeta_3 t^2, \zeta_2 + \zeta_4 t) + \]
\[ + \int_1^\infty dt t^{n_A + L} F_n(\zeta_1 t^2 + \zeta_3, \zeta_2 t + \zeta_4), \]  
is disposed of by the use of Gaussian numerical integrations [9]:  
\[ R_3 = \sum_{i=1}^N w_i x_i^{n_B + L} F_n(\zeta_1 + \zeta_3 x_i^2, \zeta_2 + \zeta_4 x_i) + \]
\[ + \sum_{j=1}^N w_j x_j^{n_B + L} F_n(\zeta_1 x_j^2 + \zeta_3, \zeta_2 x_j + \zeta_4), \]  
where 
\[ w_k = \frac{1}{2} \omega_k, \quad x_k = \frac{1}{2} (\eta_k + 1), \]  
and \( \eta_k \) is the \( k \)-th zero of the Legendre functions, \( P_N(\eta) \), and the corresponding weights are given by:  
\[ \omega_k = \frac{2}{(1 - \eta_k)^2} \left( P'_N(\eta_k) \right)^2. \]  
Choosing \( N \) to give at least twelfth-order integrations in eq. (26) produces integrals having at least eight decimal place accuracy over the range of orbital parameters studied here.  
E. INTEGRAL TYPE 4. — Here, two cases arise depending on the even-odd parity of the parameters \( n_A + L \). The situation in which \( n_A + L \) is an even integer is designated case A and the following expression is integrated:  
\[ R_{4A} = \int_1^\infty dt t^{n_A - L - 1} F_n(\zeta_A t^2, \zeta_B) + \]
\[ + \int_1^\infty dt t^{n_B - L - 1} F_n(\zeta_A, \zeta_B t). \]  
Using the relation in eq. (15a), the first term can be resolved by partial integrations while the second term can be integrated by parts after inverting the order of the \( t \)-integration with that embedded in \( F \) to give:  
\[ R_{4A} = \frac{1}{2} \int \left( \frac{n_A - L}{2} \right)^{-(n_A - L)/2} \]
\[ \times \epsilon^{-((n_A - L)/2)} \zeta_A^{(n_A - L)/2} \]
\[ \times \sum_{j=0}^{n_A - L - 1} \zeta_A^{j} F_{n_B + L + 2j}(\zeta_A, \zeta_B) \]
\[ \times \sum_{j=0}^{n_B - L - 1} \zeta_B^{j} F_{n_B + L + 2j}(\zeta_A, \zeta_B). \]  
If \( n_A + L \) is an odd integer, case B has the form:  
\[ R_{4B} = \int_0^1 dt t^{n_B + L} F_n(\zeta_A, \zeta_B t) + \]
\[ + \int_1^\infty dt t^{n_B - L - 1} F_n(\zeta_A, \zeta_B t). \]  
Both terms can be integrated by parts after interchanging the order of integrations. After combining summations, \( R_{4B} \) is obtained from:  
\[ R_{4B} = \frac{1}{2} (n_B + L)! \int \left( \frac{n_A - L}{2} \right)^{-(n_A - L)/2} \epsilon^{-(n_A + L + 1)} \]
\[ - \sum_{j=1}^{n_B - L - 1} \left( (n_B + L)! / (n_B + L - i)! \right) \]
\[ \times \epsilon^{-((n_B + L)/2)} \zeta_A^{j} F_{n_A + L + 2j}(\zeta_A, \zeta_B) \]
\[ \times \epsilon^{-((n_B + L)/2)} \zeta_B^{j} F_{n_B + L + 2j}(\zeta_A, \zeta_B). \]  
Eq. (32) could be used regardless of the parity of \( n_A + L \); however, eq. (30) is to be preferred when applicable since it involves only the addition of positive terms and is therefore inherently more capable of numerical accuracy.  
F. INTEGRAL TYPE 5. — The parity of \( n_A + L \) gives rise to two cases for this type of integral. When \( n_A + L \) is even, case A is used:  
\[ R_{5A} = \int_0^1 dt t^{n_A + L - 2} F_n(\zeta_A t^2 + \zeta_3, \zeta_4) + \]
\[ + \int_1^\infty dt t^{n_B - L - 1} F_n(\zeta_A t^2 + \zeta_3, \zeta_4). \]
The first term is integrated numerically as in Type $R_3$ and the second term is integrated by parts using eq. (15a) to give:

$$R_{SA} = \sum_{i} w_i x_i^{n_A+L} F_n(\zeta A x_i^2 + \zeta_3, \zeta_4) + \frac{1}{2} \Gamma \left( \frac{n_A - L}{2} \right) \varsigma_\Lambda^{-r(n_A-L)/2} \times \sum_{j=0}^{(n_A-L)/2} \left( \zeta A F_{mn+L+2j} \left( \frac{\zeta A + \zeta_3, \zeta_4}{j!} \right) \right),$$

where the weights, $w_i$, and points, $x_i$, are defined in eq. (27). Case B arises when $n_A + L$ is an odd integer:

$$R_{SB} = \int_0^1 dt t^{n_A+L} F_n(\zeta A t^2 + \zeta_3, \zeta_4) + \int_0^1 dt t^{n_B+L} F_n(\zeta A + \zeta_3 t^2, \zeta_4 t).$$

Now eq. (15a) enables partial integration of the first term and numerical integrations handle the second term:

$$R_{SB} = \frac{1}{2} \Gamma \left( \frac{n_A + L + 1}{2} \right) \varsigma_\Lambda^{-r(n_A+L+1)/2} \left[ F_{mn-L-1}(\zeta, \zeta_4) - \sum_{i=0}^{(n_A+L-1)/2} \zeta A F_{mn-L-1-2i} \left( \frac{\zeta A + \zeta_3, \zeta_4}{i!} \right) \right]$$

$$+ \sum_{j=0}^{N} w_j x_j^{n_A+L} F_n(\zeta A + \zeta_3 x_j^2, \zeta_4 x_j).$$

In both cases, if the order $N$ of the numerical integrations is taken to be at least twelve, the accuracy of the integral is assured to about eight decimals.

**G. INTEGRAL TYPE 6.** — The pure GTO integrals split into three cases depending on the even-odd parity of both $n_A + L$ and $n_B + L$. Case A is the most familiar situation where both $n_A + L$ and $n_B + L$ are even integers:

$$R_{6A} = \int_0^\infty dt t^{n_A+L-1} \int_0^\infty \int_0^\infty dr^m \exp[-(\zeta A t^2 + \zeta B r^2)] + \int_0^\infty t^{n_B+L-1} \int_0^\infty dr^m \exp[-(\zeta A t^2 + \zeta B r^2)] + \int_0^\infty dr^m \exp[-(\zeta A t^2 + \zeta B r^2)].$$

The most tractable manner of handling case C, where $n_A + L$ is odd and $n_B + L$ is even, is to define $R_{6C}$ as follows:

$$R_{6C} = \int_0^\infty dt t^{n_B+L} \int_0^\infty \int_0^\infty dr^m \exp[-(\zeta A t^2 + \zeta B r^2)] + \int_0^\infty dr^m \exp[-(\zeta A t^2 + \zeta B r^2)] + \int_0^\infty dr^m \exp[-(\zeta A t^2 + \zeta B r^2)].$$
Although the second term can again be integrated by parts as in case A, the first term is most easily handled by performing the r-integration analytically and using numerical integration for the remaining t-integration:

\[
R_{6C} = \frac{1}{2} \int \left( \frac{n+1}{2} \right)^N \frac{\sum_{i} w_i x_i^{n_a+2}(\zeta_A + \zeta_B x_i^2)^{-(n+1)/2}}{\left( \frac{n_B - L}{2} \right)^{\zeta_B - (n_B - L)/2} \zeta^{-(n_A + L + 1)/2} \sum_{j=0}^{(n_A - L - 2)/2} \left( \frac{j}{\zeta} \right) \frac{N_A + L + 1 + 2j}{2}} \, ,
\]

(42)

where \( w_i \) and \( x_i \) are defined in eq. (27). Only a very low integration order, \( N \), is required if \( \zeta_B \) is smaller than \( \zeta_A \) but in the most difficult situations, where \( \zeta_B \) is much larger than \( \zeta_A \), an order as high as sixteen might be required to achieve eight decimal accuracy.

Only case A arises when the orbitals are restricted to the classes, 1 s, 3 s, ..., 1 2 p, 4 p, ..., 3 d, etc. The other two cases enter only when the orbitals 2 s, 4 s, ..., 3 p, 5 p, ..., 4 d, etc. are introduced.

H. DISCUSSION. — The auxiliary function \( F_\beta(\alpha, \beta) \) defined in eq. (8) provides the means of transforming the mixed STO-GTO two-electron integrals into tractable forms for computer evaluation. Since the computed accuracy of \( F \) is greatest when \( \beta^2/4 \alpha \) is small, the choice of final expressions is always governed by this criteria.

A number of the integral types allow for more than one possible integration scheme and moreover, aside from the labelling of orbital parameters, many of the final expressions are quite similar in form. Thus, certain blocks of computer code can be used for the partial evaluation of more than one integral type. Also, an alternative form of a given integral can be evaluated for checking purposes by using appropriate blocks of computer code written for some other integral type. In this way, cross checks are provided for the formulations and their subsequent translation for the computer.

Although the technique of transforming exponentials into Gaussian form through eq. (1) might prove to be the most useful approach to the multi-center integrals, its application in the single center case would be cumbersome compared to the present schemes; in particular, this is true since one would plan to perform the transform integrations of eq. (1) numerically. The development of multi-center procedures would be facilitated by having available independent expressions for special situations such as those presented here for the limiting case where all of the orbital centers coalesce.

For calculations of atomic wavefunctions, the Slater-type orbital is the optimal choice of basis function since the STO's give better characterizations of atomic properties than GTO's and the integrals that arise are the easiest to evaluate. For molecules, a combination of STO's and GTO's might prove to give the best compromise between an accurate description of molecular properties and the least time consuming integral evaluation and data handling processes. In this case, it would be desirable to have available the most direct means of processing each of the types of integrals involved including the various single-center integrals examined here. The formulas given are particularly well suited to automatic computer calculation and have been used to perform a preliminary study of SCF wavefunctions for several small atoms using basis sets composed of both Gaussian and Slater-type atomic orbitals [5].

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References

[8] Silver (D. M.) and Ruedenberg (K.), J. Chem. Phys., 1968, 49, 4306; eq. (11) to (14) and table I.