Brief Reports

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Analytical evaluation of multicenter molecular integrals over Slater-type orbitals using expanded Löwdin alpha functions

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The Löwdin alpha functions, which are the functions associated with the spherical-harmonic expansion of a displaced Slater-type orbital, are expressed using C matrices to represent the polynomials in terms of the displacement distance a and the radial distance r. These polynomials are multiplied by the sum and difference of exponentials. The expansion of the exponentials leads to the use of E and F matrices. By keeping only the r variable identifiable, further simplifications of the alpha functions are possible, which makes for easy programming of all multicenter integrals. Also, no singularities appear in these developments. Everything is demonstrated by using 1s orbitals as prototypes.

I. INTRODUCTION

The author has shown[1] how an infinite series of formulas may be generated by computer algebra to represent the potential produced by the product of two separated Slater-type orbitals (STO's); also, a triple infinite set of formulas may be generated to represent the value of a four-center integral.[2] These procedures can be generalized for all STO's. However, the programming effort necessary for carrying out this task presents a formidable obstacle. In addition, it appears that all formulas so developed must be expanded in a Taylor series using integer arithmetic for formula evaluation for certain ranges of parameter values.[3]

The advantages of expanding the alpha function using an E-matrix representation were demonstrated in a paper[4] on the charge density about the origin. (Several E matrices are shown.) An F matrix is necessary for $r > a$, but for s orbitals this matrix is the transpose of the E matrix. These matrices are generated using integer arithmetic and are stored; they are considered to be part of the data base when using STO's. It was also shown that a further simplification of the alpha function is possible if all parameters except the radial variable r are absorbed into appropriate coefficients leading to one-dimensional matrices or vectors $Y_l(j)$ and $Z_l(j)$. Another advantage of the expanded alpha function is that the troublesome factor $\zeta_a - \zeta_b$, which often leads to singularities, does not appear in the course of developments.

To demonstrate the feasibility of our method, values for an overlap, a three-center nuclear-attraction integral (potential), an exchange integral, and a four-center integral are produced. It should be clear that the 1s orbital is an adequate prototype for any orbital because every STO is characterized by a C matrix,[5] and in the integrals the radial and angular parts always separate.

II. E AND F MATRICES

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 a along the z axis it may be expanded in spherical harmonics or Legendre polynomials in the original coordinate system as

$$\chi = \frac{\zeta^{3/2}}{\sqrt{\pi}} \sum_{l=0}^{\infty} \alpha_l P_l(\cos\vartheta) ,$$

where

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

and

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

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. It is also expedient to expand $e^{\zeta a}$ and $e^{-\zeta a}$ to arrive at an F matrix, which for s orbitals is the transpose of the E matrix. In this work, by trial and error, we found that 36 terms in our expansions are sufficient

($J_{\max}=36$), and $l_{\max}=24$ is used.

Thus

$$\alpha_l=\begin{cases}\dfrac{e^{-\zeta a}}{(\zeta a)^{l+1}}\displaystyle\sum_{i=0}^{l+1}\sum_{j=l}^{J_{\max}}E_l(i,j)(\zeta a)^i(\zeta r)^j, & r<a \quad (2)\\ \dfrac{e^{-\zeta r}}{(\zeta r)^{l+1}}\displaystyle\sum_{j=0}^{l+1}\sum_{i=l}^{36}F_l(i,j)(\zeta a)^i(\zeta r)^j, & r>a\ . \quad (3)\end{cases}$$

A further simplification results by just keeping r intact,

$$Y_l(j)=\xi^j\sum_{i=0}^{l+1}E_l(i,j)(\zeta a)^{i-l-1}e^{-\zeta a}\ , \quad (4)$$

$$Z_l(j)=\xi^{j-l-1}\sum_{i=l}^{36}F_l(i,j)(\zeta a)^i\ , \quad (5)$$

leading to

$$\alpha_l=\begin{cases}\displaystyle\sum_{j=l}^{J_{\max}}Y_l(j)r^j, & r<a \quad (6)\\ e^{-\zeta r}\displaystyle\sum_{j=0}^{l+1}Z_l(j)r^{j-l-1}, & r>a\ . \quad (7)\end{cases}$$

With these simplifications the programming of multicenter integrals becomes manageable, and singularities do not appear.

III. EXAMPLES OF VARIOUS MULTICENTER MOLECULAR INTEGRALS

A. Overlap

The simplest multicenter integral is the overlap

$$S=\int\chi_a(1)\chi_b(1)dv_1\ . \quad (8)$$

Locating χ_a at the origin and χ_b at (0,0,a) we have

$$\chi_a=\frac{\xi_a^{3/2}}{\sqrt{\pi}}e^{-\zeta a r}\text{ and }\chi_b=\frac{\xi_b^{3/2}}{\sqrt{\pi}}\sum_l\alpha_l P_l(\cos\vartheta)\ .$$

Using orthogonality of the Legendre polynomials,

$$S=4(\zeta_a\zeta_b)^{3/2}\left[\sum_{j=l}^{36}Y_0(j)\int_0^a dr\,e^{-\zeta_a r}r^j+\sum_{j=0}^{l+1}Z_0(j)\int_a^\infty dr\,e^{-(\zeta_a+\zeta_b)r}r^{j+1}\right]\ . \quad (9)$$

With $a=2$, $\zeta_a=\zeta_b=1$, we get 10-digit accuracy, as confirmed by the overlap formula $S=e^{-a}(1+a+a^2/3)$.

B. Three-center nuclear-attraction integral (electrostatic potential)

These two integrals differ only by a constant. Working with the potential, we seek the potential at the point (r_2,ϑ_2) due to the charge density given as the product of two 1s orbitals, χ_a located at the origin and χ_b at (0,0,a), $a=2$, $\zeta_a=\zeta_b=1$. Hence,

$$V(r_2,\vartheta_2)=\int dv_1\,\chi_a(1)\chi_b(1)/r_{12}\ . \quad (10)$$

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

$$\frac{1}{r_{12}}=4\pi\sum_{\lambda=0}^{\infty}\sum_{m=-\lambda}^{\lambda}(2\lambda+1)^{-1}\frac{r_<^\lambda}{r_>^{\lambda+1}}\times Y_\lambda^{m*}(\vartheta_1,\varphi_1)Y^m(\vartheta_2,\varphi_2)\ , \quad (11)$$

where $r_>$ is the larger of r_1 and r_2 and $r_<$ is the smaller. Using orthogonality of the angular functions we obtain

$$V(r_2,\vartheta_2)=\sum_l V_l(r_2)P_l(\cos\vartheta_2)\ ,$$

with

$$V_l(r_2)=\frac{4(\zeta_a\zeta_b)^{3/2}}{2l+1}\int_0^\infty dr_1\,r_1^2e^{-\zeta_a r_1}\frac{r_<^l}{r_>^{l+1}}\alpha_l(r)\ . \quad (12)$$

Explicitly,

$$V_l(r_2)=\frac{4(\zeta_a\zeta_b)^{3/2}}{2l+1}\left[\frac{1}{r_2^{l+1}}\sum_{j=l}^{J_{\max}}Y_l(j)\int_0^{r_2}dr_1\,r_1^{l+j+2}e^{-\zeta_a r_1}+r_2^l\sum_{j=l}^{J_{\max}}Y_l(j)\int_{r_2}^a dr_1\,r_1^{j+1-l}e^{-\zeta_a r_1}\right.$$
$$\left.+r_2^l\sum_{j=0}^{l+1}Z_l(j)\int_a^\infty dr_1\,r_1^{j-2l}e^{-(\zeta_a+\zeta_b)r_1}\right],\quad r_2<a \quad (13)$$

$$V_l(r_2)=\frac{4(\zeta_a\zeta_b)^{3/2}}{2l+1}\left[\frac{1}{r_2^{l+1}}\sum_{j=l}^{J_{\max}}Y_l(j)\int_0^a dr_1\,r_1^{l+j+2}e^{-\zeta_a r_1}+\frac{1}{r_2^{l+1}}\sum_{j=0}^{l+1}Z_l(j)\int_a^{r_2}dr_1\,r_2^{j+1}e^{-(\zeta_a+\zeta_b)r_1}\right.$$
$$\left.+r_2^l\sum_{j=0}^{l+1}Z_l(j)\int_{r_2}^\infty dr_1\,r_1^{j-2l}e^{-(\zeta_a+\zeta_b)r_1}\right],\quad r_2>a\ . \quad (14)$$

To obtain numerical results we must change the integrals to summations by use of three formulas (the first one due to Silverstone[6]):

$$\int_0^a dr\, r^n e^{-wr} = a^{n+1} \sum_{k=0}^{\infty} \frac{(-wa)^k}{k!(n+k+1)} ,$$

$$\int x^n e^{-wx} dx = -e^{-wx} \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{x^{n-k}}{w^{k+1}}, \quad n \geq 0$$

$$\int \frac{e^{-wx}}{x^n} dx = -e^{-wx} \sum_{k=1}^{n-1} \frac{(n-k-1)!}{(n-1)!} \frac{(-w)^{k-1}}{x^{n-k}} + \frac{(-w)^{n-1}}{(n-1)!} \mathrm{Ei}(-wx), \quad n > 0 .$$

For an example, we found the potential at the point (0,0,0.5) due to 1s orbitals ($\zeta = 1$) at the origin and at the point (0,0,2) to have the same 10-digit accuracy as in the formula case.[1]

C. Exchange integral

For the two-center exchange integral we place the orbitals $\chi_a(1)$ and $\chi_b(1)$, the product of which represents the electron density of electron "1," at the origin and at the point (0,0,a), respectively ($a = 2$, $\zeta = 1$). The orbitals $\chi_c(2)$ and $\chi_d(2)$ for electron "2" are placed in corresponding positions. We write this two-electron repulsion integral as

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

Performing the first integral we have the potential as given in Sec. III B. Making the substitutions and using orthogonality we obtain

$$K = \sum_l K_l ,$$

with

$$K_l = \frac{4}{2l+1} \int_0^{\infty} dr\, r^2 V_l \alpha_l e^{-r} . \tag{16}$$

To carry out this integration we must find V_l as a function of r (dropping the subscript 2). Let us consider the case $r_2 < a$. In the second term of Eq. (13), we replace an integral,

$$\int_{r_2}^a dr_1\, r_1^{j+1-l} e^{-\zeta_a r_1} = \int_0^a dr_1\, r_1^{j+1-l} e^{-\zeta_a r_1} - \int_0^{r_2} dr\, r_1^{j+1-l} e^{-\zeta_a r_1} .$$

Expanding the Silverstone integrals that are functions of r into 37 terms we get

$$V_l(r) = \frac{4}{2l+1} \left[\sum_{j=l}^{36} \sum_{k=0}^{36} \frac{Y_l(j)(-1)^k}{k!(l+j+k+3)} r^{2+j+k} + r^l \sum_{j=l}^{36} Y_l(j) \int_0^a dr\, r^{j+1-l} e^{-r} + \sum_{j=l}^{36} \sum_{k=0}^{36} \frac{Y_l(j)(-1)^k r^{2+j+k}}{k!(-l+j+k+2)} + r^l \sum_{j=l}^{36} Z_l(j) \int_a^{\infty} dr\, r^{j-2l} e^{-2r} \right], \quad r < a . \tag{17}$$

Now we use an in-house version of computer algebra to sort, add, and group terms with equal r exponents. This results in a simple power series. The $r > a$ case is somewhat more complicated. We find terms $1/r^{l+1}$, $r^l \mathrm{Ei}(-2r)$, e^{-2r}/r^n, and $r^n e^{-2r}$, where n is an integer, multiplied by polynomials.

To get the value of the exchange integral we must integrate over the charge density $\chi_c \chi_d$. This is a straightforward procedure, but we do need another integral,

$$\int_a^{\infty} dr\, e^{-2r} \mathrm{Ei}(-2r) r^n = \sum_{k=0}^{n} \frac{n!}{(n-k)!} \frac{1}{2^{k+1}} \times \left[a^{n-k} e^{-2a} \mathrm{Ei}(-2a) + \int_a^{\infty} dr\, e^{-4r} r^{n-k-1} \right] . \tag{18}$$

In our example, we get 9-decimal-digit accuracy using 5s of central-processing-unit (CPU) time; the accuracy is confirmed by using the Sugiura formula.[7]

D. Four-center integral

A completely formula approach has been given for this integral.[2] Orbitals $\chi_a(1)$ and $\chi_b(1)$ are again located at the origin and at (0,0,a), $a = 1$, $\zeta = 1$. Orbital $\chi_c(2)$ for electron "2" is at (a,γ,Γ) in spherical coordinates (r,ϑ,φ) and $\chi_d(2)$ is at (a,δ,Δ). Using the Legendre addition theorem we may write

$$\chi_c = 2 \sum_{m=0}^{\infty} \sum_{\mu=-m}^{m} \frac{(4\pi)^{1/2}}{2m+1} \alpha_m Y_m^{\mu}(\Gamma,\gamma) Y_m^{\mu}(\vartheta,\varphi)^* \tag{19}$$

and

$$\chi_d = 2 \sum_{n=0}^{\infty} \sum_{\nu=-n}^{n} \frac{(4\pi)^{1/2}}{2n+1} \alpha_n Y_n^{\nu}(\Delta,\delta)^* Y_n^{\nu}(\vartheta,\varphi) . \tag{20}$$

Making the proper substitutions for this electron repulsion integral we may write the resulting integral as the sum of the product of radial functions multiplied by angular functions,

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

where

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

and

$$A_{lmn} = \frac{(4\pi)^{3/2}}{(2l+1)^{1/2}} \sum_{\mu} \sum_{\nu} Y_m^{\mu}(\Gamma,\gamma)^* \times Y_n^{\nu}(\Delta,\delta)\langle m,\mu \mid l,0 \mid n,\nu\rangle \ , \tag{21}$$

where the angular bracket represents Gaunt coefficients. The evaluation of I_{lmn} is quite similar to that of K_l, since we use the same V_l. However, an additional integral is required.[2]

We take l from 0 to 9 and m and n to a maximum of 20 with $m+n \leq 20$. We compared the hybrid integral[8] I_h with I when $\gamma=\Gamma=\delta=\Delta=0$. We obtained 6-digit accuracy ($I_h = 0.507\,045$).

IV. CONCLUSION

Computations have shown that the analytic method presented here in which only the identity of the r variable is maintained is as accurate as the complete formula method; in addition the programming is much simpler and easier to generalize. Also the troublesome $\zeta_a - \zeta_b$ reciprocal does not appear, and therefore only one expression is necessary for all parameter values, and the computations appear to be completely stable. We believe that the clarity of the method presented here will lead to many improvements, the most obvious being the inclusion of look-up tables and vectorization.

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