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Computer-generated formulas for three-center nuclear-attraction integrals (electrostatic potential) for Slater-type orbitals

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The computer-assisted C-matrix, Löwdin-alpha-function, single-center expansion method in spherical harmonics has been applied to the three-center nuclear-attraction integral (potential due to the product of separated Slater-type orbitals). Exact formulas are produced for 13 terms of an infinite series that permits evaluation to ten decimal digits of an example using $1s$ orbitals.

I. INTRODUCTION

Efforts continue to be made to facilitate the use of Slater-type orbitals (STO's), or, more generally speaking, exponential-type orbitals in problems of *ab initio* quantum chemistry and molecular physics.[1,2] Here, we apply our method of computer-assisted single-center expansion in spherical harmonics to the difficult case of the three-center nuclear-attraction integral, which is the same as the problem of finding the potential due to a charge distribution that is given by the product of separated STO's. Earlier, partial results had been achieved for this integral by the use of elliptical coordinates[3] and transform methods.[4] We will make numerical comparisons with results recently obtained by Trivedi and Steinborn[5] in which a transform method using the Steinborn B function is employed.

The initial work in single-center expansion methods was carried out by Coolidge.[6] A suggestive formulation of this method with the use of coefficient matrices and the α-function notation was introduced by Löwdin.[7] An essential simplification and the use of a "C matrix" was given to the closed form of the α function by Jones and Weatherford[8] after its presentation by Sharma.[9] Thus far, computer-generated formulas have been produced for two-center overlap,[10,11] Coulomb,[12] hybrid,[13] and exchange integrals;[14] some three-center Coulomb-type formulas also have been generated.[15]

II. DERIVATION OF THE POTENTIAL

We place a STO, χ_a, at the origin of our coordinate system (r,θ,ϕ) to represent one of the factors of the expression for the electron density of electron 1:

$$\chi_a(1)=A_a r_1^{N_a-1}e^{-\zeta_a r_1}Y_{L_a}^{M_a}(\theta_1,\phi_1)\ . \tag{1}$$

$A_a=(2\zeta_a)^{N_a+1/2}[(2N_a)!]^{-1/2}$ is the normalization factor; N_a, L_a, and M_a are the quantum numbers of the orbital; and ζ_a is the screening constant. We place the other factor χ_b for the density of electron 1 in its local coordinate system (R,Θ,ϕ) that has been translated a distance a along the z axis:

$$\chi_b(1)=A_b R_1^{N_b-1}e^{-\zeta_b R_1}Y_{L_b}^{M_b}(\Theta_1,\phi_1)\ . \tag{2}$$

In terms of the original coordinate system, the expansion in spherical harmonics is as follows:[8]

$$\chi_b(1)=\frac{A_b}{\zeta_b^{N_b-1}}\left[\frac{(2L_b+1)(L_b+M_b)!}{4\pi(L_b-M_b)!}\right]^{1/2}\sum_{l=M_b}^{\infty}\left[\frac{4\pi(l+M_b)!}{(2l+1)(l-M_b)!}\right]^{1/2}(-1)^{M_b}\alpha_l^{N_bL_bM_b}(\zeta_b a,\zeta_b r_1)Y_l^{M_b}(\theta_1,\phi_1)\ ,$$

where

$$\alpha_l^{N_bL_bM_b}(\zeta_b a,\zeta_b r_1)=\frac{(2l+1)(l-M_b)!}{2(l+M_b)!}\sum_{i=0}^{N_b+L_b+l}\sum_{j=0}^{N_b+l}C_l^{N_bL_bM_b}(i,j)H_{ij}(\zeta_b a,\zeta_b r_1)(\zeta_b a)^{i-L_b-l-1}(\zeta_b r_1)^{j-l-1}$$

and

$$H_{ij}(\zeta_b a,\zeta_b r_1)=\begin{cases}e^{-\zeta_b a}[(-1)^j e^{\zeta_b r_1}-e^{-\zeta_b r_1}]\ , & r_1<a\\ e^{-\zeta_b r_1}[(-1)^i e^{\zeta_b a}-e^{-\zeta_b a}]\ , & r_1>a\ .\end{cases} \tag{3}$$

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For completeness, we write an expression that can be used to determine the C-matrix elements:

$$\sum_{i=0}^{N+L+l}\sum_{j=0}^{N+l} C_l^{NLM}(i,j)\alpha^i r^j = \sum_{P=0}^{[(L+M)/2]}\sum_{q=0}^{L+M-2p}\sum_{v=0}^{L+M-2p-q}\sum_{p'=0}^{[(l-M)/2]}\sum_{q'=0}^{l-M-2p'}\sum_{v'=0}^{l-M-2p'-q}\sum_{k=0}^{t}\sum_{k'=0}^{t-k}\frac{\alpha^x}{4^{L+l-p-p'}}$$
$$\times\frac{r^y(-1)^{v+q'+p+p'}(2L-2p)!(2l-2p')!}{(L-p)!p!p'!q!q'!v!v'!(L+M-2p-q-v)!}\frac{(N-L+2p+2q+2q')![(N-L-2p+2q+2q'-k-k')!]^{-1}}{(l-p')!(L-M-2p'-q'-v')!k!}, \quad (4)$$

where

$$x=N+L+2l-2p'-2v'-2v-k-k',$$

$$y=2(p'+v+v')+k',$$

and

$$t=N-L+2p+2q+2q'.$$

The symbols [ ] mean reduce to integer. [By multiplying by $(-1)^{l+M}$ it is possible to have all positive elements.]

We seek the potential at an arbitrary point (r_2,θ_2,ϕ_2) due to the charge distribution $\chi_a(1)\chi_b(1)$. Thus

$$V(\vec{r}_2)=\int dv_1\frac{\chi_a\chi_b}{r_{12}}. \quad (5)$$

The Laplace expansion of $1/r_{12}$ is

$$\frac{1}{r_{12}}=4\pi\sum_{\lambda=0}^{\infty}\sum_{m=-\lambda}^{\lambda}(2\lambda+1)^{-1}r_<^{\lambda}/r_>^{\lambda+1}Y_\lambda^{m*}(\theta_1,\phi_1)Y_\lambda^m(\theta_2,\phi_2), \quad (6)$$

where $r_<$ is to be replaced by r_1 or r_2, depending on which is smaller, and $r_>$ is to be replaced by r_1 or r_2, depending on which is larger. By making the appropriate substitutions in Eq. (5), the radial and angular variables separate and we get

$$V(\vec{r}_2)=k_0\sum_{\lambda}\sum_{m}Y_\lambda^m(\theta_2,\phi_2)\sum_{l}(2\lambda-1)^{-1}\left[\frac{(l+M_b)!}{(2l+1)(l-M_b)!}\right]^{1/2}$$
$$\times\int r_1^2dr_1r_1^{N_a-1}e^{-\zeta_a r_1}\alpha_l^{N_bL_bM_b}(\zeta_b\alpha,\zeta_b r_1)\frac{r_<^{\lambda}}{r_>^{\lambda+1}}\langle\lambda,m\mid L_aM_a\mid l,M_b\rangle, \quad (7)$$

where

$$k_0=\frac{A_aA_b}{\zeta_b^{N_b-1}}(-1)^{M_b}\left[\frac{(2L_b+1)(L_b+M_b)!}{(L_b-M_b)!}\right]^{1/2},$$

and the angular brackets represent the angular integration over the product of three spherical harmonics, i.e., the Gaunt coefficients.[16] Let us examine the case of $1s$ orbitals with screening constants of 1. Carrying out the algebra and using

$$Y_l^0(\theta,\phi)=\left[\frac{2l+1}{4\pi}\right]^{1/2}P_l(\cos\theta), \quad (8)$$

we get

$$V(r_2,\theta_2)=\sum_{l=0}^{\infty}V_l(r_2)P_l(\cos\theta_2) \quad (9)$$

with

$$V_l(r_2)=2\sum_{i=0}^{l+1}\sum_{j=0}^{l+1}C_l(i,j)\alpha^{-l-1+i}\int dr_1\,r_1^2e^{-r_1}\frac{r_<^l}{r_>^{l+1}}H_{ij}(\alpha,r_1)r_1^{-l-1+j}. \quad (10)$$

The integral can be reduced to a summation by employing formulas (slightly modified) from a standard integral table:[17]

$$\int x^ne^{-wx}dx=-e^{-wx}\sum_{k=0}^{n}\frac{n!}{(n-k)!}\frac{x^{n-k}}{w^{k+1}},\quad n\geq 0 \quad (11)$$

$$\int\frac{e^{-wx}}{x^n}dx=-e^{-wx}\sum_{k=1}^{n-1}\frac{(n-k-1)!}{(n-1)!}\frac{(-w)^{k-1}}{x^{n-k}}+\frac{(-w)^{n-1}}{(n-1)!}\mathrm{Ei}(-wx),\quad n>0. \quad (12)$$

For formula generation we use a very simple form of computer algebra.[18] For instance, the expression $4\alpha^2r^3$ would be

represented by the array element (2,3)=4. Hence, to multiply terms we multiply the coefficients and add the powers of the variables separately. This can be expeditiously done under iteration. We end up with obvious functions multiplied by computer-generated polynomial coefficients. The potentials for $r<a$ and $r>a$ must be determined separately. Here, we examine the $r<a$ case. For every l value we anticipate a formula with ten kinds of functions, each multiplied by a polynomial in a and r. The ten functions are as follows: e^{-a}, $e^{-a}\mathrm{Ei}(-2r)$, $e^{-a}\gamma$, $e^{-a}\ln 2$, $e^{-a}\ln a$, $e^{-a}\ln r$, e^{-3a}, $e^{-a}e^{-2r}$, $e^{-a}\mathrm{Ei}(-2a)$, and $e^{a}\mathrm{Ei}(-2a)$, where $\gamma=0.577\cdots$ (Euler's constant). Actually, only two functions appear with nonzero coefficients for all l values, namely, e^{-a} and $e^{-a}e^{-2r}$. Only in the cases of $l=1$ and 2 must we consider more than two functions. To be explicit, we write the formulas for $l=0$ and 1, dropping the subscript 2 on r:

$$V_0(r)=a^{-1}(-1/r+1.5-r+r^2/3)e^{-a}+a^{-1}(1/r+0.5)e^{-a-2r}+a^{0}(-0.5/r+2-r)e^{-a}$$
$$+a^{0}(0.5/r)e^{-a-2r}+a^{1}(1.0)e^{-a}\ , \tag{13}$$

$$V_1(r)=a^{-2}(3.75/r^2-9+13r+1.5r^2)e^{-a}+a^{-2}(6r)e^{-a}\mathrm{Ei}(-2r)+a^{-2}(6r)e^{-a}\ln a+a^{-2}(6r)e^{-a}\ln r$$
$$+a^{-2}(-3.75/r^2-7.5/r+1.5)e^{-a-2r}+a^{-2}(6r)e^{a}\mathrm{Ei}(-2a)$$
$$+a^{-1}(3.75/r^2-9+r+1.5r^2)e^{-a}+a^{-1}(6r)e^{-a}\mathrm{Ei}(-2r)+a^{-1}(6r)e^{-a}\ln a$$
$$+a^{-1}(-6r)e^{-a}\ln r+a^{-1}(-3.75/r^2-7.5/r+1.5)e^{-a-2r}+a^{-1}(6r)e^{a}\mathrm{Ei}(-2a)$$
$$+a^{0}(1/r^2-3-4r^2/3)e^{-a}+a^{0}(2r)e^{-a}\mathrm{Ei}(-2r)+a^{0}(2r)e^{-a}\ln a$$
$$+a^{0}(-2r)e^{-a}\ln r+a^{0}(-1/r^2-2/r+1)e^{-a-2r}+a^{0}(-2r)e^{a}\mathrm{Ei}(-2a)\ . \tag{14}$$

The lowest powers of a and r in the polynomials appear to be $-l-1$, with the highest power of a being 1 and the highest power of r being $l+2$. For the values $a=2$, $r=0.5$ we obtain

$$V_0=0.388\,330\,440\,4\ ,\quad V_1=0.053\,464\,134\,5\ ,$$
$$V_2=0.007\,004\,740\,9\ ,\quad V_3=0.000\,977\,590\,4\ ,$$
$$V_4=0.000\,148\,745\,9\ ,\quad V_5=0.000\,024\,463\,7\ ,$$
$$V_6=0.000\,004\,283\,0\ ,\quad V_7=0.000\,000\,787\,3\ ,$$
$$V_8=0.000\,000\,150\,4\ ,\quad V_9=0.000\,000\,029\,6\ ,$$
$$V_{10}=0.000\,000\,006\,0\ ,\quad V_{11}=0.000\,000\,001\,2\ ,$$
$$V_{12}=0.000\,000\,000\,3\ .$$

Hence,

$$V(0.5,0^\circ)=\sum_{l=0}^{12}V_l=0.449\,955\,373\,9\ , \tag{15}$$

and

$$V(0.5,180^\circ)=\sum_{l=0}^{12}V_l(-1)^l$$
$$=0.341\,021\,359\,6\ . \tag{16}$$

These two values given to ten decimal digits agree with the eight figures of Trivedi and Steinborn.[5] (We note that the table given by Hirschfelder and Weygandt[19] is only accurate to six figures.)

If we are satisfied with eight-decimal digit accuracy, we may run our program in a purely numerical mode and only use 1.4 sec central processing unit (CPU) time (on the Florida State University CDC-Cyber 170-760). For higher accuracy we must generate exact formulas for V_l, which for $l=12$ requires 44 sec CPU time, but of course these formulas need only be generated once and then put on magnetic tape. To avoid intolerable cancellation errors at high l values, the formulas must be expanded by machine in a Taylor series.[11]

III. CONCLUSION

Although in some respects our method is formally equivalent to the single-center method of Harris and Michels[20] and that of Barnett and Coulson[21] (at least for s orbitals), it is our insistence on algebra that is decisive. The fact that the C-matrix elements are integers permits exact formulas to be developed. The extensive use of algebra gives us a penetrating insight into numerical calculations that allows us to proceed with confidence. Our method gives us the ability to establish benchmark values; the use of high-speed mass storage devices makes it possible to efficiently store and retrieve formula coefficients for further developments.

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