Brief Reports

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Exact formulas and their evaluation for Slater-type-orbital overlap integrals with large quantum numbers

Herbert W. Jones
Department of Physics, Florida A&M University, Tallahassee, Florida 32307

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Using the Löwdin α-function method with a computer-generated C-matrix associated with a displaced Slater-type orbital, an exact closed formula as well as a Taylor series with exact coefficients is produced for the overlap integral over two $7g\gamma$ orbitals. It is shown how ten-decimal-digit accuracy is achieved throughout the entire range of parameter values. A noteworthy development is the great simplification of this overlap formula made possible by factoring out $(1-t)^{20}$ by means of computer algebra.

I. INTRODUCTION

There is still discussion and disagreement in the literature[1–7] as to how best to evaluate two-center overlap integrals over Slater-type orbitals (STO's). Everyone agrees that two different methods must be used for integral evaluation depending on the relative values of the screening constants (exponential scaling factors) and the distance between orbitals.

The present author[5] showed how to evaluate the overlap integral $(1s,1s)$, i.e., (100,100), over a full range of parameter values to 12-decimal-digit accuracy by use of a closed formula and a Taylor series. In this paper this method is extended to an example of orbitals with large quantum numbers, namely, two $7g\gamma$ orbitals, i.e., $(N=7,L=4,M=4)$, to obtain the formulas $S(744,744)$ and $T(744,744)$. As was pointed out by Weniger and Steinborn,[4] it is not obvious that this can be done without unwanted complications. Here, by a more careful analysis of errors, we demonstrate the feasibility of extending our original method.

II. DERIVATION OF THE OVERLAP FORMULA

We will quickly summarize our derivation of the overlap formula.[5,8] Our approach is based on the Löwdin α-function method of expanding an orbital about a displaced center in terms of spherical harmonics. We call the coefficients of the spherical harmonics (which are functions of the radial distance) α functions, and each orbital has a "C-matrix" associated with it obtained by use of computer algebra.[9,10]

The overlap integral is given by

$$S=\int \psi_A^* \psi_B \, dv \; . \tag{1}$$

We place the STO $\psi_A=A_a r^{N'-1}e^{-\zeta' r}Y_{L'}^{M'}(\vartheta,\varphi)$ at the origin and the displaced STO $\psi_B=A_b R^{N-1}e^{-\zeta R}Y_L^M(\theta,\varphi)$ at a distance a along the z axis. A_a and A_b are normalization constants. The expansion of the displaced orbital is[9,10]

$$\psi_B=\frac{A_b}{\zeta^{N-1}}\left[\frac{(2L+1)(L+M)!}{4\pi(L-M)!}\right]^{1/2} \times\sum_{l=M}^{\infty}\left[\frac{4\pi(l+M)!}{(2l+1)(l-M)!}\right]^{1/2}(-1)^M\alpha_l^{NLM}(\zeta a,\zeta r) \times Y_l^M(\vartheta,\varphi) \; , \tag{2}$$

where

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

TABLE I. The formula for the overlap integral $S(744,744)$. $p=(\zeta'+\zeta)(a/2)$ and $t=(\zeta'-\zeta)/(\zeta'+\zeta)$. The expression $t\to -t$ means that the polynomial is obtained from the first polynomial by replacing t by $-t$.

$$
\begin{aligned}
S(744,744)=\frac{(1-t^2)^{15/2}}{2002}e^{-p}\{e^{pt}[&t^{-15}(-99\,324\,225/p^9-99\,324\,225/p^8-42\,567\,525/p^7-9\,459\,540/p^6-945\,945/p^5)\\
&+t^{-14}(+99\,324\,225/p^8+99\,324\,225/p^7+42\,567\,525/p^6+9\,459\,450/p^5+945\,945/p^4)\\
&+t^{-13}(147\,349\,125/p^9+147\,349\,125p^8+19\,646\,550/p^7\\
&\quad -29\,469\,825/p^6-17\,307\,675/p^5-4\,209\,975/p^4-436\,590/p^3)\\
&+t^{-12}(-147\,349\,125/p^8-147\,349\,125/p^7-52\,754\,625/p^6\\
&\quad -3\,638\,250/p^5+3\,118\,500/p^4+1\,056\,825/p^3+121\,275/p^2)\\
&+t^{-11}(-147\,349\,125/p^9-147\,349\,125/p^8+49\,116\,375/p^6+24\,475\,500/p^5+4\,828\,950/p^4\\
&\quad +56\,700/p^3-149\,625/p^2-22\,050/p)\\
&+t^{-10}(147\,349\,125/p^8+147\,349\,125/p^7+49\,116\,375/p^6\\
&\quad -4\,683\,420/p^4-1\,408\,995/p^3-150\,255/p^2+7560/p+2646)\\
&+t^{-9}(99\,324\,225/p^9+99\,324\,225/p^8-19\,646\,550/p^7\\
&\quad -52\,754\,625/p^6-24\,475\,500/p^5-4\,683\,420/p^4+178\,605/p^2+32\,130/p+1190-196p)\\
&+t^{-8}(-99\,324\,225/p^8-99\,324\,225/p^7-29\,469\,825/p^6\\
&\quad +3\,638\,250/p^5+4\,828\,950/p^4+1\,408\,995/p^3+178\,605/p^2-2\,835-245p+7p^2)\\
&+t^{-7}(42\,567\,525/p^7+42\,567\,525/p^6+17\,307\,675/p^5\\
&\quad +3\,118\,500/p^4-56\,700/p^3-150\,255/p^2-32\,130/p-2\,835+15p^2)\\
&+t^{-6}(-9\,459\,450/p^6-9\,459\,450/p^5-4\,209\,975/p^4-1\,056\,825/p^3\\
&\quad -149\,625/p^2-7560/p+1190+245p+150p^2)\\
&+t^{-5}(945\,945/p^5+945\,945/p^4+436\,590/p^3+121\,275/p^2\\
&\quad +22\,050/p+2646+196p+7p^2)]+e^{-pt}[(t\to -t)]\}
\end{aligned}
$$

and

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

Invoking the orthogonality properties of spherical harmonics, we conclude that $M'=M$ and that only one α function is needed. Using the results of an integral table, we are able to program the formula for S, in terms of an in house version of computer algebra, and obtain functions in terms of ζ',ζ and a. Now we make a change in variables using Mulliken's notation:[11]

$$p=(\zeta'+\zeta)\frac{a}{2}$$

and

$$t=\frac{\zeta'-\zeta}{\zeta'+\zeta}$$

to get the final formula

TABLE II. The Taylor series to the t^6 power, with the requisite powers in p, give for the overlap integral the formula $T(744,744)$.

$$
\begin{aligned}
T(744,744)=(1-t^2)^{15/2}e^{-p}\Big[&1+p+\tfrac{477}{1001}p^2+\tfrac{430}{3003}p^3+\tfrac{1180}{39\,039}p^4\\
&+\tfrac{307}{65\,065}p^5+\tfrac{3587}{6\,441\,435}p^6+\tfrac{64}{1\,288\,287}p^7+\tfrac{1}{306\,735}p^8+\tfrac{59}{405\,810\,405}p^9+\tfrac{1}{289\,864\,575}p^{10}\\
&+t^2\Big[\tfrac{1}{22}p^2+\tfrac{1}{22}p^3+\tfrac{51}{2366}p^4+\tfrac{250}{39\,039}p^5+\tfrac{569}{429\,429}p^6\\
&\quad+\tfrac{41}{204\,490}p^7+\tfrac{991}{43\,801\,758}p^8+\tfrac{16}{8\,423\,415}p^9+\tfrac{59}{511\,020\,510}p^{10}+\tfrac{1}{212\,270\,058}p^{11}+\tfrac{1}{9\,855\,395\,550}p^{12}\Big]\\
&+t^4\Big[\tfrac{1}{1144}p^4+\tfrac{1}{1144}p^5+\tfrac{43}{104\,104}p^6+\tfrac{19}{156\,156}p^7+\tfrac{181}{7\,300\,293}p^8\\
&\quad+\tfrac{1069}{292\,011\,720}p^9+\tfrac{2209}{5\,548\,222\,680}p^{10}+\tfrac{2}{63\,047\,985}p^{11}+\tfrac{37}{20\,561\,060\,520}p^{12}+\tfrac{71}{1\,048\,614\,086\,520}p^{13}+\tfrac{1}{74\,901\,061\,800}p^{14}\Big]\\
&+t^6\Big[\tfrac{1}{102\,960}p^6+\tfrac{1}{102\,960}p^7+\tfrac{81}{17\,697\,680}p^8+\tfrac{1}{5\,972\,967}p^9\\
&\quad+\tfrac{2693}{9\,986\,800\,824}p^{10}+\tfrac{6497}{166\,446\,680\,400}p^{11}+\tfrac{1423}{3\,456\,969\,516}p^{12}\\
&\quad+\tfrac{8}{25\,534\,433\,925}p^{13}+\tfrac{1}{59\,920\,804\,944}p^{14}+\tfrac{1}{1\,715\,913\,959\,760}p^{15}+\tfrac{1}{94\,375\,267\,786\,800}p^{16}\Big]\Big]
\end{aligned}
$$

$$
\begin{aligned}
S=K(1+t)^{N'+1/2}(1-t)^{-2L'-L-1/2}e^{-p}&\sum_{i=0}^{N+L+L'}\sum_{j=0}^{N+L'}\sum_{l=0}^{m} n!C_{L'}^{NLM}(i,j)(-1)^l\frac{m!}{(m-l)!l!}\\
&\times\left[e^{pt}\left[\frac{(-1)^j}{2^{n+1}}p^u t^r-\frac{1}{2^{n+1}}p^u t^l\right]\right.\\
&\left.+e^{-pt}\sum_{k=0}^{n}\frac{1}{(n-k)!}\left[\frac{(-1)^i}{2^{k+1}}p^v t^l-\frac{(-1)^j}{2^{k+1}}p^v t^w\right]\right],
\end{aligned}
\tag{3}
$$

where

$m=i+j$,

$n=N'-L'+j$,

$r=l-n-1$,

$u=N'-2L'-L+m-n-1$,

$v=N'-2L'-L+m-k-1$,

$w=l-k-1$,

and

$$K=2^{N'+N}(-1)^M\left[\frac{(2L+1)(2L'+1)(L+M)!(L'-M)!}{(2N')!(2N)!(L'+M)!(L-M)!}\right]^{1/2}.$$

III. EXAMINATION OF THE OVERLAP BETWEEN $7g\gamma$ ORBITALS

As an example using high quantum numbers, we generate the exact overlap formula between two $7g\gamma$ orbitals,

TABLE III. Above the jagged lined $pt \leq 0.1$ the numbers are produced by the Taylor series $T(744,744)$. Below the line $pt > 0.1$ the numbers are produced by evaluation of the closed formula $S(744,744)$. The table is accurate to ten decimal digits.

p	$t=0.01$	$t=0.02$	$t=0.05$	$t=0.10$	$t=0.20$	$t=0.50$	$t=0.90$
0.01	0.999 247 898 3	0.997 001 558 3	0.981 399 354 6	0.927 391 176 7	0.736 263 561 3	0.115 600 296 9	0.000 003 896 3
0.02	0.999 240 862 0	0.996 994 542 0	0.981 382 476 2	0.927 384 771 6	0.736 258 777 5	0.115 599 876 8	0.000 003 896 3
0.05	0.999 191 609 6	0.996 945 428 8	0.981 344 328 3	0.927 339 937 3	0.736 225 291 4	0.115 596 936 3	0.000 003 896 4
0.10	0.999 015 729 6	0.996 770 046 2	0.981 172 392 6	0.927 179 834 0	0.736 105 711 7	0.115 586 435 0	0.000 003 896 8
0.20	0.998 312 544 2	0.996 068 848 9	0.980 484 975 3	0.926 539 719 0	0.735 627 601 8	0.115 544 437 7	0.000 003 898 4
0.50	0.993 405 196 2	0.991 175 366 6	0.975 687 598 1	0.922 072 253 3	0.732 290 171 5	0.115 250 802 9	0.000 003 909 3
1.00	0.976 090 600 4	0.973 909 567 6	0.958 760 028 1	0.906 305 899 0	0.720 503 110 6	0.114 207 072 8	0.000 003 948 0
2.00	0.910 022 607 3	0.908 025 934 9	0.894 154 410 7	0.846 090 003 6	0.675 356 533 3	0.110 110 477 8	0.000 004 099 5
5.00	0.563 074 787 4	0.561 991 607 5	0.554 456 732 4	0.528 21l4 649 1	0.433 154 062 9	0.084 966 982 3	0.000 005 030 3
10.00	0.115 070 643 1	0.114 949 568 6	0.114 102 866 4	0.111 091 160 0	0.099 272 620 5	0.034 151 040 7	0.000 007 138 5
20.00	0.000 647 114 8	0.000 648 430 8	0.000 657 667 7	0.000 690 995 9	0.000 828 571 8	0.001 602 358 9	0.000 008 914 8
50.00	0.000 000 000 0	0.000 000 000 0	0.000 000 000 0	0.000 000 000 0	0.000 000 000 0	0.000 000 005 7	0.000 002 751 5

i.e., $S(744,744)$, and present it in Table I. The expression $t \rightarrow -t$ in the second part of the formula means that the polynomial for this part is obtained from the first polynomial by replacing t by $-t$. In the development of this formula we were able to effect a remarkable simplification by factoring out the binomial $1-t$ 20 times in the originally generated formula. This step undoubtedly makes for a rapidly convergent Taylor series. We should anticipate this factorization because the $S(744,744)$ formula must be independent of the interchange of orbitals. In unsymmetric cases, $1+t$ might also be factored out of the polynomials. The expression of this formula in a Taylor series $T(744,744)$ is presented in Table II. Because the C matrix elements are integers, we were able to use integer arithmetic to arrive at exact coefficients for the expansion. We note that if we set $t=0$ we obtain the polynomial in p that gives the formula for the equal zeta case. The expansion is carried to t^6 which automatically produces terms up to p^{16}.

An important consideration is to decide which expression to use when required to produce a value for given parameters and to estimate the error. Let us consider the case $p=0.01$ and $t=0.01$. Using the formula $S(744,744)$ we obtain the number $0.495\,87\times 10^{53}$ for the positive part of the evaluation and $-0.495\,87\times 10^{53}$ for the negative part. Actually, these numbers are identical to all the machine digits and we get the absurd result $S(744,744)=-72\,536\times 10^{25}$. On the other hand, we find $T(744,744)=0.999\,247\,898\,3$. We find the t^6 term to be $0.970\,51\times 10^{-29}$. Hence, the Taylor series is obviously converged, assuming we are seeking an accuracy of $\pm 10^{-10}$. We now state a criterion corresponding to this accuracy for the evaluation of the formula $S(744,744)$: Using double precision accurate to 28 decimal digits, the absolute value of the positive and negative evaluations must not exceed 10^{17}, and for single precision accurate to 14 decimal digits, the absolute values must not exceed 10^3. The criteria are easy to arrive at since all overlap values must be equal to or less than 1.0. Investigation has shown that a more convenient criterion is as follows: for $pt \leqq 0.1$ use the Taylor series, evaluated to t^6, and for $pt > 0.1$ use the S formula with double precision arithmetic (see Table III). If S is evaluated in single precision, then the Taylor series must be evaluated to t^{12} and the dividing line is $pt=1.0$. Addition study has shown that one must be very cautious in going beyond this line, even if using more terms for the Taylor series.

IV. CONCLUSION

The Löwdin α-function method implemented by computer algebra and the C-matrix characterization of a displaced STO is capable of accurately evaluating all overlap integrals between orbitals up to $7g\gamma$. The accuracy of evaluation is readily determined and simple criteria can be used to select the method of evaluation, i.e., closed formula or Taylor series. Additional efforts will determine if this method is suitable for computer programs for molecular computations.

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