Symbolic Calculation of Two-Center Overlap Integrals Over Slater-Type Orbitals

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Two-center overlap integrals over Slater type orbitals (STOs) have been expressed in terms of the well-known Mulliken’s integrals $B_{pq}$ using Rodrigues’s formula for normalized associated Legendre functions. A computer program is written in Mathematica 4.0 for the evaluation of two-center overlap integrals over STOs. Using this computer program, symbolic tables are presented for two-center overlap integrals up to quantum numbers $l \leq n, n' \leq 3, 0 \leq l, l' \leq 2, -2 \leq m, m' \leq 2$. Numerical results of this work, for some quantum sets, have also been compared with prior literature and best agreement achieved with recent works of Barnett while some discrepancies were obtained with works of Öztekin et al. and Guseinov et al.

**Keywords:** Overlap integrals; Slater type orbitals; Symbolic calculation.

INTRODUCTION

The calculation of multicenter integrals have prime importance when LCAO-MO approximation is employed in the molecular properties calculations. Two-center overlap integrals constitute basic building blocks of other multicenter integrals since the expectation values of one-electron operators can be expressed as linear combinations of two-center overlap integrals, and also since Coulomb integrals can be calculated by taking quadrature of two-center overlap integrals. Therefore, an accurate and efficient method for the numeric calculation of two-center overlap integrals is essential. It is well known that the accuracy of molecular properties calculations depends deeply on the nature of the type of the basis functions used in the calculations. Among the basis functions, Slater-type orbitals (STOs) are able to represent density of electrons more accurately than other basis functions.

A variety of approaches on the evaluation of two-center overlap integrals over STOs exists in the literature, for example, expansion of STOs, elliptical coordinates method, integral transformation methods, and recurrence schemes and other methods.

It is well known from the literature that in the calculation of two-center overlap integrals some discrepancies occur for smaller quantum numbers, higher quantum numbers, higher or lower internuclear distances and, equal or nearly equal orbital exponents. Therefore, the symbolic calculation of two-center overlap integrals and also other multicenter integrals are needed to compare with the values in the literature.

Recently, we have presented recurrence relations and a series expansion formula for the evaluation of two-center overlap integrals over STOs. In order to test the efficiency of our recent work and formula in the literature, the symbolic calculation of two-center overlap integrals over STOs constitutes the aim of this work. Symbolic calculation of two-center overlap integrals for researchers in this field can be highlighted to the relative benefits of all the different methods. In addition, the symbolic results from this paper can be used for the energy calculations and the crystal field properties of some small molecules, such as molecules $H_2^+$, $H_2$, $CO_2$, $HCN$ and $LiH$.

DEFINITIONS

Two-center overlap integrals in line-up coordinate systems are as follows

$$S_{a\delta b\gamma}(\zeta, \zeta') = \int \chi_{a\delta}(\zeta, \vec{r}) \chi_{b\gamma}(\zeta', \vec{r'}) dV$$

(1)

where $\vec{R} = \vec{R}_{ab} = \vec{r} - \vec{r'}$ is the radius vector of the spherical-polar coordinates and $\chi_{a\delta}(\zeta, \vec{r})$ and $\chi_{b\gamma}(\zeta', \vec{r'})$ are normalized complex or real STOs centered on the nuclei $a$ and $b$, respectively, defined by

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plex or real spherical harmonics defined by:

\[ S_\ell (\theta, \phi) = P_\ell (\cos \theta) \Phi_\ell (\phi) \]

where \( \Phi_\ell (\phi) \) are orthonormal functions given by

\[ \Phi_\ell (\phi) = \frac{1}{\sqrt{2\pi}} e^{i\delta_\ell} \]

for complex spherical harmonics and

\[ \Phi_\ell (\phi) = \frac{1}{\sqrt{\pi \left(1 + \delta_\ell^2\right)}} \begin{cases} \cos \lambda \phi & \text{for } \lambda \geq 0, \\ \sin \lambda \phi & \text{for } \lambda < 0, \end{cases} \]

for real spherical harmonics. In Eq. (3), \( P_\ell \) is a normalized associated Legendre function and can be defined as in the following\(^1\) by using Rodrigues’s formula:

\[ P_\ell (\cos \theta) = W_\ell (1 - \cos^2 \theta)^{\ell/2} \]

\[ \times \sum_{i=0}^{\ell} A_{\ell i} (\cos \theta + 1)^{i}(\cos \theta - 1)^{\ell-i}, \]

with

\[ W_\ell = \left[ \frac{(2\ell+1)F_\ell (\ell + \lambda)}{2^{\ell+1} F_\ell (\ell)} \right]^{1/2} \]

\[ A_{\ell i} = F_\ell (\ell) F_{\ell-1+i} (i). \]

In Eqs. (6), the quantity \( F_\ell (j) = \frac{j!}{r(j-i)!} \) is the usual binomial coefficients.

### THE EVALUATION OF TWO-CENTER OVERLAP INTEGRALS USING ELLIPTICAL COORDINATES

It is well known that two-center overlap integrals over STOs are dealt with at their best in the elliptical coordinates. Therefore, for the integration in Eq. (1), we use the definitions for elliptical coordinates

\[ \rho = (r_1 + r_2)/R, \quad 1 \leq \rho < \infty, \]

\[ \nu = (r_1 - r_2)/R, \quad -1 \leq \nu \leq 1, \]

\[ \varphi = \varphi_1 - \varphi_2, \quad 0 \leq \varphi \leq 2\pi, \]

\[ dV = \frac{1}{2} \left( \mu^2 - \nu^2 \right) d\mu d\nu d\varphi. \]

With substitution of the relationships

\[ \cos \theta_\pm = (1 \pm \mu)(1 \pm \nu)/(\mu + \nu), \]

\[ \cos \theta_\pm = (1 \pm \mu)(1 \pm \nu)/(\mu - \nu), \]

into Eq. (5) and the expansions below

\[ (\mu \pm \nu)^\ell = \sum_{i=0}^{\ell} \sum_{j \leq i} F_\ell (k) (1 - i + j, i + j - k), \]

\[ (\mu \pm 1)^\ell = \sum_{k=0}^{\ell} F_\ell (k) 2^k (\mu - 1)^{\ell-k}, \]

we have the expression for the two-center overlap integrals over STOs as follows:

\[ S_{\alpha\beta;\nu\lambda} (\zeta, \xi, R) = (-1)^j P_{\lambda\nu/2} P_{\lambda\nu/2} e^{-p} \]

\[ \times \sum_{i, j} \sum_{k, l} F_i (i' + i - j, j + j' - i - j'), \]

\[ \times Q_{\nu^\lambda;\nu^\xi} (n_1, n_1', \lambda; \rho) B_i (pt), \]

where, the variables \( p_\rho, p_\lambda, p_\nu, p_\tau, p \) and \( t \) are defined as follows

\[ p_\rho = \frac{\zeta R}{\zeta' R}, \quad p_\lambda = \frac{\zeta R}{\zeta' R}, \quad p = \frac{1}{2} (p_\rho + p_\lambda), \quad t = \left( \frac{\zeta - \zeta'}{\zeta + \zeta'} \right), \]

and the symbol \( F_\ell (N, N') \) is the expansion coefficient in product

\[ (\mu + \nu)^N (\mu - \nu)^{N'} = \sum_{s=0}^{N+N'} F_\ell (N, N') \mu^{N-N'-s} \]

and defined by\(^18,19\)

\[ F_\ell (N, N') = \left[ \frac{\min(n, N')}{n + 1} \right]^{1/2} F_\ell (N) F_\ell (N'). \]

In Eq. (12), the quantity \( Q_{\nu^\lambda;\nu^\xi} (n_1, n_1', \lambda; \rho) \) is defined as

\[ Q_{\nu^\lambda;\nu^\xi} (n_1, n_1', \lambda; \rho) = q_{\sigma} (n_\lambda; \rho) q_{\sigma'} (n_\lambda'; \rho) \]

\[ \times F_i (i + i' + \lambda) (n + n' - j - j' - k)(2p)^i, \]

with

\[ q_{\sigma} (n_\lambda; \rho) = (-1)^{-j} \frac{W_{\rho} A_{\ell i} (n - l)}{\sqrt{(2\pi)^i}} \]

and the summation indices \( i, i', j, j', k \) and \( s \) run as follows:
Table 1. Symbolic Results of Two-Center Overlap Integrals Over STOs for \( t \neq 0 \)

\[
(1s \mid 1s) = \frac{\text{e}^{\gamma (t^2)} (-1 + t) (p (1 - t))^{1/2}}{\sqrt{p - p_t}} \cdot \frac{\text{e}^{\gamma p_t} (1 + t) (-1 + t + p_t) - (-1 + t) (1 + t + p_t)}{p_t^2 t^3}
\]
\[
\langle S | \mathcal{P}_3 \rangle = -\frac{1}{6 \sqrt{\frac{3}{10}}} \frac{\sigma^{-2 (1-t)} (-1 + t)^3 (\mathcal{P} (1 + t))^5}{\sqrt{\mathcal{P} - 2 \mathcal{E}}} \\
(\mathcal{E}^2 t^2 \left(3 - t - (3 - 3 t^2) \right) + 3 \left(5 - 3 t^2 - 5 t^4 \right) + \sigma^2 t \left(12 + 3 t - 8 t^2 + 3 t^3 - 12 t^4 \right) + \\
3 \left(5 - 3 t^2 - 3 t^3 - 5 t^4 - 5 t^5 \right) + \\
\sigma_{\phi}^{-2} \left(2 \mathcal{E}^4 (1 + t^2) + 3 \mathcal{E}^3 \left(3 - 3 t^2 - 3 t^3 \right) - 3 \left(5 - 5 t^2 - 3 t^3 - 5 t^4 - 3 t^5 \right) \right) \\
\mathcal{E}^2 t \left(10 - 3 t - 3 t^2 - 3 t^3 + 10 t^4 \right) + 3 \sigma \left(-5 + 5 t + 3 t^2 - 5 t^3 - 5 t^4 + 5 t^5 \right) \rangle)
\]
\[
\langle \mathbf{P}_n | \mathbf{p} \mathbf{P}_n \rangle = \frac{1}{2\sqrt{30}} \frac{\mathbf{p}^3 \mathbf{e}^3 \mathbf{t}^3}{\mathbf{p}^2 \mathbf{t}^3} \left( \mathbf{p}^2 (1 + \mathbf{t}) (1 + \mathbf{t}) (1 - \mathbf{t})^4 (1 - \mathbf{t})^5 (1 + \mathbf{t})^2 (1 + \mathbf{t})^2 \right) \nabla^2 \mathbf{P} - \mathbf{p} \mathbf{t}^3
\]

\[
\left( \mathbf{p}^2 \mathbf{t}^2 (3 - 4 \mathbf{t} + 3 \mathbf{t}^2) + 3 \mathbf{p} (1 + \mathbf{t})^2 (5 - 8 \mathbf{t} + 5 \mathbf{t}^2) + 6 \mathbf{p}^2 \mathbf{t} (2 - \mathbf{t} - \mathbf{t}^2 + 2 \mathbf{t}^2) + \right.
\]

\[
3 (3 - 3 \mathbf{t} - 3 \mathbf{t}^2 + 5 \mathbf{t}^3) + \mathbf{p}^2 \mathbf{e}^2 \mathbf{t}^2 (1 + \mathbf{t}) (9 \mathbf{p}^2 (1 - \mathbf{t})^2 + 2 \mathbf{p}^4 \mathbf{t}^2 + 6 \mathbf{p}^2 \mathbf{t} (3 - 5 \mathbf{t} + 3 \mathbf{t}^2) -
\]

\[
3 (5 - 5 \mathbf{t} + 5 \mathbf{t}^2) + 3 \mathbf{p} (-5 + 13 \mathbf{t} - 13 \mathbf{t}^2 + 5 \mathbf{t}^3) \left) \right)
\]
\[
\begin{align*}
&\langle 3 \psi_2 \mid 3 \Delta \psi \rangle = \frac{1}{6 \sqrt{15}} \frac{\alpha^{2\alpha}(2\alpha\alpha)}{p^4 t^2} \\
& \quad \left\{ 3(-1-t) \left( p^2 t^2 (1+t)^2 + 45 (3 - 5t + 3t^2) + 3 p^2 t^2 (2 - 5t - 5t^2 + 2t^3) + 45 p (3 - 8t - 8t^2 + 3t^3) + \\
& \quad p^4 t (15 + 90t + 31t^2 + 30t^3 + 15t^4) + p^6 t^2 (60 + 270t + 140t^2 + 235t^3 + 60t^4) + \\
& \quad p^8 (15 + 85t + 176t^2 + 176t^3 + 85t^4 + 15t^5)) \right\} + \\
& \quad \alpha^2 \beta^2 \left( 135 p (-1-t)^2 (1 + 5t + 3t^2) - p^2 t^2 (-3 - t + 2t^2 + 3t^3) - 135 (-3 - 2t + 2t^2 + 3t^3) + \\
& \quad 3 p^2 (-1-t)^2 (15 - 20t - 44t^2 + 20t^3 + 15t^4) + p^4 t^2 (18 - 3t - 10t^2 - 3t^3 + 18t^4) + \\
& \quad 9 p^4 t (-5 + 5t + 3t^2 - 3t^3 + 5t^4 + 5t^5) - 3 p^6 (-60 + 95t + 69t^2 - 69t^3 - 95t^4 + 60t^5) \right\}.
\end{align*}
\]
In Eq. (12), $B_p t n$ is the well-known Mulliken’s integral and for readers’ interest in the calculating of this integral we refer to Refs. [15a, 20, 21].

RESULTS AND DISCUSSIONS

An algorithm has been presented for the evaluation of two-center overlap integrals over STOs using ellipsoidal coordinates methods and Rodrigues’ formula for normalized associated Legendre functions. The obtained formula contains the finite sum of binomial coefficients and Mulliken integral $B_p (pt)$.

On the basis of Eq. (12), a computer program, in Mathematica 4.0 symbolic programming language, has been constructed and presented in the Appendix for two-center overlap integrals over STOs.

Symbolic computer results for two-center overlap integrals over STOs between some quantum sets have been

$$\langle 1 \mid 1 \rangle = \frac{1}{3} z^2 \{1 \cdot 2 \cdot y - y^2\}$$
listed in Table 1 for unequal orbital exponents and in Table 2 for equal orbital exponents. Numerical values obtained from the results in Tables 1 and 2 agree best with the available literature.

Also, comparative values of some pilot calculations have been presented in Table 3 for higher quantum numbers and for a wide range of molecular parameters. As can be seen from Table 3 our computer results agree best with the recent work of Barnett.\textsuperscript{23} We mention also that our results are in best agreement with the values in Refs. [8-12, 15, 24, 25]. On the other hand, despite the fact that Öztekin \textit{et al.}\textsuperscript{26} and Guseinov\textsuperscript{27} claim that their algorithm can be used in the evaluation of other multicenter integrals when translation of STOs is employed in the calculations, we have found some discrepancies with our values even for small quantum numbers. We think that these discrepancies may originate from their recurrence relations, that is, it is well known that the subtraction of two smaller numbers is a big problem for coding in computers. This fact is investigated in a detailed way in the excellent work of Barnett\textsuperscript{23} and called "Digital Erosion".

The agreement with the prior literature shows that the algorithm presented here does not suffer from possible instability problems (higher or lower quantum numbers, higher or lower internuclear distances and, equal and nearly equal orbital exponents), and we stress that the algorithm we presented can be used in molecular orbital calculations when Hartree-Fock-Roothaan approximation is employed.

Work is being continued in our laboratory and some preliminary symbolic results on two-center two-electron integrals over STOs will be reported shortly.

\begin{table}[h]
\centering
\begin{tabular}{cccccccc}
$\nu$ & $\xi$ & $\nu$ & $\xi$ & $\nu$ & $\xi$ & $\nu$ & $\xi$
\hline
3 & 2 & 3 & 2 & 1 & 25 & 0.6 & -4.42287766981
4 & 2 & 3 & 2 & 1 & 25 & 0.0 & -5.65554471491
4 & 2 & 4 & 3 & 1 & 80 & 0.4 & 4.03505950321
7 & 3 & 4 & 3 & 2 & 150 & 0.7 & 1.7686105069
9 & 5 & 8 & 4 & 3 & 45 & 0.2 & -5.4651024302
10 & 7 & 8 & 2 & 1 & 60 & 0.2 & -1.8418902617
10 & 9 & 10 & 9 & 9 & 15 & 0.6 & 6.2312231819
13 & 12 & 13 & 12 & 12 & 25 & 0.01 & 1.3531056039
14 & 13 & 14 & 13 & 13 & 15 & 0.4 & 4.5355131215
15 & 4 & 8 & 4 & 4 & 25 & 0.0 & 2.5432413255
15 & 14 & 15 & 14 & 14 & 15 & 0.0 & 3.7472249703
16 & 15 & 16 & 15 & 15 & 35 & 0.0 & 1.2368656225
17 & 8 & 8 & 7 & 4 & 50 & 0.1 & -1.0062336711
17 & 16 & 17 & 16 & 16 & 25 & -0.5 & 3.0676956518
18 & 10 & 18 & 17 & 9 & 20 & 0.0 & -1.1490869323
18 & 12 & 18 & 12 & 12 & 20 & -0.6 & 6.6393181365
21 & 10 & 9 & 8 & 6 & 45 & 0.0 & 5.3898068535
25 & 12 & 20 & 17 & 11 & 30 & 0.0 & 4.8812971401
27 & 8 & 9 & 8 & 7 & 35 & -0.2 & -1.7330098279
30 & 10 & 14 & 10 & 8 & 35 & 0.0 & 1.3507470959
30 & 15 & 29 & 10 & 8 & 50 & 0.0 & 7.3665917323
34 & 14 & 34 & 12 & 10 & 75 & 0.0 & 1.3001639359
37 & 8 & 12 & 10 & 6 & 10 & -0.6 & 3.9821984900
40 & 4 & 12 & 4 & 3 & 15 & 0.6 & 9.4837926559
43 & 10 & 18 & 8 & 6 & 60 & -0.4 & -1.1590768712
50 & 4 & 50 & 4 & 4 & 25 & 0.7 & 1.8439590103
50 & 15 & 15 & 13 & 11 & 10 & 0.0 & 2.9010070720
50 & 17 & 25 & 15 & 13 & 10 & 0.0 & 2.6746565012
\end{tabular}
\end{table}

\textsuperscript{a} Ref. 27, \textsuperscript{b} Ref. 26.
Appendix: Computer program written for two-center overlap integrals over STOs in Mathematica 4.0

Clear[bs, as]; Clear[p, t, n1, n2, l1, m, nun];

Off[Overlap::spelll'];

as[s_, p_] := s! / p^n (p + 1) Exp[-p] * Sum[p^j / j!, {j, 0, n}];

bs[s_, p_] := If[p != 0, (-1)^(s + 1) as[s, -p] -

fsum1[m_, n_, n1_] := Sum[(-1)^s Binomial[n, m] * (m - n) + nbs[m - n] / 2, Min[m, n1]];


kil[i_, l_, l_] := Binomial[l, i] * Binomial[1, 1];

qij111[i_, j_, n1_, l1_, 1_] := (-1)^i * (l + 1) / 2;

qijk[i, j, k, l, m, n1] := qij111[i, j, n1, l1, 1] * qij111[k, i, j, l, j1, n, l, n1] + qij111[i, j, 0, l, p1, n, 1, l1, 1];

Overlap[n1, 1, l1, m, p, t1] := Module[{a, pa, pb, txt, l1}, a - (-1)^(l + 1) * (l + 1 - l - 1) / 2; a + Sum[fsum1[1, 1 + 1 - 1 + l, 1 + l + 1 + j] * nbs[s, p, t], {s, 0, 1 + l + 1 + j - 1}];

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REFERENCES