Evaluation of Two-Center Overlap Integrals in Molecular Coordinate System over Slater Type Orbitals

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Using Talman’s formulae for overlap integrals in lined-up coordinate systems and Guseinov’s transformation technique, a new algorithm is presented for computing the two-center overlap integrals over Slater type orbitals (STOs) with respect to the molecular coordinate system (nonlined-up coordinate systems) appearing in the Hartree-Fock-Roothaan (HFR) equations. The numerical stability of the computational results is analyzed.

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I. INTRODUCTION

Approximation methods can be categorized as being either ab initio or semiempirical [1, 2]. Semiempirical methods use parameters that compensate for neglecting some of the time consuming mathematical terms in Schrödinger’s equation, whereas ab initio methods include all such terms. The parameters used by semiempirical methods can be derived from experimental measurements or by performing ab initio calculations on model systems.

Semiempirical approximations involve the neglect of the three- and four-center molecular integrals arising in the Hartree-Fock-Roothaan (HFR) equations [3]. For molecules with a large numbers of electrons, the evaluation of these integrals can be computationally impractical. Experimentally determined parameters (or in some cases, parameters determined from ab initio calculations on model systems) are used to compensate for the missing integrals. Such parameters are obtained from the measured or calculated ionization potentials, electron affinities, and spectroscopic quantities [4, 5].

It is well known that the evaluation of these integrals and a choice of basis functions plays a decisive role in the quality of the calculations of the various molecular parameters. Hydrogen-like wave functions modified for electron correlations are generally not used per se, because they lead to mathematical complications and time-consuming calculations. The most commonly used basis functions are the Slater type orbitals (STOs) and the Gaussian type orbitals (GTOs). The Gaussian orbitals are mathematically simpler than the STOs, but less accurate. All of the one-electron orbitals can be built by combining sets of Gaussian functions (Gaussian primitives) that approximate each STO [6, 7]. The result is called a contracted Gaussian function.

The STO screening constants are calculated for small model molecules using rigorous self-consistent field methods, then generalized for use with the actual molecules of interest.
This data is supplied with the various software implementations that use STOs. The mathematical requirements for solving the integrals of the wave equation using STOs are time consuming. As shown in the literature, with the great progress of applied mathematics and computers, significant progress has been made in several long-standing computing problems with STOs [8–23].

As is well known, the overlap integrals over STOs play a decisive role in both semiempirical and ab initio molecular calculations. Therefore, it is important to use different kinds of approaches for the evaluation of the overlap integrals. The aim of this work is to present a new algorithm for the calculation of two-center overlap integrals in a molecular coordinate system, using the formulas for two-center overlap integrals in the lined-up coordinate systems [24] and transformation formulas [25, 26].

II. ANALYTICAL EXPRESSION FOR OVERLAP INTEGRALS WITH STOS

The Slater-type orbitals are defined by

\[
\chi_{nlm}(\zeta, r) = R_n(\zeta, r)S_{lm}(\theta, \varphi),
\]

\[
R_n(\zeta, r) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2}r^{n-1}e^{-\zeta r}.
\]

Here \(n\) and \(\zeta\) are the principal quantum number and the orbital exponent, respectively. The spherical harmonics \(S_{lm}(\theta, \varphi)\) in Eq. (1) are determined by the relation

\[
S_{lm}(\theta, \varphi) = P_{l|m}(\cos \theta)\Phi_m(\varphi),
\]

where \(P_{l|m}\) are the normalized associated Legendre functions [27], and, for complex spherical harmonics \((S_{lm} = Y_{lm})\)

\[
\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi},
\]

while for real spherical harmonics

\[
\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1 + \delta_{m0})}}\begin{cases} 
\cos |m|\varphi, & m \geq 0 \\
\sin |m|\varphi, & m < 0
\end{cases}.
\]

The overlap integrals over STOs in the molecular coordinate system are defined as

\[
S_{nlm, n'l'm'}(\zeta, \zeta'; R) = \int \chi_{nlm}^*(\zeta, r_a)\chi_{n'l'm'}(\zeta', r_b)dV.
\]

To evaluate the overlap integrals, Eq. (6), in the molecular coordinate system we use Guseinov’s transformational formulae [25, 26] and Talman’s method [24] in lined up coordinate systems. We then obtain:

\[
S_{nlm, n'l'm'}(\zeta, \zeta'; R) = \sum_{\lambda=0}^{\min(l',l)} T_{lm, l'm'}^{*\lambda}(\theta, \varphi)S_{n\lambda, n'l'm'}(\zeta, \zeta'; R),
\]

where

\[
T_{lm, l'm'}^{*\lambda}(\theta, \varphi) = \int S_{nlm}(\zeta, r)S_{n'l'm'}(\zeta', r)dV.
\]
where \( S_{nlm,n'm';\lambda}(\zeta, \zeta'; R) \) are the overlap integrals in the lined up coordinate systems, defined in Refs. [24] as
\[
S_{nlm,n'm';\lambda}(\zeta, \zeta'; R) = \frac{(2\zeta)^{n+1/2}(2\zeta')^{n'+1/2}}{\sqrt{(2n)!((2n')!)}} \sum_{\lambda, L} C(l'l'm, \lambda L)Q_{\lambda L}.
\]  
(8)

The rotation coefficients \( T^\lambda \) in Eq. (7) are determined by the following relationships [25]: for complex STOs
\[
T_{lm,l'm'}^\lambda(\theta, \varphi) = \frac{2}{1 + \delta_{\lambda 0}} \sum_{L=|l-l'|}^{l+l'} \sum_{i=1}^{2} (\epsilon_{m0})^{i}C_{m, -m', m-m'}^{l+l'}C_{\lambda, \lambda - \lambda, 0}^{l+l'} \left( \frac{4\pi}{2L+1} \right)^{1/2} Y_{L,m-m'}(\theta, \varphi),
\]  
(9)

and for real STOs
\[
T_{lm,l'm'}^\lambda(\theta, \varphi) = \frac{2}{(1 + \delta_{\lambda 0})((1 + \delta_{m0})(1 + \delta_{m'0}))^{1/2}} \sum_{L=|l-l'|}^{l+l'} \sum_{i=-1}^{1} \sum_{i'=-1}^{1} (\epsilon_{m0})^{i}C_{m, -m', m-m'}^{l+l'}C_{\lambda, \lambda - \lambda, 0}^{l+l'} \left( \frac{2\pi(1 + \delta_{M0})}{2L+1} \right)^{1/2} S_{LMi}(\theta, \varphi),
\]  
(10)

where \( \gamma = |m|, \gamma' = |m'| \), and \( M_i = \epsilon_{mm'}i\gamma + \gamma' \). In Eqs. (9) and (10) the symbol \( \sum_{i=1}^{2} \) indicates that the summation is to be performed in steps of two. For \( \gamma = \gamma' \) and \( \epsilon_{mm'} = -1 \), the terms with a negative index value \( i (i = -1) \) contained in Eq. (9) should be equated to zero. We note that the symbol \( \epsilon_{mm'} \) in Eq. (9) may have the values \( \pm 1 \) and is determined by the product of the signs of \( m \) and \( m' \) (the sign of zero is regarded as positive). The quantities \( C^{l'l'}_{\lambda} \) in Eqs. (9) and (10) are the Clebsch-Gordan coefficients in the case of our phases \( Y_{lm}^* = Y_{l-m}, \) see Ref. [27]).

The coefficients \( C(l'l'm, \lambda L) \) and \( Q_{\lambda L} \) in Eq. (8) are determined by the following relationships:
\[
C(l'l'm, \lambda L) = (-1)^{l+m-\lambda} \left[ (2l+1)(2l'+1)F_{\lambda+m}(l+m)F_{\lambda-m}(l-m) \right]^{1/2}
\]  
(11)

\[
Q_{\lambda L} = \sum_{k=0}^{[L/2]} \sum_{p=0}^{L-2k} D_{Lkp}R^{l+\lambda-L-2k-2p-1}J(n'+\lambda+2k-L,n-1,p).
\]  
(12)

In Eqs. (11) and (12) the coefficients \( D \) and \( J \) have the form
\[
D_{Lkp} = \frac{(-1)^k}{2L-2k} \frac{F_k(L)F_L(2L-2k)F_p(L-2k)},
\]  
(13)
\[ J(M, N, p) = R^{M+N+2p+2} \sum_{\mu=0}^{M+N} B_{MN\mu} A_{\mu+p}(u) B_{M+N-\mu+p}(\nu), \] (14)

where \( u = (\zeta + \zeta')R/2, \nu = (\zeta - \zeta')R/2 \) and
\[ B_{MN\mu} = \frac{1}{2^{M+N+1}} \sum_{i} (-1)^{N-\mu+i} F_i(M) F_{\mu-i}(N). \] (15)

Here \( F_n(n) = n!/[((m!(n-m)!)] \) are the binomial coefficients and \( A_n \) are \( B_n \) the well known auxiliary functions [28]:
\[ A_n(u) = \int_{-1}^{1} \mu^n e^{-u\mu} d\mu = \frac{n!e^{-u}}{u^{n+1}} \sum_{i=0}^{n} u^i i!, \] (16)
\[ B_n(u) = \int_{-1}^{1} \nu^n e^{-u\nu} d\nu = \begin{cases} (-1)^{n+1} A_n(-u) - A_n(u) & u \neq 0, \\ \frac{1}{n+1}[1 + (-1)^n] & u = 0. \end{cases} \] (17)

The quantities \( \left[ \begin{array}{ccc} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{array} \right] \) in Eq. (11) are the 3-\( j \) coefficients (see Ref. [28]). We express the 3-\( j \) coefficients in terms of the binomial coefficients
\[ \left[ \begin{array}{ccc} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{array} \right] = (-1)^{(l_1+l_2+l_3)/2} \Delta(l_1l_2l_3) \]
\[ \times \begin{cases} F_{l_3}((l_1 + l_2 + l_3)/2) F_{(l_2+l_3-l_1)/2}(l_3) & \text{for even } l_1 + l_2 + l_3, \\ 0 & \text{for odd } l_1 + l_2 + l_3, \end{cases} \] (18)

where
\[ \Delta(l_1l_2l_3) = \frac{1}{\sqrt{F_{l_1+l_2-l_3}(l_1 + l_2 + l_3 + 1) F_{2l_3}(2l_3 + 1) F_{l_2+l_3-l_1}(2l_3)}}. \] (19)

As can be seen from the equations in this study, all of the coefficients appearing in the formulas for overlap integrals are expressed in terms of binomial coefficients.

III. DISCUSSION

On the basis of the new algorithm presented in this paper we constructed a program for evaluating the two-center overlap integrals over STOs in the molecular coordinate system. The results of the calculations, done on a PENTIUM III 800 MHz computer (using Turbo Pascal language), for various values of the parameters are presented in Table I. We note, for the exact and rapid calculation of the overlap integrals, the need to avoid the use...
TABLE I: The values of the two-center overlap integrals over STOs in the molecular coordinate system (a.u.).

<table>
<thead>
<tr>
<th>n</th>
<th>l</th>
<th>m</th>
<th>n'</th>
<th>l'</th>
<th>m'</th>
<th>ζ</th>
<th>ζ'</th>
<th>R</th>
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of factorials with large values. Therefore, in this study, the coefficients $3-j$, $C$, and $D$ of Ref. [24] have been expressed in terms of binomial coefficients. For quick calculation, the binomial coefficients are stored in the memory of the computer. For the binomial coefficients we use the following recurrence expression:

$$F_m(n) = F_m(n-1) + F_{m-1}(n-1).$$

(20)

In order to put these coefficients into or to retrieve them from the memory, the positions of certain coefficients $F_m(n)$ can be determined by the following relation:

$$F(n,m) = n(n+1)/2 + m + 1.$$  

(21)

As can be seen from Table I, our results are satisfactory compared with the values obtained in Ref. [30] from other analytical expressions. It is should be noted that we have also presented in Ref. [26] an algorithm for the evaluation of overlap integrals over STOs in lined-up and non lined-up coordinate systems, using the orthonormal sets of Lambda and Coulomb Sturmians exponential-type orbitals.

References