A New Algorithm for the Calculation of Two-Center Overlap Integrals Over Slater-Type Orbitals

B. A. Mamedov[1], M. Kara[2], and M. Orbay[2]

[1]Department of Physics, Faculty of Arts and Sciences, Gaziosmanpaşa University, Tokat, Turkey

[2]Department of Physics, Faculty of Education, Ondokuz Mays University, Amasya, Turkey

(Received September 14, 2001)

In this study, a new algorithm is presented for two-center overlap integrals, using translation formulas for residual and regular solid spherical harmonics in Slater-type orbitals. The compulational results obtained are in good agreement with the literature and also show a good rate of convergence and good numerical stability under a wide range of quantum numbers, orbital exponents and internuclear distances.

PACS. 31.15.-p – Calculations and mathematical techniques in atomic and molecular physics.
PACS. 31.20.Ej – Ab initio MO calculations.

I. Introduction

It is known that the Schrödinger equation is exactly solvable only for a few quantum mechanical systems, among which is the well-known hydrogen atom. Therefore we have no choice in the treatment of more complicated systems, namely many-electron systems, but to turn to approximation methods; the most commonly used in the realm of quantum chemistry is the variational technique. It is natural to expect that the trial function used in the variation procedure should converge rapidly to the exact solution and also has to satisfy the following criteria:

a) Kato cups condition at the nuclei [1],

b) Exponential decrease at infinity [2].

Among the basis functions commonly used, or proposed for molecular calculations, the Gaussian type orbitals (GTOs) are the most widely used since the multicenter molecular integrals occurring in *ab initio* calculations that it yields are both easy to derive and fast to compute. However GTOs do not satisfy the above mentioned criteria. Thus interest has been renewed in different exponential type functions [3-9], *i.e.*, Bessel function type orbitals (BTO), Sturmians. A group of well-known exponential functions are the Slater type orbitals (STOs), which are of fundamental importance in the study of various properties for molecules since they can satisfy the above mentioned criteria. However they have not been used extensively in the widely diffused molecular computational program, due to the difficulty of computing the notorious multicenter integrals. Fortunately, with the great progress made in both applied mathematics and computers, significant progress has been made in several quarters of long-standing problems of computing with STOs.

In quantum mechanical calculations of the electronic structure of molecules, one has to evaluate the two-center overlap integrals over STOs accurately and efficiently. These integrals arise not only in the Hartree-Fock-Roothaan (HFR) equations of molecules, but are central to the

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calculation of arbitrary multicenter integrals based on the series expansion formulas for STOs about a new center. Also, they are needed in semiemprical quantum mechanical calculations [10]. The existing literature (see. E.g. Refs. [3-9] and references quoted in these works) contains a number of formulas which are not satisfactory for large quantum numbers.

In our previous papers [11], the multicenter integrals have been expressed in terms of two-center overlap integrals over STOs. The aim of this work is to present a new algorithm for the calculation of two-center overlap integrals using translation formulas for the radial [8] and angular [12] part of the STOs.

II. General definitions and method

The two-center overlap integrals over STOs in an aligned coordinate system examined in this study have the following form:

$$S_{n_a l_a \lambda, n_b l_b \lambda}(\zeta_a, \zeta_b; \vec{R}) = \int \chi_{n_a l_a \lambda}(\zeta_a, \vec{r}_a) \chi_{n_b l_b \lambda}(\zeta_b, \vec{r}_b) dV, \tag{1}$$

where $\lambda = |m_a| = |m_b|$, $\vec{R} = \vec{r}_a - \vec{r}_b$, $\chi_{n_a l_a \lambda}(\zeta_a, \vec{r}_a)$ and $\chi_{n_b l_b \lambda}(\zeta_b, \vec{r}_b)$ are normalized STOs centered on the nuclei a and b, respectively.

In the most general case, an STO is defined as follows:

$$\chi_{nlm}(\zeta, r) = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} r^{n-1} exp(-\zeta r) \left\{ \begin{array}{l} Y_{lm}(\theta, \varphi) \\ S_{lm}(\theta, \varphi) \end{array} \right. \quad \text{with} \left\{ \begin{array}{l} n = 1, 2, 3, ... \\ l = 0, 1, 2, ..., n-1 \\ m = -l, -l+1, ..., l \end{array} \right. \tag{2}$$

where ζ is the orbital exponent, $Y_{lm}(\theta, \varphi)$ and $S_{lm}(\theta, \varphi)$ are the complex or real spherical harmonics [13], respectively.

In the calculation of two-center overlap integrals our algorithm involves the translation of the residual [8] and regular solid spherical harmonics $M_{lm}(\vec{r})$ [12] parts of the STOs. Since the translation and rotational properties of regular solid spherical harmonics are well-known [12,14], we express STOs centered on the nuclei b in terms of $M_{lm}(\vec{r})$ as follows

$$\chi_{n_b l_b \lambda}(\zeta_b, \vec{r}_b) = \frac{(2\zeta_b)^{n_b+\frac{1}{2}}}{\sqrt{(2n_b)!}} \sqrt{\frac{2l_b+1}{4\pi}} r_b^{n_b-l_b-1} \exp(-\zeta_b r_b) M_{l_b \lambda}(\vec{r}_b), \tag{3}$$

where $M_{l_b \lambda}(\vec{r}_b)$ is a regular solid spherical harmonic of degree l_b and order λ on the nuclei b and is given by

$$M_{l_b \lambda}(\vec{r}_b) = \sqrt{\frac{4\pi}{2l_b+1}} r_b^{l_b} S_{l_b \lambda}(\theta_b, \varphi) \tag{4}$$

and $r_b^{n_b-l_b-1} exp(-\zeta_b r_b)$ is called the residual part of the STOs.

For the evaluation of the integral (1), we will use translation formulae:
First, a translation of $M_{l_b \lambda}(\vec{r}_b)$ from b to nuclei a [12]

$$M_{l_b \lambda}(\vec{r}_b) = \sum_{l'=0}^{l_b} \sum_{m'=-l'}^{l'} {}_{l_b \lambda, l' m'}(\vec{R}) M_{l' m'}(\vec{r}_a), \tag{5}$$

where $\ _{l_b\lambda,l'm'}(\vec{R})$ is the expansion coefficients for the translation of regular solid spherical harmonics (see: Ref. [12] for the exact definition of $\ _{l_b\lambda,l'm'}(\vec{R})$).
Second, the translation of the residual part of the STOs

$$r_b^q e^{-\zeta_b r_b} = \sqrt{2\pi}\sum_{k=0}^{\infty} R_k(q,\zeta_b r_>,\cos\theta) r_<^k\ r_>^{q-k}\ e^{\zeta_b r_>}, \tag{6}$$

where $R_k(q,\zeta_b r_>,\cos\theta)$ and $r_<, r_>$ are defined in Ref. [8].

Similarly, by expanding the residual spherical parts of the orbitals [8], the two-center overlap integrals between the STOs χ_a and χ_b can be obtained by integrating over spherical coordinates for complex STOs :

$$\begin{aligned} &S_{n_a l_a\lambda,n_b l_b\lambda}(\zeta_a,\zeta_b;\vec{R}) \\ &= N_{n_a n_b}(\zeta_a,\zeta_b)\sum_{k=0}^{\infty}\sum_{j=0}^{k}\frac{\zeta_b^j}{k!}\sum_{l'=0}^{l_b}\sum_{m'=-l'}^{l'}\sqrt{\frac{2l_b+1}{2l'+1}}R^{l'+j-l_b}\ \ _{l_b\lambda,l'm'}(\vec{R}) \\ &\quad (e^{-\zeta_b R}A^{(0,1)}_{n_a+l'+k+1}(\zeta_a R) + A^{(1,\infty)}_{n_a+l'+q+j-k+1}(2p))\delta_{\lambda m'} \\ &\quad \times \sum_{\nu=max(0,l_b-j-\delta_{k,0})}^{mn(k-j,q)}(-1)^{\nu}\nu! F_{\nu}(q)F_j(j+\nu)\sum_{L=|l_a-l'|}^{l_a+l'}\beta_L^{k,j+\nu}C^L(l_a\lambda,l'm'), \end{aligned} \tag{7}$$

for real STOs :

$$\begin{aligned} &S_{n_a l_a\lambda,n_b l_b\lambda}(\zeta_a,\zeta_b;\vec{R}) \\ &= N_{n_a n_b}(\zeta_a,\zeta_b)\sum_{k=0}^{\infty}\sum_{j=0}^{k}\frac{\zeta_b^j}{k!}\sum_{l'=0}^{l_b}\sum_{m'=-l'}^{l'}\sqrt{\frac{2l_b+1}{2l'+1}}R^{l'+j-l_b}\ \ _{l_b\lambda,l'm'}(\vec{R}) \\ &\quad (e^{-\zeta_b R}A^{(0,1)}_{n_a+l'+k+1}(\zeta_a R) + A^{(1,\infty)}_{n_a+l'+q+j-k+1}(2p))\delta_{\lambda m'} \\ &\quad \times \sum_{\nu=max(0,l_b-j-\delta_{k,0})}^{mn(k-j,q)}(-1)^{\nu}\nu! F_{\nu}(q)F_j(j+\nu)\sum_{L=|l_a-l'|}^{l_a+l'}\beta_L^{k,j+\nu}C^L(l_a\lambda,l'm')A^0_{\lambda m'}. \end{aligned} \tag{8}$$

In Eqs. (7-8)

$$N_{n_a n_b}(\zeta_a\zeta_b) = \frac{(2\zeta_a)^{n_a+1/2}(2\zeta_b)^{n_b+1/2}}{\sqrt{(2n_a)!(2n_b)!}}(2p)^{n_a+n_b+1}, \tag{9}$$

$$p = \frac{R}{2}(\zeta_a+\zeta_b);\ q = n_b - l_b - 1 \text{ and } F_m(n) = \frac{n!}{m!(n-m)!}, \tag{10}$$

and $\beta_L^{k,j+\nu}$ is defined in Ref. [8], $C^L(l_a\lambda,l'm')$ is the Gaunt coefficient, the functions $A_n^{(1,\infty)}(p)$ and $A_n^{(0,1)}(p)$ contained in Eq. (6) are called Mulliken integrals [15]. The detailed discussion on these integrals and the $A^0_{\lambda m'}$ coefficient can be found in Refs. [6.i, 8, 16].

TABLE I. The comparative values of two-center overlap integrals over STOs in an aligned coordinate system for various quantum sets.

n_a	l_a	n_b	l_b	λ	ζ_a	ζ_b	R	**Eq. (7)**	**Ref.[11.e]**
2	1	2	1	1	2.5	1.5	3	9.13540567807555E-02	9.13540578540051E-02
2	1	2	1	0	7.5	2.5	2	-5.35972415539902E-02	-5.35972546055632E-02
3	2	2	1	1	1.5	2.5	6	1.05874608206221E-02	1.05874614533263E-02
3	2	3	2	2	2	1.8	10	1.21803001685809E-05	1.21905596272555E-05
4	2	3	2	2	9	1	0.1	4.68807067044795E-02	4.68806402653854E-02
4	3	4	3	2	10.5	9.5	2	-2.19276977388729E-04	-2.19276990356843E-04
4	3	4	3	0	3	2	13	-1.82631233180015E-06	-1.82628807205050E-06
4	3	2	1	1	8	2	0.8	8.445354308841430E-02	8.445354518346451E-02
4	3	4	3	3	7	3	0.2	4.35674443901789E-01	4.35674412810698E-01
5	1	4	1	1	7	7	1.2	2.01643259847683E-01	2.0164325959111E-01
5	2	4	2	2	30.7	10.5	0.03	4.06775977565192E-01	4.0671032820270E-01
5	3	4	2	0	40	30	0.01	1.10079788367633E-01	1.1007985633392E-01
5	2	5	1	1	4	3	8	1.45746553590791E-05	1.45732108034643E-05
5	2	5	2	2	6	7	4	4.75662464102031E-06	4.75215500164643E-06

III. Numerical results and discussion

We have established a new algorithm for the evaluation of two-center overlap integrals in aligned coordinate systems. Our algorithm consists of the translation of the regular solid spherical harmonics and the residual part of a STOs. The formula obtained in this study is in terms of auxiliary integrals $A_n^{(0,1)}(p)$ and $A_n^{(1,\infty)}(p)$ and Gaunt coefficients. The auxiliary function $A_n^{(1,\infty)}(p)$ and Gaunt coefficient have been discussed in our previous works [16, 17].

On the basis of Eq. (7), computer programs have been constructed in the Turbo Pascal 7.0 programming language. The computer results for the two-center overlap integrals are given in Table I. As can be seen from the Table I, our results agree well with the studies in Refs. [3-9]. In addition, our results show a good rate of convergence and great numerical stability under a wide range of quantum numbers, orbital exponents and internuclear distances. This is most promising in view of further application of the expansion to the many center case.

Work is in progress for the evaluation of the multicenter molecular integrals over STOs based on two-center overlap integrals given in this paper.

Acknowledgement

We are very grateful to Prof. V. Magnasco for useful help and also one of the authors (B. A. Mamedov) thanks TUBITAK for financial support for his visit to Gaziosmanpaşa University.

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