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Computation of multicenter overlap integrals with Slater-type orbitals using Ψ^{α}-ETOs

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Abstract Multicenter overlap integrals appearing in the evaluation of multicenter–multielectron integrals of central and noncentral interaction potentials are calculated using complete orthonormal sets of Ψ^{α}-ETOs (α=1, 0, −1, −2, ...). The final results are expressed in terms of two-center overlap integrals between STOs. The convergence of the series is tested by calculating concrete cases for arbitrary quantum numbers, screening constants and location of STOs.

Keywords Slater-type orbitals · Multicenter overlap integrals · Central and noncentral potentials · Multicenter–multielectron integrals

Introduction

It is well known that the computation of atomic and molecular multielectron properties requires solutions of the Schrödinger equation more accurate than the results obtained from the Hartree–Fock (HF) equations. The variational method for improving the HF solutions in which the interelectronic coordinates are explicitly included in the wave functions was first introduced by Hylleraas. [1, 2] The variational solutions obtained by the Hylleraas method converge to the exact solution of Schrödinger equation with any desired degree of accuracy if a sufficient number of terms are included. However, it is difficult to evaluate the multicenter integrals that arise in Hylleraas theory. The Hylleraas method developed first by James and Coolidge [3] has been used for determining the ground state energy of the H_2 molecule [4, 5] and still valid for two-, three- and four-electron atomic and molecular systems. [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]

In [23], we established the general formulae for the multicenter–multielectron integrals of central and noncentral interaction potentials in terms of multicenter overlap integrals, which arise in the solution of multielectron atomic and molecular problems when a Hylleraas approximation in Hartree–Fock theory is employed. The purpose of this paper is to present an evaluation of t-center overlap integrals:

$$S^{acd\ldots gb}_{p_1p_2p_3\cdots p_{t-1}p_t}(\zeta_1\zeta_2\zeta_3\ldots\zeta_{t-1}\zeta_t) = (\sqrt{4\pi})^{t-2}\int \chi^{*}_{p_1}(\zeta_1,\vec{r}_a)\chi_{p_2}(\zeta_2,\vec{r}_c)\chi_{p_3}(\zeta_3,\vec{r}_d)\ldots\chi_{p_{t-1}}\cdot\cdot(\zeta_{t-1},\vec{r}_g)\chi_{p_t}(\zeta_t,\vec{r}_b)dv \quad (1)$$

where $t \geq 2$, $p_i \equiv n_i l_i m_i$ and the functions χ_{p_i} are the normalized Slater-type orbitals (STOs):

$$\chi_{nlm}(\zeta,\vec{r}) = R_n(\zeta,r)S_{lm}(\theta,\varphi) \quad (2)$$

$$R_n(\zeta,r) = (2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}}r^{n-1}e^{-\zeta r} \quad (3)$$

Here S_{lm} are complex $S_{lm} \equiv Y_{lm}$ or real spherical harmonics determined by the relation

$$S_{lm}(\theta,\varphi) = P_{l|m|}(\cos\theta)\Phi_m(\varphi) \quad (4)$$

where $P_{l|m|}$ are normalized associated Legendre functions and for complex SH

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi} \quad (5)$$

for real SH

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$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \begin{cases} \cos|m|\varphi & \text{for} \quad m \geqslant 0 \\ \sin|m|\varphi & \text{for} \quad m < 0. \end{cases} \tag{6}$$

We note that our definition of phases for complex spherical harmonics $S^*_{lm}(\theta,\varphi) = S_{l-m}(\theta,\varphi)$ differs from the Condon–Shortley phases by the sign factor $(-1)^m$.

The multicenter overlap integrals arise in the determination of various t-electron properties for N-electron atomic and molecular systems ($2 \leq t \leq N$) when a Hylleraas-type approximation is employed in Hartree–Fock–Roothaan theory. These integrals are required in the calculation of multicenter–multielectron integrals for a t-electron operator of arbitrary central and noncentral interaction potentials, [23] the linear combination of which gives the matrix elements of the same operator between N-dimensional determinantal wavefunctions of the N-electron system. [24] With the help of formulae for the expansion of STOs in terms of STOs at a new origin, [25] the multicenter overlap integrals, (Eq. 1), are expressed through the two-center overlap integrals, for the computation of which efficient computer programs specially useful for large quantum numbers are available in our group. [26]

Expansion for products of STOs

In order to evaluate multicenter overlap integrals we shall require the expansion relation for product of STOs:

$$\chi^*_{n_1 l_1 m_1}(\zeta_1,\vec{r})\chi_{n_2 l_2 m_2}(\zeta_2,\vec{r})\ldots\chi_{n_k l_k m_k}(\zeta_k,\vec{r}) = R_{n_1 n_2 \ldots n_k}(\zeta_1\zeta_2\ldots\zeta_k, r)\Theta_{l_1 m_1, l_2 m_2 \ldots, l_k m_k}(\theta,\varphi) \tag{7}$$

where

$$R_{n_1 n_2 \ldots n_k}(\zeta_1\zeta_2\ldots\zeta_k, r) = R_{n_1}(\zeta_1, r)R_{n_2}(\zeta_2, r)\ldots R_{n_k}(\zeta_k, r) \tag{8}$$

$$\Theta_{l_1 m_1, l_2 m_2, \ldots, l_k m_k}(\theta,\varphi) = S^*_{l_1 m_1}(\theta,\varphi)S_{l_2 m_2}(\theta,\varphi)\ldots S_{l_k m_k}(\theta,\varphi) \tag{9}$$

Taking into account Eq. (3) for the radial part of STOs in Eq. (8), it is easy to establish the following relation:

$$R_{n_1 n_2 \ldots n_k}(\zeta_1\zeta_2\ldots\zeta_k, r) = R_{n_1 n_2 \ldots n_k}(\zeta_1\zeta_2\ldots\zeta_k)R_{N_k}(z_k, r) \tag{10}$$

$$R_{n_1 n_2 n_3 \ldots n_k}(\zeta_1\zeta_2\ldots\zeta_k) = \left[\frac{(2N_k)!}{(2n_1)!(2n_2)!\ldots(2n_k)!}\right]^{1/2} \cdot \cdot (\sqrt{2z_k})^{3(k-1)} x_1^{n_1+1/2} x_2^{n_2+1/2} \ldots x_k^{n_k+1/2} \tag{11}$$

where

$$N_k = n_1 + n_2 + \ldots + n_k - k + 1,$$
$$z_k = \zeta_1 + \zeta_2 + \ldots + \zeta_k, \; x_i = \zeta_i / z_k$$

and the function $R_{N_k}(z_k, r)$ is the radial part of normalized STOs determined by Eq. (3).

In order to derive the expansion relation for Eq. (9) we utilize the orthonormality relation of spherical harmonics and the expansion formula: [27]

$$S^*_{lm}(\theta,\varphi)S_{l'm'}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}} \sum_{L=|l-l'|}^{l+l'} \sum_{M=-L}^{L} d^{L|M|}(lm, l'm')S^*_{LM}(\theta,\varphi) \tag{12}$$

$$d^{LM}(lm, l'm') = (2L+1)^{1/2} C^{L|M|}(lm, l'm')A^M_{mm'} \tag{13}$$

where

$$C^{L|M|}(lm, l'm') = \begin{cases} C^L(lm, l'm') & \text{for} \quad |M| = |m - m'| \\ C^L(lm, l' - m') & \text{for} \quad |M| = |m + m'| \end{cases} \tag{14}$$

$$A^M_{mm'} = \begin{cases} \frac{1}{\sqrt{2}}(2 - \left|\eta^{m-m'}_{mm'}\right|)^{1/2}\, \delta_{M,\varepsilon|m-m'|} + \frac{1}{\sqrt{2}}\eta^{m+m'}_{mm'}\delta_{M,\varepsilon|m+m'|} & \text{for real STOs} \\ \delta_{M,m-m'} \quad \text{for complex STOs.} \end{cases} \tag{15}$$

Here, the quantities $C^{L|M|}(lm, l'm')$ are the Gaunt coefficients. [28] We notice that in recent years several articles have appeared in which properties of Gaunt coefficients as well as their efficient and reliable computation were discussed. [29, 30, 31, 32, 33] The symbol $\varepsilon \equiv \varepsilon_{mm'}$ in Eq. (15) may have the values ±1 and is determined by the product of the signs m and m' (the sign of zero regarded as positive). The symbols $\eta^{m\pm m'}_{mm'}$ may have the ±1 and 0: if among the indices m, m' and $m \pm m'$ there occurs a value equal to zero, then $\eta^{m\pm m'}_{mm'}$ is also zero; if all the indices differ from zero, $\eta^{m\pm m'}_{mm'} = \pm 1$ and the sign is determined by the product of the signs of m, m' and $m \pm m'$.

Taking into account Eq. (12) we obtain the following expansion relation in terms of spherical harmonics:

$$\Theta_{l_1 m_1, l_2 m_2, \ldots, l_k m_k}(\theta,\varphi) = \frac{1}{(\sqrt{4\pi})^{k-1}} \sum_{L_2 M_2, L_3 M_3, \ldots, L_k M_k} d^{L_2 M_2}(l_1 m_1, l_2 m_2) \cdot \cdot d^{L_3 M_3}(L_2 M_2, l_3 m_3)\ldots d^{L_k M_k}(L_{k-1} M_{k-1}, l_k m_k) \cdot \cdot S^*_{L_k M_k}(\theta,\varphi). \tag{16}$$

Use of translation formulae for STOs

Now we can move on to the evaluation of multicenter overlap integrals, (Eq. 1). For this purpose, we utilize the translation formulae for STOs established in [25] with the help of Ψ^{α}-ETOs (see Eq. 15 of [25]):

$$\chi_{nlm}(\zeta,\vec{r}_{a1}) = \lim_{N\to\infty}\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'} V^{\alpha N*}_{nlm,n'l'm'}(\zeta,\zeta;\vec{R}_{ab})\chi_{n'l'm'}(\zeta,\vec{r}_{b1}) \quad (17)$$

where $\alpha = 1, 0, -1, -2, \ldots$ and

$$V^{\alpha N}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab}) = \sum_{n''=l'+1}^{N}\Omega^{\alpha l'}_{n'n''}(N)S_{nlm,n''-\alpha l'm'}(\zeta,\zeta';\vec{R}_{ab}) \quad (18)$$

$$\Omega^{\alpha l}_{nk}(N) = \left[\frac{[2(k-\alpha)]!}{(2k)!}\right]^{\frac{1}{2}}\sum_{n'=\max(n,k)}^{N}(2n')^{\alpha}\omega^{\alpha l}_{n'n}\omega^{\alpha l}_{n'k} \quad (19)$$

$$\omega^{\alpha'}_{nn'} = (-1)^{n'-l-1}\left[\frac{(n'+l+1)!}{(2n)^{\alpha}(n'+l+1-\alpha)!}F_{n'+l+1-\alpha}\cdot \cdot(n+l+1-\alpha)F_{n'-l-1}(n-l-1)F_{n'-l-1}(2n')\right]^{1/2} \quad (20)$$

Here $F_k(n) = n!/[k!(n-k)!]$ and the quantities $S_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab}) \equiv S^{ab}_{nlm,n'l'm'}(\zeta,\zeta')$ are the two-center overlap integrals of STOs defined by

$$S_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ab}) = \int \chi^{*}_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm'}(\zeta',\vec{r}_b)dv \quad (21)$$

Taking into account the translation relation (17), it is easy to express the t-center overlap integrals through the two-center integrals $S^{aaa\ldots ab}$:

$$S^{acd\ldots gb}_{p_1p_2p_3\ldots p_{t-1}p_t}(\zeta_1\zeta_2\zeta_3\ldots\zeta_{t-1}\zeta_t) = \lim_{N_2N_3\ldots N_{t-1}\to\infty}\sum_{q_2q_3\ldots q_{t-1}} V^{\alpha N^*_2}_{p_2q_2}(\zeta_2,\zeta_2;\vec{R}_{ca})\cdot \cdot V^{\alpha N^*_3}_{p_3q_3}(\zeta_3,\zeta_3;\vec{R}_{da})\times\ldots V^{\alpha N^*_{t-1}}_{p_{t-1}q_{t-1}}(\zeta_{t-1},\zeta_{t-1};\vec{R}_{ga})\cdot \cdot S^{aaa\ldots ab}_{p_1q_2q_3\ldots q_{t-1}p_t}(\zeta_1\zeta_2\zeta_3\ldots\zeta_{t-1}\zeta_t), \quad (22)$$

where

$\vec{R}_{ik} = \vec{r}_i - \vec{r}_k$ $(i,k = a,b,c$ and $d)$

$q_i \equiv \mu_i\nu_i\sigma_i,\ 1 \le \mu_i \le N_i,\ 0 \le \nu_i \le \mu_i - 1$

and

$-\nu_i \le \sigma_i \le \nu_i$ $(2 \le i \le t-1)$;

μ_i, ν_i and σ_i stand for the quantum numbers.

In order to evaluate the two-center integrals $S^{aaa\ldots ab}$ that occur in Eq. (22), we take into account Eqs. (7), (10) and (16) for k=t−1 in Eq. (1). Then, it is easy to express the integral $S^{aaa\ldots ab}$ in terms of two-center overlap integrals:

$$S^{aaa\ldots ab}_{p_1q_2q_3\ldots q_{t-1}q_t}(\zeta_1\zeta_2\zeta_3\ldots\zeta_{t-1}\zeta_t) = R_{n_1\mu_2\mu_3\ldots\mu_{t-1}}(\zeta_1\zeta_2\zeta_3\ldots\zeta_{t-1})\sum_{L_2M_2,L_3M_3,\ldots,L_{t-1}M_{t-1}}\cdot \cdot d^{L_2M_2}(l_1m_1,\nu_2\sigma_2)d^{L_3M_3}(L_2M_2,\nu_3\sigma_3) \times\ldots d^{L_{t-1}M_{t-1}}(L_{t-2}M_{t-2},\nu_{t-1}\sigma_{t-1})\cdot \cdot S_{N_{t-1}L_{t-1}M_{t-1},n_tl_tm_t}(z_{t-1},\zeta_t;\vec{R}_{ab}). \quad (23)$$

As can be seen from Eqs. (22),(18) and (23), the evaluation of t-center overlap integrals for the N-electron system ($2 \le t \le N$) is reduced to the evaluation of two-center overlap integrals over STOs. Thus, with the aid of the formulae that have been established in this study, we can calculate the multicenter–multielectron integrals of arbitrary central and noncentral potentials by the use of two-center overlap integrals. (see [23]).

Discussion

Explicit formulae have been presented for computation of the multicenter overlap integrals that arise in multielectron atomic and molecular calculations which use central and noncentral interaction potentials. The two-center overlap integrals can be utilized as a basis in the calculation of these integrals, therefore, in the solution of multielectron problem when a Hylleraas approximation is employed in HFR theory.

Multicenter overlap integrals have not been studied in the literature so far. For these integrals in this work we obtained analytical formulae in terms of two-center overlap integrals. The accuracy of the resulting calculations of multicenter overlap integrals was tested by the use of four different methods in which we utilize the different complete orthonormal sets of Ψ^1, Ψ^0, Ψ^{-1} and Ψ^{-1}-ETOs.

The results of calculations for three- and four-center overlap integrals on a Pentium III 800-MHz computer (using Turbo Pascal) are given in Table 1. The comparative values obtained from Ψ^1, Ψ^0 and Ψ^{-1}-ETOs and the CPU time in milliseconds are given in the table. As can be seen from the table, the accuracy and the CPU time are satisfactory. We notice that the convergence for a given α, is more rapid for small R, and it deteriorates as R increases. An accuracy of 10^{-5} is obtained for N_2=N_3=12. Greater accuracy is easily attainable by the use of more terms of expansion (22).

It should be noted that the algorithm presented in this study can be used to calculate any multicenter overlap integral for the arbitrary values of screening constants, quantum numbers and location of STOs.

Table 1 Comparison of methods of computing three- and four-center overlap Integrals S^{acb} and S^{acdb} (in a.u.); N_2=N_3=12, θ_{ca}=θ_{ba}=120°, φ_{ca}=φ_{ba}=180°, θ_{db}=60°, φ_{db}=135°

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	n_3	l_3	m_3	ζ_3	n_4	l_4	m_4	ζ_4	R_{ca}	R_{ab}	R_{db}
Equation (<equationcite>22</equationcite>)			CPU (ms)															
α=0	α=1	α=−1																
1	0	0	3	1	0	0	2	1	0	0	5					0.7	0.7	
2	1	0	4	1	0	0	1	1	0	0	3					0.6	0.5	
2	1	0	6	2	1	0	4	1	0	0	3					0.8	1.2	
2	1	0	2.6	2	1	0	1.4	2	1	0	2.3					0.2	0.3	
2	1	1	4.6	2	1	1	2.1	2	1	0	5.2					0.4	0.8	
2	1	1	8.4	2	1	1	6.2	2	1	1	7.5					0.5	0.7	
1	0	0	5.3	1	0	0	2.2	1	0	0	3.5	1	0	0	2	0.5	0.5	0.7
2	1	0	7.5	1	0	0	4.2	1	0	0	6.3	1	0	0	4.2	0.7	0.8	0.4
2	1	0	3.7	2	1	0	1.4	1	0	0	4.6	1	0	0	2.4	1.1	0.6	0.3
2	1	1	4.3	2	1	0	3.1	2	1	0	2.4	1	0	0	4.2	0.6	0.4	0.5
2.190828047E−1	2.190827954E−1	2.190837363E−1	70.6															
−1.350659363E−1	−1.35064399E−1	−1.35067989E−1	87.1															
3.244658422E−2	3.244656994E−2	3.244670201E−2	123.4															
−4.927563426E−2	−4.927556250E−2	−4.927558702E−2	138.1															
4.562199931E−1	4.562214398E−1	4.562362691E−1	157.3															
−1.175969306E−1	−1.177677760E−1	−1.177460754E−1	212.5															
8.869542008E−1	8.869561104E−1	8.869398105E−1	131.4															
−8.817423599E−2	−8.817416446E−2	−8.817259170E−2	187.2															
4.733405848E−1	4.733402453E−1	4.73357161 2E−1	322.7															
1.612331135E−2	1.612347813E−2	1.612426277E−2	410.0															

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