ORIGINAL PAPER

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Addition theorems for Slater-type orbitals and their application to multicenter multielectron integrals of central and noncentral interaction potentials

Abstract By the use of complete orthonormal sets of ψ^{α}-ETOs (α=1, 0, −1, −2, ...) introduced by the author, new addition theorems are derived for STOs and arbitrary central and noncentral interaction potentials (CIPs and NCIPs). The expansion coefficients in these addition theorems are expressed through the Gaunt and Gegenbauer coefficients. Using the addition theorems obtained for STOs and potentials, general formulae in terms of three-center overlap integrals are established for the multicenter t-electron integrals of CIPs and NCIPs that arise in the solution of the N-electron atomic and molecular problem ($2 \leq t \leq N$) when a Hylleraas approximation in Hartree–Fock–Roothaan theory is employed. With the help of expansion formulae for translation of STOs, the three-center overlap integrals are expressed through the two-center overlap integrals. The formulae obtained are valid for arbitrary quantum numbers, screening constants and location of orbitals.

Keywords Addition theorems · Two- and three-center overlap integrals · Central and noncentral potentials · Multicenter multielectron integrals

Introduction

It is well known that the determination of multielectron properties for atoms and molecules requires more accurate solutions of Hartree–Fock (HF) equations. [1] In order to obtain better approximate solutions in HF theory, Hylleraas first introduced the two standard variational approaches in a series of papers on helium-like systems: [2, 3] (1) the Hylleraas (Hy) method, [3, 4] in which the interelectronic coordinates $r_{\mu\nu}$ are explicitly included in the terms of the wave function; (2) the configuration interaction (CI) method, [2, 4] in which the wave function is determined by linear combination of determinantal functions arising from different configurations. [5] There are theoretical grounds [5, 6] for thinking that both the CI and the Hy methods are general methods capable of yielding variational solutions that converge to the exact solution of the Schrödinger equation with any desired degree of accuracy if a sufficient number of terms are included. We notice that the CI expansions converge much more slowly than the Hy-method expansions. Recent work on the hybrid technique Hy–CI, [7] which avoids many of the complicated integrals, converges rather quickly for small systems. A drawback in the Hy-type expansions, however, is the complexity of the calculation of multicenter multielectron integrals. The Hy method first developed by James and Coolidge [8] has been used for determination of the ground state energy of the H_2 molecule [9, 10] and is still valid for two- and three-electron atomic and molecular systems (see, e.g., [11, 12, 13] and references quoted therein).

The purpose of the present paper is to derive formulae for the multicenter integrals of an arbitrary t-electron operator that arise in calculations on atoms and molecules with N electrons, where $2 \leq t \leq N$. These integrals are expressed in terms of two-center overlap integrals for the calculation of which efficient computer programs especially useful for large quantum numbers are available in our group. Therefore, by using the computer programs for the overlap integrals, one can calculate the multicenter integrals of CIPs and NCIPs appearing in the determination of atomic and molecular multielectron properties when the Hartree–Fock–Roothaan approximation is employed.

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Definitions and basic formulae

The general t-electron operator of interaction potentials with the screening parameter η for the N-electron atomic and molecular systems ($2 \leq t \leq N$) can be constructed from

$$O_{uvs}(\eta, \vec{r}_{12...t}) =$$

$$f_{uvs}(\eta, \vec{r}_{21})f_{uvs}(\eta, \vec{r}_{31})f_{uvs}(\eta, \vec{r}_{41})...$$

$$f_{uvs}(\eta, \vec{r}_{t-11})f_{uvs}(\eta, \vec{r}_{t1})f_{uvs}(\eta, \vec{r}_{32}) \times f_{uvs}(\eta, \vec{r}_{42})...$$

$$f_{uvs}(\eta, \vec{r}_{t-12})f_{uvs}(\eta, \vec{r}_{t2})...$$

$$f_{uvs}(\eta, \vec{r}_{t-1t-2})f_{uvs}(\eta, \vec{r}_{tt-2})f_{uvs}(\eta, \vec{r}_{tt-1}) \tag{1}$$

by changing the names of the electrons: [14]

$$F_{uvs}^{(t)} = \sum_{\mu_1 < \mu_2 < ... < \mu_t}^{N} O_{uvs}(\eta, \vec{r}_{\mu_1 \mu_2 ... \mu_t}) \tag{2}$$

Here $f_{uvs}(\eta, \vec{r}_{\mu v})$ are the screened NCIPs which have the form: [15]

$$f_{uvs}(\eta, \vec{r}_{21}) = f_u(\eta, r_{21})\left(\frac{4\pi}{2v+1}\right)^{1/2} S_{vs}(\theta_{21}, \varphi_{21}) \tag{3}$$

where S_{vs} is the complex ($S_{vs}=Y_{vs}$) or real spherical harmonic; $f_u(\eta, r_{21})=f_{u00}(\eta, r_{21})$ denotes a radial part of potential (central potential) with positive or negative integer values of u. We notice that the number of NCIPs $f_{uvs}(\eta, \vec{r}_{\mu v})$ in Eq. (1) is $t(t-1)/2$.

The interaction potentials $f_{uvs}(\eta, \vec{r}_{\mu v})$ and the operator $O_{uvs}(\eta, \vec{r}_{12...t})$ with respect to the permutations of subscripts have the following symmetry properties:

$$\hat{P}_{\mu v}f_{uvs}(\eta, \vec{r}_{\mu v}) = (-1)^v f_{uvs}(\eta, \vec{r}_{\mu v}) \tag{4}$$

$$\hat{P}_{\mu v}O_{uvs}(\eta, \vec{r}_{12...t}) = (-1)^v O_{uvs}(\eta, \vec{r}_{12...t}) \tag{5}$$

where $2 \leq v \leq t$ and $1 \leq \mu \leq v$. It should be noted that the operators $F_{uvs}^{(t)}$ and $O_{uvs}(\eta, \vec{r}_{12...t})$ for even values of v are not changed in application of $N!$ and $t!$ permutations, respectively.

In [14] we have established a theorem for matrix elements of a general t-electron operator, (Eq. 2), between N-dimensional determinantal wave functions arising in the solution of the atomic and molecular multielectron problem by the Hartree–Fock method. According to this theorem, the required matrix elements of this operator between N-dimensional determinantal wave functions are sums of matrix elements over t-dimensional basic determinantal wave functions. Therefore, the matrix elements between N-dimensional determinantal wave functions can be expressed, in general, through the following $2t$-center integrals of STOs with the t-electron operator (see Eq. 11 of [14]):

$$I_{p_1 p_1', p_2 p_2', p_3 p_3', ..., p_t p_t'; \tau}^{ac, bd, gh, ..., ef}(\zeta_1 \zeta_1', \zeta_2 \zeta_2', \zeta_3 \zeta_3', ..., \zeta_t \zeta_t'; \eta)$$

$$= \int \chi_{p_1}^*(\zeta_1, \vec{r}_{a1})\chi_{p_1'}(\zeta_1', \vec{r}_{c1})\chi_{p_2}(\zeta_2, \vec{r}_{b2})\chi_{p_2'}$$

$$\cdot(\zeta_2', \vec{r}_{d2})\chi_{p_3}(\zeta_3, \vec{r}_{g3})\chi_{p_3'}(\zeta_3', \vec{r}_{h3})...\chi_{p_t}(\zeta_t, \vec{r}_{et})$$

$$\times \chi_{p_t'}(\zeta_t', \vec{r}_{ft})O_\tau(\eta, \vec{r}_{123...t})dv_1 dv_2 dv_3...dv_t \tag{6}$$

where $2 \leq t \leq N$, $p_i \equiv n_i l_i m_i$, $p'_i \equiv n'_i l'_i m'_i$, $\tau \equiv uvs$. Here, the normalized STOs are determined by

$$\chi_{nlm}(\zeta, \vec{r}) = R_n(\zeta, r)S_{lm}(\theta, \varphi) \tag{7}$$

$$R_n(\zeta, r) = (2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}}r^{n-1}e^{-\zeta r} \tag{8}$$

Addition theorems for STOs and potentials

For the evaluation of integral (6) we require addition theorems for STOs and potentials. For this purpose we use the formulae for the expansion of STOs in terms of STOs at a new origin established with the help of ψ^α-ETOs: [16]

$$\chi_{nlm}(\zeta, \vec{r}_{a1})$$

$$= \lim_{N \to \infty} \sum_{n'=1}^{N} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} V_{nlm,n'l'm'}^{\alpha N*}(\zeta, \zeta; \vec{R}_{ab})\chi_{n'l'm'}(\zeta, \vec{r}_{b1}) \tag{9}$$

Here the translation coefficients $V^{\alpha N}$ are determined by

$$V_{nlm,n'l'm'}^{\alpha N}(\zeta, \zeta; \vec{R}_{ab})$$

$$= \sum_{n''=l'+1}^{N} \Omega_{n'n''}^{\alpha l'}(N) S_{nlm,n''-\alpha l'm'}(\zeta, \zeta; \vec{R}_{ab}) \tag{10}$$

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

$$\Omega_{n\kappa}^{\alpha l}(N) = \left[\frac{[2(k-\alpha)]!}{(2\kappa)!}\right]^{\frac{1}{2}} \sum_{n'=\max(n,\kappa)}^{N} (2n')^\alpha \omega_{n'n}^{\alpha l}\omega_{n'\kappa}^{\alpha l} \tag{11}$$

$$\omega_{nn'}^{\alpha l} = (-1)^{n'-l-1}$$

$$\cdot \left[\frac{(n'+l+1)!}{(2n)^\alpha(n'+l+1-\alpha)!}F_{n'+l+1-\alpha}(n+l+1-\alpha)\right.$$

$$\left.\times F_{n'-l-1}(n-l-1)F_{n'-l-1}(2n')\right]^{1/2} \tag{12}$$

Here $Fk(n)=n!/[k!(n-k)!]$ and the quantities $S_{nlm,n'l'm'}$ are overlap integrals between normalized STOs:

$$S_{nlm,n'l'm'}(\zeta, \zeta; \vec{R}_{ab}) = \int \chi_{nlm}^*(\zeta, \vec{r}_{a1})\chi_{n'l'm'}(\zeta, \vec{r}_{b1})dv_1 \tag{13}$$

The overlap integrals with the same screening constants ($\zeta = \zeta'$) can be expressed in terms of STOs: [17]

$$S_{nlm,n'l'm'}(\zeta, \zeta; \vec{R}_{ab})$$

$$= \frac{\sqrt{4\pi}}{\zeta^{3/2}} \sum_{\mu-1}^{n+n'+1} \sum_{v=0}^{\mu-1} \sum_{\sigma=-v}^{v} g_{nlm,n'l'm'}^{\alpha\mu v\sigma}\chi *_{\mu v\sigma}(\zeta, \bar{R}_{ab}) \tag{14}$$

where

$$g_{nlm,n'l'm'}^{\alpha\mu v\sigma} = \frac{1}{\sqrt{4\pi}} \sum_{\mu'=1}^{n+n'+1} \Omega_{\mu\mu'}^{\alpha v}(n+n'+1)T_{nlm,n'l'm'}^{\mu'-\alpha v\sigma} \tag{15}$$

The relation for coefficients $T_{nlm,n'l'm'}^{\mu'-\alpha v\sigma}$ in terms of Gaunt and Gegenbauer coefficients is given in [17].

Using Eqs. (10) and (14) in (9) it is easy to establish for STOs the following addition theorems:

$$\chi_{nlm}(\zeta, \vec{r}_{a1}) = \frac{\sqrt{4\pi}}{\zeta^{3/2}} \lim_{N \to \infty} \sum_{n'=1}^{N} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} \sum_{\mu=1}^{N+n-\alpha+1} \sum_{v=0}^{\mu-1} \sum_{\sigma=-v}^{v}$$

$$Z_{nlm,n'l'm'}^{\alpha N,\mu v\sigma} \chi_{n'l'm'}(\zeta, \vec{r}_{b1}) \chi_{\mu v\sigma}^{*}(\zeta, \vec{R}_{ab}) \quad (16)$$

where

$$\alpha = 1, 0, -1, -2, ..., \quad \vec{R}_{ab} = \vec{r}_{a1} - \vec{r}_{b1},$$

$$g_{nlm,n'l'm'}^{\alpha\mu v\sigma} \equiv 0 \text{ for } \mu gt; n + n' + 1$$

and

$$Z_{nlm,n'l'm'}^{\alpha N,\mu v\sigma} = \sum_{n''=l'+1}^{N} \Omega_{n'n''}^{\alpha l'}(N) g_{nlm,n''-\alpha l'm'}^{\alpha\mu v\sigma} \quad (17)$$

Now we can move on to the derivation of addition theorems for potentials, Eq. (3). For this purpose we utilize the following one-center expansion of potentials through the STOs: [15]

$$f_{uvs}(\eta, \vec{r}_{21}) = \left(\frac{4\pi}{2v+1}\right)^{1/2} \frac{\sqrt{(2u)!}}{(2\eta)^{u+1/2}} \chi_{uvs}(\eta, \vec{r}_{21}) \text{ for } u \geq 0$$

$$(18a)$$

$$f_{uvs}(\eta, \vec{r}_{21}) = \left(\frac{4\pi}{2v+1}\right)^{1/2} \lim_{N \to \infty}$$

$$\cdot \sum_{u'=v+1}^{N} b_{uv,u'v}^{\alpha N}(\eta, \eta') \chi_{u'vs}(\eta', \vec{r}_{21}) \text{ for } u < 0 \quad (18b)$$

where

$$b_{uv,u'v}^{\alpha N}(\eta, \eta') = \sum_{u''=v+1}^{N} \Omega_{u'u''}^{\alpha v}(N) P_{uu''}^{\alpha}(\eta, \eta') \quad (19)$$

See [15] for the exact definition of the quantity P^α.

Taking into account the addition theorem (16) for $a \to 2$, $b \to a$, $\vec{R}_{ab} \to \vec{r}_{2a} = \vec{r}_{21} - \vec{r}_{a1}$ and the symmetry property

$$\chi_{uvs}(\eta, \vec{r}_{2a}) = (-1)^v \chi_{uvs}(\eta, \vec{r}_{a2}) \quad (20)$$

we obtain the following addition theorems for STOs appearing in Eqs. (18a) and (18b):

$$\chi_{uvs}(\eta, \vec{r}_{21}) = \frac{\sqrt{4\pi}}{\eta^{3/2}} \lim_{N \to \infty} \sum_{\mu=1}^{N} \sum_{v=0}^{\mu-1} \sum_{\sigma=-v}^{v} \sum_{\mu'=1}^{N+u-\alpha+1} \sum_{v'=0}^{\mu'-1} \sum_{\sigma'=-v'}^{v'}$$

$$\cdot Y_{uvs,\mu v\sigma}^{\alpha N,\mu' v'\sigma'} \chi_{\mu v\sigma}(\eta, \vec{r}_{a1}) \chi_{\mu' v'\sigma'}^{*}(\eta, \vec{r}_{a2}) \quad (21)$$

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

$$Y_{uvs,\mu v\sigma}^{\alpha N,\mu' v'\sigma'} = (-1)^{v'} Z_{uvs,\mu v\sigma}^{\alpha N,\mu' v'\sigma'} \quad (22)$$

Equation (21) is the desired addition theorem for interaction potentials IP: any IP having the difference of the radius vectors, $\vec{r}_{21} = \vec{r}_{a1} - \vec{r}_{a2}$, as its argument, is expanded into a series over products of STOs depending on $\vec{r}_{a1}$ and $\vec{r}_{a2}$, separately.

Formulae in terms of overlap integrals

The multicenter t-electron integrals (Eq. 6) can be evaluated by a reduction to overlap integrals. For this purpose we should utilize the addition theorems for interaction potentials (Eq. 21). Then, we obtain:

$$I_{p_1p_1',p_2p_2',p_3p_3',...,p_tp_t';\tau}^{ac,bd,gh...,ef}(\zeta_1\zeta_1',\zeta_2\zeta_2',\zeta_3\zeta_3',...,\zeta_t\zeta_t',\eta)$$

$$= \frac{1}{(\eta\sqrt{\eta})^{t(t-1)}} \lim_{N \to \infty} \sum_{qq'}^{N} (Y_{\tau q21}^{\alpha N21 q_{21}'} Y_{\tau q31}^{\alpha N31 q_{31}'} ...$$

$$Y_{\tau q_{t-1}1}^{\alpha N_{t-1}1 q_{t-1}'1} Y_{\tau q_{t1}}^{\alpha N_{t1} q_{t1}'})(Y_{\tau q32}^{\alpha N32 q_{32}'} Y_{\tau q42}^{\alpha N42 q_{42}'} ...$$

$$Y_{\tau q_{t2}}^{\alpha N_{t2} q_{t2}'}) \times (Y_{\tau q43}^{\alpha N43 q_{43}'} ... Y_{\tau q_{t3}}^{\alpha N_{t3} q_{t3}'}) ...$$

$$(Y_{\tau q_{tt-1}}^{\alpha N_{tt-1} q_{tt-1}'}) S_{p_1 q_{21} q_{31} \cdots q_{t-1}1 q_{t1} p_1'}^{aaa...aac}(\zeta_1 \eta\eta ... \eta\eta\zeta_1')$$

$$\times S_{q_{21}' q_{32} q_{42} \cdots q_{t2} p_2 p_2'}^{aaa...abd}(\eta\eta\eta ... \eta\zeta_2\zeta_2')$$

$$\cdot S_{q_{31}' q_{32}' q_{43} \cdots q_{t3} p_3 p_3'}^{aaa...agh}(\eta\eta\eta ... \eta\zeta_3\zeta_3') ...$$

$$\times S_{q_{t1}' q_{t2}' q_{t3}' \cdots q_{tt-1}' p_t p_t'}^{aaa...aef}(\eta\eta\eta ... \eta\zeta_t\zeta_t') \quad (23)$$

where $\alpha = 1, 0, -1, -2, ...,$ $N \equiv [(N_{21}N_{31}N...N_{t1}), (N_{32}N_{42}...N_{t2}),...,(N_{t-1-2}N_{tt-2}), N_{t-1}]$, $q \equiv [(q_{21}q_{31}...q_{t1}), (q_{32}q_{42}...q_{t2}), ..., (q_{t-1t-2}q_{tt-2}), (q_{tt-1})]$, $q' \equiv [(q_{21}'q_{31}'...q_{t1}'), (q_{32}'q_{42}'...q_{t2}'), ..., (q_{t-1t-2}'q_{tt-2}'), (q_{tt-1}')]$, $q_{ik} \equiv \mu_{ik}v_{ik}\sigma_{ik}q_{ik}' \equiv \mu_{ik}'v_{ik}'\sigma_{ik}'$, $1 \leq \mu_{ik} \leq N_{ik}$, $0 \leq v_{ik} \leq \mu_{ik}-1$, $-v_{ik} \leq \sigma_{ik} \leq v_{ik}$, $1 \leq \mu_{ik}' \leq N_{ik}+u-\alpha+1$,

$$0 \leq v_{ik}' \leq \mu_{ik}' - 1, \quad -v_{ik}' \leq \sigma_{ik}' \leq v_{ik}', \quad g_{\tau q_{ik}}^{\alpha q_{ik}'} \equiv 0$$

for

$$\mu_{ik}' gt; u + \mu_{ik} + 1$$

and the quantities S in Eq. (23) are the one-electron integrals defined by

$$S_{p_1 q_{21} q_{31} \cdots q_{t-1}1 q_{t1} p_1'}^{aaa...aac}(\zeta_1 \eta\eta ... \eta\eta\zeta_1')$$

$$= (\sqrt{4\pi})^{t-1} \int \begin{array}{l} \chi_{p_1}^{*}(\zeta_1, \vec{r}_{a1}) \chi_{q_{21}}(\eta, \vec{r}_{a1}) \chi_{q_{31}}(\eta, \vec{r}_{a1}) ... \\ \times \chi_{q_{t-1}1}(\eta, \vec{r}_{a1}) \chi_{q_{t1}}(\eta, \vec{r}_{a1}) \chi_{p_1'}(\zeta_1', \vec{r}_{c1}) \mathrm{d}v_1 \end{array}$$

$$(24.1)$$

$$S_{q_{21}' q_{32} q_{42} \cdots q_{t2} p_2 p_2'}^{aaa...abd}(\eta\eta\eta ... \eta\zeta_2\zeta_2')$$

$$= (\sqrt{4\pi})^{t-1} \int \begin{array}{l} \chi_{q_{21}'}^{*}(\eta, \vec{r}_{a2}) \chi_{q_{32}}(\eta, \vec{r}_{a2}) \chi_{q_{42}}(\eta, \vec{r}_{a2}) ... \\ \times \chi_{q_{t2}}(\eta, \vec{r}_{a2}) \chi_{p_2}(\zeta_2, \vec{r}_{b2}) \chi_{p_2'}(\zeta_2', \vec{r}_{d2}) \mathrm{d}v_2 \end{array}$$

$$(24.2)$$

$$S_{q_{31}' q_{32}' q_{43} \cdots q_{t3} p_3 p_3'}^{aaa...agh}(\eta\eta\eta ... \eta\zeta_3\zeta_3')$$

$$= (\sqrt{4\pi})^{t-1} \int \begin{array}{l} \chi_{q_{31}'}^{*}(\eta, \vec{r}_{a3}) \chi_{q_{32}'}^{*}(\eta, \vec{r}_{a3}) \chi_{q_{43}}(\eta, \vec{r}_{a3}) ... \\ \times \chi_{q_{t3}}(\eta, \vec{r}_{a3}) \chi_{p_3}(\zeta_3, \vec{r}_{g3}) \chi_{p_3'}(\zeta_3', \vec{r}_{h3}) \mathrm{d}v_3 \end{array}$$

$$(24.3)$$

$$S^{aaa...aef}_{q'_{t1}q'_{t2}q'_{t3}...q'_{tt-1}p_tp'_t}(\eta\eta...\eta\zeta_t\zeta'_t)$$

$$= (\sqrt{4\pi})^{t-1} \int \begin{array}{l} \chi^*_{q'_{t1}}(\eta,\vec{r}_{at})\chi^*_{q'_{t2}}(\eta,\vec{r}_{at})\chi^*_{q'_{t3}}(\eta,\vec{r}_{at})... \\ \times\chi^*_{q'_{tt-1}}(\eta,\vec{r}_{at})\chi_{p_t}(\zeta_t,\vec{r}_{et})\chi_{p'_t}(\zeta'_t,\vec{r}_{ft}) \end{array} \mathrm{d}v_t$$

$$(24.t)$$

The analytical relationships for one-electron integrals (Eqs. 24.1, 24.2, 24.3, ..., 24.t)] in terms of two-center overlap integrals have been established, and these are discussed in the Appendix. We notice that the number of summation terms over the indices N_{ik} in Eq. (23) is $t(t-1)/2$.

As can be seen from Eq. (23) and the formulae of the Appendix, the evaluation of multicenter t-electron integrals of arbitrary screened NCIPs ($\eta\neq0$) for the N-electron atomic and molecular system ($2\leq t\leq N$) is reduced to the calculation of two-center overlap integrals over STOs. It should be noted that the formulae obtained in this work are also correct in the case where $\eta=0$ (see [15]). Thus, with the aid of the formulae obtained in this study, we can calculate also the multicenter multielectron integrals of nonscreened central and noncentral interaction potentials.

Appendix

As can be seen from Eq. (23), the multicenter t-electron integrals are expressed through the following basic three-center one-electron integrals over STOs:

$$S^{aaa...acb}_{p_1p_2p_3...p_{t-1}p_tp_{t+1}}(\zeta_1\zeta_2\zeta_3...\zeta_{t-1}\zeta_t\zeta_{t+1})$$

$$= (\sqrt{4\pi})^{t-1} \int \begin{array}{l} \chi^*_{p_1}(\zeta_1,\vec{r}_a)\chi_{p_2}(\zeta_2,\vec{r}_a)\chi_{p_3}(\zeta_3,\vec{r}_a)... \\ \times\chi_{p_{t-1}}(\zeta_{t-1},\vec{r}_a)\chi_{p_t}(\zeta_t,\vec{r}_c)\chi_{p_{t+1}}(\zeta_{t+1},\vec{r}_b) \end{array} \mathrm{d}v$$

$$= (\sqrt{4\pi})^{t-1}$$

$$\cdot \int \begin{array}{l} R_{n_1n_2n_3...n_{t-1}}(\zeta_1\zeta_2\zeta_3...\zeta_{t-1},r_a)\mathrm{T}_{l_1m_1,l_2m_2,l_3m_3,...,l_{t-1}m_{t-1}} \\ (\theta_a\varphi_a)\chi_{p_t}(\zeta_t,\vec{r}_c)\chi_{p_{t+1}}(\zeta_{t+1},\vec{r}_b) \end{array} \mathrm{d}v$$

$$(25)$$

where

$$R_{n_1n_2n_3...n_k}(\zeta_1\zeta_2\zeta_3...\zeta_k,r)$$

$$= R_{n_1}(\zeta_1,r)R_{n_2}(\zeta_2,r)R_{n_3}(\zeta_3,r)...R_{n_k}(\zeta_k,r)$$

$$= \left[\frac{(2N_k)!}{(2n_1)!(2n_2)!(2n_3)!...(2n_k)!}\right]^{1/2}$$

$$\times (\sqrt{2z_k})^{3(k-1)}x_1^{n_1+1/2}x_2^{n_2+1/2}x_3^{n_3+1/2}...x_k^{n_k+1/2}R_{N_k}(z_k,r)$$

$$(26)$$

$$N_k = n_1 + n_2 + n_3 + ... + n_k - k + 1,$$

$$z_k = \xi_1 + \xi_2 + \xi_3 + ... + \xi_k, x_i = \xi_i/z_k, \ i = 1,2,3,...,k$$

$$(27)$$

and

$$\Theta_{l_1m_1,l_2m_2,l_3m_3,...,l_km_k}(\theta,\varphi)$$

$$= S^*_{l_1m_1}(\theta,\varphi)S_{l_2m_2}(\theta,\varphi)S_{l_3m_3}(\theta,\varphi)...S_{l_km_k}(\theta,\varphi)$$

$$= \frac{1}{(\sqrt{4\pi})^{k-1}} \times \sum_{L_2M_2,L_3M_3,...,L_kM_k}$$

$$d^{L_2M_2}(l_1m_1,l_2m_2)d^{L_3M_3}(L_2M_2,l_3m_3)...$$

$$d^{L_kM_k}(L_{k-1}M_{k-1},l_km_k)S^*_{L_kM_k}(\theta,\varphi) \qquad (28)$$

$$d^{LM}(lm,l'm') = (2L+1)^{1/2}C^{L|M|}(lm,l'm')A^M_{mm'} \qquad (29)$$

Here, $R_{N_k}(z_k,r)$ and $S_{L_kM_k}(\theta,\varphi)$ are the radial parts of normalized STOs and the spherical harmonics, respectively. See [18] for the exact definition of the Gaunt coefficients $C^{L|M|}$ and the quantities $A^M_{mm'}$. We notice that, Eq. (28) can easily be derived by the use of the following expansion relation for the product of two spherical harmonics both with one and the same center [18]:

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

$$(30)$$

Inserting Eqs. (26) and (28) into the integral in Eq. (25) leads to the three-center overlap integrals

$$S^{acb}_{nlm,n'l'm',\mu'v'\sigma'}(\zeta,\zeta',z')$$

$$= \sqrt{4\pi} \int \chi^*_{nlm}(\zeta,\vec{r}_a)\chi_{n'l'm'}(\zeta',\vec{r}_c)\chi_{\mu'v'\sigma'}(z',\vec{r}_b)\mathrm{d}v \qquad (31)$$

Using the expansion formulae for electron charge densities (see Eq. (19) of [15]), the three-center overlap integrals [Eq. (31)] can be expressed through the two-center overlap integrals:

$$S^{acb}_{nlm,n'l'm',\mu'v'\sigma'}(\zeta,\zeta',z')$$

$$= \lim_{N\to\infty}\sum_{\mu=1}^N\sum_{v=0}^{\mu-1}\sum_{\sigma=-v}^v W^{\alpha N}_{nlm,n'l'm',\mu v\sigma}(\zeta,\zeta',z;\vec{R}_{ca},0)$$

$$\cdot S_{\mu v\sigma,\mu'v'\sigma'}(z,z';\vec{R}_{ab}) \qquad (32)$$

where

$$z = \zeta + \zeta', \ S_{\mu v\sigma,\mu'v'\sigma'}(z,z';\vec{R}_{ab}) \equiv S^{ab}_{\mu v\sigma,\mu'v'\sigma'}(z,z')$$

and $W^{\alpha N}$ is the two-center charge density expansion coefficient. Thus, the basic three-center one-electron integrals (Eq. 25) are determined solely from the two-center overlap integrals.

The results of calculation for the two-center two-electron integrals of central interaction potential $f_{000}(0, r_{21})=1/r_{21}$ obtained with a Pentium III 800 MHz computer (using TURBO Pascal 7.0) are shown in Table 1. The comparative values obtained from the expansions in terms of different complete orthonormal sets of ψ^α-ETOs are shown in this table. As can be seen from the table, the computation time and accuracy of the computer results for different expansion formulae obtained from ψ^0-ETOs, ψ^1-ETOs and ψ^{-1}-ETOs are satisfactory. Work is in

Table 1 Comparison of methods of computing two-center two-electron integrals of central interaction potential $f_{000}(0,r_{21})=1/r_{21}$ obtained in the molecular coordinate system in a.u. for $N_{21}=15$, $\theta_{ba}=\theta_{db}=45°$, $\phi_{ba}=\phi_{db}=270°$

n_1	l_1	m_1	ζ_1	n'_1	l'_1	m'_1	ζ'_1	n_2	l_2	m_2	ζ_2	n'_2	l'_2	m'_2	ζ'_2
2	0	0	5.3	2	0	0	7.1	2	1	1	3.5	2	1	1	1.3
2	1	0	3.1	2	1	0	1.4	2	1	−1	5.1	2	1	−1	1.3
2	1	0	10.8	2	1	0	8.5	2	1	1	12.2	2	1	1	8.6
2	1	1	8.4	2	1	1	5.4	2	1	−1	10.5	2	1	−1	6.5
2	1	−1	4.1	2	1	−1	4.2	2	1	−1	5.2	2	1	−1	5.7
1	0	0	2.8	1	0	0	4.5	2	0	0	6.6	2	0	0	4.8
2	1	0	7.2	2	1	1	5.4	2	1	0	9.6	2	1	1	7.4
2	1	1	10.7	2	1	1	2.5	2	1	0	19.3	2	1	0	7.7
2	1	1	9.1	2	1	1	6.2	2	1	1	12.7	2	1	1	9.7
2	1	−1	1.1	2	1	−1	4.2	2	1	1	5.2	2	1	1	7.9
2	1	−1	4.1	2	1	−1	4.2	2	1	−1	5.2	2	1	−1	5.7

R_{ca}	R_{db}	R_{ba}	Eq. (23), $\alpha=1$	Eq. (23), $\alpha=0$	Eq. (23), $\alpha=-1$	CPU (ms)
0	0.5	0	5.2265660306E−1	5.2265660306E−1	5.2265660306E−1	22.5
0	8.4	0	−5.3206382155E−5	−5.3206382148E−5	−5.3206382171E−5	40.3
0	3.6	0	4.0009374438E−12	4.0009374610E−12	4.0009374522E−12	39.4
0	12.1	0	−1.2826395140E−31	−1.2826397066E−31	−1.2826396515E−31	45.4
0	1.1	0	−1.2711391438E−1	−1.2711391440E−1	−1.2711391445E−1	43.1
0	0	8.7	9.9253681754E−2	9.9253681754E−2	9.9253681752E−2	7.9
0	0	12.8	−9.3617985464E−9	−9.3617985454E−9	−9.3617985449E−9	25.8
0	0	5.2	3.4083931212E−2	3.4083931200E−2	3.4083931233E−2	27.6
0	0	10.5	8.3039888591E−2	8.3039888587E−2	8.3039888579E−2	26.9
0	0	10.5	3.0014944352E−2	3.0014944344E−2	3.0014944370E−2	37.1
0	0	1.1	9.0417470379E−1	9.0417470395E−1	9.0417470357E−1	35.4

progress for the computation of multicenter multielectron integrals of central and noncentral interaction potentials over STOs based on the formulae given in this work.

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