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Letter

Calculation of three-center electric and magnetic multipole moment integrals using translation formulas for Slater-type orbitals

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Abstract. By the use of translation formulas for the expansion of Slater-type orbitals (STOs) in terms of STOs at a new origin, three-center electric and magnetic multipole moment integrals are expressed in terms of two-center multipole moment integrals for the evaluation of which closed analytical formulas are used. The convergence of the series is tested by calculating concrete cases. Computer results with an accuracy of 10^{-7} are obtained for 2^{ν} – pole electric and magnetic multipole moment integrals for $1 \leq \nu \leq 5$ and for arbitrary values of screening constants of atomic orbitals and internuclear distances.

Key words: Multipole moments – Slater-type orbitals – Overlap integrals

1 Introduction

It is well known that in the majority of expansion methods for Slater-type orbitals (STOs) about a displaced center the single-center expansion method in spherical harmonics has been applied [1–8]. For the evaluation of radial coefficients of a spherical harmonic expansion, methods of numerical integration have been used or analytical formulas have been obtained. For obtaining the spherical harmonic expansion of STOs about a new center one of us presented a particular method [9] in which the analytical expressions were derived for the expansion of STOs in terms of STOs at a new origin. The expansion coefficients in these formulas are expressed through the overlap integrals over STOs. Using the expansion formulas for the translation of STOs, in Ref. [10] simpler expressions in terms of binomial coefficients have been established for the multicenter molecular integrals with an arbitrary multielectron operator appearing in the determination of various multielectron properties for molecules when the Hartree–Fock–Roothaan theory is employed and also in the evaluation of the correlation energy when the Hylleraas approximation is used. For the efficient and accurate calculation of molecular properties one needs to study the convergence of these series expansion formulas. The aim of this report is to investigate the convergence of the infinite series expressions for the translation of STOs by calculating three-center electric and magnetic multipole moment integrals through the overlap integrals.

The three-center electric and magnetic multipole moment integrals examined in this work have the following form [11]:

$$M^{k}_{nlm,\nu\sigma,n'l'm'}\left(\zeta,\zeta';\vec{R}_{0\mathrm{b}},\vec{R}_{\mathrm{ab}}\right) = \int \chi^{*}_{nlm}(\zeta,\vec{r}_{\mathrm{a}})\hat{M}^{(k)}_{\nu\sigma}(\vec{r}_{0})\chi_{n'l'm'}(\zeta',\vec{r}_{\mathrm{b}})\mathrm{d}V \ , \tag{1}$$

where the quantities $M^{(k)}_{\nu\sigma}$ for $k \equiv \mathrm{e}$ and for $k \equiv \mathrm{m}$ are the electric and magnetic multipole moment operators, respectively.

2 Method

In order to evaluate three-center electric and magnetic multipole moment integrals we use in Eq. (1) the translation formula for the STOs $\chi_{nlm}(\zeta,\vec{r}_{\mathrm{a}})$ in the form (see Eqs. 5, and 6 of Ref. [9])

$$\chi_{nlm}(\zeta,\vec{r}_{\mathrm{a}}) = \lim_{N\to\infty}\sum_{n'=1}^{N}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'} V^{*N}_{nlm,n'l'm'} \times\left(\zeta,\zeta;\vec{R}_{\mathrm{ab}}\right)\chi_{n'l'm'}(\zeta,\vec{r}_{\mathrm{b}}) \ , \tag{2}$$

where

$$V^{N}_{nlm,n'l'm'}\left(\zeta,\zeta';\vec{R}_{\mathrm{ab}}\right) = \sum_{n''=l'+1}^{N}\Omega^{l'}_{n'n''}(N)S^{*}_{nlm,n''l'm'}\left(\zeta,\zeta';\vec{R}_{\mathrm{ab}}\right) \ , \tag{3}$$

$$\Omega^{l}_{n\kappa}(N) = \sum_{n'=\max(n,\kappa)}^{N}\omega^{l}_{n'n}\omega^{l}_{n'\kappa} \ , \tag{4}$$

$$\omega^{l}_{n'n} = (-1)^{n+l+1}\left[F_{n+l+1}(n'+l+1)F_{n-l-1}(n'-l-1) \times F_{n-l-1}(2n)\right]^{\frac{1}{2}} \quad \text{and} \quad F_{m}(n) = \frac{n!}{m!(n-m)!} \ . \tag{5}$$

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The quantities $S_{nlm,n'l'm'}$ in Eq. (3) are the overlap integrals between the normalized STOs:

$$S_{nlm,n'l'm'}\left(\zeta,\zeta';\vec{R}_{\mathrm{ab}}\right) = \int \chi^*_{nlm}(\zeta,\vec{r}_{\mathrm{a}})\chi_{n'l'm'}(\zeta',\vec{r}_{\mathrm{b}})\mathrm{d}V \ . \tag{6}$$

Now we take into account Eq. (2) for $\zeta = \zeta'$ in Eq. (1). Then, it is easy to express the given three-center 2^v – pole moment integrals in terms of two-center multipole moment integrals by the following relation:

$$M^{(k)}_{nlm,v\sigma,n'l'm'}\left(\zeta,\zeta';\vec{R}_{0\mathrm{b}},\vec{R}_{\mathrm{ab}}\right) = \lim_{Q\to\infty}\sum_{N=1}^{Q}\sum_{L=0}^{N-1}\sum_{M=-L}^{L} V^{*Q}_{nlm,NLM}\left(\zeta',\zeta';\vec{R}_{\mathrm{ab}}\right) \times M^{(k)}_{NLM,v\sigma,n'l'm'}\left(\zeta,\zeta';\vec{R}_{0\mathrm{b}},0\right) \ . \tag{7}$$

The quantities $M^{(k)}_{NLM,v\sigma,n'l'm'}\left(\zeta,\zeta';\vec{R}_{0\mathrm{b}},0\right)$ on the right-hand side of Eq. (7) are two-center electric and magnetic multipole moment integrals for which the closed analytical relations were established in Ref. [11].

As can be seen from the series expansion formula Eq. (7) and Eq. (3), three-center electric and magnetic multipole moment integrals are expressed through the overlap integrals over STOs. The numerical aspects of overlap integrals for large quantum numbers have recently been investigated using the auxiliary functions [12] and the recursive relations [13].

3 Numerical results and discussion

The convergence of the series in Eq. (7) for $N' \leq Q$, $L' \leq Q-1$ and $M' \leq Q-1$ has been tested, where N', L' and M' are the upper limits of the indices N, L and M, respectively. The calculation of three-center electric and magnetic multipole moment integrals on a computer in concrete cases shows that for the given value of N' the convergence of the series with respect to L and M is rapid; therefore, it is sufficient to include only a few terms in the summation over indices L and M. The results of tests of Eq. (7) on series accuracy $\Delta M^{(k)}_{QLM} = M^{(k)}_{QQ-1Q-1} - M^{(k)}_{QLM}$ for $Q = 17$ are shown in Figs. 1 and 2. Here the quantities $M^{(k)}_{QQ-1Q-1}$ are the values of the integrals (Eq. 7) for $N' = Q$, $L' = Q-1$ and $M' = Q-1$. The values of the integrals for $Q = 17$, $L' = 5$ and $M' = 3$ are given in Tables 1 and 2. The last columns of these tables give the comparison values of the integrals obtained from the closed analytical formulas of Ref. [11]. As can be seen from Figs. 1 and 2 and Tables 1 and 2, an overall accuracy of between 10^{-7} and 10^{-8} hartree was sought for $Q = 17$, $L' = 5$ and $M' = 3$.

The convergence of the series in Eq. (7) with respect to the indices N was also examined in numerous calculations, for which Figs. 3 and 4 show only results for three-center electric and magnetic multipole moment integrals $M^{(k)}_{nlm,v\sigma,n'l'm'}$ in some values of ζ and ζ' for $R_{\mathrm{ab}} = 5.5, \theta_{\mathrm{ab}} = 123°, \phi_{\mathrm{ab}} = 330°$ and $R_{0\mathrm{b}} = 2.7$, $\theta_{0\mathrm{b}} = 80°, \phi_{0\mathrm{b}} = 300°$. As can be seen from these figures an accuracy of 10^{-7} is obtained for $Q = 17$.

From Figs. 1–4 and Tables 1 and 2 we see that in all the calculations (up to $v = 5$) the computer results obtained from the series expansion formula Eq. (7) and the analytical relations of Ref. [11] are in agreement with each other for at least seven decimal digits.

The examples shown in Tables 1 and 2 and in Figs. 1–4 indicate that three-center electric and magnetic multipole moment integrals can be computed to arbitrary

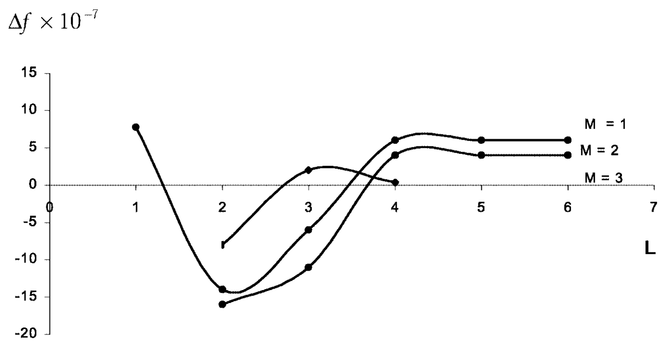

Fig. 1. The convergence of the series in Eq. (7) for $Q = 17$ as a function of the upper limits of the indices L and M for three-center electric multipole moment integrals $M^{(e)}_{421,2-2,321}$ for $\zeta = 3.5, \zeta' = 6.5$ and $R_{0\mathrm{b}} = 2.33, \theta_{0\mathrm{b}} = 143°, \phi_{0\mathrm{b}} = 115°$ and $R_{\mathrm{ab}} = 4.75, \theta_{\mathrm{ab}} = 122°, \phi_{\mathrm{ab}} = 262°$ (in atomic units)

Table 1. The values of three-center electric multipole moment integrals for $Q = 17$, $L' = 5$ and $M' = 3$ for the upper limits of the indices L and M in Eq. (7) for $R_{\mathrm{ab}} = 2.33$, $\theta_{\mathrm{ab}} = 143°$, $\phi_{\mathrm{ab}} = 115°$ and $R_{0\mathrm{b}} = 4.75$, $\theta_{0\mathrm{b}} = 122°$, $\phi_{0\mathrm{b}} = 262°$ (in atomic units)

n	l	m	v	σ	n'	l'	m'	ζ	ζ'	Eq. (7)	Eq. (20) in Ref. [11]
										Values	Values
1	0	0	4	4	2	1	0	15	5	−0.0186739482	−0.0186739487
2	1	−1	1	0	2	1	−1	9	1	−0.0177021271	−0.0177021214
3	1	0	5	0	3	1	0	4	4	13.907592094	13.907592022
3	2	0	2	1	4	1	1	6	4	−0.0883820356	−0.0883820398
3	1	0	5	2	3	1	0	8	5	1.8299480612	1.8299480725
4	1	0	3	1	2	1	0	7	7	0.0019355948	0.0019355589
5	3	−2	2	2	3	2	0	4.5	5.5	−0.0908327914	−0.0908327364
6	3	2	3	0	3	2	−1	13	8	−0.0040523263	−0.0040523192
7	2	1	3	1	2	1	1	6.5	3.5	0.3607899443	0.3607899443
8	4	0	4	0	5	2	2	9	1	−0.0336474579	−0.0336474146
9	3	1	1	1	4	1	0	8	2	0.0305219752	0.0305219378
10	5	−4	1	−1	5	3	2	12	2	0.0002712678	0.0002712226
11	5	4	2	2	4	2	1	10	4	0.1753468792	0.1753468982
12	2	1	4	0	2	1	0	9	6	0.4782267577	0.4782267122
13	3	2	2	−1	5	3	−1	9.5	0.5	0.0120375489	0.0120375415
15	6	1	3	2	7	4	2	13	3	0.4398876521	0.4398876778

Table 2. The values of three-center magnetic multipole moment integrals for $Q = 17$, $L' = 5$ and $M' = 3$ for the upper limits of the indices L and M in Eq. (7) for $R_{ab} = 3.5$, $\theta_{ab} = 34°$, $\phi_{ab} = 239°$ and $R_{0b} = 4.7$, $\theta_{0b} = 40°$, $\phi_{0b} = 240°$ (in atomic units)

n	l	m	v	σ	n'	l'	m'	ζ	ζ'	Eq. (7) Values	Eq. (10) in Ref. [11] Values
2	1	−1	2	1	2	1	0	5.2	4.8	−0.0002484254	−0.0002484252
2	0	0	2	0	2	1	0	7.5	2.5	0.0015961484	0.0015961422
3	2	0	3	1	2	1	−1	5.5	4.5	0.0017558203	0.0017558298
3	2	0	3	−2	2	1	0	12	2	−0.0009294500	−0.0009294526
3	2	2	5	4	2	1	0	3	9	0.0309343768	0.0309343712
4	2	1	1	1	2	0	0	2	7	−0.0028050745	−0.0028050743
4	2	1	3	2	2	1	1	3	9	−0.0025959679	−0.0025959636
4	2	1	2	1	2	0	0	2	7	0.0868284477	0.0868284421
2	1	0	4	−3	3	2	−2	13	5	−0.0000116282	−0.0000116247
2	1	0	3	2	3	2	1	6	5	0.0021036789	0.0021036722
3	2	−2	3	−3	3	2	−1	7	4	−0.0067120087	−0.0067120015
3	1	−1	5	2	3	2	−1	7	4	−0.0339178844	−0.0339178875
3	2	1	2	1	2	1	−1	5	10	0.0000727956	0.0000727910
3	2	0	4	1	2	1	−1	5.7	4.3	−0.0002718383	−0.0002718394
3	2	1	2	1	2	1	−1	6	4	0.0006772829	0.0006772899
5	3	1	2	2	3	2	0	5.5	4.5	0.0169289000	0.0169289061
9	4	1	1	0	3	2	0	6	4	−0.0285621599	−0.0285621565
10	3	2	4	2	2	1	0	7.5	7.5	−0.0005192578	−0.0005192546

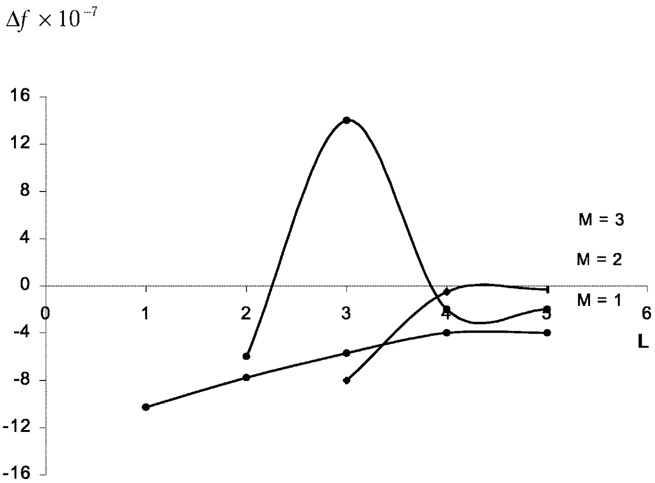

Fig. 2. The convergence of the series in Eq. (7) for $Q = 17$ as a function of the upper limits of the indices L and M for three-center magnetic multipole moment integrals $M^{(m)}_{211,3-2,321}$ for $\zeta = 12$, $\zeta' = 7$ and $R_{0b} = 2.33$, $\theta_{0b} = 143°$, $\phi_{0b} = 115°$ and $R_{ab} = 4.75$, $\theta_{ab} = 122°$, $\phi_{ab} = 262°$ (in atomic units)

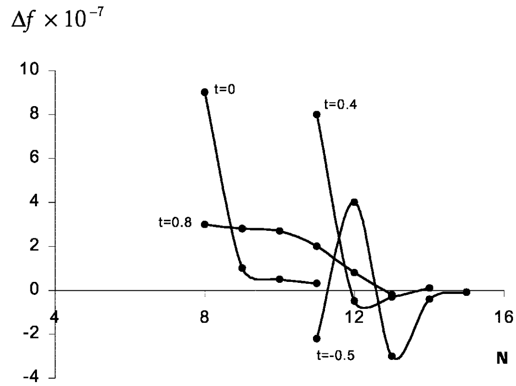

Fig. 3. The convergence of the series in Eq. (7) for different values of parameters ζ and ζ' for three-center electric multipole moment integrals $M^{(e)}_{431,21,321}$ as a function of the indices N ($R_{0b} = 5.5, \theta_{0b} = 123°, \phi_{0b} = 330°$ and $R_{ab} = 2.7, \theta_{ab} = 80°, \phi_{ab} = 300°$)

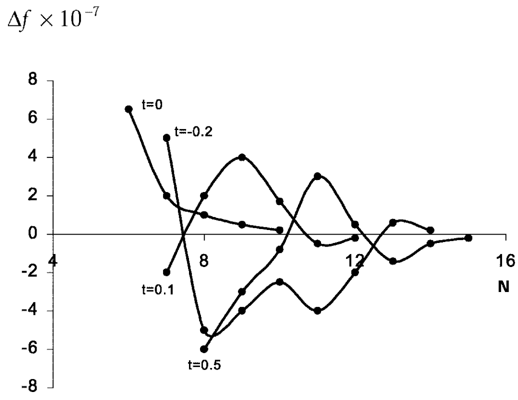

Fig. 4. The convergence of the series in Eq. (7) for different values of parameters ζ and ζ' for three-center magnetic multipole moment integrals $M^{(m)}_{321,2-2,21-1}$ as a function of the indices N ($R_{0b} = 5.5, \theta_{0b} = 123°, \phi_{0b} = 330°$ and $R_{ab} = 2.7, \theta_{ab} = 80°, \phi_{ab} = 300°$)

accuracy for wide-ranging parameters of STOs. It is important in developing methods to have available completely trustworthy benchmarks for all parameter ranges. This is assured because the convergence rates of the overlap integrals in Eq. (7) are independent of the values of the parameters [12, 13]; therefore, it is not necessary to use here the convergence accelerator method for overlap integrals of Ref. [14] related to the rate of convergence of the series.

By the use of the translation formula Eq. (2) for the expansion of STOs in terms of STOs at a new origin, our studies are being continued to perform computer calculations for the molecular integrals appearing in the Hartree–Fock–Roothaan equations and also in the determination of molecular properties.

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