

Calculation of multicenter electric field gradient integrals over Slater-type orbitals using unsymmetrical one-range addition theorems

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Abstract The electric field induced within a molecule by its electrons determines a whole series of important physical properties of the molecule. In particular, the values of the gradient of this field at the nuclei determine the interaction of their quadrupole moments with the electrons. Using unsymmetrical one-range addition theorems introduced by one of the authors, the sets of series expansion relations for multicenter electric field gradient integrals over Slater-type orbitals in terms of multicenter charge density expansion coefficients and two-center basic integrals are presented. The convergence of the series is tested by calculating concrete cases for different values of quantum numbers, parameters and locations of orbitals.

Keywords Slater-type orbitals · Electric field gradient integrals · Hartree–Fock–Roothaan equations · Unsymmetrical one-range addition theorems

Introduction

It is well known that a whole series of important physical properties of a molecule are determined by the electrostatic potential created by the electrons of the molecule at the nuclei and its derivatives with respect to their Cartesian coordinates [1]. In particular, electron–nuclei quadrupole

interactions, the interactions between the nuclear quadrupole moment and the electric field gradient (EFG) created at the nucleus by the electrons of the atom or molecule, can be studied by calculating second derivatives of the electrostatic potential [2, 3]. The Hamiltonian of this interaction in atomic units is given by [4]:

$$H'_{EQ} = B \left[\frac{\frac{3}{2}\vec{I} \cdot \vec{J}(2\vec{I} \cdot \vec{J} + 1) - I^2 J^2}{2I(2I - 1)j(2j - 1)} \right]. \quad (1)$$

The quantum numbers I and j in Eq. 1 correspond to the nuclear spin and the total electronic orbital angular momentum, respectively. The nuclear quadrupole coupling constant B is determined by

$$B = Q \langle V_{zz} \rangle, \quad (2)$$

where the quantity Q is the quadrupole moment that describes the degree to which the charge distribution in the nucleus deviates from a sphere. The quantity Q is positive for nuclei elongated in the z -direction and negative for those contracted in this direction [5]. The expectation value $\langle V_{zz} \rangle = \left\langle \frac{\partial^2 V_e}{\partial z^2} \right\rangle$ is the zz -component of the electric field gradient tensor created at the nucleus, which has a quadrupole moment Q . The first-order energy shift obtained from Eq. 1 for the interaction between the electric field and the quadrupole moment is defined by [6]

$$\begin{aligned} \Delta E &= \langle jIFM_F | H'_{EQ} | jIFM_F \rangle \\ &= \frac{B}{4} \left[\frac{\frac{3}{2}K(K + 1) - 2I(I + 1)j(j + 1)}{I(2I - 1)j(2j - 1)} \right], \end{aligned} \quad (3)$$

where $F = |I - j|, |I - j| - 1, \dots, I + j - 1, I + j$ and $K = F(F + 1) - I(I + 1) - j(j + 1)$. For a spherically symmetric electronic charge distribution, $\langle V_{zz} \rangle = 0$, i.e., there is no

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energy shift. Moreover, nuclei with $I=0$ or $1/2$ nuclear spins have zero quadrupole moments, thus giving no energy shift. The quadrupole coupling constant B cannot be measured by experiment. This constant must therefore be calculated. As can be seen from Eq. 3, when the value of $\langle V_{zz} \rangle$ is known, an experimental measurement of the ΔE energy shift can be used to obtain the nuclear quadrupole moment Q . The quadrupole coupling constant B is obtained by comparing the theoretical value of the electron–nuclei quadrupole interactions with an experimental measurement of the energy shift ΔE . Thus, the structure of the nucleus can be obtained from a comparison between theory and experiment.

According to the Hartree–Fock–Roothaan method (HFR) [7], the matrix elements of the EFG operator between the determinantal wavefunctions of atomic or molecular systems are expressed in terms of multicenter EFG integrals. Therefore, the accurate evaluation of EFG integrals is very important for atomic and molecular ab initio calculations. It is well known that electron–nuclei quadrupole interactions are sensitive to minor errors in wavefunctions [8]. Therefore, the basis sets of functions used for theoretical calculations of molecular structure are of prime importance, since the quality of several molecular properties can depend strongly on the nature of these basis functions. The most popular functions used in ab initio calculations are Gaussian-type orbitals (GTOs) [9, 10]. The great advantage of using GTOs is that multicenter molecular integrals are easily evaluated. However, GTOs are not able to correctly describe the asymptotic behavior of exact molecular wavefunctions either in the vicinity of the nuclei [11] or at large distances away from the nuclei [12]. Exponential-type orbitals (ETOs) are a viable alternative to GTOs because they are better than GTOs at representing electronic wavefunctions near the nucleus and at long ranges [1]. Therefore, for the calculations of EFG integrals, it is desirable to use an ETO that describes the physical situation more accurately than a GTO does.

In the literature, the wide use of ETOs as basis sets has been pursued with considerable enthusiasm by a growing number of investigators because of the huge advances made in applied mathematics and computer science [13–18]. Among these ETOs, Slater-type orbitals (STO) are certainly the simplest analytical functions and are used as atomic basis sets in molecular structure calculations (see [19–21] and references therein).

One of the most promising methods for the evaluation of multicenter molecular integrals over STOs is the use of addition theorems for STOs, which are established through the use of complete orthonormal sets of ψ^α -exponential type orbitals (ψ^α -ETO, $\alpha=1, 0, -1, -2, \dots$), where the eigenfunctions ψ^α -ETO correspond to the total centrally symmetric potential which contains the core attraction

potential and the Lorentz potential of the field produced by the particle itself. The index α that arises from the use of the total potential and occurs in the ψ^α -ETO is the frictional quantum number [22]. In the context of atomic and molecular electronic structure calculations, two fundamentally different types of addition theorems occur in the literature [23–25]. Addition theorems of the first type all have the typical two-range form of the Laplace expansion of the Coulomb potential:

$$\frac{1}{r_{21}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} S_{lm}^*(\theta_2, \varphi_2) S_{lm}(\theta_1, \varphi_1), \quad (4)$$

where S_{lm} is the complex (for $S_{lm} \equiv Y_{lm}$) or real spherical harmonic and $r_{<} = \min(r_1, r_2)$, $r_{>} = \max(r_1, r_2)$. There is a second class of addition theorems: unsymmetrical and symmetrical one-range addition theorems [23, 26], which can be constructed by expanding a function located at a center a in terms of a complete orthonormal set located at a center b . It should be noted that the two-range addition theorems can lead to nontrivial technical problems during application. The use of one-range addition theorems would be highly desirable, as they are capable to simplify subsequent integrations in multicenter integrals substantially. Therefore, it is desirable to use the unsymmetrical or symmetrical one-range addition theorems for STOs in which the problems associated with the evaluation of multicenter integrals do not arise. The expansion coefficients of unsymmetrical and symmetrical one-range addition theorems are the overlap integrals and STOs, respectively.

Using ψ^α -ETO, different analytical expressions were derived for the expansion of one- and two-center electron charge densities over STOs in terms of STOs about a new center (see [27]). The expansion coefficients in these formulae are expressed through the overlap integrals with the same screening parameters. The aim of this work is to calculate, with the help of unsymmetrical one-range addition theorems of STOs, the multicenter electric field gradient integrals that appear in the HFR approach. The relations obtained for the multicenter electric field gradient integrals can be used to model nuclear quadrupole interactions.

Definition

The multicenter EFG integrals over STOs examined in this work have the following form:

$$I_{p_1, p_1'}^{ijac, b}(\zeta_1, \zeta_1') = \frac{\partial^2}{\partial X^i \partial X^j} I_{p_1, p_1'}^{ac, b}(\zeta_1, \zeta_1') \quad (5a)$$

$$= \int \chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p_1'}(\zeta_1', \vec{r}_{c1}) O^{ij}(\vec{r}_{b1}) dV_1, \quad (5b)$$

where $p_1 \equiv n_1 l_1 m_1, p_1' \equiv n_1' l_1' m_1'$ and

$$I_{p_1 p_1'}^{ac,b}(\zeta_1, \zeta_1') = \int \chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p_1'}(\zeta_1', \vec{r}_{c1}) \frac{1}{r_{b1}} dV_1 \quad (6)$$

$$O^{ij}(\vec{r}_{b1}) = \left[\frac{3x_{b1}^i x_{b1}^j - \delta_{ij} r_{b1}^2}{r_{b1}^5} - \frac{4\pi}{3} \delta_{ij} \delta(\vec{r}_{b1}) \right]. \quad (7)$$

Here, $I_{p_1 p_1'}^{ac,b}(\zeta_1, \zeta_1')$ and $O^{ij}(\vec{r}_{b1})$ are the multicenter electronic attraction integrals [26] and the electron–nuclei quadrupole interaction potentials, respectively. The quantities $x^1 = x, x^{-1} = y, x^0 = z$ and $X^1 = X, X^{-1} = Y, X^0 = Z$ in these equations are the Cartesian coordinates of the electron and nucleus b , respectively. $\delta(\vec{r})$ is the Dirac delta function, while $\chi_{nlm}(\zeta_1, \vec{r}_{a1})$ and $\chi_{n'l'm'}(\zeta_1, \vec{r}_{b1})$ are the normalized STOs centered on nuclei a and b , which are defined by

$$\chi_{nlm}(\zeta, \vec{r}) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi) \quad (8)$$

$$S_{lm}(\theta, \varphi) = P_{l|m|}(\cos \theta) \Phi_m(\varphi), \quad (9)$$

where $P_{l|m|}$ are the normalized associated Legendre functions [28]. For complex spherical harmonics (for $S_{lm} \equiv Y_{lm}$)

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \quad (10)$$

and for real spherical harmonics

$$\Phi_m(\varphi) = \frac{1}{\sqrt{\pi(1 + \delta_{m0})}} \begin{cases} \cos|m|\varphi & \text{for } m \geq 0 \\ \sin|m|\varphi & \text{for } m < 0 \end{cases}. \quad (11)$$

It should be noted that the definition of the phases used in this work for complex spherical harmonics, $Y_{lm}^*(\theta, \varphi) = Y_{l-m}(\theta, \varphi)$, [29] differs from that of Condon–Shortley phases [30] by the sign factor $(-1)^m$.

Use of unsymmetrical one-range addition theorems

In order to evaluate the multicenter EFG integrals (5b), we use the following expansion formulae for the unsymmetrical one-range addition theorems for STO charge density [26]. For three-center cases we have:

$$\chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p_1'}(\zeta_1', \vec{r}_{c1}) = \frac{1}{\sqrt{4\pi}} \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{ca}, \vec{R}_{ab}) \chi_p^*(z, \vec{r}_{b1}) \quad (12a)$$

$$\chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p_1'}(\zeta_1', \vec{r}_{c1}) = \frac{1}{\sqrt{4\pi}} \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{cb}, \vec{R}_{ab}) \chi_p^*(z, \vec{r}_{b1}), \quad (12b)$$

for two-center cases:

$$\chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p_1'}(\zeta_1', \vec{r}_{c1}) = \frac{1}{\sqrt{4\pi}} \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0) \chi_p^*(z, \vec{r}_{a1}) \quad (13a)$$

$$\chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p_1'}(\zeta_1', \vec{r}_{b1}) = \frac{1}{\sqrt{4\pi}} \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; 0, \vec{R}_{ab}) \chi_p^*(z, \vec{r}_{b1}), \quad (13b)$$

and for the one-center case:

$$\chi_{p_1}^*(\zeta_1, \vec{r}_1) \chi_{p_1'}(\zeta_1', \vec{r}_1) = \frac{1}{\sqrt{4\pi}} \sum_{v=|l_1-l_1'|}^{l_1+l_1'} \sum_{\sigma=-v}^v W_{p_1 p_1' q}(\zeta_1, \zeta_1', z) \chi_q^*(z, \vec{r}_1), \quad (14)$$

where $p \equiv nlm, q \equiv \mu\nu\sigma, \mu = n_1 + n_1' - 1, z = \zeta_1 + \zeta_1', \vec{R}_{ca} = \vec{R}_a - \vec{R}_c, \vec{R}_{ab} = \vec{R}_b - \vec{R}_a$ and $\vec{R}_{cb} = \vec{R}_b - \vec{R}_c$. The index N is a positive integer number. See [31] for the exact definitions of the multicenter charge density expansion coefficients $W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{ca}, \vec{R}_{ab}), W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{cb}, 0), W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; 0, \vec{R}_{ab})$ and $W_{p_1 p_1' q}(\zeta_1, \zeta_1', z)$ that occur in these equations. These three- and two-center charge density expansion coefficients are determined by the

use of two-center overlap integrals with the same screening constants. It should be noted that Eqs. 12a, 12b, 13a and 13b are obtained through the use of the unsymmetrical one-range addition theorems presented in [23].

Substituting Eqs. 12a, 12b, 13a, 13b and 14 for the charge densities into (5b), we obtain the series expansion formulae for the multicenter EFG integrals in terms of two-center

basic electric field gradient integrals. For three-center integrals, we have:

$$I_{p_1 p_1'}^{jac,b}(\zeta_1, \zeta_1') = \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0) J_p^{ij}(z, \vec{R}_{ab}) \tag{15a}$$

$$I_{p_1 p_1'}^{ijac,b}(\zeta_1, \zeta_1') = \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{cb}, \vec{R}_{ab}) J_p^{ij}(z, 0) \tag{15b}$$

$$I_{p_1 p_1'}^{ijac,b}(\zeta_1, \zeta_1') = \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{ca}, \vec{R}_{ab}) J_p^{ij}(z, 0), \tag{15c}$$

for two-center integrals:

$$I_{p_1 p_1'}^{jaa,b}(\zeta, \zeta') = \sum_{\nu=|l_1-l_1'|}^{l_1+l_1'} \sum_{\sigma=-\nu}^{\nu} W_{p_1 p_1' q}(\zeta_1, \zeta_1', z) J_q^{ij}(z, \vec{R}_{ab}) \tag{16a}$$

$$I_{p_1 p_1'}^{jab,b}(\zeta, \zeta') = \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; 0, \vec{R}_{ab}) J_p^{ij}(z, 0) \tag{16b}$$

$$I_{p_1 p_1'}^{jac,a}(\zeta, \zeta') = \lim_{N \rightarrow \infty} \sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^l W_{p_1 p_1' p}^{\alpha N}(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0) J_p^{ij}(z, 0), \tag{16c}$$

and for one-center integrals:

$$I_{p_1 p_1'}^{ij}(\zeta_1, \zeta_1') \equiv I_{p_1 p_1'}^{jaa,a}(\zeta_1, \zeta_1') = \lim_{N \rightarrow \infty} \sum_{\mu=1}^N \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W_{p_1 p_1' p}^{\alpha N}(\zeta, \zeta', z) J_p^{ij}(z, 0). \tag{17}$$

Table 1 Comparison of methods of computing two- and three-center electric field gradient integrals over STOs obtained in the molecular coordinate system in a.u. for $X^1 = -0.7, X^{-1} = 0.5, X^0 = 0.2$ and $N=15$

i	j	n ₁	l ₁	m ₁	ζ ₁	n ₁	l ₁	m ₁	ζ ₁	Eqs. 15a and 16c			α=1			α=0			α=-1			α=-2		
										R _{ca}	θ _{ca}	φ _{ca}	R _{ab}	θ _{ab}	φ _{ab}	R _{ca}	θ _{ca}	φ _{ca}	R _{ab}	θ _{ab}	φ _{ab}	R _{ca}	θ _{ca}	φ _{ca}
1	0	2	1	1	0.6	2	1	0	0.4	0.2	100	135	0	0	0.0224711589593146	0.0224782509105851	0.0224848772839253	0.0224908588946610						
0	0	2	1	-1	1.2	2	1	-1	0.8	0.2	60	36	0	0	-0.117175947022725	-0.117350316158520	-0.117540641351530	-0.117724769229690						
-1	0	3	2	1	3.4	3	1	1	3.5	0.8	100	120	0	0	-0.1659053609216	-0.16599590314987	-0.16521348469835	-0.16130470517651						
0	-1	3	1	0	1.4	2	1	1	1.1	0.5	126	200	0	0	0.126030759486263	0.126017514416321	0.126002807030017	0.126095572858067						
1	1	1	0	0	5.3	2	1	0	2.5	1.8	90	63	1.2	45	0.0146374533381824	0.0146056145211002	0.0146078627972581	0.0145925751212836						
-1	0	2	1	1	4.5	2	1	1	1.8	0.9	30	125	1.5	120	0.0310873848899115	0.0310698025349309	0.0310617184848114	0.0310574704724762						
-1	1	3	0	0	5.5	2	0	0	2.8	1.2	45	90	1.9	60	-0.015074428301370	-0.015074363553180	-0.015071867786193	-0.015070595842217						
1	1	3	1	0	2.7	2	1	0	1.2	0.8	65	85	1.9	53	-0.143740311839084	-0.143716655594771	-0.143685951551224	-0.143658647526262						

The two-center basic EFG integrals $J_p^{ij}(z, \vec{R}_{ab})$ in Eqs. 15a and 16a are defined as

$$J_{nlm}^{ij}(z, \vec{R}_{ab}) = \frac{\partial^2}{\partial X^i \partial X^j} J_{nlm}(z, \vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int \chi_{nlm}^*(z, \vec{r}_{a1}) \left[\frac{3x_{b1}^i x_{b1}^j - \delta_{ij} r_{b1}^2}{r_{b1}^5} - \frac{4\pi}{3} \delta_{ij} \delta(\vec{r}_{b1}) \right] dV_1. \tag{18}$$

We notice that the following translations on the right-hand sides of Eqs. 15a, 15b and 15c should be made: $(c \rightarrow a, a \rightarrow b)$, $(c \rightarrow b, a \rightarrow b)$ and $(c \rightarrow a, a \rightarrow b)$, respectively.

In Eq. 18, $J_{nlm}(z, \vec{R}_{ab})$ are the two-center basic electronic attraction integrals determined by

$$J_{nlm}(\zeta, \vec{R}) = \frac{1}{\sqrt{4\pi}} \int \chi_{nlm}^*(\zeta, \vec{r}_{a1}) \frac{1}{r_{b1}} dV_1 = \frac{2^{n+1}(n+l+1)!}{[(2l+1)(2n)!(2\zeta)]^{1/2}(\zeta R)^{l+1}} \left(1 - e^{-\zeta R} \sum_{\sigma=0}^{n+l} \gamma_{\sigma}^l(n)(\zeta R)^{\sigma} \right) \bar{S}_{lm}^*(\theta, \varphi) \tag{19}$$

where $\vec{R} = \vec{R}_{ab}$ and

$$\bar{S}_{lm}(\theta, \varphi) = \left(\frac{4\pi}{2l+1} \right)^{1/2} S_{lm}(\theta, \varphi) \tag{20}$$

$$\gamma_{\sigma}^l(n) = \frac{1}{\sigma!} - \frac{(n-l)!}{(n+l+1)!(\sigma-2l-1)!}. \tag{21}$$

Here, $\gamma_{\sigma}^l(n) = 0$ for $\sigma < 0$ and $\sigma > n+l$. In Eq. 21, terms with negative factorials should be equated to zero.

In order to evaluate the two-center basic EFG integrals (18), we need the derivatives of the function

$$M_{lm}(x, y, z) = r^l \bar{S}_{lm}(\theta, \varphi), \tag{22}$$

where $M_{lm}(x, y, z)$ are the complex or real regular solid spherical harmonics. With the aid of the well-known

characteristics of spherical harmonics, we can show that the derivatives of these functions with respect to Cartesian coordinates can be expressed in terms of M_{l-1m} :

$$\frac{\partial M_{lm}}{\partial x_i} = \sum_{m'=-l}^{l-1} a_{lm,m'}^i M_{l-1m'} \tag{23}$$

$$\frac{\partial^2 M_{lm}}{\partial x_i \partial x_j} = \sum_{m'=-l}^{l-2} a_{lm,m'}^{ij} M_{l-2m'}. \tag{24}$$

See [32] for the exact definitions of the coefficients $a_{lm,m'}^i$ and $a_{lm,m'}^{ij}$. We use the following formulae for the derivatives of the product of the functions $M_{lm}(x, y, z)$ and $f(r)$:

$$\frac{\partial(M_{lm}f)}{\partial x_i} = \frac{\partial M_{lm}}{\partial x_i} f + M_{lm} x_i \left(\frac{1}{r} \frac{\partial f}{\partial r} \right) \tag{25}$$

Table 2 Convergence of the series expansion relation (15a) for the three-center electric field gradient integral $I_{300,200}^{-11ac,b}(5.5, 2.8)$ as a function of R_{ab} (with $\theta_{ab}=90^\circ$, $\varphi_{ab}=60^\circ$) for $R_{ca}=1.2$, $\theta_{ca}=45^\circ$, $\varphi_{ca}=90^\circ$ and $N=15$

R_{ab}	$\alpha=1$	$\alpha=0$	$\alpha=-1$	$\alpha=-1$
0.7	-0.1956433187831	-0.1699397878935	-0.1356788830337	-0.08272806910867
1.9	-0.0150744283013	-0.0150743635531	-0.0150718677861	-0.01507059584221
3.0	-0.0013156605035	-0.0013157021814	-0.0013157168517	-0.00131571648886
5.0	-0.0000859524732	-0.0000859524339	-0.0000859539717	-0.00008595485734
9.0	$-3.973250062 \times 10^{-6}$	$-3.973265486 \times 10^{-6}$	$-3.973317539 \times 10^{-6}$	$-3.9733419335 \times 10^{-6}$
12.0	$-9.006847754 \times 10^{-7}$	$-9.006862281 \times 10^{-7}$	$-9.006959790 \times 10^{-7}$	$-9.0070040875 \times 10^{-7}$
15.0	$-2.868906255 \times 10^{-7}$	$-2.868905224 \times 10^{-7}$	$-2.868932211 \times 10^{-7}$	$-2.8689444554 \times 10^{-7}$
19.0	$-8.586400620 \times 10^{-8}$	$-8.5863810353 \times 10^{-8}$	$-8.586451644 \times 10^{-8}$	$-8.5864841722 \times 10^{-8}$
23.0	$-3.250230264 \times 10^{-8}$	$-3.250218476 \times 10^{-8}$	$-3.250242759 \times 10^{-8}$	$-3.2502541857 \times 10^{-8}$

$$\begin{aligned} \frac{\partial^2(M_{lm}f)}{\partial x_i \partial x_j} &= \frac{\partial^2 M_{lm}}{\partial x_i \partial x_j} f + \frac{\partial M_{lm}}{\partial x_i} x_j \left(\frac{1}{r} \frac{\partial f}{\partial r} \right) + \frac{\partial M_{lm}}{\partial x_j} x_i \left(\frac{1}{r} \frac{\partial f}{\partial r} \right) \\ &+ M_{lm} \left[\delta_{ij} \left(\frac{1}{r} \frac{\partial f}{\partial r} \right) + x_i x_j \frac{1}{r} \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial f}{\partial r} \right) \right] \end{aligned} \quad (26)$$

where $r = (x^2 + y^2 + z^2)^{1/2}$.

Taking into account Eqs. 19 and 22–26, it is easy to show that the two-center basic EFG integrals (18) are determined by the following relations:

$$\begin{aligned} J_{nlm}^{ij}(\zeta) &= J_{nlm}^{ij}(\zeta, 0) = \frac{(n-2)!}{(n+3)!} N_{n2}^2(2\zeta) a_{2m,0}^{ij} \delta_{l2} \\ &- \frac{\sqrt{2}}{6} (2\zeta)^{3/2} \delta_{ij} \delta_{n1} \delta_{l0} \delta_{m0} \text{ for } \vec{R} = 0 \end{aligned} \quad (27a)$$

$$\begin{aligned} J_{nlm}^{ij}(\zeta, \vec{R}) &= \sum_{m'=-l-2}^{l-2} a_{lm,m'}^{ij} f_{nl,l-2m'}^{20}(\zeta, \vec{R}) - (2l+1) \\ &\times \sum_{m'=-l-1}^{l-1} \left[a_{lm,m'}^i \left(\frac{X^j}{R} \right) \right. \\ &+ a_{lm,m'}^j \left(\frac{X^i}{R} \right) \left. \right] f_{nl,l-1m'}^{21}(\zeta, \vec{R}) \\ &- (2l+1) \delta_{ij} f_{nl,lm}^{21}(\zeta, \vec{R}) \end{aligned}$$

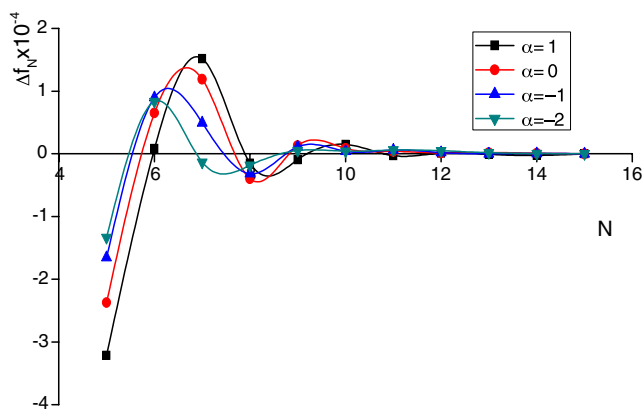


Fig. 1 The convergence of the series expansion relation (15a) for the three-center electric field gradient integral $I_{300,200}^{-11}(5.5, 2.8)$ as a function of the upper limit of the index N for $R_{ca}=1.2$, $\theta_{ca}=45^\circ$, $\varphi_{ca}=90^\circ$, $R_{ab}=1.9$, $\theta_{ab}=90^\circ$, and $\varphi_{ab}=60^\circ$ in a.u.

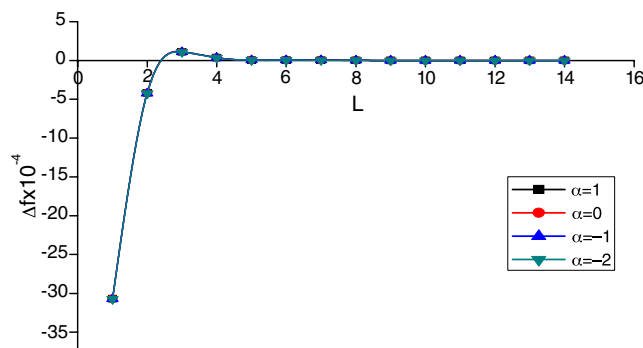


Fig. 2 Convergence of the series expansion relation (15a) for the three-center electric field gradient integral $I_{300,200}^{-11}(5.5, 2.8)$ as a function of the limit L ($0 \leq l \leq L$ and $-l \leq m \leq l$) for $R_{ca}=1.2$, $\theta_{ca}=45^\circ$, $\varphi_{ca}=90^\circ$, $R_{ab}=1.9$, $\theta_{ab}=90^\circ$, $\varphi_{ab}=60^\circ$, and $N=15$

$$\begin{aligned} &+ (2l+1)(2l+3) \left(\frac{X^j}{R} \right) \left(\frac{X^i}{R} \right) f_{nl,lm}^{22}(\zeta, \vec{R}) \\ &- \frac{\sqrt{4\pi}}{3} \delta_{ij} \chi_{nlm}^*(\zeta, \vec{R}), \text{ for } \vec{R} \neq 0, \end{aligned} \quad (27b)$$

where $X^1 = X$, $X^{-1} = Y$, $X^0 = Z$ and $i, j = 1, 0, -1$. Here, $f_{nl,vm}^{tk}(\zeta, \vec{R})$ are the potential functions determined by

$$f_{nl,vm}^{tk}(\zeta, \vec{R}) = f_{nl}^{tk}(\zeta, R) \bar{S}_{vm}(\theta, \varphi) \quad (28)$$

$$f_{nl}^{tk}(\zeta, \vec{R}) = f_{nl,00}^{tk}(\zeta, R) = \frac{N_{nl}^t(2\zeta)}{(\zeta R)^{l+t+1}} \left(1 - e^{-\zeta R} \sum_{\sigma=0}^{n+l+k} \gamma_{\sigma}^{lk}(n) (\zeta R)^{\sigma} \right) \quad (29)$$

$$N_{nl}^t(2\zeta) = 2^{n-t+1} (n+l+1)! \left[\frac{(2\zeta)^{2t-1}}{(2l+1)(2n)!} \right]^{1/2}, \quad (30)$$

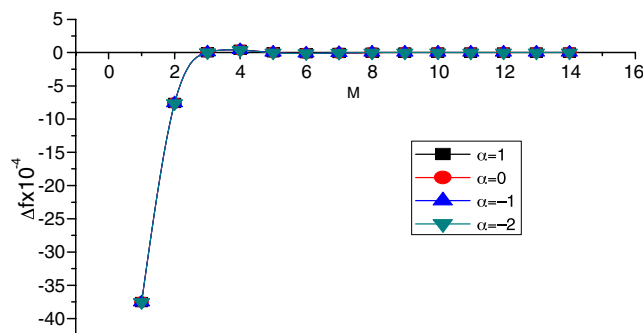


Fig. 3 Convergence of the series expansion relation (15a) for the three-center electric field gradient integral $I_{300,200}^{-11}(5.5, 2.8)$ as a function of the summation limit M ($0 \leq l \leq N-1$ and $-M \leq m \leq M$) for $R_{ca}=1.2$, $\theta_{ca}=45^\circ$, $\varphi_{ca}=90^\circ$, $R_{ab}=1.9$, $\theta_{ab}=90^\circ$, $\varphi_{ab}=60^\circ$, and $N=15$

where $0 \leq k \leq 2$ and

$$\gamma_{\sigma}^{l0}(n) = \gamma_{\sigma}^l(n) \tag{31} \quad \gamma_{\sigma}^{l1}(n) = \frac{1}{2l+1} [(2l+1-\sigma)\gamma_{\sigma}^l(n) + \gamma_{\sigma-1}^l(n)] \tag{32}$$

$$\gamma_{\sigma}^{l2}(n) = \frac{1}{(2l+1)(2l+3)} [(2l+1-\sigma)(2l+3-\sigma)\gamma_{\sigma}^l(n) + (4l+5-2\sigma)\gamma_{\sigma-1}^l(n) + \gamma_{\sigma-2}^l(n)]. \tag{33}$$

Numerical results and discussion

As can be seen from the equations obtained in this study, the multicenter EFG integrals determined by Eqs. 15a, 15b, 15c, 16a, 16b, 16c and 17 can be calculated with the help of one-, two- and three-center expansion approaches based on the use of overlap integrals over STOs with the same screening constants. To do this, we need only the Cartesian coordinates of the nuclei relative to a common axial frame, the quantum numbers and screening constants of the STOs.

The applicability of unsymmetrical one-range addition theorems is tested by calculating the multicenter EFG integrals determined by Eqs. 15a, 15b, 15c, 16a, 16b, 16c and 17. Using these formulae, we constructed programs that are performed in the Mathematica 7.0 software package.

The numerical results for the three-center EFG integrals (15a) and two-center EFG integrals (16c) for arbitrary values of screening constants, quantum numbers and locations of orbitals are shown in Table 1. This table shows that good agreement is obtained for $\alpha = 1, 0, -1, -2$. The convergence properties of the series expansion relation for the three-center EFG integral $I_{300,200}^{-11ac,b}(5.5, 2.8)$ are shown in Table 2 and Figs. 1, 2 and 3. The convergences in these figures are described by $10^4 \Delta f_N = I_{300,200}^{-11ac,b}(5.5, 2.8)_N - I_{300,200}^{-11ac,b}(5.5, 2.8)_{N=15}$, $10^2 \Delta f_L = I_{300,200}^{-11ac,b}(5.5, 2.8)_L - I_{300,200}^{-11ac,b}(5.5, 2.8)_{L=14}$ and $10^4 \Delta f_M = I_{300,200}^{-11ac,b}(5.5, 2.8)_M - I_{300,200}^{-11ac,b}(5.5, 2.8)_{M=14}$, respectively. The partial summations corresponding to progressively increasing upper summation limits in Eq. (15a) are denoted by N , L and M . As can be seen from Fig. 1, Eq. 15a displays the most rapid convergence to the numerical results (with five digits stable) as a function of the summation limit for $N=11$ (for $\alpha=1, 0$), $N=12$ (for $\alpha=-1$) and $N=14$ (for $\alpha=-2$). Figure 1 shows that the calculation accuracy is satisfactory for the summation index N . As can be seen from Figs. 2 and 3, Eq. 15a displays the most rapid convergence to the numerical results (with five digits

stable) as a function of the summation limits for $L=6$ and $M=8$ (for $\alpha = 1, 0$), and for $L=8$ and $M=7$ (for $\alpha = -1, -2$). Therefore, the series rapidly converges with respect to l and m , so only a few terms can be included in the summations over indices l and m .

The dependences of the three-center EFG integrals on the internuclear distances for $\alpha = 1, 0, -1, -2$ and $N=15$ are shown in Table 2. The convergence is also satisfactory here. Note that greater accuracy is attainable through the use of more terms in the series expansion relations.

As can be seen from our tests, the series expansion formulae obtained with the help of unsymmetrical one-range addition theorems for STOs are useful tools for evaluating multicenter electric field gradient integrals with arbitrary values of quantum numbers, orbital parameters and internuclear distances.

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