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Calculation of multicenter electronic attraction, electric field and electric field gradient integrals of Coulomb potential over integer and noninteger *n* Slater orbitals

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With the help of complete orthonormal sets of Ψ^{α}- ETOs, where $\alpha = 1, 0, -1, -2, \ldots$ a large number of series expansion formulas for the multicenter electronic attraction (EA), electric field (EF) and electric field gradient (EFG) integrals of integer and noninteger *n* Slater type orbitals (ISTOs and NISTOs) is established through the overlap integrals with the same screening constants and the new central and noncentral interaction potentials depending on the coordinates of the nuclei of a molecule are introduced. The convergence of the series is tested by calculating concrete cases for arbitrary quantum numbers, screening constants and location of ISTOs and NISTOs.

KEY WORDS: electronic attraction integrals, electric field integrals, electric field gradient integrals, noninteger principal quantum numbers

1. Introduction

It is well known that the vast majority of all molecular electronic structure calculations are nowadays performed on the basis of the Hartree-Fock-Roothaan (HFR) equations [1] combined with the so-called LCAO MO approach. In this approach, the multi-electron wave functions are approximated by linear combinations of suitably symmetrized products of one-electron wave functions (Slater determinants), and the spatial part of such a one-electron wave function is approximated by a linear combination of so-called basis functions centered at the nuclei of the different atoms of the molecule. The HFR approach inevitably leads to the so-called molecular multicenter integrals one- and two-electron integrals whose numerical values are needed in the subsequent iterative solution of the HFR equations. Unfortunately, even today and in spite of all the recent

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progress in mathematical techniques and in computer hard- and software, this integral problem of computational quantum chemistry is not yet solved in a completely satisfactory way.

The computational problems, which have to be overcome, depend strongly on the basis functions being used. The stater type orbitals (STOs) are the first basis functions, were used on a larger scale in atomic calculations [2]. These functions are able to describe correctly the asymptotic behavior of exact solutions of atomic and molecular Schrödinger equation both in the vicinity of the nuclei [3] or at large distances away from the nuclei [4]. Accordingly, the STOs are apparently very close to physical reality. Nevertheless, STOs nowadays play a negligible role in ab initio calculations. The reason is that so far, nobody has been able to compute the multicenter integrals at the same time efficiently and reliable. This would be necessary to make molecular electronic structure calculations with a Slater basis feasible. Instead, ab initio calculations are routinely performed with the help of Gaussian functions, as proposed by Boys [5]. These functions have many obvious disadvantages. In particular, they are nonphysical in that sense that they are not able to describe correctly the asymptotic behavior of exact molecular wave functions either in the vicinity of the nuclei [3] or at large distances away from the nuclei [4]. Consequently, relatively large basis sets of Gaussian functions are needed to compensate their nonphysical nature and to accomplish a satisfactory accuracy. In particular, for the investigation of the derivatives of the electrostatic potential created by the electrons and the interactions between electrons and nuclei of a molecule, the slow convergence of Gaussian functions may lead to serious computational problems. The only, but nevertheless decisive advantage of Gaussian functions is that their molecular multicenter integrals can be computed comparatively easily.

In principle, it is quite obvious how to overcome the inherent limitations of Gaussian basis functions. One only has to use alternative basis functions that are physically better motivated. As explained above, exponentially decaying basis functions like STOs are the most natural candidates: many test calculations have shown that already relatively small basis of STOs suffice to produce a good accuracy.

Recently, we have had some encouraging developments in this direction. With the help of complete orthonormal sets of Ψ^{α}-ETOs [6–8], we could show that the arbitrary multicenter multielectron molecular integrals of ISTOs and NISTOs arising in the determination of various multielectron properties for a given molecule can be computed both efficiently and reliable. The convergence, accuracy and CPU time have been tested in our previous papers (see: figures and tables in refs. 9–13) by calculating different kinds of one and two-electron multicenter integrals over ISTOs and NISTOs. We notice that 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 over ISTOs and NISTOs appearing in the determination of molecular multielectron properties when the HFR approximation is employed.

In this paper, we wish, using our treatment of the expansion problem for STOs based upon the complete orthonormal sets of Ψ^{α}-ETOs, to establish the combined formulas for the multicenter EA, EF and EFG integrals of STOs with integer and noninteger principal quantum numbers. We notice that the method used in this work is an extension of the approach presented in refs. 14 and 15 for ISTOs to the case of NISTOs. The new and older works are reviewed in ref. 15.

2. Definitions and basic formulas

In order to evaluate the multicenter integrals of Coulomb potential appearing in the study of electric field induced within a molecule by its electrons, the following integrals must be solved:

multicenter EA integrals

$$U_{pp'}(\zeta, \zeta'; \vec{R}_{ca,} \vec{R}_{ab}) = \int \chi_p^*(\zeta, \vec{r}_{a1}) \chi_{p'}(\zeta', \vec{r}_{c1}) O(r_{b1}) \mathrm{d}V_1, \tag{1}$$

multicenter EF integrals,

$$U^i_{pp'}(\zeta, \zeta'; \vec{R}_{ca,} \vec{R}_{ab}) = \int \chi_p^*(\zeta, \vec{r}_{a1}) \chi_{p'}(\zeta', \vec{r}_{c1}) O^i(\vec{r}_{b1}) \mathrm{d}V_1 \tag{2a}$$

$$= \frac{\partial}{\partial X^i} U_{pp'}(\zeta, \zeta'; \vec{R}_{ca,} \vec{R}_{ab}), \tag{2b}$$

multicenter EFG integrals,

$$U^{ij}_{pp'}(\zeta, \zeta'; \vec{R}_{ca,} \vec{R}_{ab}) = \int \chi_p^*(\zeta, \vec{r}_{a1}) \chi_{p'}(\zeta', \vec{r}_{c1}) O^{ij}(\vec{r}_{b1}) \mathrm{d}V_1 \tag{3a}$$

$$= \frac{\partial^2}{\partial X^i \partial X^j} U_{pp'}(\zeta, \zeta'; \vec{R}_{ca}, \vec{R}_{ab}), \tag{3b}$$

where $i, j = 1, -1, 0$, $p \equiv nlm$, $p' \equiv n'l'm'$, $\vec{R}_{ca} = \vec{r}_{c1} - \vec{r}_{a1,} \vec{R}_{ab} = \vec{r}_{a1} - \vec{r}_{b1,} n$ and n' are the integer or noninteger principal quantum numbers and

$$O(r_{b1}) = \frac{1}{r_{b1}}, \tag{4}$$

$$O^i(\vec{r}_{b1}) = \frac{\partial}{\partial X^i} O(\vec{r}_{b1}) = \frac{x^i_{b1}}{r^3_{b1}}, \tag{5}$$

$$O^{ij}(\vec{r}_{b1}) = \frac{\partial^2}{\partial X^i \partial X^j} O(\vec{r}_{b1}) = \frac{3x^i_{b1}x^j_{b1} - \delta_{ij} r^2_{b1}}{r^5_{b1}} - \frac{4\pi}{3} \delta_{ij} \delta(\vec{r}_{b1}). \tag{6}$$

Here $x^1 = x, x^{-1} = y, x^0 = z$ and $X^1 = X, X^{-1} = Y, X^0 = Z$ are the Cartesian coordinates of the electron and nucleus b, respectively; $\delta(\vec{r})$ is the Dirac delta function. The normalized complex or real STOs in equations (1), (2a) and (3a) are determined by

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

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

where ζ is the screening constant and $\Gamma(n)$ is the gamma function defined by [16]

$$\Gamma(n) = \int_0^\infty t^{n-1} \mathrm{e}^{-t} \mathrm{d}t. \tag{9}$$

The Coulomb potential $O(r_{b1})$, equation (4), satisfies the Poisson's equation [17]:

$$O^{11}(\vec{r}) + O^{-1-1}(\vec{r}) + O^{00}(\vec{r}) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) O(r) = -4\pi \delta(\vec{r}). \tag{10}$$

3. Expressions in terms of basic integrals

In order to evaluate the multicenter EA, EF and EFG integrals, equations (1)–(3), we first make use of the following expansion formulas for the electron charge density over NISTOs in terms of ISTOs [7]:

$$\chi_p(\zeta, \vec{r}_{a1}) \chi^*_{p'}(\zeta', \vec{r}_{c1}) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta, \zeta', z; \vec{R}_{ca,} \vec{R}_{ab}) \chi_q(z, \vec{r}_{b1}), \tag{11}$$

$$\chi_p(\zeta, \vec{r}_{a1}) \chi^*_{p'}(\zeta', \vec{r}_{c1}) = \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{\mu=1}^{N} \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta, \zeta', z; \vec{R}_{ca,} 0) \chi_q(z, \vec{r}_{a1}), \tag{12}$$

where $\alpha = 1, 0, -1, -2, \ldots, q \equiv \mu\nu\sigma$ and $z = \zeta + \zeta'$. The quantities $W^{\alpha N}_{pp'q}(\zeta, \zeta', z; \vec{R}_{ca,} \vec{R}_{ab})$ and $W^{\alpha N}_{pp'q}(\zeta, \zeta', z; \vec{R}_{ca,} 0)$ are the three- and two-center charge density expansion coefficients determined by the use of two-center overlap integrals between ISTOs and NISTOs with the same screening constants.

Substituting in equations (1)–(3) the charge densities $\chi_p(\zeta, \vec{r}_{a1}) \chi^*_{p'}(\zeta', \vec{r}_{c1})$ by their expressions, namely, equations (11) and (12), we get the following relations

in terms of one- and two-center basic integrals over ISTOs:

$$U_{pp'}(\zeta,\zeta';\vec{R}_{ca,}\vec{R}_{ab})=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W_{pp'q}^{\alpha N}(\zeta,\zeta',z;\vec{R}_{ca,}\vec{R}_{ab})J_q(z), \quad (13)$$

$$U^{i}_{pp'}(\zeta,\zeta';\vec{R}_{ca,}\vec{R}_{ab})=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W_{pp'q}^{\alpha N}(\zeta,\zeta',z;\vec{R}_{ca,}\vec{R}_{ab})J^{i}_q(z), \quad (14)$$

$$U^{ij}_{pp'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab})=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W_{pp'q}^{\alpha N}(\zeta,\zeta',z;\vec{R}_{ca,}\vec{R}_{ab})J^{ij}_q(z), \quad (15)$$

and

$$U_{pp'}(\zeta,\zeta';\vec{R}_{ca,}\vec{R}_{ab})=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W_{pp'q}^{\alpha N}(\zeta,\zeta',z;\vec{R}_{ca,}0)J_q(z,\vec{R}_{ab}), \quad (16)$$

$$U^{i}_{pp'}(\zeta,\zeta';\vec{R}_{ca,}\vec{R}_{ab})=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W_{pp'q}^{\alpha N}(\zeta,\zeta',z;\vec{R}_{ca,}0)J^{i}_q(z,\vec{R}_{ab}), \quad (17)$$

$$U^{ij}_{pp'}(\zeta,\zeta';\vec{R}_{ca,}\vec{R}_{ab})=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W_{pp'q}^{\alpha N}(\zeta,\zeta',z;\vec{R}_{ca,}0)J^{ij}_q(z,\vec{R}_{ab}). \quad (18)$$

The basic integrals in these equations are determined by one-center integrals

$$J_q(z)=\frac{1}{\sqrt{4\pi}}\int\chi_q^*(z,\vec{r}_1)O(r_1)\mathrm{d}V_1, \quad (19)$$

$$J^{i}_q(z)=\frac{1}{\sqrt{4\pi}}\int\chi_q^*(z,\vec{r}_1)O^{i}(\vec{r}_1)\mathrm{d}V_1, \quad (20)$$

$$J^{ij}_q(z)=\frac{1}{\sqrt{4\pi}}\int\chi_q^*(z,\vec{r}_1)O^{ij}(\vec{r}_1)\mathrm{d}V_1 \quad (21)$$

and
two-center integrals

$$J_q(z;\vec{R})=\frac{1}{\sqrt{4\pi}}\int\chi_q^*(z,\vec{r}_{a1})O(r_{b1})\mathrm{d}V_1, \quad (22)$$

$$J^{i}_q(z;\vec{R})=\frac{1}{\sqrt{4\pi}}\int\chi_q^*(z,\vec{r}_{a1})O^{i}(\vec{r}_{b1})\mathrm{d}V_1 \quad (23a)$$

$$=\frac{\partial}{\partial X^{i}}J_q(z;\vec{R}), \quad (23b)$$

$$J_q^{ij}(z;\vec{R}) = \frac{1}{\sqrt{4\pi}} \int \chi_q^*(z,\vec{r}_{a1}) O^{ij}(\vec{r}_{b1}) \mathrm{d}V_1 \tag{24a}$$

$$= \frac{\partial^2}{\partial X^i \partial X^j} J_q(z;\vec{R}), \tag{24b}$$

where $J_q(z) = J_q(z,0)$, $J_q^i(z) = J_q^i(z,0)$, $J_q^{ij}(z) = J_q^{ij}(z,0)$ and $\vec{R} = \vec{R}_{ab}$. Thus, the multicenter EA, EF and EFG integrals over ISTOs and NISTOs can be calculated with the help of one- or two-center basic integrals of ISTOs.

4. Use of central and noncentral potential functions in evaluation of basic integrals

In order to evaluate the one-center basic integrals we take into account equations (4)–(6) for operators in equations (19)–(21). Then we find finally for the one-center basic integrals the following relations:

$$J_{\mu\nu\sigma}(z) = \frac{2^{\mu+1}\Gamma(\mu+1)}{\sqrt{\Gamma(2\mu+1)}} (2z)^{-1/2} \delta_{\nu 0}\delta_{\sigma 0}, \tag{25}$$

$$J^i_{\mu\nu\sigma}(z) = \frac{2^{\mu}\Gamma(\mu)}{\sqrt{3\Gamma(2\mu+1)}} (2z)^{1/2} \delta_{\nu 1}\delta_{\sigma i}, \tag{26}$$

$$J^{ij}_{nlm}(\zeta) = \frac{2^{\mu-1}\Gamma(\mu-1)}{\sqrt{5\Gamma(2\mu+1)}} (2z)^{3/2} a^{ij}_{2\sigma,0}\delta_{\nu 2} - \frac{\sqrt{2}}{6}(2z)^{3/2}\delta_{ij}\delta_{\mu 1}\delta_{\nu 0}\delta_{\sigma 0}, \tag{27}$$

where

$$a^{ij}_{2\sigma,0} = 5C^{2|\sigma|}(1i,1j)A^{\sigma}_{ij}. \tag{28}$$

See refs. 15 and 21 for exact definition of coefficients a^{ij}, A^{σ} and $C^{\nu|\sigma|}$, respectively.

Now we move on the evaluation of two-center basic integrals. For this purpose we use equations (25) and (26) of ref 12 for the two-center basic EA integrals in equations (22), (23b) and (24b). Then with the aid of the method set out in ref. 15 we find for the two-center basic integrals the following analytical expressions in terms of potential functions:

$$J_{\mu\nu\sigma}(z,\vec{R}) = f^{00}_{\mu\nu,\nu\sigma}(z,\vec{R}), \tag{28}$$

$$J^i_{\mu\nu\sigma}(z,\vec{R}) = \sum_{\sigma'=-(\nu-1)}^{\nu-1} a^i_{\nu\sigma,\sigma'} f^{10}_{\mu\nu,\nu-1\sigma'}(z,\vec{R}) - (2\nu+1)\left(\frac{X^i}{R}\right) f^{11}_{\mu\nu,\nu\sigma}(z,\vec{R}), \tag{29}$$

$$J^{ij}_{\mu\nu\sigma}(z,\vec{R}) = \sum_{\sigma'=-(\nu-2)}^{\nu-2} a^{ij}_{\nu\sigma,\sigma'} f^{20}_{\mu\nu,\nu-2\sigma'}(z,\vec{R}) - (2\nu+1)$$

$$\sum_{\sigma'=-(\nu-1)}^{\nu-1}\left[a^{i}_{\nu\sigma,\sigma'}\left(\frac{X^j}{R}\right)+a^{j}_{\nu\sigma,\sigma'}\left(\frac{X^i}{R}\right)\right]f^{21}_{\mu\nu,\nu-1\sigma'}(z,\vec{R})$$
$$-(2\nu+1)\delta_{ij}f^{21}_{\mu\nu,\nu\sigma}(z,\vec{R})+(2\nu+1)(2\nu+3)\left(\frac{X^i}{R}\right)\left(\frac{X^j}{R}\right)f^{22}_{\mu\nu,\nu\sigma}(z,\vec{R})-\frac{\sqrt{4\pi}}{3}\delta_{ij}\chi^{*}_{\mu\nu\sigma}(z,\vec{R}). \tag{30}$$

The potential functions $f^{tk}_{\mu\nu,\upsilon\sigma}(z,\vec{R})$ occurring in these equations are determined by

$$f^{tk}_{\mu\nu,\upsilon\sigma}(z,\vec{R})=f^{tk}_{\mu\nu}(z,R)\bar{S}_{\upsilon\sigma}(\theta,\varphi),\quad \bar{S}_{\upsilon\sigma}(\theta,\varphi)=\sqrt{\frac{4\pi}{2\upsilon+1}}S_{\upsilon\sigma}(\theta,\varphi), \tag{31}$$

$$f^{tk}_{\mu\nu}(z,R)\equiv f^{tk}_{\mu\nu,00}(z,R)=\frac{N^{t}_{\mu\nu}(2z)}{x^{\nu+t+1}}\left(1-\frac{1}{\Gamma(\mu+\nu+2)}\sum_{\sigma=0}^{k}\beta^{tk}_{\sigma}[\Gamma(\mu+\nu+2+\sigma,x)\right.$$
$$\left.-x^{2\nu+1}\Gamma(\mu-\nu+2+\sigma,x)]\right), \tag{32}$$

where $x=zR$ and $t=0,1,2$ for EA, EF and EFG basic integrals, respectively, $0\leqslant k\leqslant t$,

$$\beta^{00}_{0}=\beta^{10}_{0}=\beta^{20}_{0}=1,\quad \beta^{11}_{0}=\beta^{21}_{0}=-\frac{\mu-\nu+1}{2\nu+1},\quad \beta^{11}_{1}=\beta^{21}_{1}=\frac{1}{2\nu+1},$$
$$\beta^{22}_{0}=\frac{(\mu-\nu+1)(\mu-\nu-1)}{(2\nu+1)(2\nu+3)},$$
$$\beta^{22}_{1}=-\frac{2\mu-2\nu+1}{(2\nu+1)(2\nu+3)},\quad \beta^{22}_{2}=\frac{1}{(2\nu+1)(2\nu+3)}\ \text{and}$$
$$N^{t}_{\mu\nu}(2z)=2^{\mu-t+1}\Gamma(\mu+\nu+2)\left[\frac{(2z)^{2t-1}}{(2\nu+1)\Gamma(2\mu+1)}\right]^{1/2}. \tag{33}$$

Here $\Gamma(\sigma,x)$ is the incomplete gamma function defined by [16]

$$\Gamma(\sigma,x)=\int_{x}^{\infty}t^{\sigma-1}\mathrm{e}^{-t}\mathrm{d}t. \tag{34}$$

The accuracy of computer results for the multicenter EA, EF and EFG integrals with NISTOs obtained from the analytical equations of this work can also be determined by the use of the following different sets of one- center series expansion formulas:

$$U_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab})=\lim_{\substack{N\to\infty\\ N'\leftarrow\infty}}\sum_{\mu=l+1}^{N}\sum_{\mu'=l'+1}^{N'}V^{\alpha N^{*}}_{nl,\mu l}V^{\alpha N'}_{n'l',\mu l'}U_{\mu lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab}), \tag{35}$$

$$U^{i}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab}) = \lim_{\substack{N\to\infty\\ N'\leftarrow\infty}} \sum_{\mu=l+1}^{N}\sum_{\mu'=l'+1}^{N'} V^{\alpha N*}_{nl,\mu l} V^{\alpha N'}_{n'l',\mu l'} U^{i}_{\mu lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab}), \tag{36}$$

$$U^{ij}_{nlm,n'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab}) = \lim_{\substack{N\to\infty\\ N'\leftarrow\infty}} \sum_{\mu=l+1}^{N}\sum_{\mu'=l'+1}^{N'} V^{\alpha N*}_{nl,\mu l} V^{\alpha N'}_{n'l',\mu l'} U^{ij}_{\mu lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab}), \tag{37}$$

where $U_{\mu lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab})$, $U^{i}_{\mu lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab})$ and $U^{ij}_{\mu lm,\mu'l'm'}(\zeta,\zeta';\vec{R}_{ca},\vec{R}_{ab})$ are the multicenter EA, EF and EFG integrals with ISTOs and $\alpha = 1, 0, -1, -2, \ldots$. In ref. 15 we derived the analytical expressions for the multicenter EA, EF and EFG integrals with ISTOs. Here the quantities $V^{\varepsilon N}$ are the one-center expansion coefficients for NISTOs in terms of ISTOs obtained with the help of complete orthonormal sets of Ψ^{α}-ETOs (see ref. 6)

$$\chi_{n^*lm}(\zeta,\vec{r}) = \lim_{N\to\infty} \sum_{n=l+1}^{N} V^{\alpha N}_{n^*l,nl}\chi_{nlm}(\zeta,\vec{r}), \tag{38}$$

where

$$V^{\alpha N}_{n^*l,nl} = \sum_{n'=l+1}^{N} \Omega^{\alpha l}_{nn'}(N)\Gamma(n^*+n'-\alpha+1)/\sqrt{\Gamma(2n^*+1)\Gamma(2n'-2\alpha+1)}, \tag{39}$$

$$\Omega^{\alpha l}_{n\kappa}(N) = \left[\frac{[2(k-\alpha)]!}{(2\kappa)!}\right]^{1/2} \sum_{n'=\max(n,\kappa)}^{N} (2n')^{\alpha}\omega^{\alpha l}_{n'n}\omega^{\alpha l}_{n'\kappa}, \tag{40}$$

$$\omega^{\alpha l}_{nn'} = (-1)^{n'-l-1} \times\left[\frac{(n'+l+1)!}{(2n)^{\alpha}(n'+l+1-\alpha)!}F_{n'+l+1-\alpha}(n+l+1-\alpha) \times F_{n'-l-1}(n-l-1)F_{n'-l-1}(2n')\right]^{1/2}. \tag{41}$$

5. Numerical results and discussion

As can be seen from the formulas of this paper, the multicenter EA, EF and EFG integrals with the integer and noninteger principal quantum numbers can be calculated by the use of two-center overlap integrals with the same screening constant and potential function. For this purpose we need only the cartesian coordinates of the nuclei of a molecule relative to a common axial frame and the screening constants and quantum numbers of STOs. Thus, the computation of different formulas for any multicenter EA, EF and EFG integral obtained by the use of complete orthonormal sets of $\Psi^{1}_{nlm}, \Psi^{0}_{nlm}, \Psi^{-1}_{nlm}, \Psi^{-2}_{nlm}, \ldots$ ETOs can be reduced to the calculation of overlap integrals and the potential containing the incomplete gamma function. One has to be able to compute the overlap integrals

and the incomplete gamma function with sufficient accuracy even for relatively large summation indices because otherwise convergence cannot be obtained. The numerical aspects of overlap integrals for large quantum numbers have recently been investigated in our papers [12] and [19,20]. For the calculation of incomplete gamma function we used the computer program presented in ref. 21.

In figure 1, we present the convergence of the series, in equation (18) for $L = M < N - 1$. Here N, L and M are upper limits of the indices μ, ν and σ, respectively. The series accuracy $\Delta f = f_{NN-1N-1} - f_{NLM}$ is shown in figure 1, where the quantities $f = f_{NN-1N-1}$ are the values of integral for $L = N - 1$ and $M = N - 1$. We see that the convergence series with respect to $\alpha = 0$ is rapid.

The results of calculations on a PENTIUM III 800 MHz computer (using TURBO PASCAL 7.0 language) for various values of parameters of multicenter

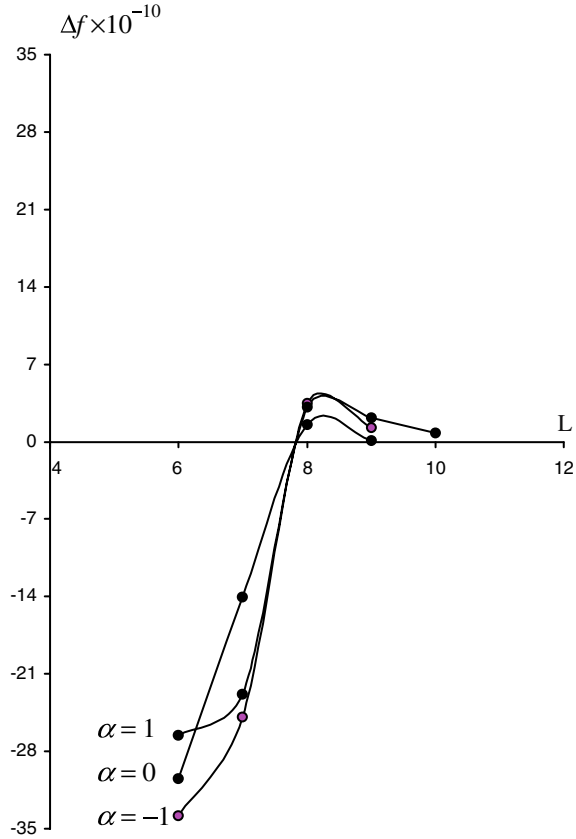

Figure 1. The convergence of series in equation (18) for the three-center EFG integral $U^{1-1}_{2.551-1,2.3411}$ for $\alpha = 1, 0, -1$ in a.u.: $\zeta = 10.6$, $\zeta' = 4.7$, $R_{ab} = 3.2$, $\theta_{ab} = 150^0$, $\varphi_{ab} = 180^\circ$, $R_{ca} = 0.6$, $\theta_{ca} = 54^\circ$, $\varphi_{ca} = 60^\circ$.

Table 1
The values of two- and three-center EF integrals with NISTOs and ISTOs in molecular coordinate system for $X^1 = -0.7$, $X^{-1} = 0.5$, $X^0 = 0.2$ (in a.u.).

														Equations (14) and (17) for $N = 12$		
n	l	m	ζ	n'	l'	m'	ζ'	i	R_{ab}	θ_{ab}	ϕ_{ab}	R_{ca}	θ_{ca}	φ_{ca}	$\alpha = 0$	$\alpha = 1$	$\alpha = -1$
2	1	0	5.4	1	0	0	3.6	1	0	0	0	0.5	120	20	3.6624477143E-01	3.6624578768E-01	3.6624481993E-01
1.2	0	0	5.7	1.5	0	0	3.4	−1	0	0	0	0.5	120	160	3.6781908793E-01	3.67819229082E-01	3.6781775279E-01
2	1	0	4.6	2	1	0	1.3	1	0	0	0	0.7	60	60	2.5770033767E-02	2.5770313535E-02	2.5772043583E-02
2.6	1	0	8.5	2.3	1	0	2.3	−1	0	0	0	1.2	60	60	1.4061814826E-02	1.4061848254E-02	1.4061609791E-02
2	1	1	8.4	2	1	1	6.1	1	0	0	0	0.3	10	45	−8.8761880078E-01	−8.8761697943E-01	−8.8761733518E-01
2.4	1	1	10.8	2.8	1	0	6.2	−1	0	0	0	0.7	30	80	5.0402729511E-02	5.0402918457E-02	5.0404920212E-02
1	0	0	5.3	1	0	0	2.4	1	1.5	60	30	1.3	40	135	1.7532267585E-02	1.7532282499E-02	1.7532413286E-02
1.4	0	0	6.1	1.2	1	0	4.6	−1	2.4	30	120	0.6	120	40	4.2350062283E-03	4.2350064609E-03	4.2350081283E-03
2	1	1	4.6	2	1	1	3.1	1	1.6	45	120	0.5	60	225	8.8161402611E-02	8.8161431989E-02	8.8162766627E-02
2.14	1	0	8.6	2.32	1	0	3.4	−1	1.2	60	180	0.4	150	120	−2.7010462501E-02	−2.7010482292E-02	−2.7010375359E-02
2	1	0	5.4	2	1	1	7.3	1	0.8	135	150	0.4	70	270	−9.5243334684E-01	−9.5241594854E-01	−9.5243494500E-01
2.56	1	1	9.8	2.72	1	1	6.3	−1	0.8	120	240	0.6	180	140	−1.8125508646E-01	−1.8125535977E-01	−1.8128315590E-01

Table 2
The values of two- and three-center EFG integrals with NISTOs and ISTOs in molecular coordinate system for $X^1 = -0.7$, $X^{-1} = 0.5$, $X^0 = 0.2$ (in a.u.).

															Equations (15) and (18) for $N = 12$		
n	l	m	ζ	n'	l'	m'	ζ'	i	j	R_{ab}	θ_{ab}	ϕ_{ab}	R_{ca}	θ_{ca}	φ_{ca}	$\alpha = 0$	$\alpha = 1$	$\alpha = -1$
1	0	0	7.5	2	1	0	2.3	1	−1	0	0	0	0.4	20	45	2.2533282211E-01	2.2533265208E-01	2.2533385003E-01
2.5	0	0	9.8	2.7	0	0	6.3	−1	0	0	0	0	0.6	45	20	−5.6852326371E-01	−5.6852513177E-01	−5.6852342029E-01
2	1	0	8.7	2	1	0	6.2	1	−1	0	0	0	0.7	100	135	−4.4621117717E-01	−4.4621017139E-01	−4.4624038073E-01
2.25	1	0	7.7	2.66	1	0	2.4	−1	0	0	0	0	0.8	126	200	3.8289381944E-01	3.8289335553E-01	3.8289652363E-01
2	1	0	7.4	2	1	0	3.6	−1	−1	0.8	135	90	1.2	100	120	−1.2578403784E-01	−1.2578525132E-01	−1.257689631E-01
2.7	0	0	8.5	2.4	1	0	3.1	1	−1	0.8	120	240	1.3	54	140	−2.4439343431E-01	−2.4439342338E-01	−2.443625327E-01
2	1	1	9.7	2	1	0	2.3	−1	−1	1.5	180	120	1.1	110	240	−4.0944510974E-03	−4.0944535596E-03	−4.094549853E-03
2.86	1	0	10.8	2.75	1	0	5.3	1	−1	1.4	150	180	0.6	18	20	1.0092388430E-01	1.00923191405E-01	1.0092376102E-01
2	1	1	12.5	2	1	1	4.2	−1	−1	1.8	120	150	1.4	120	300	3.0989593427E-04	3.0989575902E-04	3.0988727875E-04
2.86	1	1	12.2	2.75	1	−1	7.5	1	−1	2.1	120	135	0.8	36	40	4.2395405405E-03	4.2394371408E-03	4.2395405405E-03

EF and EFG integrals are given in tables 1 and 2. As can be seen from these tables, the accuracy of computer calculations obtained in the present algorithm is satisfactory.

The computer time required for the calculation of multicenter EF and EFG integrals are not given in the tables due to the fact that the comparison cannot be made with the different computers used in the literature. It is seen from the algorithm presented for multicenter EF and EFG integrals that our CPU times are satisfactory. For instance, for two-center EF integrals with quantum sets $n^* = 2, l = 1, m = 1, \zeta = 3.8, n' = 2, l' = 1, m' = 0, \zeta' = 4.1, i = 1$ and $R_{ca} = 1.1, \theta_{ab} = 90^\circ, \varphi_{ca} = 30^\circ$, CPU time takes about 0.34 ms.

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