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ORIGINAL PAPER

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Use of Ψ^{α}-ETOs in the unified treatment of electronic attraction, electric field and electric field gradient multicenter integrals of screened Coulomb potentials over Slater orbitals

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Abstract In this study, using complete orthonormal sets of Ψ^{α}-ETOs (where α=1, 0, −1, −2, ...)introduced by the author, a large number of series expansion formulae for the multicenter electronic attraction (EA), electric field (EF) and electric field gradient (EFG) integrals of the Yukawa-like screened Coulomb potentials (SCPs) is presented through the new central and noncentral potentials and the overlap integrals with the same screening constants. The final results obtained are valid for arbitrary locations of STOs and their parameters.

Keywords Screened Coulomb potentials · Multicenter electric field integrals · Multicenter electric field gradient integrals · Central and noncentral potential functions

Introduction

For many years there has been considerable interest in calculating the multicenter EA, EF and EFG integrals of Yukawa-like screened Coulomb potentials. These potentials are important in several contexts. For example, the Yukawa potential may be used to approximate the potential experienced by electrons in an atom of a molecule where the remaining electrons screen the nuclear charge. It describes the shielding effect in plasmas, where it is called the Debye–Hückel potential, and is known as the Thomas–Fermi potential in solid-state physics [1]. This potential is also important in studying hydrogen under pressure [2, 3, 4]. Therefore, it is desirable to have available as many different representations for the Yukawa potential as possible.

It is well known that there is a large body of existing formulae for expansion methods for STOs about a displaced center [5, 6, 7, 8], the Gaussian transform method [9], the Fourier transform method [10, 11, 12], the B-function method [13, 14] then also, new methods [15, 16, 17, 18, 19, 20, 21, 22] developed for the evaluation of multicenter molecular integrals of nonscreened potentials do not generally apply to screened Coulomb potentials. In previous papers, we have presented a method for obtaining the translation formula for STOs [23] by the use of complete orthonormal set of lambda ETOs introduced in [24, 25, 26] (see Eqs. 1 and 2 of [27] for α=0). These have been used for the evaluation of multicenter integrals of nonscreened potentials.

The aim of this article is to obtain different expressions for the multicenter EA, EF and EFG integrals with the Yukawa-like screened Coulomb potentials by the use of complete orthonormal sets of ψ^{α}-ETOs.

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Definitions and basic formulae

For the purpose of evaluating the multicenter integrals with the Yukawa-like screened Coulomb potentials required for the study of the electric field induced within a molecule by its electrons, the following integrals must be solved:

EA integrals of SCPs:

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

EF integrals of SCPs:

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

EFG integrals of SCPs:

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

where $\eta>0$, $i,j=1,-1,0$; $p=nlm$, $p'=n'l'm'$, $\vec{R}_{ca}=\vec{r}_{c1}-\vec{r}_{a1}, \vec{R}_{ab}=\vec{r}_{a1}-\vec{r}_{b1}$ and

$$O(\eta, r_{b1})=\frac{e^{-\eta r_{b1}}}{r_{b1}} \tag{4}$$

$$O^i(\eta, \vec{r}_{b1})=\frac{\partial}{\partial X^i}O(\eta, r_{b1})=\frac{x^i_{b1}}{r^3_{b1}}(1+\eta r_{b1})\mathrm{e}^{-\eta r_{b1}} \tag{5}$$

$$\begin{aligned}O^{ij}(\eta, \vec{r}_{b1})&=\frac{\partial}{\partial X^i \partial X^j}O(\eta, r_{b1})\\&=\frac{3x^i_{b1}x^j_{b1}-\delta_{ij}r^2_{b1}}{r^5_{b1}}\left(1+\eta r_{b1}+\frac{\eta^2}{3}r^2_{b1}\right)\mathrm{e}^{-\eta r_{b1}}\\&\quad+\frac{\eta^2\mathrm{e}^{-\eta r_{b1}}}{3r_{b1}}\delta_{ij}-\frac{4\pi}{3}\delta_{ij}\delta(\vec{r}_{b1})\end{aligned} \tag{6}$$

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 containing in Eqs. (1), (2) and (3) are given by

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

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

We note that the definition of phases in this work for the complex spherical harmonics ($Y^*_{lm}=Y_{l-m}$, where $S_{lm}=Y_{lm}$ differs from the Condon–Shortley phases [28] by the sign factor $(-1)^m$.

The Yukawa-like screened Coulomb potential, Eq. (4), satisfies the modified Helmholtz equation: [29]

$$\begin{aligned}&O^{11}(\eta, \vec{r})+O^{-1-1}(\eta, \vec{r})+O^{00}(\eta, \vec{r})-\eta^2 O(\eta, r)\\&=\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}-\eta^2\right)\frac{e^{-\eta r}}{r}=-4\pi\delta(\vec{r})\end{aligned} \tag{9}$$

Since this equation is one of the important partial differential equations of mathematical physics, it is not surprising that the Yukawa and Yukawa-like screened Coulomb potentials are useful in various branches of science.

Now we express the operators $O(\eta, r_{b1})$, $O^i(\eta, \vec{r}_{b1})$ and $O^{ij}(\eta, \vec{r}_{b1})$ in terms of screening central and non-central potentials introduced in [30]:

$$f_{u\upsilon s}\left(\eta, \overrightarrow{r}\right)=f_u(\eta, r)\bar{S}_{\upsilon s}(\theta, \varphi) \tag{10}$$

$$f_u(\eta, \vec{r})=f_{u00}(\eta, \vec{r})=r^{n-1}e^{-\eta r} \tag{11}$$

where $u\geq-\upsilon$ and

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

Taking into account Eqs. (10) and (11) in Eqs. (4), (5) and (6) we obtain:

$$O(\eta, r)=f_{000}(\eta, r) \tag{12}$$

$$O^i(\eta, \vec{r})=f_{-11i}(\eta, \vec{r})+\eta f_{01i}(\eta, \vec{r}) \tag{13}$$

$$\begin{aligned}O^{ii}(\eta, \vec{r})=(1+\delta_{i0})\times\Big\{&\left[(-1)^i f_{-220}(\eta, \vec{r})+i\sqrt{3}f_{-222}(\eta, \vec{r})\right]\\&+\eta\left[(-1)^i f_{-120}(\eta, \vec{r})+i\sqrt{3}f_{-122}(\eta, \vec{r})\right]\\&+\frac{\eta^2}{3}\left[(-1)^i f_{020}(\eta, \vec{r})+i\sqrt{3}f_{022}(\eta, \vec{r})\right]\Big\}\\&+\frac{\eta^2}{3}f_{000}(\eta, r)-\frac{4\pi}{3}\delta(\vec{r})\end{aligned} \tag{14}$$

and for $i\neq j$

$$O^{ij}(\eta, \vec{r})=\frac{1}{\sqrt{3}}\left[f_{-22s}(\eta, \vec{r})+\eta f_{-12s}(\eta, \vec{r})+\frac{\eta^2}{3}f_{02s}(\eta, r)\right] \tag{15}$$

where $s=i$ for $i=\pm1$, $j=0$ or $s=j$ for $i=0$, $j=\pm1$ and $s=-2$ for $i=1$, $j=-1$ or $i=-1$, $j=1$.

In order to evaluate the multicenter EA, EF and EFG integrals, Eqs. (1), (2) and (3), we shall use here Eq. (11) of [30] for the one-center expansion of the potentials in terms of STOs for $\eta'=z$:

$$f_{u\upsilon s}(\eta, \vec{r})=\sqrt{4\pi}\lim_{N\to\infty}\sum_{u'=\upsilon+1}^{N}b^{\alpha N}_{u\upsilon, u'\upsilon}(\eta, z)\chi_{u'\upsilon s}(z, \vec{r}) \tag{16}$$

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

$$b^{\alpha N}_{u\upsilon, u'\upsilon}(\eta, z)=\left(\frac{1}{2\upsilon+1}\right)^{1/2}\sum_{u''=\upsilon+1}^{N}\Omega^{\alpha\upsilon}_{u'u''}(N)P^{\alpha}_{uu''}(\eta, z) \tag{17}$$

$$P^{\alpha}_{uu''}(\eta, z)=\frac{(u+u''-\alpha)!}{[(2(u''-\alpha))!]^{1/2}(\eta+z)^{u+1/2}}\left(\frac{2z}{\eta+z}\right)^{u''-\alpha+1/2} \tag{18}$$

Expressions in terms of basic integrals

We first make use of the following expansion formulae for the electron charge density, [30] i.e.:

$$\begin{aligned}&\chi_p(\zeta, \vec{r}_{a1})\chi^*_{p'}(\zeta', \vec{r}_{c1})\\&=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W^{\alpha N}_{pp'q}\left(\zeta, \zeta', z; \overrightarrow{R}_{ca}, \overrightarrow{R}_{ab}\right)\chi_q(z, \vec{r}_{b1})\end{aligned} \tag{19}$$

$$\begin{aligned}&\chi_p(\zeta, \vec{r}_{a1})\chi^*_{p'}(\zeta', \vec{r}_{c1})\\&=\frac{1}{\sqrt{4\pi}}\lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu}W^{\alpha N}_{pp'q}\left(\zeta, \zeta', z; \overrightarrow{R}_{ca}, 0\right)\chi_q(z, \vec{r}_{a1})\end{aligned} \tag{20}$$

where α=1,0,–1,–2,..., $z=\zeta+\zeta'$ and $q=\mu\nu\sigma$. The quantities $W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\overrightarrow{R}_{ca},\overrightarrow{R}_{ab})$ and $W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\overrightarrow{R}_{ca},0)$ are the three- and two-center charge-density expansion coefficients defined by

$$W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\vec{R}_{ca},\vec{R}_{ab}) = \lim_{N'\to\infty}\sum_{\mu'=0}^{N'}\sum_{\nu'=0}^{\mu'-1}\sum_{\sigma'=-\nu'}^{\nu'} V^{*\alpha N'}_{p'q'}(\zeta',\zeta';\vec{R}_{ca}) \cdot W^{\alpha N}_{pq'q}(\zeta,\zeta',z;0,\vec{R}_{ab}) \tag{21}$$

$$W^{\alpha N}_{pp'q}(\zeta,\zeta',z;0,\vec{R}_{ab}) = \sum_{\nu'=0}^{\mu'-1}\sum_{\sigma'=-\nu'}^{\nu'} W_{pp'q'}(\zeta,\zeta';z)V^{\alpha N}_{q'q}(z,z;\vec{R}_{ab}) \tag{22}$$

and

$$W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\vec{R}_{ca},0) = \sum_{\nu'=0}^{\mu'-1}\sum_{\sigma'=-\nu'}^{\nu'} W_{pq'q}(\zeta,\zeta';z)V^{*\alpha N}_{p'q'}(\zeta',\zeta';\vec{R}_{ca}) \tag{23}$$

Here $W_{pp'q}(\zeta,\zeta';z)$ and $V^{\alpha N}_{qq'}(z,z;\overrightarrow{R}_{ab})$ are the electron charge density expansion coefficients for the one-center case and the translation coefficients for STOs (see [30]). We note that the coefficients $V^{\alpha N}{}_{q'q}$ are determined by the use of overlap integrals with the same screening parameters. Substituting the charge densities $\chi_p(\zeta,\vec{r}_{a1})\chi^*_{p'}(\zeta',\vec{r}_{c1})$ in Eqs. (1), (2) and (3) by their expressions in terms of STOs, namely, Eqs. (19) and (20), we get the following relations in terms of one- and two-center basic integrals:

$$U_{pp'}(\zeta,\zeta',\eta;\vec{R}_{ca},\vec{R}_{ab}) = \lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\vec{R}_{ca},\vec{R}_{ab})J_q(z,\eta) \tag{24}$$

$$U^{i}_{pp'}\left(\zeta,\zeta',\eta;\overrightarrow{R}_{ca},\overrightarrow{R}_{ab}\right) = \lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\overrightarrow{R}_{ca},\overrightarrow{R}_{ab})J^{i}_q(z,\eta) \tag{25}$$

$$U^{ij}_{pp'}(\zeta,\zeta',\eta;\vec{R}_{ca},\vec{R}_{ab}) = \lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\vec{R}_{ca},\vec{R}_{ab})J^{ij}_q(z,\eta) \tag{26}$$

and

$$U_{pp'}(\zeta,\zeta',\eta;\vec{R}_{ca},\vec{R}_{ab}) = \lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\vec{R}_{ca},0)J_q(z,\eta;\vec{R}_{ab}) \tag{27}$$

$$U^{i}_{pp'}(\zeta,\zeta',\eta;\vec{R}_{ca},\vec{R}_{ab}) = \lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\vec{R}_{ca},0)J^{i}_q(z,\eta;\vec{R}_{ab}) \tag{28}$$

$$U^{ij}_{pp'}(\zeta,\zeta',\eta;\vec{R}_{ca},\vec{R}_{ab}) = \lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} W^{\alpha N}_{pp'q}(\zeta,\zeta',z;\vec{R}_{ca},0)J^{ij}_q(z,\eta;\vec{R}_{ab}) \tag{29}$$

The basic integrals in these equations are determined by

One-center integrals

$$J_q(z,\eta) = \frac{1}{\sqrt{4\pi}}\int \chi^*_q(z,\vec{r}_1)O(\eta,r_1)\,\mathrm{d}V_1 \tag{30}$$

$$J^{i}_q(z,\eta) = \frac{1}{\sqrt{4\pi}}\int \chi^*_q(z,\vec{r}_1)O^{i}(\eta,\vec{r}_1)\,\mathrm{d}V_1 \tag{31}$$

$$J^{ij}_q(z,\eta) = \frac{1}{\sqrt{4\pi}}\int \chi^*_q(z,\vec{r}_1)O^{ij}(\eta,\vec{r}_1)\,\mathrm{d}V_1 \tag{32}$$

and

Two-center integrals

$$J_q(z,\eta;\vec{R}) = \frac{1}{\sqrt{4\pi}}\int \chi^*_q(z,\vec{r}_{a1})O(\eta,r_{b1})\,\mathrm{d}V_1 \tag{33}$$

$$J^{i}_q(z,\eta;\vec{R}) = \frac{1}{\sqrt{4\pi}}\int \chi^*_q(z,\vec{r}_{a1})O^{i}(\eta,\vec{r}_{b1})\,\mathrm{d}V_1 \tag{34}$$

$$J^{ij}_q(z,\eta;\vec{R}) = \frac{1}{\sqrt{4\pi}}\int \chi^*_q(z,\vec{r}_{a1})O^{ij}(\eta,\vec{r}_{b1})\,\mathrm{d}V_1 \tag{35}$$

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

With the evaluation of integrals (30), (31) and (32) we use the expansion formulae (12), (13), (14) and (15) for the operators in terms of potential functions. Then we find finally for the one-center basic integrals the following relations:

$$J_{\mu\nu\sigma}(z,\eta) = \delta_{\nu0}\delta_{\sigma0}F_{\mu0}(z,\eta) \tag{36}$$

$$J^{i}_{\mu\nu\sigma}(z,\eta) = \frac{1}{\sqrt{3}}\delta_{\nu1}\delta_{\sigma i}\left[F_{\mu,-1}(z,\eta)+\eta F_{\mu0}(z,\eta)\right] \tag{37}$$

$$J^{ii}_{\mu\nu\sigma}(z,\eta) = \frac{1}{\sqrt{5}}\delta_{\nu2}(1+\delta_{i0})\left[(-1)^{i}\delta_{\sigma0}+i\sqrt{3}\,\delta_{\sigma2}\right] \cdot\left[F_{\mu,-2}(z,\eta)+\eta F_{\mu,-1}(z,\eta)+\frac{\eta^2}{3}F_{\mu0}(z,\eta)\right] +\delta_{\nu0}\delta_{\sigma0}\frac{\eta^2}{3}F_{\mu0}(z,\eta)-\frac{2}{3}\zeta^{3/2}\delta_{\mu1}\delta_{\nu0}\delta_{\sigma0} \tag{38}$$

and for $i \neq j$

$$J^{ij}_{\mu\nu\sigma}(z,\eta) = \frac{1}{\sqrt{15}}\delta_{\nu 2}\delta_{\sigma s} \cdot \left[F_{\mu,-2}(z,\eta) + \eta F_{\mu,-1}(z,\eta) + \frac{\eta^2}{3}F_{\mu 0}(z,\eta)\right] \tag{39}$$

where s is the above-mentioned symbol (see Eq. 15) and

$$F_{\mu u}(z,\eta) = \frac{(\mu+u)!}{\sqrt{(2\mu)!}(z+\eta)^{u+1/2}}\left(\frac{2z}{z+\eta}\right)^{\mu+1/2} \tag{40}$$

Now we move on to the evaluation of two-center basic integrals. For this purpose we use Eq. (19) for the one-center expansion of potentials in Eqs. (33), (34) and (35). Then we obtain:

$$J_{\mu\nu\sigma}\left(z,\eta;\vec{R}\right) = \lim_{N\to\infty}\sum_{u'=1}^{N} b^{\alpha N}_{00,u'0}(\eta,z)S_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) \tag{41}$$

$$J^{i}_{\mu\nu\sigma}\left(z,\eta;\vec{R}\right) = \lim_{N\to\infty}\sum_{u'=1}^{N} b^{\alpha N}_{00,u'0}(\eta,z)S^{i}_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) \tag{42}$$

$$J^{ij}_{\mu\nu\sigma}\left(z,\eta;\vec{R}\right) = \lim_{N\to\infty}\sum_{u'=1}^{N} b^{\alpha N}_{00,u'0}(\eta,z)S^{ij}_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) - \delta_{ij}\frac{\sqrt{4\pi}}{3}\chi^{*}_{\mu\nu\sigma}\left(z,\vec{R}_{ab}\right) \tag{43}$$

The overlap integrals with the same screening parameters and derivatives contained in these equations are defined by

$$S_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) = \int \chi^{*}_{\mu\nu\sigma}(z,\vec{r}_{a1})\chi_{u'00}(z,\vec{r}_{b1})\,\mathrm{d}V_1 \tag{44}$$

$$S^{i}_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) = \frac{\partial}{\partial X^i}S_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) \tag{45}$$

$$S^{ij}_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) = \frac{\partial^2}{\partial X^i\partial X^j}S_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) \tag{46}$$

The overlap integrals with the same screening parameters are determined by [31]

$$S_{\mu\nu\sigma,u'00}\left(z,z;\overrightarrow{R}\right) = \left[\sum_{N=\nu+1}^{\mu+u'+1} g^{\alpha N\nu\sigma}_{\mu\nu\sigma,u'00}2^N\left[(2\nu+1)/(2N)!\right]^{1/2}(zR)^{N-1}\mathrm{e}^{-zR}\right] \bar{S}^{*}_{\nu\sigma}(\theta,\varphi) \tag{47}$$

$$g^{\alpha N\nu\sigma}_{\mu\nu\sigma,u'00} = \sum_{N'=\nu+1}^{\mu+u'+1}\Omega^{\alpha\nu}_{NN'}(\mu+u'+1)Q^{N'-\alpha\nu}_{\mu\nu,u'0} \tag{48}$$

See [31] for the exact definitions of the quantities $\Omega^{\alpha\nu}$ and $Q^{N\nu}$.

Use of screening noncentral potentials in evaluation of two-center basic integrals

As can be seen from Eq. (47), for the calculation of two-center basic EF and EFG integrals, Eqs. (45) and (46), we need the derivatives of the function

$$F_{\nu\sigma}\left(z,\vec{R}\right) = M_{\nu\sigma}(X,Y,Z)f(R) \tag{49}$$

where $R=(X^2+Y^2+Z^2)^{1/2}$ and

$$M_{\nu\sigma}(X,Y,Z) = R^{\nu}\bar{S}_{\nu\sigma}(\theta,\varphi) \tag{50}$$

$$f(R) = R^{N-\nu-1}e^{-zR} \tag{51}$$

In order to obtain the derivatives of the function $F_{\nu\sigma}\left(z,\vec{R}\right)$, we use the following formulae for the derivatives of a product of the functions $M_{\nu\sigma}(X,Y,Z)$and $f(R)$:

$$\frac{\partial(M_{\nu\sigma}f)}{\partial X^i} = \frac{\partial M_{\nu\sigma}}{\partial X^i}f + M_{\nu\sigma}X^i\left(\frac{1}{R}\frac{\partial f}{\partial R}\right) \tag{52}$$

$$\frac{\partial^2(M_{\nu\sigma}f)}{\partial X^i\partial X^j} = \frac{\partial^2 M_{\nu\sigma}}{\partial X^i\partial X^j}f + \frac{\partial M_{\nu\sigma}}{\partial X^i}X^j\left(\frac{1}{R}\frac{\partial f}{\partial R}\right) + \frac{\partial M_{\nu\sigma}}{\partial X^j}X^i\left(\frac{1}{R}\frac{\partial f}{\partial R}\right) + M_{\nu\sigma}\left[\delta_{ij}\left(\frac{1}{R}\frac{\partial f}{\partial R}\right) + X^iX^j\frac{1}{R}\frac{\partial}{\partial R}\left(\frac{1}{R}\frac{\partial f}{\partial R}\right)\right] \tag{53}$$

where

$$\frac{\partial M_{\nu\sigma}}{\partial X^i} = \sum_{\sigma'=-(\nu-1)}^{\nu-1} a^{i}_{\nu\sigma,\sigma'}M_{\nu-1\sigma'} \tag{54}$$

$$\frac{\partial^2 M_{\nu\sigma}}{\partial X^i\partial X^j} = \sum_{\sigma'=-(\nu-2)}^{\nu-2} a^{ij}_{\nu\sigma,\sigma'}M_{\nu-2\sigma'} \tag{55}$$

and

$$\frac{1}{R}\frac{\partial f}{\partial R} = \left[(N-\nu-1)R^{N-\nu-3} - zR^{N-\nu-2}\right]\mathrm{e}^{-zR} \tag{56}$$

$$\frac{1}{R}\frac{\partial}{\partial R}\left(\frac{1}{R}\frac{\partial f}{\partial R}\right) = \left[(N-\nu-1)(N-\nu-3)R^{N-\nu-5} - z(N-\nu-1)R^{N-\nu-4} + z^2R^{N-\nu-3}\right]\mathrm{e}^{-zR} \tag{57}$$

Here $a^{i}_{lm,m'}$=0 for l=0, $a^{ij}_{lm,m'}$ = for l=0,1 and

$$a^{1}_{lm,m'} = -\frac{\varepsilon_m}{2}\left\{\left[(1+\delta_{m0})\left(1-\delta_{m,-1}\right)(l-m) \cdot (l-m-1)\right]^{1/2}\delta_{m',m+1} - \left[(1-\delta_{m0})(1+\delta_{m1})(l+m) \cdot (l+m-1)\right]^{1/2}\delta_{m',m-1}\right\} \tag{58}$$

$$a_{lm,m'}^{-1} = -\frac{\varepsilon_m}{2}\left\{\left[(1+\delta_{m0})(1+\delta_{m,-1})(l-m)\right.\right.$$
$$\left.\cdot(l-m-1)\right]^{1/2}\delta_{m',-m-1}$$
$$+\left[(1-\delta_{m0})(1-\delta_{m1})(l+m)\right.$$
$$\left.\left.\cdot(l+m-1)\right]^{1/2}\delta_{m',-m+1}\right\} \tag{59}$$

$$a_{lm,m'}^{0} = \left[(l+m)(l-m)\right]^{1/2}\delta_{m'm} \quad \text{for} \quad l \geqslant 1 \tag{60}$$

$$a_{lm,m'}^{ij} = a_{lm,m'}^{ji} = \sum_{m''=-(l-1)}^{l-1} a_{lm,m''}^{j} a_{l-1m'',m'}^{i} \quad \text{for} \quad l \geqslant 2 \tag{61}$$

where ε_m=sgn m is the sign functions, i.e. $\varepsilon_m=\pm 1$. The sign of the symbol ε_m is determined by the sign of m, i.e. $\varepsilon_m=+1$ for $m\geq 0$and $\varepsilon_m=-1$ for $m<0$.

Taking into account Eqs. (50), (51), (52), (53), (54), (55), (56) and (57) in Eq. (47) we find finally for the overlap integrals with the same screening constants and other derivatives in terms of noncentral potentials the following relationships:

$$S_{\mu\nu\sigma,u'00}\left(z,z;\vec{R}\right) = f_{\mu\nu\sigma,u'00,\nu\sigma}^{00}\left(z,z;\vec{R}\right) \tag{62}$$

$$S_{\mu\nu\sigma,u'00}^{i}\left(z,z;\vec{R}\right) = \sum_{\sigma'=-(\nu-1)}^{\nu-1} a_{\nu\sigma,\sigma'}^{i} f_{\mu\nu\sigma,u'00,\nu-1\sigma'}^{10}\left(z,z;\vec{R}\right) + \left(\frac{X^i}{R}\right) f_{\mu\nu\sigma,u'00,\nu\sigma}^{11}\left(z,z;\vec{R}\right) \tag{63}$$

$$S_{\mu\nu\sigma,u'00}^{ij}\left(z,z;\vec{R}\right) = \sum_{\sigma'=-(\nu-2)}^{\nu-2} a_{\nu\sigma,\sigma'}^{ij} f_{\mu\nu\sigma,u'00,\nu-2\sigma'}^{20}\left(z,z;\vec{R}\right)$$
$$+\sum_{\sigma'=-(\nu-1)}^{\nu-1}\left[a_{\nu\sigma,\sigma'}^{i}\left(\frac{X^j}{R}\right)+a_{\nu\sigma,\sigma'}^{j}\left(\frac{X^i}{R}\right)\right]$$
$$\cdot f_{\mu\nu\sigma,u'00,\nu-1\sigma'}^{21}\left(z,z;\vec{R}\right)$$
$$+\delta_{ij}R^2 f_{\mu\nu\sigma,u'00,\nu\sigma}^{21}\left(z,z;\overrightarrow{R}\right)$$
$$+\left(\frac{X^i}{R}\right)\left(\frac{X^j}{R}\right) f_{\mu\nu\sigma,u'00,\nu\sigma}^{22}\left(z,z;\vec{R}\right) \tag{64}$$

Here, the screening noncentral potentials are determined as

$$f_{\mu\nu\sigma,u'00,\upsilon s}^{tk}\left(z,z;\vec{R}\right) = f_{\mu\nu\sigma,u'00}^{tk}\left(z,z;\vec{R}\right)\bar{S}_{\upsilon s}(\theta,\varphi) \tag{65}$$

$$f_{\mu\nu\sigma,u'00}^{tk}\left(z,z;\vec{R}\right) = f_{\mu\nu\sigma,u'00,00}^{tk}\left(z,z;\vec{R}\right)$$
$$= z^{t+2k}\sum_{N=\nu+1}^{\mu+u'+1} g_{\mu\nu\sigma,u'00}^{\alpha N\nu\sigma} 2^N\left[(2\nu+1)/(2N)!\right]^{1/2}$$
$$\cdot(zR)^{N-t-2k-1}\sum_{\sigma'=0}^{k}\beta_{\sigma'}^{k}(N,\nu)(zR)^{\sigma'}\,\mathrm{e}^{-zR} \tag{66}$$

Table 1 Comparison of methods of computing EF multicenter integrals of screened Coulomb potentials obtained in the molecular coordinate system in a.u. for N=15, X^0=0.71896457, X^1=−1.77059622

n	l	m	ζ	n'	l'	m'	ζ'	η	i	R ca	θ ca	ϕ ca	R ab	θ ab	ϕ ab	Eq. (28), α=0	Eq. (28), α=−1	CPU (ms)
1	0	0	2.8	1	0	0	1.6	3.2	0	2.4	60	90	0.8	30	45	−9.8924352751E−03	−9.8924369506E−03	10.2
2	1	0	4.2	2	1	0	6.1	5.3	0	0.5	45	180	0.2	60	30	−5.0258308316E−01	−5.0258316718E−01	15.3
2	1	0	3.4	2	1	0	1.1	4.6	1	1.8	120	20	1.2	60	60	−1.0044301269E−02	−1.0044509645E−02	18.4
2	1	1	4.3	2	1	1	2.1	6.4	1	0.8	135	360	0.3	120	90	−3.6556986874E−01	−3.6555995101E−01	25.7
2	1	−1	2.4	2	1	−1	1.2	5.6	1	0.5	180	180	1.3	180	36	−9.6558338374E−03	−9.6558189082E−03	24.1

where t=0, 1, 2 for EA, EF and EFG integrals, respectively ($0 \leq k \leq t$) and $\beta^0{}_0(N,\nu)=1$; $\beta^1{}_0(N,\nu)=N-\nu-1$, $\beta^1{}_1(N,\nu)=-1$; $\beta^2{}_0(N,\nu)=(N-\nu-1)(N-\nu-3)$, $\beta^2{}_1(N,\nu)=-(N-\nu-1)$, $\beta^2{}_2(N,\nu)=1$.

As can be seen from the equations of this study, all the multicenter EA, EF and EFG integrals can be calculated by the use of one-center or two-center expansion approaches. For this purpose we need only the Cartesian coordinates of the nuclei relative to a common axial frame and the quantum numbers and screening constants of the STOs. We notice that the charge-density expansion coefficients $W^{\alpha N}{}_{pp'q}$ needed for calculation of multicenter integrals are expressed through the translation coefficients $V^{\alpha N}{}_{qq'}$, which can be defined by linear combinations of overlap integrals (see Eq. 22 of [30]).Thus, the computation of different formulae for any integral obtained by the use of complete orthonormal sets of $\psi^1{}_{nlm}$, $\psi^0{}_{nlm}$, $\psi^{-1}{}_{nlm}$, $\psi^{-2}{}_{nlm}$,.... ETOs can be reduced to the calculation of the overlap integrals with the same screening constants. One must be able to compute these overlap integrals 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 [32].

The results of calculation in atomic units for the EF multicenter integrals of screened Coulomb potentials obtained with a Pentium III 800-MHz computer (using TURBO Pascal 7.0) are shown in Table 1. The comparative values obtained from the expansion of different ψ^α-ETOs are also shown in this table. We see from the table that the computation time and accuracy of the computer results for different expansion formulae obtained from ψ^0-ETOs and ψ^{-1}-ETOs are satisfactory.

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