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ORIGINAL PAPER

Analytical evaluation for two-center nuclear attraction integrals over slater type orbitals by using Fourier transform method

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Abstract In this study, we shall suggest analytical expressions for two-center nuclear attraction integrals over STO's with a one-center charge distribution by using Fourier transform method. The derivation is based on partial-fraction decompositions and Taylor expansions of rational functions. Analytical expressions obtained by this method are expressed in terms of Gegenbauer, and binomial coefficients and linear combinations of STO's. Finally, it is relatively easy to express the Fourier integral representations of two-center nuclear attraction integrals with a one-center charge distribution mentioned above as finite and infinite of series of STO's and irregular solid harmonics which may be considered to be limiting cases of STO's.

Keywords Slater type orbitals · Gegenbauer polynomials · Irregular solid harmonics · Two-center nuclear attraction integrals

1 Introduction

As is well known, in molecular electronic structure calculations based on the linear combination of atomic orbitals (LCAO)-molecular orbitals (MO) approximation, the estimation of energies and other properties of molecular systems require the calculation of a large number of molecular integrals over atomic orbitals (AOs). The choice of reliable basis functions is of prime importance in accurate quantum chemistry

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calculations since the quality of several molecular properties may depend strongly on the nature of these functions.

Slater type orbitals (STOs) are able to satisfy cusp condition at the nuclei [1] and decrease exponentially at the large distances they behave as exact eigenstates of atomic and molecular Hamiltonians [2]. Consequently, it is not surprising that the use of STOs as basis functions in atomic calculations would be highly desirable. This explains the continued effort of theoretical research in this field, since the early work of Roothaan and Ruedenberg [3], Coulson [4], Löwdin [5], up to more recent work by Silverstone [6], Steinborn [7], Jones [8], and Rinaldi's Groups [9].

While two-center integrals over STOs are dealt with at their best in confocal spheroidal coordinates [3,10], few attempts have been made to extend this approach to the three- and four-center case [11]. This many-center case has, however, been mostly approached either in terms of one-center expansions about a displaced center [4,5,8,12] or by Fourier-transform techniques [6,13].

Fourier transform convolution theorem where multicenter integrals are transformed into inverse Fourier integrals is one of the most important methods for the evaluation of the complicated multicenter molecular integrals. The main advantages of this method allow the transformation of the two-centric convolution integral into one-centric Fourier integral that usually is easier to calculate. There is an extensive literature on the use Fourier transform convolution theorem in the evaluation multicenter molecular integrals [14].

In this paper we shall present new analytical expressions for two-center nuclear attraction integrals with a one-center charge distribution by using Fourier transform method and Gegenbauer polynomials over STOs. These formulas are obtained by purely analytical methods and don't require any numerical integrations. They are very compact and surprisingly simple also for arbitrarily high quantum numbers and atomic parameters. Therefore obtained formulas in this study are well suited for practical applications. All rather old expressions for two-center one-electron nuclear attraction integrals over STO's are much more complicated than the new formulas derived in this paper. Especially for higher quantum numbers the use of older formulas is very difficult. Because they usually hold for special cases only, a special computer program is required for each case [15]. Therefore we feel that the new formulas presented in this paper meet a real demand and offer a satisfying solution of the problem for two-center one-electron nuclear attraction integrals over STO's.

2 Definitions and basic relations

In this section we want to give the definitions of STOs, Gegenbauer polynomials, and other spherical tensors that are used in this paper. We first give definitions and some basic relations for spherical, regular, and irregular solid harmonics. Then, the Fourier transform of irregular solid harmonics is presented. After this, Fourier transform of STOs are defined, their interrelationship is discussed, the originally expressions of Gegenbauer polynomials and denominators which appear in two-center nuclear-attraction integrals over STOs are presented, and the advantageous properties of STOs in the treatment of molecular integrals with the Fourier transform method are pointed out.

As the well-known, Slater type orbitals that are given in normalized form by

$$\chi_{n,l}^{m}(\alpha,\mathbf{r})=\frac{(2\alpha)^{n+1/2}}{\sqrt{(2n)!}}r^{n-1}e^{-\alpha r}Y_{l}^{m}(\theta,\phi) \tag{1}$$

where α is screening parameters and spherical harmonics $Y_l^m(\theta,\phi)$ obeying Condon Shortley phase conventions are given by

$$Y_{l}^{m}(\theta,\phi)=(-1)^{m}\left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2}P_{l}^{m}(\cos\theta)\,e^{im\phi} \tag{2}$$

where $P_l^m(\cos\theta)$ denotes an associated Legendre polynomials [16].

For a given value l, only $2l+1$ linearly independent harmonic polynomials exist. Hence it is possible to span the space of harmonic polynomials by the so-called regular and irregular solid harmonics, respectively,

$$\begin{aligned}S_{l}^{m}(\mathbf{r})&=r^{l}Y_{l}^{m}(\theta,\phi)\\ \pounds_{l}^{m}(\mathbf{r})&=r^{-l-1}Y_{l}^{m}(\theta,\phi)\end{aligned} \tag{3}$$

We can write the relationship to define the Fourier transform of an irregular solid harmonics by following form [17];

$$\begin{aligned}\pounds_{l}^{m}(\mathbf{p})&=(2\pi)^{-3/2}\int e^{-i\mathbf{r}\cdot\mathbf{p}}\pounds_{l}^{m}(\mathbf{r})\,d\mathbf{r}\\ &=\frac{\sqrt{2/\pi}}{p^{2}(2l-1)!!}S_{l}^{m}(-i\mathbf{p})\end{aligned} \tag{4}$$

The representation of the irregular solid harmonics as an inverse Fourier integral is presented in the same reference [17,21].

$$\pounds_{l}^{m}(\mathbf{r})=\left[2\pi^{2}(2l-1)!!\right]^{-1}\int e^{i\mathbf{p}\cdot\mathbf{r}}\frac{S_{l}^{m}(-i\mathbf{p})}{p^{2}}d\mathbf{p} \tag{5}$$

For the evaluation of the Fourier transforms of STOs we only have to insert the well-known Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics [18];

$$e^{\pm i\mathbf{x}\cdot\mathbf{y}}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(\pm i)^{l}j_{l}(xy)\left(Y_{l}^{m}(\mathbf{x}/x)\right)^{*}Y_{l}^{m}(\mathbf{y}/y) \tag{6}$$

where

$$j_{l}(xy)=\left(\frac{\pi}{2xy}\right)^{1/2}J_{l+1/2}(xy) \tag{7}$$

is the spherical Bessel function.

We are in a position to give explicit integral representations for the integrals of the product of spherical harmonics and the spherical Bessel functions as following form,

$$Y_l^m(\theta,\phi)\int_0^\infty j_l(pr)\,p^l dp=\pi\frac{(2l-1)!!}{2}\alpha^{l+1}\pounds_l^m(\alpha\mathbf{r}) \tag{8}$$

In this paper we shall use the symmetric version of the Fourier transformation, i.e., a given function of STO and its Fourier transform $U(\mathbf{p})$ are connected by [19];

$$\begin{aligned} U_{n,l}^m(\alpha,\mathbf{p}) &= (2\pi)^{-3/2}\int e^{-i\mathbf{p}\cdot\mathbf{r}}\chi_{n,l}^m(\alpha,\mathbf{r})\,d\mathbf{r} \\ &= \frac{2^{n+l+1}\alpha^{n+1/2}\left(\alpha^2+p^2\right)^{-(n+l+2)/2}}{F_l(n)\sqrt{\pi F_n(2n)}}C_{n-l}^{l+1}\left(\frac{\alpha}{\sqrt{\alpha^2+p^2}}\right)S_l^m(-i\mathbf{p}) \end{aligned} \tag{9}$$

where $F_l(n)$ are the binomial coefficients and $C_n^\alpha(x)$ is the Gegenbauer polynomial defined by the following relation [16];

$$C_n^\alpha(x)=\sum_{s=0}^{E(n/2)}(-1)^s a_s(\alpha,n)(2x)^{n-2s} \tag{10}$$

where

$$E(n/2)=\frac{n}{2}-\frac{1-(-1)^n}{4}, \tag{11}$$

and

$$a_m(\alpha,n)=F_{\alpha-1}(\alpha+n-m-1)\,F_m(n-m) \tag{12}$$

Gaunt coefficients defined as the integral of the product of three spherical harmonics over the surface of the unit sphere are used to simplify the following product expansions of spherical harmonics,

$$\left[Y_{l_1}^{m_1}(\Omega)\right]^* Y_{l_2}^{m_2}(\Omega)=\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2m_2|l_1m_1|lm_2-m_1\rangle\,Y_l^{m_2-m_1}(\Omega) \tag{13}$$

The symbol $\sum^{(2)}$ indicates that the summation proceeds in steps of 2. The summation limits in Eq. 13 are determined by the selection rules satisfied by the Gaunt coefficients.

3 Two-center nuclear-attraction integrals

We shall also consider for the two-center nuclear-attraction integrals of STOs with a one-center charge distribution given by following form;

$$A_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R}) = \int \left[\chi_{n_1, l_1}^{m_1}(\alpha, \mathbf{r})\right]^* \frac{1}{|\mathbf{r}-\mathbf{R}|} \chi_{n_2, l_2}^{m_2}(\beta, \mathbf{r})\, d\mathbf{r} \tag{14}$$

In order to evaluate Eq. 14, the potential at the point $\mathbf{R}$ is generated by a charge distribution product of two STO's. Now, we have applied to the coupling rule for spherical harmonics according to Eq. 13. Therefore, the product of the STO's can be written as a linear combination of STO's,

$$\begin{aligned} \left[\chi_{n_1, l_1}^{m_1}(\alpha, \mathbf{r})\right]^* \chi_{n_2, l_2}^{m_2}(\beta, \mathbf{r}) &= \sqrt{2^3 \frac{(2(n_1+n_2-1))!}{(2n_1)!\,(2n_2)!}} \frac{\alpha^{n_1+1/2} \beta^{n_2+1/2}}{(\alpha+\beta)^{n_1+n_2-1/2}} \\ &\quad \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle\, \chi_{n_1+n_2-1, l}^{m_2-m_1}((\alpha+\beta), \mathbf{r}) \end{aligned} \tag{15}$$

Then, we have rewritten the two-center nuclear-attraction integrals of STOs with a one-center charge distribution

$$\begin{aligned} A_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R}) &= \sqrt{2^3 \frac{(2(n_1+n_2-1))!}{(2n_1)!\,(2n_2)!}} \frac{\alpha^{n_1+1/2} \beta^{n_2+1/2}}{(\alpha+\beta)^{n_1+n_2-1/2}} \\ &\quad \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle\, A_{n_1+n_2-1 l}^{m_2-m_1}(\alpha+\beta; \mathbf{R}) \end{aligned} \tag{16}$$

$$\begin{aligned} &= \sqrt{16\pi \frac{(2(n_1+n_2-1))!}{(2n_1)!\,(2n_2)!}} \frac{\alpha^{n_1+1/2} \beta^{n_2+1/2}}{(\alpha+\beta)^{n_1+n_2-1/2}} \\ &\quad \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle \\ &\quad \lim_{\varepsilon \to 0} \left\{ \frac{1}{\sqrt{\varepsilon}} S_{000}^{n_1+n_2-1 l m_2-m_1}(\varepsilon, (\alpha+\beta); \mathbf{R}) \right\} \end{aligned} \tag{17}$$

where basic nuclear attraction integrals over STO's is denoted by following form

$$A_{nl}^{m}(\alpha; \mathbf{R}) = \int \frac{\chi_{n,l}^{m}(\alpha, \mathbf{r})}{|\mathbf{r}-\mathbf{R}|} d\mathbf{r} \tag{18}$$

and S is overlap integrals given by

$$S_{000}^{Nlm}(a,b;\mathbf{R}) = \int \left[\chi_{0,0}^{0}(a,\mathbf{r}-\mathbf{R})\right]^{*} \chi_{N,l}^{m}(b,\mathbf{r})d\mathbf{r} \tag{19}$$

4 Fourier transform of nuclear-attraction integrals

In this paper, we shall use the symmetric version of the Fourier transformation a given function Fourier transform of STOs with Eq. 9. This relationship can be used to derive representations as inverse Fourier integrals for nuclear attraction integrals given by Eq. 18 over STO's;

$$A_{nl}^{m}(\alpha;\mathbf{R}) = \lim_{\beta\to 0}\left\{\sqrt{\frac{2\pi}{\beta}}\int e^{-i\mathbf{R}\cdot\mathbf{p}}\left[U_{0,0}^{0}(\beta,\mathbf{p})\right]^{*} U_{n,l}^{m}(\alpha,\mathbf{p})\,d\mathbf{p}\right\} \tag{20}$$

$$= \sqrt{\frac{2}{\pi}}\int \frac{e^{-i\mathbf{R}\cdot\mathbf{p}}}{p^{2}} U_{n,l}^{m}(\alpha,\mathbf{p})\,d\mathbf{p} \tag{21}$$

Finally, we are in a position to give explicit integral representation for the two-center nuclear attraction-integrals over STOs via Fourier transform methods, which will be treated in this paper. If we use the Fourier transform of STOs given by Eq. 9 in Eq. 21, we obtain following expression for nuclear attraction integral,

$$A_{nl}^{m}(\alpha;\mathbf{R}) = \frac{2^{n+l+3/2}\alpha^{n+1/2}}{\pi F_{l}(n)\sqrt{F_{n}(2n)}}$$
$$\int \frac{e^{-i\mathbf{R}\cdot\mathbf{p}}}{p^{2}\left(\alpha^{2}+p^{2}\right)^{(n+l+2)/2}} C_{n-l}^{l+1}\left(\frac{\alpha}{\sqrt{\alpha^{2}+p^{2}}}\right) S_{l}^{m}(-i\mathbf{p})\,d\mathbf{p} \tag{22}$$

By the use of Rayleigh expansions of a plane wave given by Eq. 6 and orthogonality relationship of spherical harmonics, the two-center nuclear attraction integral representation can be obtained in terms of Gegenbauer polynomials, spherical harmonics and spherical Bessel functions:

$$A_{nl}^{m}(\alpha;\mathbf{R}) = (-1)^{l}\,\frac{2^{n+l+7/2}\alpha^{n+1/2}}{F_{l}(n)\sqrt{F_{n}(2n)}} Y_{l}^{m}(\theta,\phi)$$
$$\int_{0}^{\infty} \frac{j_{l}(pR)}{p^{2}\left(\alpha^{2}+p^{2}\right)^{(n+l+2)/2}} C_{n-l}^{l+1}\left(\frac{\alpha}{\sqrt{\alpha^{2}+p^{2}}}\right) p^{l+2}dp \tag{23}$$

Then one has to compute radial integrals of the type given by Eq. 23. Let us first consider Gegenbauer polynomials, which occur in the integral representation Eq. 23. These polynomials can be expressed in terms of simpler functions by using fraction decompositions given by Eqs. (4.2, 4.13, 4.27 and 4.7) in Ref. [17]:

$$C_a^b(x) = \frac{2^a}{x^{a+2b}} \sum_{s=0}^{E\left(\frac{a}{2}\right)} (-1)^s \frac{a_s(b,a)}{2^{2s}} \left(1 - (1-x^2) \sum_{v=0}^{a+b-s-1} (x)^{2v}\right) \tag{24}$$

$$= (2x)^a \left(1 - x^2\right) \sum_{v=0}^{\infty} \sum_{s=0}^{E\left(\frac{a}{2}\right)} (-1)^s \frac{a_s(b,a)}{2^{2s}} x^{2(v-s)} \tag{25}$$

$$= \frac{\alpha^{2(a+b+1)}\left(1-x^2\right)}{x^{a+2b+2}} \sum_{v=0}^{\infty} \sum_{s=0}^{E\left(\frac{a}{2}\right)} (-1)^s \frac{a_s(b,a)}{(2\alpha)^{2s}} 2^{2a+b-s+1} F_v(a+b-s+v)$$
$$\alpha^{2v} \left(\frac{x^2}{\alpha^2(2-x^2)}\right)^{a+b-s+v+1} {}_2F_1(-v, a+b-s; a+b-s+1; 2) \tag{26}$$

$$= \alpha^{2(a+b)} (2x)^a \sum_{s=0}^{E\left(\frac{a}{2}\right)} (-1)^s \frac{a_s(b,a)}{(2\alpha x)^{2s}} \left(\frac{1}{\alpha^2 + x^2(\beta^2-\alpha^2)}\right)^{a+b-s}$$
$${}_1F_0\left(a+b-s; \frac{x^2(\beta^2-\alpha^2)}{\alpha^2 + x^2(\beta^2-\alpha^2)}\right) \tag{27}$$

As can be use Eqs. 23 and 24, the two-center nuclear attraction integral is expressed by the following formula,

$$A_{nl}^m(\alpha; \mathbf{R}) = \frac{2^{2n+7/2}}{F_l(n)\sqrt{F_n(2n)}} \sum_{s=0}^{E\left(\frac{n-l}{2}\right)} (-1)^{l+s} \frac{a_s(l+1; n-l)}{2^{2s}\alpha^{l+3/2}}$$
$$Y_l^m(\theta,\phi) \left\{ \int_0^\infty j_l(pR)\, p^l dp - \sum_{v=0}^{n-s} \alpha^{2v} \int_0^\infty \frac{j_l(pR)\, p^{l+2}}{\left(\alpha^2+p^2\right)^{v+1}} dp \right\} \tag{28}$$

If we use the results given by Eq. 8 and Eq. (A2) in the Appendix together with Eq. 28, the two-center nuclear-attraction integrals can be expressed in terms of Gegenbauer coefficients, irregular solid harmonics and finite sum of STOs:

$$A_{nl}^m(\alpha; \mathbf{R}) = \pi \frac{2^{2n+5/2}}{F_l(n)\sqrt{\alpha F_n(2n)}} \sum_{s=0}^{E\left(\frac{n-l}{2}\right)} (-1)^{l+s} \frac{a_s(l+1; n-l)}{2^{2s}}$$
$$\left((2l-1)!!\pounds_l^m(\alpha\mathbf{R}) - \sum_{v=0}^{n-s} \frac{\alpha^{-3/2}}{2^{2v+1/2}} \sum_{q=1}^{v-l} g_{v,q}^l \chi_{q+l,l}^m(\alpha, \mathbf{R})\right) \tag{29}$$

With respect to Eq. 25, we can write the two-center nuclear-attraction integrals in terms of infinite sums of STOs as following forms:

$$A_{nl}^{m}(\alpha;\mathbf{R}) = \frac{2^{2n+7/2}\alpha^{2n-l+1/2}}{F_l(n)\sqrt{F_n(2n)}} \sum_{s=0}^{E\left(\frac{n-l}{2}\right)} (-1)^{l+s}\frac{a_s(l+1;n-l)}{(2\alpha)^{2s}} \times \sum_{v=0}^{\infty} \alpha^{2v} Y_l^m(\theta,\phi) \int_0^{\infty} \frac{j_l(pR)\,p^{l+2}}{(\alpha^2+p^2)^{n-s+v+2}}dp \tag{30}$$

$$= \frac{\pi}{\alpha^2 F_l(n)\sqrt{F_n(2n)}} \sum_{s=0}^{E\left(\frac{n-l}{2}\right)} (-1)^{l+s} a_s(l+1,n-l) \times \sum_{v=0}^{\infty} 2^{-2v} \sum_{q=1}^{n-s+v-l+1} g_{n-s+v+1,q}^{l}\,\chi_{q+l,l}^{m}(\alpha,\mathbf{R}) \tag{31}$$

Substituting Eqs. 26 into 23, the two-center nuclear attraction integral is obtained in terms of hypergeometric functions and STOs:

$$A_{nl}^{m}(\alpha;\mathbf{R}) = \frac{2^{2n+7/2}\alpha^{2n-l+1/2}}{F_l(n)\sqrt{F_n(2n)}} \sum_{s=0}^{E\left(\frac{n-l}{2}\right)} (-1)^{l+s}\frac{a_s(l+1;n-l)}{(2\alpha)^{2s}} \times \sum_{v=0}^{\infty} \frac{F_v(n+v-s+1)}{2^v\alpha^{-2v}}\,{}_2F_1(-v,n-s+1;n-s+2;2)\; Y_l^m(\theta,\phi)\int_0^{\infty}\frac{j_l(pR)\,p^{l+2}}{(\alpha^2/2+p^2)^{n-s+v+2}}dp \tag{32}$$

$$= \pi\frac{2^{n-l/2+5/4}}{\alpha^2 F_l(n)\sqrt{F_n(2n)}} \sum_{s=0}^{E\left(\frac{n-l}{2}\right)} (-1)^{l+s}\frac{a_s(l+1;n-l)}{2^s} \times \sum_{v=0}^{\infty} \frac{F_v(n+v-s+1)}{2^{2v}}\,{}_2F_1(-v,n-s+1;n-s+2;2) \times \sum_{q=1}^{n+v-s-l+1} g_{n+v-s+1,q}^{l}\,\chi_{q+l,l}^{m}\left(\alpha/\sqrt{2},\mathbf{R}\right) \tag{33}$$

Finally, by the use of Eq. 27 in Eq. 23, the two-center nuclear attraction integrals can be obtained as the following forms,

$$A_{nl}^{m}(\alpha,\beta;\mathbf{R})=\frac{2^{2n+7/2}\alpha^{2n-l+1/2}}{F_l(n)\sqrt{F_n(2n)}}\sum_{s=0}^{E\left(\frac{n-l}{2}\right)}(-1)^{l+s}\frac{a_s(l+1,n-l)}{(2\alpha)^{2s}}Y_l^m(\theta,\phi)$$
$$\times\int_0^\infty j_l(pR)\frac{p^{l+2}{}_1F_0\left(n-s+1;(\beta^2-\alpha^2)/(\beta^2+p^2)\right)}{p^2(\beta^2+p^2)^{n-s+1}}dp \quad (34)$$

$$=\pi\frac{2^{2n+5/2}(\alpha/\beta)^{2n-l+1/2}}{F_l(n)\sqrt{\beta F_n(2n)}}\sum_{s=0}^{E\left(\frac{n-l}{2}\right)}(-1)^{l+s}\frac{a_s(l+1,n-l)}{(2\alpha/\beta)^{2s}}$$
$$\times\sum_{k=0}^{\infty}\left(\frac{\beta^2-\alpha^2}{\beta^2}\right)^k F_{n-s}(n+k-s)$$
$$\times\left((2l-1)!!\pounds_l^m(\beta\mathbf{R})-\sum_{\upsilon=0}^{n+k-s}\frac{\beta^{-3/2}}{2^{2\upsilon+1/2}}\sum_{q=1}^{\upsilon-l}g_{\upsilon,q}^{l}\chi_{q+l,l}^{m}(\beta,\mathbf{R})\right) \quad (35)$$

5 Numerical results and discussion

In this article, various mathematical representations of Gegenbauer polynomials were analyzed given by Eqs. 24–27. And then by using Fourier transform of STOs and Gegenbauer polynomials, we first derived the nuclear attraction integrals with a one-center charge distribution in terms of basic nuclear attraction integrals. The basic nuclear attraction integrals were written by using the connection between a basic overlap integral and the Fourier transform of STOs as can be seen Eqs. 20, 21. The standard way of computing the Fourier transform of an STO, overlap integrals, nuclear attraction integrals and coulomb integrals with two-center consists in using the Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics. Due to orthonormality of the spherical harmonics the angular distribution is then trivial and only radial integral involving a spherical Bessel function remains to be alone. However, the evaluation of the integrals involving radial part is usually not all easy and in some cases even impossible. In this cases, the another mathematical tools as partial-fraction decomposition and Taylor expansion of rational functions have been used except for Fourier transform method. Our approach leads to considerable simplification of the derivation for analytical representation of the nuclear attraction integrals with different screening parameters.

In order to calculate the two-center nuclear attraction integrals with a one-center charge distribution over STOs via the Fourier transform methods, the values of the Gaunt coefficients, Gegenbauer coefficients, binomial coefficients, the normalized associated Legendre functions and irregular solid harmonics were calculated using the methods in Ref. [20–22], while the basic nuclear attraction integrals were calculated using Eqs. 23, 29, 31 of this study. The results are given in Table 1. As can be seen in Table 1, the comparative values of the basic nuclear attraction integrals $A_{nl}^{m}(\alpha;\mathbf{R})$

Table 1 Comparative results of two-center nuclear attraction integrals over STOs $\left(A_{nl}^{m}(\alpha; \mathbf{R})\right)$

n	l	m	α	R	θ	ϕ	Eq. 23	Eq. 29	Eq. 31
3	2	1	1.2	1	30	60	2.42280668397678E−01	2.42280668397678E−01	2.42280668379755E−01
5	4	2	4	2.2	30	30	1.14478940942409E−01	1.14478940942409E−01	1.14478940914585E−01
6	3	3	3.4	0.8	60	0	−1.45301661470911E−01	−1.45301661470911E−01	−1.45301661448647E−01
8	5	4	1.5	8.6	60	20	−6.27837715909328E−02	−6.27837715909328E−02	−6.27837715819115E−02
9	7	1	5	2.6	45	30	1.08255816997327E−01	1.08255816997327E−01	1.08255816968399E−01
10	8	−2	0.5	5	60	60	2.78440275257209E−04	2.78440275257209E−01	2.78440275713403E−01
12	6	5	6.7	1.8	40	120	−4.67577117224796E−02	−4.67577117224796E−02	−4.67577117132093E−02
15	8	−4	0.6	6	90	160	−1.77588119621249E−04	−1.77588119621249E−04	−1.77588119574672E−04

Table 2 Numerical results for two-center nuclear attraction integrals of STOs with a one-center charge distribution $A_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R})$

n_1	l_1	m_1	n_2	l_2	m_2	α	β	R	θ	ϕ	Eq. 16	Ref. [23]
2	1	0	2	1	1	7.6	1.5	2.3	45	180	2.00987043440502E−03	2.00987043387478E−03
3	1	0	2	1	1	8.6	7.4	4	54	40	−5.42130987411028E−04	−5.42130987268004E−04
3	2	1	3	2	1	13.8	7.3	3.5	18	80	2.01794411622562E−01	2.01752673993300E−01
3	2	2	3	2	2	12.4	10.6	6.1	0	0	1.60316721578661E−01	1.60316721578661E−01
4	3	2	3	2	2	7.4	5.3	5.9	144	200	−5.46598678548996E−03	−5.46603780760789E−03
4	3	2	4	3	2	8.7	7.5	4.5	162	220	2.16776864777679E−01	2.16776797962649E−01

was checked for quantum numbers, screening parameters, radial distances and angles using Eqs. 23, 29 and 31. It is seen from Table 1, Eqs. 23 and 29 are consistent with each other all decimal digits. For the results of Eqs. 23, 29 and 31, the accuracy is given as a sum of at least of 12 decimal digits, it is decreased to 11 decimal digits for $n = 10$, $l = 8$ and $m = -2$.

The comparative values of the nuclear attraction integrals with a one-center charge distribution over STOs by using Fourier transform methods are given in Table 2. The accuracy of the results for $A^{n_2 l_2 m_2}_{n_1 l_1 m_1}(\alpha, \beta; \mathbf{R})$ with different screening parameters given in Eq. (16) was checked for various quantum numbers using the results of Ref. [23]. As can be seen from Table 1, all the calculations were made in range of $1 \leq n \leq 15$, $-4 \leq l \leq n$ and $-4 \leq m \leq 4$ and $0.8 \leq atomicdistances$. All the calculations in Table 2 are in agreement with the results of Ref. [23] to at least 11 decimal digits. The reason that the accuracy is getting weaken for various atomic parameters is due to the basic nuclear attraction integrals as can be seen in Table 1. This can clearly seen from Eq. 31, the upper limit of second total is go to infinitive.

The algorithm of calculation of nuclear attraction integrals over STOs has been implemented in a computer program, written in Mathematica 6.0, and performed an P. IV 2.8 GHz computer for a moderate range of physically significant values of atomic orbital parameters.

Appendix

We can establish the following formula for the integrals $G^m_{v,l}(\alpha, R)$ in Eqs. 28, 30, 32 and 34. The radial integral, $G^m_{v,l}(\alpha, R)$, can be calculated with help of the relationship:

$$G^m_{v,l}(\alpha, R) = Y^m_l(\theta, \phi) \int_0^\infty \frac{j_l(pR)\, p^{l+2}}{(\alpha^2 + p^2)^{v+1}} dp \tag{A1}$$

which can be proved with the help of [16]

$$\begin{aligned} G^m_{v,l}(\alpha, R) &= \sqrt{\pi} \frac{R^{v-1/2} \alpha^{l+1/2-v}}{2^{v+1/2} v!} Y^m_l(\theta, \phi) K_{l-v+1/2}(\alpha R) \\ &= \pi \frac{\alpha^{l-2v-1/2}}{2^{2v+3/2}} \sum_{q=1}^{v-l} g^l_{v,q} \chi^m_{q+l,l}(\alpha, \mathbf{R}) \end{aligned} \tag{A2}$$

where

$$g^l_{v,q} = \frac{q}{(2v - 2l - q)} \frac{F_l(q + l)\, F_{v-l}(2v - 2l - q)}{F_l(v)} \sqrt{F_{q+l}(2(q + l))} \tag{A3}$$

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