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Overlap integrals between irregular solid harmonics and STOs via the Fourier transform methods

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In this paper, a unified analytical and numerical treatment of overlap integrals between Slater type orbitals (STOs) and irregular Solid Harmonics (ISH) with different screening parameters is presented via the Fourier transform method. Fourier transform of STOs is probably the simplest to express of overlap integrals. Consequently, it is relatively easy to express the Fourier integral representations of the overlap integrals as finite sums and infinite series of STOs, ISHs, Gegenbauer, and Gaunt coefficients. The another mathematical tools except for Fourier transform have used partial-fraction decomposition and Taylor expansions of rational functions. Our approach leads to considerable simplification of the derivation of the previously known analytical representations for the overlap integrals between STOs and ISHs with different screening parameters. These overlap integrals have also been calculated for extremely large quantum numbers using Gegenbauer, Clebsch-Gordan and Binomial coefficients. The accuracy of the numerical results is quite high for the quantum numbers of Slater functions, irregular solid harmonic functions and for arbitrary values of internuclear distances and screening parameters of atomic orbitals.

KEY WORDS: overlap integrals, slater type orbitals, irregular solid harmonics, gegenbauer polynomials

1. Introduction

Electronic structure calculations for molecules are built from LCAO-MO approach. In that approach the choice of basis functions for the reliability basis set for the electronic distribution is of utmost importance. It is well known that a good atomic orbital basis satisfy the cusp condition and exponential decay at large distances [1,2]. It is not surprising that exponentially decreasing orbitals (ETOs) could be used successfully as basis functions in large arguments. Among the ETOs, the Slater Type Orbitals (STOs) have assumed a dominating position as basis functions in molecular multi-center integrals calculations. In addition to, STOs have

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the simplest analytical structure of all ETOs. Other ETOs, for instance, Bessel type or Gaussian type orbitals, can be expressed quite easily as linear combinations of STOs [3]. This declines that multicenter molecular integrals over other ETOs can be expressed in terms of the basic multicenter molecular integrals over STOs. Consequently, STOs have been used quite frequently and successfully as basis functions in atomic Hartree–Fock calculations.

Historically, difficulties with molecular integrals appeared at the very beginning of quantum chemistry with the study of hydrogen molecule by Heitler and London [4]. Sugiura [5] was able to solve exactly their approximated $1s$–$1s$ exchange integral by using elliptical coordinates. Eventually, a wide range of two-center molecular integrals were examined by many workers [6]. However, the more general case of integrals over four orbitals, each centered on a different nucleus, proved to be virtually intractable. Yet, substantial progress was recorded by Collidge [7] when he introduced a new method by expanding all orbitals in an infinite series of spherical harmonics about a common center (single-center expansion). Löwdin [8] pursued these methods using the α-function notation for the radial functions associated with the spherical harmonics and wrote suggestive matrix arrays for polynomial coefficients. Barnett and Coulson [9] found some success using combinations of Bessel functions (zeta function) in their single-center expansions. Harris and Michels [10] used recursion relations for α-functions, but numerical instabilities sometimes appeared. Transform methods and expansions in orthogonal functions have been applied to this problem and have produced some notable results [11]. More recent references can be found in Ref. [12].

Spherical harmonics play important roles in many areas of theoretical, applied and chemical physics (calculations of molecular interactions, molecular integrals, the analysis of the molecular electronic density, etc.). Some of these problems are related to calculation of the electrostatic interaction between two different charge distributions. This interaction takes a simple form in terms of the multipolar moments of distributions in line-up coordinate systems [13].

One of the most important methods for the evaluation of the complicated multi-center integrals has been the use Fourier transform. This relationship for two-center molecular integrals, which was first noted by Prosser and Blanchard [14], has subsequently been used quite frequently for the evaluation of overlap integrals [15]. Using the technique of the Fourier transform and the theory of residues, Todd et al. [16] presented an overlap formula. Within the Fourier transform method for the evaluation of STOs, multi-center integrals are transformed into inverse Fourier integrals. In this method, it is not the analytical simplicity of the ETOs used, but rather the analytical simplicity of its Fourier transform of all the normally used ETOs, BTOs have the simplest Fourier transform [17]. However, the inefficiency of BTOs arises in the evaluation of multi-center molecular integrals for higher quantum numbers, nearly equal to the screening parameters and higher and lower internuclear distances [18]. It is well known that there is no satisfactory computational method for the use of the Fourier transform convolution theorem over STOs in quantum chemistry for a higher range of quantum numbers and geometries, and for all the values of the screening parameters.

In numerous papers it was demonstrated that the STOs have the simplest analytical structure of the ETOs. Therefore, in this paper we prefer to use Fourier transforms of STOs and ISHs. The Fourier transforms of such as STOs and ISHs are of exceptional simplicity. Consequently, these functions may be considered to be some fundamental entities in momentum space. Because of simplicity of the Fourier transforms of STOs and ISHs it is an obvious idea to evaluate multicenter molecular integrals over STOs via the Fourier transform method. In section 3, we shall discuss the relevant properties the Fourier transforms of STOs and ISHs. Particular emphasis will be given to relationship between STOs, ISHs and analyze limit case. In the following sections, we shall develop all mathematical tolls which we need for the derivation of expressions for the overlap integrals between STOs and ISHs. These expressions contain product Gegenbauer, Gaunt coefficients, and linear combinations of STOs. Finally, we would like to emphasise that this paper is presented numerical results of formulas.

2. Definition and basic properties

We will use real STOs with integer values of principal quantum numbers. The normalized STOs designated by χ are given by

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

where α is the scaling parameter, the functions $Y_l^m(\theta, \phi)$ are real or complex spherical harmonics [19]

$$Y_l^m(\theta, \phi) = P_l^{|m|}(\cos\theta)\, \Phi_m(\phi). \tag{2}$$

Here $P_l^{|m|}$ are normalized associated Legendre functions and for real spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi\left(1+\delta_{m,0}\right)}} \begin{cases} \cos(m\phi) & \text{for } m \geq 0, \\ \sin(|m|\,\phi) & \text{for } m < 0 \end{cases} \tag{3}$$

for complex spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

For the regular and irregular solid harmonics we use the symbols, respectively,

$$S_l^m(\mathbf{r}) = r^l Y_l^m(\theta, \phi), \tag{4}$$

$$£_l^m(\mathbf{r}) = r^{-l-1} Y_l^m(\theta, \phi). \tag{5}$$

For the integral of the product of three spherical harmonics over the surface of the unit sphere, so-called Gaunt coefficient [17-(a)], we write

$$\langle l_3 m_3 | \, l_2 m_2 \, | l_1 m_1 \rangle = \int \left[Y_{l_3}^{m_3}(\Omega) \right]^* Y_{l_2}^{m_2}(\Omega) \, Y_{l_1}^{m_1}(\Omega) \, \mathrm{d}\Omega. \tag{6}$$

These Gaunt coefficients linearize the product of two spherical harmonics,

$$\left[Y_{l_1}^{m_1}(\Omega) \right]^* Y_{l_2}^{m_2}(\Omega) = \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 \, | l m_2 - m_1 \rangle \, Y_l^{m_2 - m_1}(\Omega). \tag{7}$$

The symbol $\sum^{(2)}$ indicates that the summation proceeds in steps of 2. The summation limits in equation (7) determined by the selection rules satisfied by the Gaunt coefficients.

In this paper, we shall use the symmetric version of the Fourier transformation a given function $f(\mathbf{r})$ and its Fourier transform $g(\mathbf{p})$ are connected by the relationships

$$\begin{aligned} g(\mathbf{p}) &= (2\pi)^{-3/2} \int \mathrm{e}^{-i\mathbf{p}.\mathbf{r}} f(\mathbf{r}) \mathrm{d}^3 r \\ f(\mathbf{r}) &= (2\pi)^{-3/2} \int \mathrm{e}^{i\mathbf{r}.\mathbf{p}} g(p) \mathrm{d}^3 p. \end{aligned} \tag{8}$$

The Fourier transform is only defined for functions that are element of $L^1(R^3)$.

The main advantage of the representation of two-center integrals as inverse Fourier integrals according to two-center integrals is that a separation of integration variables can be achieved quite easily if $f(\mathbf{r})$ and its Fourier transform $g(\mathbf{p})$ are irreducible spherical tensors. To show this we only have to insert the well-known Rayleigh expansion of a plane wave in terms of spherical Bessel functions and spherical harmonics

$$\mathrm{e}^{\pm i\mathbf{x}.\mathbf{y}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (\pm i)^l \, j_l(xy) \left(Y_l^m \left(\frac{\mathbf{x}}{x} \right) \right)^* Y_l^m \left(\frac{\mathbf{y}}{y} \right) \tag{9}$$

into the integrals in two-center molecular integrals, where

$$j_l(xy) = \left(\frac{\pi}{2xy} \right)^{1/2} J_{l+1/2}(xy). \tag{10}$$

3. Fourier transforms of irregular solid harmonics and STOs

In this section, we want to analyze how to simplicity of the convolution formulas can be related to the mathematical properties of STOs and ISHs. With the help of Rayleigh wave expansion we obtain for the Fourier transform of STOs [3-(a)]

$$U_{nl}^{m}(\beta,\mathbf{p}) = (2\pi)^{-3/2}\int \mathrm{e}^{-i\mathbf{p}.\mathbf{r}}\chi_{nl}^{m}(\beta,\mathbf{r})\,\mathrm{d}^3r$$
$$= \frac{2^{n+l+1}\beta^{n+1/2}}{F_l(n)\sqrt{\pi F_n(2n)}}\left(\beta^2+p^2\right)^{-(n+l+2)/2}$$
$$\times C_{n-l}^{l+1}\left(\frac{\beta}{\sqrt{\beta^2+p^2}}\right)S_l^m(-i\mathbf{p})$$
$$= \frac{2^{2n+1}\beta^{2n-l+1/2}}{F_l(n)\sqrt{\pi\,F_n(2n)}}S_l^m(-i\mathbf{p})\sum_{r=0}^{E\left(\frac{n-l}{2}\right)}(-1)^r\,\frac{a_r(l+1,n-l)}{(2\beta)^{2r}}$$
$$\sum_{s=0}^{\infty}F_s(n-r+s)\frac{\left(\alpha^2-\beta^2\right)^s}{\left(\alpha^2+p^2\right)^{n-r+s+1}}, \tag{11}$$

where $F_l(n)$ are the binomial coefficients, and $C_n^{\alpha}(x)$ is the Gegenbauer polynomial defined by the following relation [20];

$$C_n^{\alpha}(x) = \sum_{s=0}^{E(n/2)}(-1)^s\,a_s(\alpha,n)\,(2x)^{n-2s}, \tag{12}$$

where

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

and

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

If the screening parameters α and β differ only slightly, all expressions of the overlap integrals over the two basis functions with different screening parameters that are based upon the partial-fraction decomposition equation 5.11 of Ref. [17-(a)] become numerically unstable. As an alternative from the Fourier transform of STOs, we has to derive the another expression;

$$U_{nl}^{m}(\alpha,\mathbf{p}) = \left(\frac{2}{\pi}\right)^{1/2} S_l^m(-i\mathbf{p}) \sum\nolimits_{s=s_{\min}}^{n-l} (-1)^{n-l-s} 2^{n+2l+2s} (n-2l)!$$
$$\times \frac{F_s(n-l)\,F_{n-2l}(l+s)}{F_{s-n-l}(2s-n-l)} \left(\frac{\alpha}{\beta}\right)^{2s+l+1} \sum\nolimits_{r=0}^{\infty} \frac{(n+s+1)_r}{r!}$$
$$\times \left[1-\left(\frac{\alpha}{\beta}\right)^2\right]^r \frac{\beta^{2(s+r)+l-1}}{\left(\beta^2+p^2\right)^{s+r+l+1}}, \tag{13}$$

where $s_{\min} = \frac{n-l-((-1)^{n-l}-1)/2}{2}$ and $(a)_n = \Gamma(a+n)/\Gamma(a)$, for $n \in N$ with $(a)_0 = 1$ is a Pochhammer symbol.

If we set $n = l = 0$ and perform the limit $\alpha \to 0$ in equations (11) and (13), after some algebra we find

$$p^{-2} = \sum\nolimits_{v=0}^{\infty} \beta^{2v} \Big/ \left(\beta^2 + p^2\right)^{v+1}. \tag{14}$$

The irregular solid harmonics is written as following forms by using limited values of STOs

$$£_l^m(\mathbf{r}) = \lim\nolimits_{\alpha\to 0} \left\{ \frac{\sqrt{(2n)!}}{2^{n+1/2}} \alpha^{-n-1/2} \chi_{nl}^m(\alpha,\mathbf{r}) \Big|_{n=-l} \right\}. \tag{15}$$

The relationship to define Fourier transform of an irregular solid harmonics is given by

$$£_l^m(p) = (2\pi)^{-3/2} \int e^{-i\mathbf{p}.\mathbf{r}} £_l^m(\mathbf{r}) d^3r. \tag{16}$$

If we perform the angular integration in the above Fourier integrals using the well known Rayleigh expansion of a plane wave and orthogonality of spherical harmonics, we find that the resulting radial integrals involving spherical Bessel functions.

$$£_l^m(\mathbf{p}) = \left(\frac{2}{\pi}\right)^{1/2} (-i)^l\, Y_l^m\left(\theta_p,\phi_p\right) \int_{r=0}^{\infty} \frac{j_l(pr)}{r^{l-1}} dr. \tag{17}$$

The remaining radial integral can be computed quite easily. We use [20]

$$\int_0^{\infty} \frac{J_v(ax)}{x^{v-q}} dx = \frac{\Gamma\left(\frac{q}{2}+\frac{1}{2}\right)}{2^{v-q} a^{q-v+1} \Gamma\left(v-\frac{q}{2}+\frac{1}{2}\right)}. \tag{18}$$

With the help of radial integral in equation (18), we obtain for the Fourier transform of ISHs in terms of regular solid harmonics by following form

$$£_l^m(\mathbf{p}) = \frac{\sqrt{2/\pi}}{(2l-1)!!} \frac{S_l^m(-i\mathbf{p})}{p^2}. \tag{19}$$

Alternatively, one might also use the following representation of the Fourier transform of an ISHs are considered to Fourier transform of an ISHs by using equation (11)

$$\pounds_l^m(\mathbf{p}) = \lim_{\alpha\to 0}\left\{\frac{\sqrt{(2n)!}}{2^{n+1/2}}\alpha^{-n-1/2}U_{nl}^m(\alpha,\mathbf{p})\Big|_{n=-l}\right\}$$

$$= \left(\frac{2}{\pi}\right)^{1/2} 2^l l! S_l^m(-i\mathbf{p}) \lim_{\alpha\to 0}\left\{(n-l)!\left(\alpha^2+p^2\right)^{-(n+l+2)/2} C_{n-l}^{l+1}\left(\frac{\alpha^2}{\sqrt{\alpha^2+p^2}}\right)\Big|_{n=-l}\right\}. \quad (20)$$

For the calculated of limited values in equation (20), we must have special values of the Gegenbauer polynomials. For this aim, we can written the Gegenbauer polynomials in terms of hypergeometric functions [20]

$$C_n^\lambda(t) = F_n(2\lambda+n-1)_2F_1\left(2\lambda+n,-n;\lambda+\frac{1}{2};\frac{1-t}{2}\right). \quad (21)$$

If we take into consideration that the relationship

$$(n-l)!C_{n-l}^{l+1}(0)\Big|_{n=-l} = \frac{(n+l+1)!}{(2l+1)!}{}_2F_1\left(n+l+2,l-n;l+\frac{3}{2};\frac{1}{2}\right)\Big|_{n=-l}.$$

$$= \frac{1}{(2l)!}. \quad (22)$$

Holds, we again obtain result given by equation (19) for Fourier transform of an ISHs from equations. (20)–(22).

4. Overlap integrals between irregular solid harmonics and STOs with different screening parameters

In this section, we want to consider the overlap integrals between STOs and ISHs with exponential parameters α and β and the internuclear separation vectors $\boldsymbol{R}$ for which we write

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta;\mathbf{R}) = \int\left[\pounds_{l_1}^{m_1}(\alpha\mathbf{r})\right]^*\chi_{n_2l_2}^{m_2}(\beta,\mathbf{r}-\mathbf{R})\,\mathrm{d}^3r. \quad (23)$$

This relationship, which holds in the sense of distributions, can be used to derive representations inverse Fourier transform [17].

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta;\mathbf{R}) = \int \mathrm{e}^{-i\mathbf{R}.\mathbf{p}}\left[\pounds_{l_1}^{m_1}(\alpha\mathbf{p})\right]^* U_{n_2l_2}^{m_2}(\beta,\mathbf{p})\,\mathrm{d}^3p. \quad (24)$$

Finally, we are give explicit integral representation for overlap integrals over an ISHs and STOs with different screening parameters, which will be treated in this paper. Together with equations (11), (19), and couple of spherical harmonics according to equation (7), and after some manipulations we finally arrived at following integral representation for overlap integrals between STOs and ISHs

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R}) = i^{l_1 - l_2} \frac{2^{2n_2+3/2} \beta^{2n_2 - l_2 + 1/2}}{\alpha^{l_1+1}(2l_1-1)!!\pi F_{l_2}(n_2)\sqrt{F_{n_2}(2n_2)}}$$

$$\times \sum_{r=0}^{E\left(\frac{n_2-l_2}{2}\right)} (-1)^r \frac{a_r(l_2+1, n_2-l_2)}{(2\beta)^{2r}} \sum_{l=l_{\min}}^{l_{\max}} {}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle$$

$$\times \int e^{-i\mathbf{R}.\mathbf{p}} \frac{p^{l_1+l_2-l} S_l^{m_2-m_1}(\mathbf{p})}{p^2 (\beta^2 + p^2)^{n_2-r+1}} d^3 p. \tag{25}$$

Equation (25) is the general expressions for overlap integrals between STOs and ISHs with different screening parameters via to Fourier transform method. In this expression, $l_1 + l_2 - l = 2L$ is the even integer number or zero. To evaluate of the representations of overlap integrals, we shall show how the series expansions, which occur integral representations equation (25) can be expressed in terms of simpler functions such as p^{2L} and $p^{-2}(\beta^2 + p^2)^{-n+r-1}$ using Taylor expansions or partial-fraction decomposition. We use the relationship, which is a special case of binomial theorem [17]

$$p^{2L} = (-1)^L \beta^{2L} \sum_{t=0}^{L} (-1)^t F_t(L) \left(\frac{\beta^2 + p^2}{\beta^2}\right)^t. \tag{26}$$

Then, we start the following partial-fraction decomposition given by equations (4.2), (4.13), and (4.27) of Ref. [17-(a)]

$$p^{-2}\left(\beta^2 + p^2\right)^{-n-l-1} = \beta^{-2n-2l-4}\left[\beta^2/p^2 - \sum_{\nu=0}^{n+l}\left[\beta^2/\left(\beta^2+p^2\right)\right]^{\nu+1}\right] \tag{27}$$

$$= \left(\beta^2 + p^2\right)^{-n-l-2} \sum_{\nu=0}^{\infty} \left(\frac{\beta^2}{\beta^2 + p^2}\right)^v \tag{28}$$

$$= \left(\frac{\beta^2}{2} + p^2\right)^{-n-l-2} \sum_{\nu=0}^{\infty} {}_2F_1(-\nu, n+l+1; n+l+2; 2)$$

$$\times \frac{(n+l+2)_v}{v!} \left(\frac{\beta^2}{\beta^2 + 2p^2}\right)^v. \tag{29}$$

We may expect that these representations will allow a very efficient evaluation of the overlap integrals between STOs and ISHs with different screening parameters. If we combine equations (25)–(27), we immediately find

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R}) = \frac{2^{2n_2+3/2}\beta^{l_1-3/2} i^{l_1-l_2}}{\alpha^{l_1+1}(2l_1-1)!!\pi F_{l_2}(n_2)\sqrt{F_{n_2}(2n_2)}}$$
$$\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle$$
$$\sum_{r=0}^{E((n_2-l_2)/2)} \sum_{t=0}^{L} (-1)^{L+r+t} F_t(L) 2^{-2r} \beta^{-l} a_r(l_2+1, n_2-l_2)$$
$$\left\{ \int e^{-i\mathbf{R}.\mathbf{p}} \frac{S_l^{m_2-m_1}(\mathbf{p})}{p^2} d^3p - \sum_{v=0}^{n_2-r-t} \beta^{2v} \int e^{-i\mathbf{R}.\mathbf{p}} \frac{S_l^{m_2-m_1}(\mathbf{p})}{\left(\beta^2+p^2\right)^{v+1}} d^3p \right\}. \quad (30)$$

To evaluate first integral in equation (30), we use following expression and Rayleigh wave expansion;

$$Y_l^m(\theta, \phi) \int_0^\infty j_l(pR) p^l dp = \frac{\pi}{2}(2l-1)!!£_l^m(\mathbf{R}). \quad (31)$$

In the following step, we shall present closed-form expressions for the second integral in equation (30) which are derived very detailed in Appendix A.

$$Y_l^m(\theta, \phi) \int_0^\infty \frac{p^{l+2} j_l(pR)}{\left(\beta^2+p^2\right)^{k+1}} dp = \pi \frac{\beta^{l-2k-1/2}}{2^{2k+3/2}} \sum_{q=1}^{k-l} g_{k-l,q}^{l} \chi_{q+l,l}^{m}(\beta, \mathbf{R}). \quad (32)$$

If we insert equations (31) and (32) into the overlap integrals (30), we obtain

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R}) = \frac{\pi(-1)^{l_1} 2^{2n_2+3/2}\beta^{l_1-3/2}}{(2l_1-1)!!\alpha^{l_1+1} F_{l_2}(n_2)\sqrt{F_{n_2}(2n_2)}} \sum_{l=l_{\min}}^{l_{\max}}{}^{(2)} \langle l_2 m_2 | l_1 m_1 | l m_2 - m_1 \rangle$$
$$\times \sum_{r=0}^{E(n_2-l_2/2)} \sum_{t=0}^{(l_1+l_2-l)/2} (-1)^{l+r+t} \frac{a_r(l_2+1, n_2-l_2)}{2^{2r}} F_t\left(\frac{l_1+l_2-l}{2}\right)$$
$$\times \left\{ \beta(2l-1)!!£_l^{m_2-m_1}(\beta\mathbf{R}) - \frac{1}{\sqrt{2\beta}} \sum_{q=1}^{l+1} g_{l+1,q}^{-l-1} \chi_{q-l-1,l}^{m_2-m_1}(\beta, \mathbf{R}) \right.$$
$$\left. - \sum_{v=1}^{n_2-r-t} \left(\frac{\beta^{-1/2}}{2^{2v+1/2}} \sum_{q=1}^{v-l} g_{v-l,q}^{l} \chi_{q+l,l}^{m_2-m_1}(\beta, \mathbf{R}) \right) \right\}. \quad (33)$$

Using the expansions equations (28), (29) into equation (25), we rewrite the overlap integrals between STOs and ISH as the product STOs, Gegenbauer coefficients and hypergeometric functions in terms of infinite series

$$Z_{l_1m_1}^{n_2l_2m_2}(\alpha,\beta;\mathbf{R}) = \frac{\pi\,(-1)^{l_1}\,\beta^{l_1-2}}{(2l_1-1)!!\alpha^{l_1+1}F_{l_2}(n_2)\sqrt{F_{n_2}(2n_2)}}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2m_2\,|l_1m_1|\,lm_2-m_1\rangle$$
$$\times\sum_{r=0}^{E((n_2-l_2)/2)}\sum_{t=0}^{(l_1+l_2-l)/2}(-1)^{l+r+t}a_r(l_2+1,n_2-l_2)\,F_t\left(\frac{l_1+l_2-l}{2}\right)$$
$$\times\sum_{v=0}^{\infty}\frac{1}{2^{2v-2t}}\sum_{q=1}^{k-l}g_{k-l,q}^{l}\chi_{q+l,l}^{m_2-m_1}(\beta,\mathbf{R}) \tag{34}$$

$$= \frac{\pi(-1)^{l_1}2^{n_2+5/4}\beta^{l_1-2}}{(2l_1-1)!!\alpha^{l_1+1}F_{l_2}(n_2)\sqrt{F_{n_2}(2n_2)}}\sum_{l=l_{\min}}^{l_{\max}}{}^{(2)}\langle l_2m_2\,|l_1m_1|\,lm_2-m_1\rangle$$
$$\times\sum_{r=0}^{E(n_2-l_2/2)}\sum_{t=0}^{(l_1+l_2-l/2)}(-1)^{l+r+t}F_t\left(\frac{l_1+l_2-l}{2}\right)a_r(l_2+1,n_2-l_2)$$
$$\times\sum_{v=0}^{\infty}{}_2F_1(-v,n_2-r-t+1;n_2-r-t+2;2)\frac{F_v(n_2-r-t+v+1)}{2^{r-t+2v+l/2}}$$
$$\times\sum_{q=1}^{k-l}g_{k-l,q}^{l}\chi_{q+l,l}^{m_2-m_1}\left(\beta\big/\sqrt{2},\mathbf{R}\right), \tag{35}$$

where $k = n_2 - r - t + v + 1$.

5. Results and discussions

In this article various mathematical properties of ISHs and Fourier transforms of STOs were analyzed and the relevance of these properties in overlap integrals was discussed. For that purpose, we first derived Fourier transforms of STOs and ISHs. And then, we analyzed the connection between STOs and ISHs. The standard way of computing the Fourier transform of an irreducible spherical tensor 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 integration is then trivial and only radial integral involving a spherical Bessel function remains to be alone. However, the evaluation of the integrals involving spherical Bessel functions is usually not all easy and in some cases even impossible.

Overlap integrals with different screening parameters are much more complicated than overlap integrals with the same screening parameters. In the case of overlap integrals with the different screening parameters, two different expressions are available one by a finite numbers of terms involving linear combinations of STOs and ISHs and one by infinite series in terms of only STOs.

The important approach for the evaluation of overlap integrals is based upon the use of elliptical coordinates [21]. Elliptical or spherical coordinates leads in difficult mathematical structures. Usually, completely different special and auxiliary functions occur. Therefore, it is very hard to compare the efficiency and feasibility of formulas. In our opinion, an overlap integral can be transformed into a one-center momentum space integral by seen equations (23) and (24). This representation of the overlap integral makes it is possible to obtain a separation of the integration variables without using an addition theorem. For overlap integrals over STOs this method has been applied by many authors [22]. However, we could be shown that the overlap integrals over STOs can be represented quite conveniently in terms of STOs again; in this article and Ref. [12]. As can be seen from equations (33)–(35), final result for the overlap integrals between STOs and ISHs with different screening parameters are expressed in terms of binomial, Gaunt, and Gegenbauer coefficients.

The algorithm of calculation of overlap integrals between STOs and ISHs has been implemented in a computer program, written in Mathematica 5.0, and performed on P. IV 2.8 GHz computer for a moderate range of physically significant values of atomic orbital parameters. In table 1, we present results of our calculation of overlap integrals obtained from equation (33). As can be seen equation (33), in order to calculate overlap integrals using Gegenbauer, Gaunt coefficients, ISHs, and STOs are required. The coefficients and ISHs were calculated using the method in Refs. [23,24], respectively. The accuracy of overlap integrals was checked for various quantum numbers using following expression;

$$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta;\mathbf{R}) = \lim_{\alpha\to 0}\left\{\frac{\sqrt{(2n_1)!}}{(2\alpha)^{n_1+1/2}} S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha,\beta;\mathbf{R})\right\}\Bigg|_{n_1=-l_1} \tag{36}$$

$$\begin{aligned}
&= \lim_{\alpha\to 0}\left\{\frac{(2\alpha)^{-n_1-1/2}}{4\beta R Y_1^0(\theta,0)}\sqrt{\frac{3(2n_1)!}{\pi}}\,\lim_{K\to\infty}\sum\nolimits_{n''=l_1+1}^{K}\left\{\left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{1/2}\right.\right.\\
&\quad\times\left\{A_{n_1 l_1 m_1} f_{n_1+1 n''}^{l_1+1}(K,\varepsilon)\, S_{n'' l_1+1 m_1}^{n_2 l_2 m_2}(\beta,\beta;\mathbf{R})\right.\\
&\quad\left.+B_{n_1 l_1 m_1} f_{n_1+1 n''}^{l_1-1}(K,\varepsilon)\, S_{n'' l_1-1 m_1}^{n_2 l_2 m_2}(\beta,\beta;\mathbf{R})\right\}\\
&\quad-\left(\frac{1+\varepsilon}{1-\varepsilon}\right)^{1/2}\left\{A_{n_2 l_2 m_2} f_{n_1 n''}^{l_1}(K,\varepsilon)\, S_{n'' l_1 m_1}^{n_2+1 l_2+1 m_2}(\beta,\beta;\mathbf{R})\right.\\
&\quad\left.\left.\left.+B_{n_2 l_2 m_2} f_{n_1 n''}^{l_1}(K,\varepsilon)\, S_{n'' l_1 m_1}^{n_2+1 l_2-1 m_2}(\beta,\beta;\mathbf{R})\right\}\right\}\right\}\Bigg|_{n_1=-l_1}.
\end{aligned} \tag{37}$$

Equation (37) is obtained from equation (18) of Ref. [12-(f)] and equations (1)–(4) of Ref. [24]. In equation (37), we use following definitions;

$$\begin{aligned}
A_{nlm} &= \left[(2n+1)(2n+2)\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}\right]^{1/2},\\
B_{nlm} &= \left[(2n+1)(2n+2)\frac{(l-m)(l+m)}{(2l+1)(2l-1)}\right]^{1/2},\\
\varepsilon &= \frac{\alpha-\beta}{\alpha+\beta}
\end{aligned} \tag{38}$$

Table 1
Overlap integrals with the different screening parameters between ISHs and STOs by using equation (33).

l_1	m_1	n_2	l_2	m_2	α	β	R	θ	ϕ	$Z_{l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R})$	CPU(s)
1	0	2	1	0	3	1	5	$\pi/2$	$2\pi/3$	0.0274414392873177478	0.75
1	−1	3	2	−1	6	2	4	$\pi/6$	$\pi/3$	$-1.704172039670138 \times 10^{-3}$	0.313
4	0	5	4	2	10	3	10	$\pi/2$	$\pi/3$	$2.254149714004311 \times 10^{-11}$	1.640
6	5	7	6	5	3	1	5	0	0	$-9.885941626712943 \times 10^{-5}$	12.422
6	3	9	4	−4	2	4	10	$\pi/6$	$\pi/2$	$-6.781916333533241 \times 10^{-7}$	4.844
8	8	10	9	−9	2	4	5	$\pi/6$	$2\pi/3$	$5.932252013126985 \times 10^{-11}$	2.281
3	−3	12	3	−2	4	1	5	$\pi/8$	$\pi/4$	$-4.540647682407877 \times 10^{-3}$	3.156
10	10	15	8	−8	3	1	5	$\pi/3$	$\pi/4$	$4.032466535179790 \times 10^{-4}$	2.219
10	10	15	8	−8	3	1	50	$\pi/3$	$\pi/4$	$1.354550933551059 \times 10^{-22}$	2.422
5	4	17	12	9	2	1	15	$\pi/3$	$\pi/4$	$1.548664161477702 \times 10^{-4}$	28.656
9	3	20	5	4	2	4	5	$\pi/3$	$\pi/3$	$9.066083734140633 \times 10^{-8}$	27.469
3	−2	22	10	−2	3	5	5	$\pi/3$	$\pi/3$	$4.768854827891625 \times 10^{-3}$	21.406
12	5	26	10	−2	3	5	5	$\pi/4$	$\pi/3$	$6.031853352172510 \times 10^{-9}$	81.922
10	5	30	5	5	2	5	20	$\pi/9$	$\pi/6$	$-3.762828660160955 \times 10^{-19}$	31.828
15	5	50	4	−2	6	4	10	$\pi/4$	$\pi/6$	$-1.583065595426039 \times 10^{-25}$	63.422

and $S_{n_1 l_1 m_1}^{n_2 l_2 m_2}(\alpha, \beta; \mathbf{R})$ is overlap integrals between STOs. In equation (37) coefficients $f_{nn'}^{l}$ have been defined in Ref. [24]. In this comparison perfect matching is obtained. The accuracy and CPU time of computer results are satisfactory. Therefore, this algorithm provides a rapid and sufficiently accurate method for the calculation of the multicenter molecular integrals in the Hartree–Fock–Roothaan approximation based on the translation formulas for STOs and ISHs for arbitrary values of quantum numbers, internuclear distances and screening constants and location of STOs and ISHs. This causes us the comment that our program should be efficiently accurate for all practical purposes.

Appendix A

We can establish the following formula for the second integrals in equation (30). Because of orthonormality of the spherical harmonics and Rayleigh expansion of plane wave in terms of spherical Bessel functions and spherical harmonics it follows immediately, equation (30), is again an irreducible spherical tensor,

$$Y_l^m(\theta, \phi)\, G_\nu^l(\beta, R) = \int e^{-i\mathbf{R}.\mathbf{p}} \frac{S_l^m(\mathbf{p})}{\left(\beta^2 + p^2\right)^{\nu+1}} d^3 p. \tag{A1}$$

The radial integral, $G_\nu^l(\beta, R)$, can be calculated with help of the relationship:

$$G_\nu^l(\beta, R) = 4\pi\, (-i)^l \int_0^\infty \frac{p^{l+2} j_l(pR)}{\left(\beta^2 + p^2\right)^{\nu+1}} dp. \tag{A2}$$

The result can be derived in terms of the Bessel function of the first kind by using equation (10)

$$G_\nu^l(\beta, R) = 2\,(-i)^l \sqrt{\frac{2\pi}{R}} \int_0^\infty \frac{p^{l+3/2} J_{l+1/2}(pR)}{\left(\beta^2 + p^2\right)^{\nu+1}} dp. \tag{A3}$$

This integral can be proved with the help of Ref. [20]

$$\int_0^\infty \frac{p^{l+3/2} J_{l+1/2}(pR)}{\left(\beta^2 + p^2\right)^{\nu+1}} dp = \frac{R^\nu \beta^{l+1/2-\nu}}{2^\nu \nu!} K_{l+1/2-\nu}(\beta R). \tag{A4}$$

If $K_n(x)$ stands for the modified Bessel function of second kind, the reduced Bessel functions is defined by Gradshteyn and Ryzhik [20]

$$\hat{k}_n(x) = (2/\pi)^{1/2} x^n K_n(x). \tag{A5}$$

The reduced Bessel functions can be represented by an exponential multiplied by a polynomial [19]

$$\hat{k}_{n-1/2}(x) = e^{-x} \sum_{q=1}^{n} \frac{(2n-q-1)!}{(q-1)!\,(2n-2q)!!} x^{q-1}. \tag{A6}$$

Now, the integral given by equation (A1) can be computed quite easily with help of equations (A4)–(A6);

$$\begin{aligned} Y_l^m(\theta,\phi)\, G_\nu^l(\beta,R) &= (-i)^l \pi^2 \frac{R^l \alpha^{2l-2\nu+1}}{2^{\nu-1}\nu!} \hat{k}_{\nu-l-1/2}(\alpha R)\, Y_l^m(\theta,\phi) \\ &= (-i)^l \pi^2 \frac{\alpha^{l-2\nu-1/2}}{2^{2\nu-1/2}} \sum_{t=0}^{\nu-l} g_{\nu-l,t}^l \chi_{t+l,l}^m(\alpha,\mathbf{R}), \end{aligned} \tag{A7}$$

where

$$g_{\mu,t}^l = \frac{t}{2\mu-t} \frac{F_t(\mu)\, F_\mu(2\mu-t)}{F_{\mu-t}(\mu+l)} \sqrt{F_{t+l}(2(t+l))}. \tag{A8}$$

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