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One- and two-center ETF-integrals of first order in relativistic calculation of NMR parameters

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Abstract

The present work focuses on the analytical and numerical developments of first-order integrals involved in the relativistic calculation of the shielding tensor using exponential-type functions as a basis set of atomic orbitals. For the analytical development, we use the Fourier integral transformation and practical properties of spherical harmonics and the Rayleigh expansion of the plane wavefunctions. The Fourier transforms of the operators were derived in previous work and they are used for analytical development. In both the one- and two-center integrals, Cauchy's residue theorem is used in the final developments of the analytical expressions, which are shown to be accurate to machine precision.

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1. Introduction

Relativistic calculation of nuclear magnetic resonance (NMR) parameters is a subject of significant research [1–14] and still constitutes an important challenge for any of the standard models of quantum chemistry. Calculations involving a magnetic field should preserve gauge independence. This is conveniently accomplished by using gauge including atomic orbitals (GIAO) [15–18].

The main difficulty in the analytical and numerical developments of NMR parameters arises from the operators associated with these parameters, which in the case of the paramagnetic contribution in the relativistic calculations, involve $1/r^5$, where r stands for the modulus of the vector $\vec{r}$ that separates two particles. These operators lead to extremely complicated integrals. The finite-perturbation method [19] can be used to compute the NMR parameters [20], but it is well known that numerical differentiation can be very unstable and this is why analytic development has to be used in such calculations.

Magnetic properties of the molecules are particularly sensitive to the quality of the basis sets of atomic orbitals due to many contributing physical phenomena arising from both the vicinity of the nucleus and from the valence region. In *ab initio* calculations using the linear combination of atomic orbitals–molecular orbitals (LCAO-MO) approximation, molecular orbitals are built from a linear combination of atomic orbitals. Thus, the choice of reliable basis functions is of primary importance. A good atomic orbital basis should satisfy the cusp at the origin [21] and the exponential decay at infinity [22]. The most popular functions used in *ab initio* calculations are Gaussian-type functions (GTFs) [23]. With GTFs, the numerous molecular integrals can be evaluated rather easily. Unfortunately, these GTFs functions fail to satisfy the aforementioned mathematical conditions for atomic–electronic distributions. Consequently, a large number of GTFs have to be used in order to achieve acceptable accuracy, increasing overall computational cost. Exponential-type functions (ETFs) show the same behavior as the exact solutions of atomic or molecular Schrödinger equations satisfying Kato's conditions [24]. Thus, these functions are better suited to represent electron wavefunctions near the nucleus and within a long range. This implies that a smaller number of ETFs is needed for comparable accuracy to the same calculation using GTFs. Unfortunately, molecular multi-center integrals based on ETFs are extremely difficult to evaluate accurately and rapidly. Among ETFs, Slater-type functions (STFs) [25] have a dominating position; this is due to the fact that their analytical expression is very simple. Unfortunately the multi-center integrals over these functions turned out to be extremely difficult to evaluate.

Various studies have focused on the use of B functions [26–28], which are analytically more complicated than STFs but have much more appealing properties applicable to multi-center integral problems [27, 29]; in particular, their Fourier transform is exceptionally simple [30]. Note that STFs can be expressed as finite linear combinations of B functions [27] and that the basis set of B functions is well adapted to the Fourier transform [30–35], which led to analytic expressions for all multi-center molecular integrals over B functions.

In the present paper, we derive analytic expressions for one- and two-center integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor. The analytical development is based on the Fourier transform method. Orthogonality of spherical harmonics and the Rayleigh expansion of the plane wavefunctions are used in the development leading to analytic expressions for the first-order integrals. The obtained analytic expressions involve semi-infinite integrals and their expression is obtained using Cauchy's residue theorem.

2. General definitions and properties

The functions $B^m_{n,l}(\zeta,\vec{r})$ are defined by [27, 28]:

$$B^m_{n,l}(\zeta,\vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!}\,\hat{k}_{n-\frac{1}{2}}(\zeta r)\,Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}}), \tag{1}$$

where n, l, and m are the quantum numbers, $\hat{k}_{n-\frac{1}{2}}(z)$ stands for the reduced spherical Bessel function of the second kind defined in [26, 28] and $Y^m_l(\theta,\varphi)$ stands for the surface spherical harmonic [36].

A given function $f(\vec{r})$ and its Fourier transform $\bar{f}(\vec{k})$ are connected by the symmetric relationships:

$$\bar{f}(\vec{k}) = (2\pi)^{-3/2}\int_{\vec{r}} \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}}\, f(\vec{r})\,\mathrm{d}\vec{r} \qquad \text{and} \qquad f(\vec{r}) = (2\pi)^{-3/2}\int_{\vec{k}} \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}}\,\bar{f}(\vec{k})\,\mathrm{d}\vec{k}. \tag{2}$$

The Fourier transform $\bar{B}^m_{n,l}(\zeta,\vec{p})$ of $B^m_{n,l}(\zeta,\vec{r})$ is given by [30]

$$\bar{B}^m_{n,l}(\zeta,\vec{p}) = \sqrt{\frac{2}{\pi}}\,\zeta^{2n+l-1}\,\frac{(-\mathrm{i}\,|p|)^l}{(\zeta^2+|p|^2)^{n+l+1}}\,Y^m_l(\theta_{\vec{p}},\varphi_{\vec{p}}). \tag{3}$$

The normalized STFs are defined according to the following relationship [25]:

$$\chi_{n,l}^m(\zeta,\vec{r}) = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}}\, r^{n-1}\, \mathrm{e}^{-\zeta r}\, Y_l^m(\theta_{\vec{r}},\varphi_{\vec{r}}). \tag{4}$$

STFs can be expressed as finite linear combinations of B functions [27]:

$$\chi_{n,l}^m(\zeta,\vec{r}) = \sqrt{\frac{2^{2n+1}\,\zeta^3}{(2n)!}} \sum_{\tilde{n}=\tilde{n}_{\min}}^{\tilde{n}_{\max}} \frac{(-1)^{n-l-\tilde{n}}\; 2^{2\tilde{n}+2l-n}\;(l+\tilde{n})!}{(2\tilde{n}-n+l)!\;(n-l-\tilde{n})!}\, B_{\tilde{n},l}^m(\zeta,\vec{r}), \tag{5}$$

where $\tilde{n}_{\max} = n-l$ and $\tilde{n}_{\min} = \frac{n-l}{2}$ if $n-l$ is even, or $\tilde{n}_{\min} = \frac{n-l+1}{2}$ if $n-l$ is odd.

Gaunt coefficients are defined by [37, 38]

$$\langle l_1 m_1 | l_2 m_2 | l_3 m_3\rangle = \int_0^{2\pi}\int_0^{\pi} \left[Y_{l_1}^{m_1}(\theta,\varphi)\right]^* Y_{l_2}^{m_2}(\theta,\varphi)\, Y_{l_3}^{m_3}(\theta,\varphi)\,\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi. \tag{6}$$

The Gaunt coefficients linearize the product of two spherical harmonics:

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

where the subscript $l = l_{\min}, 2$ in the summation symbol implies that the summation index l runs in steps of 2. The constant $l_{\min}$ is given by [38]

$$l_{\min} = \begin{cases} \max(|l_1-l_2|, |m_2-m_1|) & \text{if} \quad l_1+l_2+\max(|l_1-l_2|,|m_2-m_1|) \quad \text{is even} \\ \max(|l_1-l_2|, |m_2-m_1|)+1 & \text{if} \quad l_1+l_2+\max(|l_1-l_2|,|m_2-m_1|) \quad \text{is odd.} \end{cases} \tag{8}$$

The orthogonality of spherical harmonics is defined by

$$\begin{aligned} &\int_0^{2\pi}\int_0^{\pi} \left[Y_{l_1}^{m_1}(\theta,\varphi)\right]^* Y_{l_2}^{m_2}(\theta,\varphi)\,\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi = \delta_{l_1,l_2}\delta_{m_1,m_2} \\ \text{and} \qquad &\int_0^{2\pi}\int_0^{\pi} Y_l^m(\theta,\varphi)\,\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi = \delta_{l,0}\delta_{m,0}, \end{aligned} \tag{9}$$

where δ_{l_1,l_2} stands for the Kronecker delta function.

The Rayleigh expansion of the plane wavefunctions is given by [39]

$$\mathrm{e}^{\pm \mathrm{i}\vec{k}\cdot\vec{r}} = 4\pi \sum_{l=0}^{+\infty}\sum_{m=-l}^{l} (\pm\mathrm{i})^l \left[Y_l^m(\theta_{\vec{k}},\varphi_{\vec{k}})\right]^* Y_l^m(\theta_{\vec{r}},\varphi_{\vec{r}})\, j_l(k\,r), \tag{10}$$

where $j_\lambda(x)$ stands for the spherical Bessel function of order λ.

The Pochhammer symbol $(\alpha)_n$ is defined by

$$(\alpha)_n = \begin{cases} (\alpha)_n = 1 & \text{if} \quad n = 0, \\ (\alpha)_n = \alpha\,(\alpha+1)\,(\alpha+2)\cdots(\alpha+n-1) = \dfrac{\Gamma(\alpha+n)}{\Gamma(\alpha)} & \text{if} \quad n \leqslant -\alpha, \\ (\alpha)_n = 0 & \text{if} \quad n \geqslant -\alpha+1, \end{cases} \tag{11}$$

where Γ stands for the Gamma function. For $n \in \mathbb{N}$,

$$\Gamma(n+1) = n! \qquad \text{and} \qquad \Gamma\left(n+\frac{1}{2}\right) = \frac{(2n)!}{2^{2n}\,n!}\sqrt{\pi}. \tag{12}$$

The Cartesian coordinates r_α for $\alpha \in \{x,y,z\}$ of a vector $\vec{r}$ can be expressed in terms of spherical polar coordinates and their complex conjugates as

$$r_\alpha = r \sum_{m=-1}^{1} c_{\alpha,m}\, Y_1^m(\theta_{\vec{r}},\phi_{\vec{r}}), \tag{13}$$

where the coefficients $c_{\alpha,m}$ for $\alpha \in \{x, y, z\}$ are given as follows:

$$\begin{cases} c_{x,-1} = \sqrt{\frac{2\pi}{3}}, & c_{y,-1} = \mathrm{i}\sqrt{\frac{2\pi}{3}} \quad \text{and} \quad c_{z,-1} = 0, \\ c_{x,0} = 0, & c_{y,0} = 0 \quad \text{and} \quad c_{z,0} = \sqrt{\frac{4\pi}{3}}, \\ c_{x,1} = -\sqrt{\frac{2\pi}{3}}, & c_{y,1} = \mathrm{i}\sqrt{\frac{2\pi}{3}} \quad \text{and} \quad c_{z,1} = 0. \end{cases} \tag{14}$$

3. Analytical development of NMR integrals of the first order

In the presence of an external uniform magnetic field $\vec{B}_0$, the electronic non-relativistic Hamiltonian for a system of n electrons and N nuclei is given by

$$\mathcal{H} = \sum_{i=1}^{n} \left[\frac{1}{2}\vec{p}_i^{\,2} + \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{i<j}^{n} \frac{1}{r_{ij}} \right], \tag{15}$$

where the electron momentum $\vec{p}_j$ is given by

$$\vec{p}_i = [-\mathrm{i}\,\vec{\nabla}_i + e\,\vec{A}(i)] \qquad \text{where} \quad \vec{A} = \frac{1}{2}(\vec{B}_0 \times \vec{r}_{i0}) + \frac{\mu_0}{4\pi}\sum_{N} \frac{\vec{\mu}_N \times \vec{r}_{iN}}{r_{iN}^3}, \tag{16}$$

where $\vec{A}(i)$ stands for the vector potential induced by the nuclear moments $\vec{\mu}_N$ and the external uniform magnetic field $\vec{B}_0$ and μ_0 stands for the dielectric permittivity. Z_A is the atomic number of nucleus A, $\vec{r}_{iA} = \vec{r}_i - \vec{R}_A$, $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $\vec{r}_i$ (resp. $\vec{r}_j$) represents the vector position of the electron i (resp. the electron j) and $\vec{R}_A$ is the vector position of the atom A.

Heavy atoms require the inclusion of relativistic effects [13] and this gives rise to new parameters, which do not appear in the non-relativistic Hamiltonian. In terms of perturbations with respect to $\mu_{N,\alpha}$ and $B_{0,\beta}$ where α and β stand for Cartesian coordinates ($\alpha, \beta \in (x, y, z)$), the electronic relativistic Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(r)} + \mu_{N,\alpha}\mathcal{H}_{\alpha}^{(0,1)} + B_{0,\beta}\mathcal{H}_{\beta}^{(1,0)} + \mu_{N,\alpha}B_{0,\beta}\mathcal{H}_{\alpha\beta}^{(1,1)} + \cdots, \tag{17}$$

where $\mathcal{H}^{(0)}$ is the zeroth-order Hamiltonian and $\mathcal{H}^{(r)}$ is the relativistic perturbation term, which is independent of the magnetic perturbations [1, 2].

The first-order perturbation $\mathcal{H}_{\alpha}^{(0,1)}$ of the Hamiltonian with respect to the nuclear moment involves relativistic terms including $\frac{\mu_0}{4\pi}\sum_{j=1}^{n} 3\,r_{jN,\beta}\frac{\vec{r}_{jN}\cdot\vec{\sigma}(j)}{r_{jN}^5}$, which correspond to the paramagnetic contribution in the relativistic calculations of the shielding tensor [1, 2]. In this work, we present the analytical and numerical developments of one- and two-center integrals of the first order corresponding to the aforementioned operators.

Let $L_{jN,\alpha}$ be defined by

$$L_{jN,\alpha} = 3r_{jN,\alpha}\left[\frac{\vec{r}_{jN}\cdot\vec{\sigma}_j}{r_{jN}^5}\right], \tag{18}$$

where $\vec{\sigma}_j$ stands for the Pauli spin matrix of the jth electron and its Cartesian coordinates are given by

$$\sigma_{j,x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_{j,y} = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} \qquad \text{and} \qquad \sigma_{j,z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

By developing the scalar product in the expression of $L_{jN,\alpha}$, we obtain

$$L_{jN,\alpha} = 3\, r_{jN,\alpha}\, \frac{\vec{r}_{jN} \cdot \vec{\sigma}_j}{r_{jN}^5} = 3\, r_{jN,\alpha} \sum_{\beta} \sigma_{j,\beta}\, \frac{r_{jN,\beta}}{r_{jN}^5} = -\sum_{\beta} \sigma_{j,\beta} \left[r_{jN,\alpha}\, \frac{\partial}{\partial r_{jN,\beta}} \left(\frac{1}{r_{jN}^3} \right) \right]. \tag{19}$$

One electron integrals arise from the operator $L_{jN,\alpha}$. These integrals are given by

$$\begin{aligned} \mathcal{I} &= \left\langle B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_{jA}) \middle| L_{jN,\alpha} \middle| B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB}) \right\rangle_{\vec{r}} \\ &= \int_{\vec{r}} \left[B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_{jA}) \right]^* 3 r_{jN,\alpha} \left[\frac{\vec{r}_{jN} \cdot \vec{\sigma}_j}{r_{jN}^5} \right] B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB})\, \mathrm{d}\vec{r}, \end{aligned} \tag{20}$$

where $\vec{r}_{jA} = \vec{r}_j - \overrightarrow{OA} = \vec{r}$, $\vec{r}_{jB} = \vec{r}_j - \overrightarrow{OB} = \vec{r} - \overrightarrow{AB}$ and $\vec{r}_{jN} = \vec{r}_j - \overrightarrow{ON} = \vec{r} - \overrightarrow{AN}$. A, B and N are three arbitrary points of the Euclidian space, while O stands for the origin of the fixed coordinate system.

Using equation (19), the above integrals can be expressed as a finite linear combination of integrals $\mathcal{I}^{(\alpha,\beta)}$ and $\mathcal{I}^{(\alpha)}$. The integrals $\mathcal{I}^{(\alpha,\beta)}$ correspond to the case where α and β represent two different Cartesian coordinates (say $\alpha \neq \beta$) and the integrals $\mathcal{I}^{(\alpha)}$ correspond to the case where α and β represent the same Cartesian coordinate (say $\alpha = \beta$).

The present work concerns the analytical and numerical developments of the integrals $\mathcal{I}^{(\alpha,\beta)}$ ($\alpha \neq \beta$), which are given by

$$\mathcal{I}^{(\alpha,\beta)} = \int_{\vec{r}} \left[B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_{jA}) \right]^* \left[r_{jN,\alpha}\, \frac{\partial}{\partial r_{jN,\beta}} \left(\frac{1}{r_{jN}^3} \right) \right] B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB})\, \mathrm{d}\vec{r}. \tag{21}$$

For the analytic development of the above integrals, the Fourier transform method is used. The Fourier transform of the operators was derived in [40] and is given by

$$\overline{r_{jN,\alpha}\, \frac{\partial}{\partial r_{jN,\beta}} \left(\frac{1}{r_{jN}^3} \right)} = \sqrt{\frac{2}{\pi}}\, \frac{k_\alpha\, k_\beta}{k^2}. \tag{22}$$

Note that due to the method used to develop the above Fourier transform, it is not valid for the case where α and β represent the same Cartesian coordinate. In this case, the Fourier transform does not exist in the classical sense. The integrals corresponding to $\alpha = \beta$ are a subject of ongoing research.

3.1. One-center integrals

This case occurs when $A = B = N$. Let us denote by $\vec{r} = \vec{r}_{jN} = \vec{r}_{jA} = \vec{r}_{jB}$. In the following, the one-center integrals will be referred to as $\mathcal{I}_1^{(\alpha,\beta)}$.

Using the Fourier transformation method, we obtain the following expressions for the one-center integrals:

$$\mathcal{I}_1^{(\alpha,\beta)} = \frac{1}{2\pi^2} \int_{\vec{k}} \frac{k_\alpha\, k_\beta}{k^2} \left\langle B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}) \middle| \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}} \middle| B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}) \right\rangle_{\vec{r}} \mathrm{d}\vec{k}. \tag{23}$$

In the term $\mathcal{T}_1 = \left\langle B_{n_1 l_1}^{m_1}(\zeta_1, \vec{r}) \middle| \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}} \middle| B_{n_2 l_2}^{m_2}(\zeta_2, \vec{r}) \right\rangle_{\vec{r}}$ involved in the above expression, the two B functions are centered at the same point and the radial part of their product is given by

$$\mathcal{T}_1 = \frac{\sqrt{\pi}\,\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{l_1+l_2-1}}{2^{2n_1+l_1+2n_2+l_2+1}\,(n_1+l_1)!\,(n_2+l_2)!}\sum_{l=l_{\min},2}^{l_1+l_2}\frac{(-i)^l}{(2\,\zeta_s)^l}\,\langle l_1m_1|l_2m_2|lm_1-m_2\rangle[Y_l^{m_1-m_2}(\theta_{\vec{k}},\varphi_{\vec{k}})]^*$$
$$\times\sum_{\tau=2}^{n_1+n_2}\sum_{\varsigma=\tau_1}^{\tau_2}\frac{2^\tau\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,\zeta_1^{\varsigma-1}\zeta_2^{\tau-\varsigma-1}\zeta_s^{\tau}\,\Gamma(\tau+l_1+l_2+l+1)}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma\left(l+\frac{3}{2}\right)}$$
$$\times\sum_{r=0}^{\eta'}\frac{(-1)^r\left(\frac{\eta}{2}\right)_r\left(\frac{\eta+1}{2}\right)_r}{\left(l+\frac{3}{2}\right)_r r!\zeta_s^{2r}}\,\frac{k^{l+2r}}{\left(\zeta_s^2+k^2\right)^{\tau+l_1+l_2}}, \tag{24}$$

where $\tau_1 = \max(1,\tau-n_2)$, $\tau_2 = \min(n_1,\tau-1)$, $\zeta_s = \zeta_1+\zeta_2$, $\eta = l-\tau-l_1-l_2+1$ and $\eta' = -\frac{\eta}{2}$ if η is even, otherwise $\eta' = -\frac{\eta+1}{2}$.

Using equations (13) and (14), we can obtain the following expression for $\frac{k_\alpha k_\beta}{k^2}$:

$$\frac{k_\alpha k_\beta}{k^2} = \sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_3}c_{\alpha,m_3}c_{\beta,m_4}\sum_{l'=l'_{\min,2}}^{2}\langle 1m_4|1m_3|l'm_4-m_3\rangle Y_{l'}^{m_4-m_3}(\theta_{\vec{k}},\phi_{\vec{k}}), \tag{25}$$

where

$$l'_{\min} = \begin{cases}|m_4-m_3| & \text{if} \quad |m_4-m_3| \quad \text{is even,}\\ |m_4-m_3|+1 & \text{if} \quad |m_4-m_3| \quad \text{is odd.}\end{cases} \tag{26}$$

The integration of the angular parts of equations (24) and (25) leads to

$$\int_0^{2\pi}\int_0^{\pi}\left[Y_l^{m_1-m_2}(\theta_{\vec{k}},\varphi_{\vec{k}})\right]^* Y_{l'}^{m_4-m_3}(\theta_{\vec{k}},\phi_{\vec{k}})\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi = \delta_{l,l'}\delta_{m_1-m_2,m_4-m_3}. \tag{27}$$

Using the above equation, we obtain the following for $\mathcal{I}_1^{(\alpha,\beta)}$:

$$\mathcal{I}_1^{(\alpha,\beta)} = \frac{\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{l_1+l_2-1}}{\pi^{3/2}\,2^{2n_1+l_1+2n_2+l_2+2}\,(n_1+l_1)!\,(n_2+l_2)!}\sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_3}\,c_{\alpha,m_3}\,c_{\beta,m_4}$$
$$\times\sum_{l'=l'_{\min,2}}^{2}\sum_{l=l_{\min},2}^{l_1+l_2}\frac{(-i)^l}{(2\zeta_s)^l}\,\langle 1\,m_4|1\,m_3|l'\,m_4-m_3\rangle\,\langle l_1m_1|l_2m_2|lm_1-m_2\rangle\delta_{l,l'}\delta_{m_1-m_2,m_4-m_3}$$
$$\times\sum_{\tau=2}^{n_1+n_2}\sum_{\varsigma=\tau_1}^{\tau_2}\frac{2^\tau\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,\zeta_1^{\varsigma-1}\,\zeta_2^{\tau-\varsigma-1}\,\zeta_s^{\tau}\,\Gamma(\tau+l_1+l_2+l+1)}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma\left(l+\frac{3}{2}\right)}$$
$$\times\sum_{r=0}^{\eta'}(-1)^r\,\frac{\left(\frac{\eta}{2}\right)_r\left(\frac{\eta+1}{2}\right)_r}{\left(l+\frac{3}{2}\right)_r\,r!\zeta_s^{2r}}\int_0^\infty\frac{k^{l+2r+2}}{\left(\zeta_s^2+k^2\right)^{l_1+l_2+\tau}}\,\mathrm{d}k, \tag{28}$$

which can be re-written as

$$\mathcal{I}_1^{(\alpha,\beta)} = \frac{\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{l_1+l_2-1}}{\pi^{3/2}\,2^{2n_1+l_1+2n_2+l_2+2}\,(n_1+l_1)!\,(n_2+l_2)!}\sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_3}\,c_{\alpha,m_3}\,c_{\beta,m_4}$$
$$\times\sum_{l=l_{\min},2}^{2}\frac{(-i)^l}{(2\zeta_s)^l}\,\langle 1\,m_4|1\,m_3|l\,m_4-m_3\rangle\,\langle l_1m_1|l_2m_2|lm_1-m_2\rangle\delta_{m_1-m_2,m_4-m_3}$$
$$\times\sum_{\tau=2}^{n_1+n_2}\sum_{\varsigma=\tau_1}^{\tau_2}\frac{2^\tau\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,\zeta_1^{\varsigma-1}\,\zeta_2^{\tau-\varsigma-1}\,\zeta_s^{\tau}\,\Gamma(\tau+l_1+l_2+l+1)}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma(l+\frac{3}{2})}$$
$$\times\sum_{r=0}^{\eta'}(-1)^r\,\frac{\left(\frac{\eta}{2}\right)_r\left(\frac{\eta+1}{2}\right)_r}{\left(l+\frac{3}{2}\right)_r\,r!\zeta_s^{2r}}\int_0^\infty\frac{k^{l+2r+2}}{\left(\zeta_s^2+k^2\right)^{l_1+l_2+\tau}}\,\mathrm{d}k. \tag{29}$$

The last difficulty in the development of $\mathcal{I}_1^{(\alpha,\beta)}$ lies in the semi-infinite integrals involved in its analytical expression (29). We approach this problem by considering the integral

$$\int_0^\infty \frac{k^{l+2r+2}}{\zeta_s^2 + k^2}\,\mathrm{d}k, \tag{30}$$

with the even integrand

$$f(z) = \frac{z^{l+2r+2}}{\zeta_s^2 + z^2}, \qquad z = k + \mathrm{i}\,y. \tag{31}$$

By considering a positively oriented circular contour above the real axis with a radius $R > \zeta_s$ joined at its two ends by the line along the real axis, and by applying Cauchy's residue theorem and taking the limit as $R \to \infty$, we can write

$$2\int_0^\infty f(k)\,\mathrm{d}k = 2\pi\mathrm{i}\,\operatorname*{Res}_{z=i\zeta_s} f(z). \tag{32}$$

By developing further, we obtain the formula

$$\int_0^\infty \frac{k^{l+2r+2}}{\zeta_s^2 + k^2}\,\mathrm{d}k = \frac{\pi\, i^{l+2r+2}}{2}\zeta_s^{l+2r+1}. \tag{33}$$

By applying $\frac{1}{(-2)^{\mu-1}\Gamma(\mu)}\left(\frac{\partial}{\zeta_s\,\partial\zeta_s}\right)^{\mu-1}$, for $\mu = l_1 + l_2 + \tau$ to both sides of the equation and simplifying, we obtain

$$\tilde{\mathcal{I}}_1^{(\alpha,\beta)} = \int_0^\infty \frac{k^{l+2r+2}}{\left(\zeta_s^2 + k^2\right)^{l_1+l_2+\tau}}\,\mathrm{d}k = \frac{\pi\, i^{l+2r+2}}{2}\frac{\left(-r - \frac{l+1}{2}\right)_{l_1+l_2+\tau-1}}{\Gamma(l_1 + l_2 + \tau)}\zeta_s^{l+2r+3-2l_1-2l_2-2\tau}. \tag{34}$$

Therefore, by simplifying the terms, we finally obtain

$$\begin{aligned}
\mathcal{I}_1^{(\alpha,\beta)} = &-\frac{\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{2-l_1-l_2}}{\sqrt{\pi}\,2^{2n_1+l_1+2n_2+l_2+3}\,(n_1+l_1)!\,(n_2+l_2)!}\sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_3}\,c_{\alpha,m_3}\,c_{\beta,m_4}\\
&\times\sum_{l=l_{\min},2}^{2} 2^{-l}\,\langle 1\,m_4|1\,m_3|l\,m_4 - m_3\rangle\,\langle l_1m_1|l_2m_2|lm_1 - m_2\rangle\delta_{m_1-m_2,m_4-m_3}\\
&\times\sum_{\tau=2}^{n_1+n_2}\sum_{\varsigma=\tau_1}^{\tau_2}\frac{2^\tau\,\zeta_1^{\varsigma-1}\,\zeta_2^{\tau-\varsigma-1}}{\zeta_s^\tau}\frac{(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,(\tau+l_1+l_2)_{l+1}}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma\left(l+\frac{3}{2}\right)}\\
&\times\sum_{r=0}^{\eta'}\frac{\left(\frac{\eta}{2}\right)_r\left(\frac{\eta+1}{2}\right)_r\left(-r-\frac{l+1}{2}\right)_{l_1+l_2+\tau-1}}{\left(l+\frac{3}{2}\right)_r\,r!}.
\end{aligned} \tag{35}$$

Note that expression (34) obtained using Cauchy's residue theorem implies many simplifications in the overall formula for $\mathcal{I}_1^{(\alpha,\beta)}$ in equation (29) ultimately leading to (35).

3.2. Two-center integrals

This case occurs when $A = B \neq N$. Let us denote by $\vec{r} = \vec{r}_{jA} = \vec{r}_{jB}$ and $\vec{R} = \overrightarrow{AN}$. In the following, the two-center integrals will be referred to as $\mathcal{I}_2^{(\alpha,\beta)}$.

Using the Fourier transformation method, we obtain the following expressions for the two-center integrals:

$$\mathcal{I}_2^{(\alpha,\beta)} = \frac{1}{2\pi^2}\int_{\vec{k}}\frac{k_\alpha\,k_\beta}{k^2}\,\mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{R}}\left\langle B_{n_1,l_1}^{m_1}(\zeta_1,\vec{r})\right|\mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}}\left|B_{n_2,l_2}^{m_2}(\zeta_2,\vec{r})\right\rangle_{\vec{r}}\,\mathrm{d}\vec{k}. \tag{36}$$

Following the same development as for the one-center integrals, we obtain

$$\mathcal{I}_2^{(\alpha,\beta)} = \frac{1}{2\pi^2}\int_{\vec{k}} 4\pi \sum_{\lambda=0}^{+\infty}\sum_{m=-\lambda}^{\lambda} i^{\lambda}\left[Y_\lambda^m(\theta_{\vec{k}},\varphi_{\vec{k}})\right]^* Y_\lambda^m(\theta_{\vec{R}},\varphi_{\vec{R}})\, j_\lambda(R\,k)$$
$$\times \sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_3}\, c_{\alpha,m_3}\, c_{\beta,m_4}\sum_{l'=l'_{\min,2}}^{2}\langle 1\,m_4|1\,m_3|l'\,m_4-m_3\rangle\, Y_{l'}^{m_4-m_3}(\theta_{\vec{k}},\phi_{\vec{k}})$$
$$\times \frac{\sqrt{\pi}\,\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{l_1+l_2-1}}{2^{2n_1+l_1+2n_2+l_2+1}\,(n_1+l_1)!\,(n_2+l_2)!}\sum_{l=l_{\min},2}^{l_1+l_2}$$
$$\times \frac{(-i)^l}{(2\,\zeta_s)^l}\langle l_1 m_1|l_2 m_2|l m_1-m_2\rangle\left[Y_l^{m_1-m_2}(\theta_{\vec{k}},\varphi_{\vec{k}})\right]^*\sum_{\tau=2}^{n_1+n_2}\sum_{\varsigma=\tau_1}^{\tau_2}$$
$$\times \frac{2^\tau\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,\zeta_1^{\varsigma-1}\zeta_2^{\tau-\varsigma-1}\zeta_s^\tau\,\Gamma(\tau+l_1+l_2+l+1)}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma\left(l+\frac{3}{2}\right)}$$
$$\times \sum_{r=0}^{\eta'}\frac{(-1)^r\left(\frac{\eta}{2}\right)_r\left(\frac{\eta+1}{2}\right)_r}{(l+\frac{3}{2})_r\, r!\,\zeta_s^{2r}}\,\frac{k^{l+2r}}{\left(\zeta_s^2+k^2\right)^{\tau+l_1+l_2}}\,\mathrm{d}\vec{k}. \qquad (37)$$

Using equation (7) to linearize the product of the two spherical harmonics in the above equation, we obtain

$$\mathcal{I}_2^{(\alpha,\beta)} = \frac{1}{2\pi^2}\int_{\vec{k}} 4\pi \sum_{\lambda=0}^{+\infty}\sum_{m=-\lambda}^{\lambda} i^{\lambda}\left[Y_\lambda^m(\theta_{\vec{k}},\varphi_{\vec{k}})\right]^* Y_\lambda^m(\theta_{\vec{R}},\varphi_{\vec{R}})\, j_\lambda(R\,k)$$
$$\times \sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_3}\, c_{\alpha,m_3}\, c_{\beta,m_4}\sum_{l'=l'_{\min,2}}^{2}\langle 1\,m_4|1\,m_3|l'\,m_4-m_3\rangle$$
$$\times \frac{\sqrt{\pi}\,\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{l_1+l_2-1}}{2^{2n_1+l_1+2n_2+l_2+1}\,(n_1+l_1)!\,(n_2+l_2)!}\sum_{l=l_{\min},2}^{l_1+l_2}\frac{(-i)^l}{(2\,\zeta_s)^l}\langle l_1 m_1|l_2 m_2|l m_1-m_2\rangle$$
$$\times \sum_{l''=l''_{\min,2}}^{l+l'}\langle l' m_4-m_3|l m_1-m_2|l'' m_4-m_3-m_1+m_2\rangle\, Y_{l''}^{m_4-m_3-m_1+m_2}(\theta_{\vec{k}},\phi_{\vec{k}})$$
$$\times \sum_{\tau=2}^{n_1+n_2}\sum_{\varsigma=\tau_1}^{\tau_2}\frac{2^\tau\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,\zeta_1^{\varsigma-1}\zeta_2^{\tau-\varsigma-1}\zeta_s^\tau\,\Gamma(\tau+l_1+l_2+l+1)}{(\varsigma-1)!(n_1-\varsigma)!(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\Gamma\left(l+\frac{3}{2}\right)}$$
$$\times \sum_{r=0}^{\eta'}\frac{(-1)^r\left(\frac{\eta}{2}\right)_r\left(\frac{\eta+1}{2}\right)_r}{\left(l+\frac{3}{2}\right)_r\, r!\,\zeta_s^{2r}}\,\frac{k^{l+2r}}{\left(\zeta_s^2+k^2\right)^{\tau+l_1+l_2}}\,\mathrm{d}\vec{k}. \qquad (38)$$

The integration of the angular parts $\left[Y_\lambda^m(\theta_{\vec{k}},\varphi_{\vec{k}})\right]^*$ and $Y_{l''}^{m_4-m_3-m_1+m_2}(\theta_{\vec{k}},\phi_{\vec{k}})$ involved in the above equation along with the orthogonality relation of spherical harmonics (9), lead to

$$\mathcal{I}_2^{(\alpha,\beta)} = \frac{\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{l_1+l_2-1}}{\sqrt{\pi}\,2^{2n_1+l_1+2n_2+l_2}\,(n_1+l_1)!\,(n_2+l_2)!}\sum_{l=l_{\min},2}^{l_1+l_2}\frac{(-i)^l}{(2\,\zeta_s)^l}\langle l_1 m_1|l_2 m_2|l m_1-m_2\rangle$$
$$\times \sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_3}\, c_{\alpha,m_3}\, c_{\beta,m_4}\sum_{l'=l'_{\min,2}}^{2}\langle 1\,m_4|1\,m_3|l'\,m_4-m_3\rangle$$

$$\times \sum_{\lambda=\lambda_{\min,2}}^{l+l'} i^{\lambda} \langle l'm_4 - m_3|lm_1 - m_2|\lambda m_4 - m_3 - m_1 + m_2\rangle Y_{\lambda}^{m_4-m_3-m_1+m_2}(\theta_{\vec{R}}, \varphi_{\vec{R}})$$
$$\times \sum_{\tau=2}^{n_1+n_2} \sum_{\varsigma=\tau_1}^{\tau_2} \frac{2^{\tau}\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,\zeta_1^{\varsigma-1}\zeta_2^{\tau-\varsigma-1}\zeta_s^{\tau}\,\Gamma(\tau+l_1+l_2+l+1)}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma\left(l+\frac{3}{2}\right)}$$
$$\times \sum_{r=0}^{\eta'} \frac{(-1)^r \left(\frac{\eta}{2}\right)_r \left(\frac{\eta+1}{2}\right)_r}{\left(l+\frac{3}{2}\right)_r r!\,\zeta_s^{2r}} \int_0^{\infty} \frac{k^{l+2r+2}}{\left(\zeta_s^2+k^2\right)^{l_1+l_2+\tau}} j_{\lambda}(R\,k)\,\mathrm{d}k. \tag{39}$$

Again, the last difficulty in the development of $\mathcal{I}_2^{(\alpha,\beta)}$ lies in the semi-infinite integrals involved in its analytical expression (39). By proceeding similarly as above, an analytical expression was developed for the integral in [30]. This expression is

$$\int_0^{\infty} \frac{k^{\lambda+2n_k+2}}{(k^2+\alpha^2)^{\mu+1}} j_{\lambda}(v\,k)\,\mathrm{d}k = \frac{\pi\,(-1)^{n_k}\,\alpha^{2n_k}}{2^{\mu+1}\,\Gamma(\mu+1)\,v^{\lambda-2\mu+1}} \sum_{s=0}^{n_k} \binom{n_k}{s} \frac{2^s\,(-\mu)_s}{(v\,\alpha)^{2s}}\,\hat{k}_{\lambda-\mu+s+\frac{1}{2}}(v\,\alpha). \tag{40}$$

Re-parameterizing for the integrals in $\mathcal{I}_2^{(\alpha,\beta)}$, we obtain the expression

$$\tilde{\mathcal{I}}_2^{(\alpha,\beta)} = \int_0^{\infty} \frac{k^{l+2r+2}}{(\zeta_s^2+k^2)^{l_1+l_2+\tau}} j_{\lambda}(R\,k)\,\mathrm{d}k = \frac{\pi\,i^{l+2r-\lambda}\,\zeta_s^{l+2r-\lambda}}{2^{l_1+l_2+\tau}\,\Gamma(l_1+l_2+\tau)\,R^{\lambda-2l_1-2l_2-2\tau+3}}$$
$$\times \sum_{s=0}^{r+\frac{l-\lambda}{2}} \binom{r+\frac{l-\lambda}{2}}{s} \frac{2^s\,(1-l_1-l_2-\tau)_s}{(R\,\zeta_s)^{2s}}\,\hat{k}_{\lambda-l_1-l_2-\tau+s+\frac{3}{2}}(R\,\zeta_s). \tag{41}$$

Inserting this representation into (39), we simplify and develop that

$$\mathcal{I}_2^{(\alpha,\beta)} = \frac{\sqrt{\pi}\,\zeta_1^{l_1}\,\zeta_2^{l_2}\,\zeta_s^{l_1+l_2-1}\,R^{2l_1+2l_2-3}}{4^{n_1+l_1+n_2+l_2}\,(n_1+l_1)!\,(n_2+l_2)!} \sum_{l=l_{\min,2}}^{l_1+l_2} 2^{-l}\,\langle l_1m_1|l_2m_2|lm_1-m_2\rangle$$
$$\times \sum_{m_3=-1}^{1} \sum_{m_4=-1}^{1} (-1)^{m_3}\,c_{\alpha,m_3}\,c_{\beta,m_4} \sum_{l'=l'_{\min,2}}^{2} \langle 1\,m_4|1\,m_3|l'\,m_4-m_3\rangle$$
$$\times \sum_{\lambda=\lambda_{\min,2}}^{l+l'} (R\,\zeta_s)^{-\lambda}\,\langle l'm_4-m_3|lm_1-m_2|\lambda m_4-m_3-m_1+m_2\rangle Y_{\lambda}^{m_4-m_3-m_1+m_2}(\theta_{\vec{R}},\varphi_{\vec{R}})$$
$$\times \sum_{\tau=2}^{n_1+n_2} \sum_{\varsigma=\tau_1}^{\tau_2} \frac{R^{2\tau}\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\zeta_1^{\varsigma-1}\zeta_2^{\tau-\varsigma-1}\zeta_s^{\tau}\,(\tau+l_1+l_2)_{l+1}}{(\varsigma-1)!(n_1-\varsigma)!(\tau-\varsigma-1)!(n_2-\tau+\varsigma)!\,\Gamma\left(l+\frac{3}{2}\right)}$$
$$\times \sum_{r=0}^{\eta'} \frac{\left(\frac{\eta}{2}\right)_r\left(\frac{\eta+1}{2}\right)_r}{\left(l+\frac{3}{2}\right)_r r!} \sum_{s=0}^{r+\frac{l-\lambda}{2}} \binom{r+\frac{l-\lambda}{2}}{s} \frac{2^s\,(1-l_1-l_2-\tau)_s}{(R\,\zeta_s)^{2s}}\,\hat{k}_{\lambda-l_1-l_2-\tau+s+\frac{3}{2}}(R\,\zeta_s). \tag{42}$$

4. Numerical discussion

Table 1 shows the evaluation of the integral $\tilde{\mathcal{I}}_1^{(\alpha,\beta)}$ and table 2 shows the evaluation of the integral $\tilde{\mathcal{I}}_2^{(\alpha,\beta)}$ for physically plausible parameters. The values listed as $\tilde{\mathcal{I}}_1^{(\alpha,\beta)}$ are obtained using the right-hand side of expression (34) and $\tilde{\mathcal{I}}_2^{(\alpha,\beta)}$ are obtained using the right-hand side of expression (41). The values listed as Maple 11 were obtained using the Maple evalf command applied directly to the semi-infinite integral representations of $\tilde{\mathcal{I}}_1^{(\alpha,\beta)}$ and $\tilde{\mathcal{I}}_2^{(\alpha,\beta)}$. As it can be

Table 1. Evaluation of $\tilde{\mathcal{I}}_1^{(\alpha,\beta)}$ of equation (34).

l	r	l_1	l_2	τ	ζ_s	$\tilde{\mathcal{I}}_1^{(\alpha,\beta)}$	Maple 11
0	0	1	0	2	0.1	0.196 349 540 849 3621(3)	0.196 349 540 849 3621(3)
0	1	2	1	3	0.1	0.184 077 694 546 2769(6)	0.184 077 694 546 2769(6)
0	0	3	0	4	1.0	0.322 135 965 455 9846(−1)	0.322 135 965 455 9847(−1)
0	1	4	1	5	1.0	0.342 748 832 293 1979(−2)	0.342 748 832 293 1980(−2)
2	0	0	1	2	1.0	0.589 048 622 548 0862(0)	0.589 048 622 548 0862(0)
2	1	1	2	3	1.0	0.184 077 694 546 2769(−1)	0.184 077 694 546 2769(−1)
2	2	0	3	2	10.0	0.429 514 620 607 9795(−1)	0.429 514 620 607 9795(−1)

Table 2. Evaluation of $\tilde{\mathcal{I}}_2^{(\alpha,\beta)}$ of equation (41).

l	r	l_1	l_2	τ	ζ_s	λ	R	$\tilde{\mathcal{I}}_2^{(\alpha,\beta)}$	Maple 11
0	0	1	0	2	0.1	0	0.1	0.196 339 788 577 3828(3)	0.196 339 788 577 3828(3)
0	1	2	1	3	0.1	2	1.0	0.122 514 417 148 3751(3)	0.122 514 417 148 3751(3)
0	0	3	0	4	1.0	0	0.1	0.321 957 064 925 3009(−1)	0.321 957 064 925 3011(−1)
0	1	4	1	5	1.0	2	1.0	0.839 979 613 391 3563(−4)	0.839 979 613 391 3561(−4)
2	0	0	1	2	1.0	0	1.0	0.144 465 918 723 8652(0)	0.144 465 918 723 8652(0)
2	1	1	2	3	1.0	2	10.0	−0.427 141 402 832 3236(−4)	−0.427 141 402 832 3236(−4)
2	2	0	3	2	10.0	4	1.0	−0.222 856 384 086 4297(−5)	−0.222 856 384 086 4297(−5)

Table 3. Evaluation of $\mathcal{I}_1^{(x,y)}$ of equation (35).

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	$\mathcal{I}_2^{(x,y)}$
2	1	−1	2.0	2	1	−1	1.5	0.844 938 515 752 529(−3)
2	1	0	2.0	2	1	0	1.5	0.197 895 122 059 999(−3)
3	2	−1	2.0	2	1	−1	1.5	−0.183 961 338 177 373(−4)
3	2	1	2.0	3	2	1	1.5	0.314 124 180 426 832(−4)
3	2	2	2.0	3	2	2	1.5	0.132 485 365 811 557(−3)
4	2	1	2.0	2	1	1	1.5	−0.361 569 492 726 092(−4)
4	2	1	2.0	3	2	1	1.5	0.764 186 724 377 223(−4)
4	2	2	2.0	3	2	2	1.5	0.331 525 812 542 680(−3)
4	2	0	2.0	4	2	0	1.5	−0.297 315 128 733 290(−4)
4	2	1	2.0	4	2	1	1.5	0.215 564 810 358 993(−3)
4	2	2	2.0	4	2	2	1.5	0.951 453 780 055 960(−3)

seen from tables 1 and 2, the expressions obtained from Cauchy's residue theorem are capable of attaining high accuracy.

In tables 3 and 4, we present values for the integrals $\mathcal{I}_1^{(\alpha,\beta)}$ of equation (35). In table 3, we have $\alpha = x$ and $\beta = y$ and in table 4, we have $\alpha = x$ and $\beta = z$.

In tables 5–7, we present values for the integrals $\mathcal{I}_2^{(\alpha,\beta)}$ of equation (42). In table 5, we have $\alpha = x$ and $\beta = y$. In table 6, we have $\alpha = x$ and $\beta = z$ and in table 7, we have $\alpha = y$ and $\beta = z$.

Table 4. Evaluation of $\mathcal{I}_1^{(x,z)}$ of equation (35).

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	$\mathcal{I}_2^{(x,y)}$
3	2	2	2.0	2	1	1	1.5	0.821 954 698 577 322(−3)
3	2	1	2.0	3	2	0	1.5	0.115 820 024 850 022(−3)
3	2	−1	2.0	3	2	−2	1.5	−0.511 114 095 358 989(−3)
3	2	2	2.0	3	2	1	1.5	0.738 528 227 838 956(−3)
4	3	2	2.0	3	2	1	1.5	0.684 887 168 407 806(−4)
4	3	3	2.0	3	2	2	1.5	0.465 714 740 331 515(−3)
4	3	3	2.0	4	3	2	1.5	0.487 915 417 374 633(−4)
5	4	2	2.0	4	3	3	1.5	0.172 192 762 141 693(−3)
5	4	2	2.0	4	3	1	1.5	0.949 043 394 880 123(−3)
5	4	4	2.0	4	3	3	1.5	0.245 308 514 529 775(−2)
5	4	3	2.0	4	3	2	1.5	0.312 594 481 860 128(−2)
5	4	4	2.0	4	3	3	1.5	0.476 597 518 466 772(−2)
6	5	2	2.0	5	3	3	1.5	0.258 993 584 962 462(−2)
6	5	3	2.0	5	3	2	1.5	0.147 851 833 602 632(−1)
6	5	5	2.0	5	4	4	1.5	0.209 404 505 361 548(−2)

Table 5. Evaluation of $\mathcal{I}_2^{(x,y)}$ of equation (42). $\zeta_1 = 1.0$, $\zeta_2 = 1.5$, $\vec{R} = (1.5, 75°, 0°)$ in spherical coordinates.

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	$\mathcal{I}_2^{(x,y)}$
2	1	1	1.0	2	1	−1	1.5	−0.434 843 064 459 248(0)
3	2	1	1.0	2	1	−1	1.5	−0.864 738 363 581 576(−2)
3	2	1	1.0	2	1	1	1.5	0.480 104 782 258 312(−1)
3	2	1	1.0	3	2	−1	1.5	−0.163 214 465 381 496(2)
3	2	2	1.0	3	2	−2	1.5	0.410 633 175 483 623(−1)
3	2	2	1.0	3	2	−1	1.5	−0.110 224 669 992 678(−1)
3	2	2	1.0	3	2	1	1.5	0.109 871 879 056 160(−1)
4	2	1	1.0	2	1	−1	1.5	−0.111 977 101 298 055(−1)
4	2	2	1.0	3	2	−2	1.5	0.598 123 871 812 077(−1)
4	2	2	1.0	3	2	−1	1.5	−0.160 487 351 821 931(−1)
4	2	2	1.0	3	2	1	1.5	0.160 078 508 905 662(−1)
4	2	2	1.0	4	2	−2	1.5	0.489 662 959 894 970(0)
4	2	2	1.0	4	2	−1	1.5	−0.131 339 439 243 965(0)
4	2	2	1.0	4	2	1	1.5	0.131 082 624 218 578(0)
4	3	2	1.0	4	2	1	1.5	0.135 727 821 381 524(2)

For the numerical evaluation of Gaunt coefficients which occur in the complete expressions of the integrals under consideration, we use the subroutine GAUNT.F developed by Weniger *et al* [38]. The spherical harmonics $Y_l^m(\theta, \varphi)$ are computed using the recurrence formulae presented in [38].

In all tables, the numbers in parentheses represent powers of 10.

Table 6. Evaluation of $\mathcal{I}_2^{(x,z)}$ of equation (42). $\zeta_1 = 1.0$, $\zeta_2 = 1.5$, $\vec{R} = (1.5, 75°, 0°)$ in spherical coordinates.

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	$\mathcal{I}_2^{(x,z)}$
2	1	1	1.0	2	1	−1	1.5	−0.993 394 591 541 964(−3)
3	2	1	1.0	2	1	−1	1.5	−0.321 257 181 375 785(−1)
3	2	1	1.0	2	1	1	1.5	0.868 646 553 961 828(−2)
3	2	1	1.0	3	2	−1	1.5	−0.220 418 082 414 166(−1)
3	2	2	1.0	3	2	−2	1.5	0.393 822 816 223 339(−4)
3	2	2	1.0	3	2	−1	1.5	−0.205 475 160 983 857(−1)
3	2	2	1.0	3	2	1	1.5	0.163 419 882 900 283(2)
4	2	1	1.0	2	1	−1	1.5	−0.416 483 489 210 977(−1)
4	2	2	1.0	3	2	−2	1.5	0.443 153 951 881 734(−4)
4	2	2	1.0	3	2	−1	1.5	−0.299 240 326 968 214(−1)
4	2	2	1.0	3	2	1	1.5	0.291 681 304 465 606(2)
4	2	2	1.0	4	2	−2	1.5	0.270 308 611 383 939(−3)
4	2	2	1.0	4	2	−1	1.5	−0.244 940 259 990 155(0)
4	2	2	1.0	4	2	1	1.5	0.297 907 579 119 817(3)
4	3	2	1.0	4	2	1	1.5	0.729 667 633 180 134(1)

Table 7. Evaluation of $\mathcal{I}_2^{(y,z)}$ of equation (42). $\zeta_1 = 1.0$, $\zeta_2 = 1.5$, $\vec{R} = (1.5, 75°, 0°)$ in spherical coordinates.

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	$\mathcal{I}_2^{(y,z)}$
2	1	1	1.0	2	1	−1	1.5	−0.980 852 389 239 356(−3)
3	2	1	1.0	2	1	−1	1.5	−0.319 537 014 904 337(−1)
3	2	1	1.0	2	1	1	1.5	0.858 668 805 557 491(−2)
3	2	1	1.0	3	2	−1	1.5	−0.219 369 423 462 985(−1)
3	2	2	1.0	3	2	−2	1.5	0.391 684 472 826 858(−4)
3	2	2	1.0	3	2	−1	1.5	−0.204 743 121 872 522(−1)
3	2	2	1.0	3	2	1	1.5	0.163 009 587 528 461(2)
4	2	1	1.0	2	1	−1	1.5	−0.414 819 029 773 496(−1)
4	2	2	1.0	3	2	−2	1.5	0.441 086 792 217 064(−4)
4	2	2	1.0	3	2	−1	1.5	−0.298 416 140 021 138(−1)
4	2	2	1.0	3	2	1	1.5	0.291 083 584 089 616(2)
4	2	2	1.0	4	2	−2	1.5	0.269 289 153 349 077(−3)
4	2	2	1.0	4	2	−1	1.5	−0.244 437 213 263 127(0)
4	2	2	1.0	4	2	1	1.5	0.297 418 176 922 208(3)
4	3	2	1.0	4	2	1	1.5	0.727 410 965 270 183(1)

5. Conclusion

In this paper we show that the Fourier integral transformation can be applied for the analytical development of integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor using ETFs as a basis set of atomic orbitals. These analytic expressions obtained for the one- and two-center integrals, involve semi-infinite integrals. Cauchy's residue theorem is used in the final developments of the analytical expressions, which are shown to be accurate to machine precision.

The numerical results obtained with the algorithms described in the present work for integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor over STFs show that it does not seem impossible to envisage that ETFs or related functions may compete with GTFs in accurate and rapid calculations of the NMR properties of molecules in the near future.

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