ORIGINAL PAPER

Integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor

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Abstract   Of the nuclear magnetic resonance (MMR), the nuclear shielding tensor is of a great interest. The relativistic calculation of the nuclear shielding tensor involves extremely challenging integrals of first and second order. Among the first order integrals are paramagnetic contribution integrals, which are extremely difficult to evaluate analytically and numerically, especially when using exponential type functions (ETFs). The main difficulty in the analytical development arises from the presence of $1/r^5$ in the operators. In the present contribution, we developed the Fourier transform of the operators of the paramagnetic contribution and we used the Fourier integral transformation to derive analytic expressions for the integrals under consideration over ETFs. The main difficulty in the numerical treatment of the obtained analytic expressions arises from the presence of highly oscillatory spherical Bessel integrals. Extrapolation methods and nonlinear transformations are used to develop highly accurate algorithms for the numerical evaluation of the integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor.

Keywords   Magnetic properties of molecules · Nuclear shielding tensor · Fourier integral transformations · Extrapolation methods · Nonlinear transformations · Numerical integration

1 Introduction

The computation of NMR parameters for any of the standard models of quantum chemistry constitutes an important challenge [1–11]. The heavy atoms requires the

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inclusion of the relativistic effects in order to correctly account for their magnitude and this gives raise to new parameters, which do not appear in the non-relativistic Hamiltonian. Calculations involving a magnetic field should preserve gauge invariance. This is conveniently accomplished by using gauge including atomic orbitals (GIAO) [4], which is based on atom-centered basis functions with an explicit field dependence. NMR properties are sensitive to the quality of the basis set due to many contributing physical phenomena arising from both the vicinity of the nucleus and from the valence region. This is why it is highly desirable to use ETFs as a basis set of atomic orbitals.

Since the NMR parameters are obtained as derivatives of the electronic energy, one should be able to extract these parameters using numerical differentiation of the electronic energy. This approach is known as the finite-perturbation (FP) method [7]. Although some ab initio FP calculations of NMR parameters have been reported in the literature [12] analytic rather than numerical differentiation has to be used in such calculations, since the numerical differentiation is known to be very unstable for higher-order derivatives. Analytic treatment of the aforementioned operators over GTFs was a subject of many articles (see for example [8]) and although, the interest of using ETFs in the computation of NMR parameters is increasing [9–11], no effort was dedicated to their analytic treatment over ETFs. Straightforward numerical integration was used for the computation of integrals associated with these parameters.

The main difficulty in the analytic development of NMR parameters arises from the operators associated with these parameters, which in the case of the paramagnetic contribution in the relativistic calculation are given by $3\, r_{jN,\beta}\, \left(\vec{r}_{jN} \cdot \vec{\sigma}(j)\right)/r_{jN}^5$, where β represents a cartesian coordinates, $\vec{r}_{jN}$ is the vector separating the jth electron and the Nth nuclei and σ stands for Pauli spin matrix. These operators lead to extremely complicated integrals.

The present work is concerned with the analytical development of integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor as well as their numerical evaluation. For the analytical development, we used the Fourier transform method [13–15] combined with B functions [16–18], due to the fact that their Fourier transforms are of exceptional simplicity among ETFs [19]. The Rayleigh expansion of the plane wave functions and practical properties of spherical harmonics are also used leading to analytic expressions for integrals of first order magnetic properties of molecules. This method was applied successfully to integrals of second order involved in the non-relativistic calculation of the shielding tensor [20].

The obtained analytic expressions turned out to be similar to those obtained for the so-called three-center nuclear attraction integrals (zeroth order integrals). The latter were the subject of significant research [21–31]. The analytic expressions involve highly oscillatory spherical Bessel integral functions, which are the source of severe computational difficulties in the accurate and rapid numerical evaluation of the integrals under consideration. In previous work [27–31], we demonstrated the superiority of the combination of the S transformation [27] and the nonlinear $\bar{D}$ [32] and G [33] transformations, in the evaluation of this kind of semi-infinite oscillatory integrals compared with classical methods.

In this work, we developed FORTRAN programs based on the use of the combination of S and $\bar{D}$ and the numerical tables clearly illustrate the efficacy of this method. For more details on this method and the algorithms, we send the readers to [27,28].

2 Definitions and basic properties

The functions $B_{n,l}^m(\zeta, \vec{r})$ are defined by [16,17]:

$$B_{n,l}^m(\zeta, \vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!} \hat{k}_{n-\frac{1}{2}}(\zeta r) \, Y_l^m(\theta_{\vec{r}}, \varphi_{\vec{r}}), \tag{1}$$

where n, l, and m are the quantum numbers, $Y_l^m(\theta, \varphi)$ is the surface spherical harmonic [34] and $\hat{k}_{n-\frac{1}{2}}(z)$ stands for the reduced spherical Bessel function of the second kind and is given by [16,18].

The B function can only be used as a basis functions of atomic orbitals if $n \in \mathbb{N}$ holds. For $-l \le n \le 0$, a B function is singular at the origin, and if $n = -l - \nu$ with $\nu \in \mathbb{N}$ holds, then a B function is no longer a function in the sense of classical analysis but a derivation of the 3-dimensional Dirac delta function [35].

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

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

The Fourier transform $\bar{B}_{n,l}^m(\zeta, \vec{p})$ of $B_{n,l}^m(\zeta, \vec{r})$ is given by [19]:

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

Gaunt coefficients are defined by [36,37]:

$$\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle = \int\limits_{\theta=0}^{\pi} \int\limits_{\varphi=0}^{2\pi} [Y_{l_1}^{m_1}(\theta, \varphi)]^* \, Y_{l_2}^{m_2}(\theta, \varphi) \, Y_{l_3}^{m_3}(\theta, \varphi) \, \sin(\theta) \, d\theta \, d\varphi. \tag{4}$$

The Gaunt coefficients linearize the product of two spherical harmonics:

$$\left[Y_{l_1}^{m_1}(\theta, \varphi) \right]^* Y_{l_2}^{m_2}(\theta, \varphi) = \sum_{l=l_{\min},2}^{l_1+l_2} \langle l_2 m_2 | l_1 m_1 | l\, m_2 - m_1 \rangle \, Y_l^{m_2-m_1}(\theta, \varphi), \tag{5}$$

where the summation index l runs in steps of 2 from l_{min} to $l_1 + l_2$. The constant l_{min} is given by [37]:

$$l_{min} = \begin{cases} \max(|l_1 - l_2|, |m_2 - m_1|) & \text{if } l_1 + l_2 + \max(|l_1 - l_2|, |m_2 - m_1|) \text{ is even} \\ \max(|l_1 - l_2|, |m_2 - m_1|) + 1 & \text{if } l_1 + l_2 + \max(|l_1 - l_2|, |m_2 - m_1|) \text{ is odd.} \end{cases} \tag{6}$$

The orthogonality relations between spherical harmonics is defined by:

$$\int_0^\pi \int_0^{2\pi} [Y_{l_1}^{m_1}(\theta, \varphi)]^* Y_{l_2}^{m_2}(\theta, \varphi) \, \sin(\theta) \, d\theta \, d\varphi = \delta_{l_1 l_2} \delta_{m_1 m_2} \quad \text{and}$$

$$\int_0^\pi \int_0^{2\pi} Y_l^m(\theta, \varphi) \, \sin(\theta) \, d\theta \, d\varphi = \delta_{l0} \delta_{m0}, \tag{7}$$

where δ stands for the Dirac delta function.

A useful property of spherical harmonics is given by:

$$Y_l^m(\theta, \varphi) = (-1)^m \left[Y_l^{-m}(\theta, \varphi) \right]^*. \tag{8}$$

The normalized STFs are defined according to the following relationship [38]:

$$\chi_{n,l}^m(\zeta, \vec{r}) = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} \, r^{n-1} \, e^{-\zeta r} \, Y_l^m(\theta_{\vec{r}}, \varphi_{\vec{r}}). \tag{9}$$

STFs can be expressed as finite linear combinations of B functions [17]:

$$\chi_{n,l}^m(\zeta, \vec{r}) = \sqrt{\frac{2^{2n+1} \zeta^3}{(2n)!}} \sum_{p=\tilde{p}}^{n-l} \frac{(-1)^{n-l-p} 2^{2p+2l-n} (l+p)!}{(2p-n+l)!(n-l-p)!} \, B_{p,l}^m(\zeta, \vec{r}), \tag{10}$$

where $\tilde{p} = \frac{n-l}{2}$ if $n - l$ is even or $\tilde{p} = \frac{n-l+1}{2}$ if $n - l$ is odd.

The Rayleigh expansion of the plane wave functions is given by [39]:

$$e^{\pm i \vec{k} \cdot \vec{r}} = 4\pi \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} (\pm i)^l \, [Y_l^m(\theta_{\vec{k}}, \varphi_{\vec{k}})]^* \, Y_l^m(\theta_{\vec{r}}, \varphi_{\vec{r}}) \, j_l(k\,r), \tag{11}$$

where $j_\lambda(x)$ stands for the spherical Bessel function of order $\lambda \in \mathbb{N}_0$ [40].

The Fourier integral representation of the Coulomb operator is given by [41]:

$$\frac{1}{|\vec{r}|} = \frac{1}{2\pi^2} \int_{\vec{k}} \frac{e^{-i\vec{k} \cdot \vec{r}}}{k^2} \, d\vec{k}. \tag{12}$$

The cartesian coordinates r_u for $u \in \{x, y, z\}$ of a vector $\vec{r}$ can be expressed in terms of spherical polar coordinates and their complex conjugates as follow:

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

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

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

3 Relativistic formulation of NMR shielding tensor

One of the crucial tasks of quantum mechanics is to solve the non-relativistic, time-independent Schrödinger equation, which is given by:

$$\mathcal{H}_T \, \Psi = E_T \, \Psi, \tag{15}$$

where Ψ stands for the wave function depending on electronic and nuclear coordinates, $\mathcal{H}_T$ is the Hamiltonian operator and E_T is the energy of the system as the eigenvalue. For the system of n electrons and N nuclei the general Hamiltonian (in the absence of magnetic or electric fields) is given by:

$$\mathcal{H}_T = -\sum_{A=1}^{N} \frac{\nabla_A^2}{2M_A} - \sum_{i=1}^{n} \frac{\nabla_i^2}{2} - \sum_{i=1}^{n}\sum_{A=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{A=1}^{N}\sum_{B<A}^{N} \frac{Z_A Z_B}{R_{AB}} + \sum_{i=1}^{n}\sum_{i<j}^{n} \frac{1}{r_{ij}}, \tag{16}$$

where 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. M_A stands for the mass of the nucleus A.

The Hamiltonian consists of five basic contributions: the kinetic energy of the electrons and nuclei, the attractive electrostatic interaction between the electrons and the nuclei, and the inter-electronic and internuclear repulsive interactions.

To decouple electronic and nuclear motion, we use the Born–Oppenheimer approximation, which is based on the fact that nuclei move much slower compared to electrons and that electrons respond instantaneously to the nuclear motion. In consequence the electronic energies are computed for the fixed nuclear positions. The general Hamiltonian (16) is then reduced to the electronic Hamiltonian and Eq. (15) is reduced to the pure electronic problem:

$$\mathcal{H}_e \, \Psi_e = E_e \, \Psi_e, \tag{17}$$

which depends only on the nuclear coordinates R_A. The electronic Hamiltonian $\mathcal{H}_e$ is obtained from $\mathcal{H}_T$ by leaving out the nuclear kinetic energy and internuclear repulsion terms and is given by:

$$\mathcal{H}_e = -\sum_{i=1}^{n} \left[\frac{1}{2}\nabla_i^2 + V(i) \right] + \sum_{i=1}^{n}\sum_{i<j}^{n} \frac{1}{r_{ij}} \quad \text{with} \quad V(i) = \sum_{A=1}^{N} \frac{Z_A}{r_{iA}}. \tag{18}$$

In the presence of an external uniform magnetic field $\vec{B}_0$, the electronic non-relativistic Hamiltonian is given by:

$$\mathcal{H} = \sum_{i=1}^{n} \left[\frac{1}{2}\vec{p}_i^{\,2} + V(i) + \sum_{i<j}^{n} \frac{1}{r_{ij}} \right], \tag{19}$$

where the electronic impulsion $\vec{p}_j$ is given by:

$$\vec{p}_i = \left[-i\,\vec{\nabla}_i + e\,\vec{A}_i \right] \quad \text{where} \quad \vec{A}_i = \frac{1}{2}\left(\vec{B}_0 \wedge \vec{r}_{i0} \right) + \frac{\mu_0}{4\pi}\sum_{N} \frac{\vec{\mu}_N \wedge \vec{r}_{iN}}{r_{iN}^3}, \tag{20}$$

where $\vec{A}_i$ stands for the vector potential induced by the nuclear moments $\vec{\mu}_N$ and the external uniform magnetic field $\vec{B}_0$. μ_0 stands for dielectric permittivity.

Accepting such a form of the Hamiltonian we implicitly neglect the relativistic effects (normally negligible for the first 3 rows in the periodic table, i.e. $Z < 36$, but important for the fourth and fifth rows and for transitions metals [6]. 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:

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(r)} + \mu_{N,\alpha}\mathcal{H}_\alpha^{(0,1)} + B_{0,\beta}\mathcal{H}_\beta^{(1,0)} + \mu_{N,\alpha}B_{0,\beta}\mathcal{H}_{\alpha\beta}^{(1,1)}$$
$$+ \mu_{N,\alpha}\mu_{N,\beta}\mathcal{H}_{\alpha\beta}^{(0,2)} + B_{0,\alpha}B_{0,\beta}\mathcal{H}_{\alpha\beta}^{(2,0)} + \cdots, \tag{21}$$

where $\mathcal{H}^{(0)}$ is the zeroth-order Hamiltonian (18) and $\mathcal{H}^{(r)}$ is the relativistic perturbation term, which is independent of the magnetic perturbations and is given by [42]:

$$\mathcal{H}^{(r)} = \sum_{j<k}^{n} \left[\mathcal{H}_{1,j}^{(r)} + \mathcal{H}_{2,j}^{(r)} + \mathcal{H}_{3,j}^{(r)} + \mathcal{H}_{4,j}^{(r)} + \mathcal{H}_{5,j}^{(r)} \right], \tag{22}$$

which include the contributions; $\mathcal{H}_{1,j}^{(r)}$: two-electron Darwin term, $\mathcal{H}_{2,j}^{(r)}$: two-electron spin-orbit term, $\mathcal{H}_{3,j}^{(r)}$: the retarded orbit-orbit term, $\mathcal{H}_{4,j}^{(r)}$: spin-other-orbit term and $\mathcal{H}_{5,j}^{(r)}$: spin-spin term.

The perturbations $\mathcal{H}_\alpha^{(0,1)}$, $\mathcal{H}_\beta^{(1,0)}$ and $\mathcal{H}_{\alpha\beta}^{(1,1)}$ are given by [42]:

$$
\mathcal{H}_\alpha^{(0,1)} = \left(\frac{\partial \mathcal{H}}{\partial \mu_{N,\alpha}}\right)_{\{\vec{\mu}_N=\vec{0},\vec{B}_0=\vec{0}\}} = \frac{\mu_0}{2\pi} \sum_{j=1}^{n} \frac{\vec{l}_{jN,\beta}}{r_{jN}^3}
$$

$$
+ \frac{\mu_0}{4\pi} \underbrace{\sum_{j=1}^{n} \left[\frac{8\pi}{3} \delta(\vec{r}_{jN})\sigma_\beta(j) - \frac{\sigma_\beta(j)}{r_{jN}^3} + 3 r_{jN,\beta} \frac{\vec{r}_{jN} \cdot \vec{\sigma}(j)}{r_{jN}^5} \right]}_{\text{relativistic term}} \qquad (23)
$$

$$
\mathcal{H}_\beta^{(1,0)} = \left(\frac{\partial \mathcal{H}}{\partial B_{0,\beta}}\right)_{\{\vec{\mu}_N=\vec{0},\vec{B}_0=\vec{0}\}} = \frac{1}{2} \sum_{j=1}^{n} \vec{l}_{j0,\beta} + \underbrace{\frac{1}{2} \sum_{j=1}^{n} \sigma_\beta(j)}_{\text{relativistic term}} \qquad (24)
$$

$$
\mathcal{H}_{\alpha\beta}^{(1,1)} = \left(\frac{\partial^2 \mathcal{H}}{\partial \mu_{N,\alpha} \partial B_{0,\beta}}\right)_{\{\vec{\mu}_N=\vec{0},\vec{B}_0=\vec{0}\}} = \frac{\mu_0}{8\pi} \sum_{j=1}^{n} \frac{\vec{r}_{j0} \cdot \vec{r}_{jN}\delta_{\alpha\beta} - r_{jN,\alpha} r_{j0,\beta}}{r_{jN}^3},
$$

$$
\qquad (25)
$$

where $\vec{l}_{jX} = -i\left(\vec{r}_{jX} \wedge \vec{\nabla}_j\right)$, $\vec{l}_{j0} = -i\left(\vec{r}_{j0} \wedge \vec{\nabla}_j\right)$ and $\vec{\sigma}_j$ stands for the Pauli spin matrix of the electron j.

In order to allow gauge-origin independent calculations, we use GIAO functions ϕ_v, which are defined as follows [4,5,43]:

$$
\phi_v(\vec{B}_0) = e^{-i\frac{1}{c}(\vec{A}_v \cdot \vec{r})} \chi_v, \qquad (26)
$$

where $\vec{A}_v$ is defined in Eq. (20) where $\vec{r}_{v0} = \vec{r}_v - \vec{R}_0$ and $\vec{R}_0$ is the position of the gauge origin. The function $e^{-i\frac{1}{c}(\vec{A}_v \cdot \vec{r})}$ is the gauge factor for the real basis function and χ_v represents the atomic orbital, which in this work is a B function.

4 Fourier transformation and the analytic development of the paramagnetic integrals

Let us consider the operator, which will be referred to as L_{jN}, involved in the relativistic part of the first order perturbation $\mathcal{H}^{(0,1)}$ with respect to the nuclear moment:

$$
L_{jN} = 3r_{jN,v} \left[\frac{\vec{r}_{jN} \cdot \vec{\sigma}_j}{r_{jN}^5}\right]. \qquad (27)
$$

Let A, B and N be three arbitrary points of the euclidian space and O the origin of the fixed coordinate system. The operator L_{jN} gives rise to one electron integrals of the form:

$$\mathcal{I} = \left\langle B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_{jA}) | L_{jN} | B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB}) \right\rangle_{\vec{r}_j}$$

$$= \int \left[B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_{jA}) \right]^* 3\, r_{jN,v} \left[\frac{\vec{r}_{jN} \cdot \vec{\sigma}_j}{r_{jN}^5} \right] B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB})\, d\vec{r}_j, \qquad (28)$$

where $\vec{r}_{jA} = \vec{r}_j - \overrightarrow{OA}$, $\vec{r}_{jB} = \vec{r}_j - \overrightarrow{OB}$ and $\vec{r}_{jN} = \vec{r}_j - \overrightarrow{ON}$.

The analytic development of the above integrals is difficult due to the presence of the operator L_{jN} involving $1/r^5$, which is not the case of the usual three-center molecular integrals (zeroth order molecular integrals) where the Coulomb operator $1/r$ is involved. The Fourier transform method was applied successfully to the zeroth order molecular integrals and led to analytic expressions for these molecular integrals over B functions [15,26]. It was also successfully applied to the overlap-like quantum similarity integrals [44,45]. In [20], we also used the Fourier transform formalism for the analytic development of integrals of second orders involving the operators $\frac{\vec{r}_{j0} \cdot \vec{r}_{jN} \delta_{\alpha\beta} - r_{jN,\alpha}\, r_{j0,\beta}}{r_{jN}^3}$ (25). These integrals were expressed in terms of integrals involving the operators $\frac{Y_1^m(\theta,\varphi)}{r^2}$ for $m = -1, 0, 1$ and the Fourier transforms of the new operators were derived allowing the applicability of the Fourier transform formalism, which led to analytic expressions of the second order integrals of the shielding tensor.

In the present contribution, we derived the Fourier transforms of the operators involved in the integrals $\mathcal{I}$ (28) and we applied the Fourier transform formalism and with the help of the Rayleigh expansion of the plane wave functions (11) and practical properties of spherical harmonics, we derived analytic expressions for the integrals under consideration.

4.1 Fourier transforms of the operators

By developing the scalar product in the expression of L_{jN}, we obtain:

$$L_{jN} = 3\, r_{jN,v} \frac{\vec{r}_{jN} \cdot \vec{\sigma}_j}{r_{jN}^5} = 3\, r_{jN,v} \sum_u \sigma_{j,u} \frac{r_{jN,u}}{r_{jN}^5} = -\sum_u \sigma_{j,u} \hat{L}_{jN,uv}, \qquad (29)$$

where $u, v \in \{x, y, z\}$ and for any cartesian coordinates u and v, $\hat{L}_{jN,uv}$ is given by:

$$\hat{L}_{jN,uv} = r_{jN,v} \frac{r_{jN,u}}{r_{jN}^5} = r_{jN,v} \frac{\partial}{\partial r_{jN,u}} \left(\frac{1}{r_{jN}^3} \right). \qquad (30)$$

Now, we need to derive the Fourier transform of $\hat{L}_{jN,uv}$. In the case where u and v represent two different cartesian coordinates, the Fourier transform of $r_v \frac{\partial}{\partial r_u} \left(\frac{1}{r^3} \right)$ is given by:

$$\overline{r_v \frac{\partial}{\partial r_u} \left(\frac{1}{r^3} \right)} = (2\pi)^{-3/2} \int_{\vec{r}} e^{-i\vec{k}\cdot\vec{r}} \, r_v \frac{\partial}{\partial r_u} \left(\frac{1}{r^3} \right) d\vec{r}$$

$$= (2\pi)^{-3/2} \int_{\mathbb{R}} e^{-i k_w r_w} \int_{\mathbb{R}} r_v \, e^{-i k_v r_v}$$

$$\times \int_{\mathbb{R}} e^{-i k_u r_u} \frac{\partial}{\partial r_u} \left(\frac{1}{r^3} \right) dr_u \, dr_v \, dr_w, \qquad (31)$$

where w stands for the third cartesian coordinate.

Integrating by parts with respect to dr_u leads to:

$$\int_{\mathbb{R}} e^{-i k_u r_u} \frac{\partial}{\partial r_u} \left(\frac{1}{r^3} \right) dr_u = \left[e^{-i k_u r_u} \frac{1}{r^3} \right]_{-\infty}^{+\infty} + i k_u \int_{\mathbb{R}} e^{-i k_u r_u} \frac{1}{r^3} \, dr_u$$

$$= i k_u \int_{\mathbb{R}} e^{-i k_u r_u} \frac{1}{r^3} \, dr_u. \qquad (32)$$

By using the fact that $\frac{r_v}{r^3} = -\frac{\partial}{\partial r_v} \left(\frac{1}{r} \right)$ and integration by parts with respect to dr_v, we obtain:

$$\overline{r_v \frac{\partial}{\partial r_u} \left(\frac{1}{r^3} \right)} = (2\pi)^{-3/2} (i k_u) \int_{\mathbb{R}} e^{-i k_w r_w} \int_{\mathbb{R}} e^{-i k_u r_u} \left[\int_{\mathbb{R}} e^{-i k_v r_v} \frac{r_v}{r^3} dr_v \right] dr_u dr_w$$

$$= (2\pi)^{-3/2} (i k_u) \int_{\mathbb{R}} e^{-i k_w r_w} \int_{\mathbb{R}} e^{-i k_u r_u} \left[-i k_v \int_{\mathbb{R}} e^{-i k_v r_v} \frac{1}{r} dr_v \right] dr_u dr_w$$

$$= (2\pi)^{-3/2} k_u k_v \int_{\vec{r}} \frac{e^{-i\vec{k}\cdot\vec{r}}}{r} d\vec{r}$$

$$= \sqrt{\frac{2}{\pi}} \frac{k_u k_v}{k^2}. \qquad (33)$$

In the above development, we assumed that u and v represent two different cartesian coordinates. In the case where u and v represent the same cartesian coordinate, the development in Eq. (31) is no longer correct. For that reason, we need to derive separately the Fourier transform of $\hat{L}_{jN,uu}$. Unfortunately, the calculations leads to the potential $1/r^3$, which poses serious difficulties because of the singularity and its Fourier transform does not exist in a sense of classical analysis. This case is part of ongoing research.

4.2 Analytical development of the paramagnetic integrals over ETFs

Among the three-center integrals of the paramagnetic contribution, which are of first order, we have:

$$
\begin{aligned}
\mathcal{I}_3^{(u,v)} &= \left\langle B_{n_1,l_1}^{m_1}(\varsigma_1, \vec{r}_{jA}) \left| \hat{L}_{jN,uv} \right| B_{n_2,l_2}^{m_2}(\varsigma_2, \vec{r}_{jB}) \right\rangle_{\vec{r}} \\
&= (2\pi)^{-3/2} \int_{\vec{k}} \overline{\hat{L}_{jN,uv}} \left\langle B_{n_1,l_1}^{m_1}(\varsigma_1, \vec{r}_{jA}) \left| e^{-i\vec{k}\cdot\vec{r}_{jN}} \right| B_{n_2,l_2}^{m_2}(\varsigma_2, \vec{r}_{jB}) \right\rangle_{\vec{r}} d\vec{k} \\
&= \frac{1}{2\pi^2} \int_{\vec{k}} \frac{k_u k_v}{k^2} e^{i\vec{k}\cdot\vec{R}_1} \left\langle B_{n_1,l_1}^{m_1}(\varsigma_1, \vec{r}) \left| e^{-i\vec{k}\cdot\vec{r}} \right| B_{n_2,l_2}^{m_2}(\varsigma_2, \vec{r} - \vec{R}_2) \right\rangle_{\vec{r}} d\vec{k},
\end{aligned}
$$

(34)

where $\vec{r} = \vec{r}_{jA} = \vec{r}_j - \overrightarrow{OA}$, $\vec{R}_1 = \overrightarrow{AN}$ and $\vec{R}_2 = \overrightarrow{AB}$.

An analytic expression was obtained for $\mathcal{T}_2 = \left\langle B_{n_1,l_1}^{m_1}(\varsigma_1, \vec{r}) | e^{-i\vec{k}\cdot\vec{r}} | B_{n_2,l_2}^{m_2}(\varsigma_2, \vec{r} - \vec{R}_2) \right\rangle_{\vec{r}}$ using the Fourier transform method [15]. This expression is given by:

$$
\begin{aligned}
\mathcal{T}_2 &= \frac{(4\pi)^3 (2l_1+1)!! (2l_2+1)!! (n_1+l_1+n_2+l_2+1)! \varsigma_1^{2n_1+l_1-1} \varsigma_2^{2n_2+l_2-1}}{(n_1+l_1)! (n_2+l_2)! 2^{n_1+n_2+l_1+l_2+1}} \\
&\times \sum_{l_1'=0}^{l_1} (-i)^{l_1+l_1'} \sum_{m_1'=-l_1'}^{l_1'} \frac{\langle l_1 m_1 | l_1' m_1' | l_1 - l_1' m_1 - m_1' \rangle}{(2l_1'+1)!![2(l_1-l_1')+1]!!} \\
&\times \sum_{l_2'=0}^{l_2} (-i)^{l_2+l_2'} \sum_{m_2'=-l_2'}^{l_2'} \frac{\langle l_2 m_2 | l_2' m_2' | l_2 - l_2' m_2 - m_2' \rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!} \\
&\times \sum_{l'=l_{min}',2}^{l_1'+l_2'} (-1)^{l_1'} \langle l_2' m_2' | l_1' m_1' | l' m_2' - m_1' \rangle R_2^{l'} Y_{l'}^{m_2'-m_1'}(\theta_{\vec{R}_2}, \varphi_{\vec{R}_2}) \\
&\times \sum_{l_{12}=l_{12min},2}^{l_1-l_1'+l_2-l_2'} \langle l_2 - l_2' m_2 - m_2' | l_1 - l_1' m_1 - m_1' | l_{12} m_{12} \rangle Y_{l_{12}}^{m_{12}}(\theta_{\vec{k}}, \varphi_{\vec{k}}) \\
&\times \sum_{j=0}^{\Delta l} \frac{(-2)^j \binom{\Delta l}{j}}{(n_1+n_2+l_1+l_2-j+1)!} \\
&\times \int_{\alpha=0}^{1} \alpha^{n22} (1-\alpha)^{n11} k^{l_1-l_1'+l_2-l_2'} \frac{\hat{k}_v \left[R_2 \gamma(\alpha, k) \right]}{[\gamma(\alpha, k)]^{n_\gamma}} e^{-i(1-\alpha)\vec{k}\cdot\vec{R}_2} d\alpha,
\end{aligned}
$$

(35)

where $n_\gamma = 2(n_1+n_2+l_1+l_2)-(l_1'+l_2'+l')+1$, $m_{12} = (m_2-m_2')-(m_1-m_1')$, $\Delta l = \frac{l_1'+l_2'-l'}{2}$, $n_{11} = n_1+l_1+l_2-l_2'$, $n_{22} = n_2+l_2+l_1-l_1'$, $v = n_1+n_2+l_1+l_2-l'-j+\frac{1}{2}$ and $\gamma(\alpha, k) = \sqrt{(1-\alpha)\,\zeta_1^2 + \alpha\,\zeta_2^2 + \alpha\,(1-\alpha)\,k^2}$.

Using equations (13) and (14), we obtain the following expression:

$$
\frac{k_u\,k_v}{k^2} = \sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_4}\,c_{u,m_3}\,c_{v,m_4}
$$
$$
\times \sum_{l''=l''_{\min},2}^{2}\langle 1\,m_4|1\,m_3|l''\,m_4-m_3\rangle\left[Y_{l''}^{m_3-m_4}(\theta_{\vec{k}},\phi_{\vec{k}})\right]^*, \qquad (36)
$$

where $l''_{\min} = |m_4-m_3|$ if $|m_4-m_3|$ is even or $l''_{\min} = |m_4-m_3|+1$ if $|m_4-m_3|$ is odd.

Substituting (35) and (36) in Eq. (34) and by writing the product of $e^{i\,\vec{k}\cdot\vec{R}_1}$ by $e^{-i(1-\alpha)\vec{k}\cdot\vec{R}_2}$ as $e^{-i\,\vec{k}\cdot\left((1-\alpha)\,\vec{R}_2-\vec{R}_1\right)}$ and using Rayleigh expansion of the plane wave functions (11), we obtain the following analytic expression for $\mathcal{I}_3^{(u,v)}$:

$$
\mathcal{I}_3^{(u,v)} = \frac{4^3\pi(2l_1+1)!!(2l_2+1)!!(n_1+l_1+n_2+l_2+1)!\,\zeta_1^{2n_1+l_1-1}\,\zeta_2^{2n_2+l_2-1}}{(n_1+l_1)!(n_2+l_2)!2^{n_1+n_2+l_1+l_2+2}}\int\limits_{\vec{k}}
$$

$$
\times \sum_{l_1'=0}^{l_1}(-i)^{l_1+l_1'}\sum_{m_1'=-l_1'}^{l_1'}\frac{\langle l_1m_1\,|l_1'm_1'|\,l_1-l_1'm_1-m_1'\rangle}{(2l_1'+1)!![2(l_1-l_1')+1]!!}
$$

$$
\times \sum_{l_2'=0}^{l_2}(-i)^{l_2+l_2'}\sum_{m_2'=-l_2'}^{l_2'}\frac{\langle l_2m_2\,|l_2'm_2'|\,l_2-l_2'm_2-m_2'\rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!}
$$

$$
\times \sum_{l'=l'_{\min},2}^{l_1'+l_2'}(-1)^{l_1'}\langle l_2'm_2'\,|l_1'm_1'|\,l'm_2'-m_1'\rangle\,R_2^{l'}Y_{l'}^{m_2'-m_1'}(\theta_{\vec{R}_2},\varphi_{\vec{R}_2})
$$

$$
\times \sum_{l_{12}=l_{12min},2}^{l_1-l_1'+l_2-l_2'}\langle l_2-l_2'm_2-m_2'\,|l_1-l_1'm_1-m_1'|\,l_{12}m_{12}\rangle
$$

$$
\times \sum_{m_3=-1}^{1}\sum_{m_4=-1}^{1}(-1)^{m_4}c_{u,m_3}c_{v,m_4}\sum_{l''=l''_{\min},2}^{2}\langle 1m_4|1m_3|l''m_4-m_3\rangle Y_{l_{12}}^{m_{12}}(\theta_{\vec{k}},\varphi_{\vec{k}})
$$

$$
\times \left[Y_{l''}^{m_3-m_4}(\theta_{\vec{k}},\phi_{\vec{k}})\right]^*
$$

$$
\times \sum_{j=0}^{\Delta l}\frac{(-2)^j\binom{\Delta l}{j}}{(n_1+n_2+l_1+l_2-j+1)!}\int\limits_{\alpha=0}^{1}\alpha^{n_{22}}(1-\alpha)^{n_{11}}k^{l_1-l_1'+l_2-l_2'}
$$

$$
\times \frac{\hat{k}_v\left[R_2\gamma(\alpha,k)\right]}{[\gamma(\alpha,k)]^{n_\gamma}}
$$

$$\times 4\pi \sum_{\lambda=0}^{+\infty} \sum_{m=-\lambda}^{\lambda} (-i)^{\lambda} [Y_{\lambda}^{m}(\theta_{\vec{k}}, \varphi_{\vec{k}})]^{*} Y_{\lambda}^{m}(\theta_{\vec{v}}, \varphi_{\vec{v}}) j_{\lambda}(vk) d\alpha d\vec{k}, \tag{37}$$

where $\vec{v} = (1-\alpha)\vec{R}_2 - \vec{R}_1$.

By linearizing the product of spherical harmonics as given by Eq. (5) and using the orthogonality relations between spherical harmonics (7), we obtain:

$$\mathcal{I}_3^{(u,v)} = \frac{4^3 \pi (2l_1+1)!! (2l_2+1)!! (n_1+l_1+n_2+l_2+1)! \zeta_1^{2n_1+l_1-1} \zeta_2^{2n_2+l_2-1}}{(n_1+l_1)! (n_2+l_2)! 2^{n_1+n_2+l_1+l_2+2}}$$

$$\times \sum_{l_1'=0}^{l_1} (-i)^{l_1+l_1'} \sum_{m_1'=-l_1'}^{l_1'} \frac{\langle l_1 m_1 | l_1' m_1' | l_1 - l_1' m_1 - m_1' \rangle}{(2l_1'+1)!! [2(l_1-l_1')+1]!!}$$

$$\times \sum_{l_2'=0}^{l_2} (-i)^{l_2+l_2'} \sum_{m_2'=-l_2'}^{l_2'} \frac{\langle l_2 m_2 | l_2' m_2' | l_2 - l_2' m_2 - m_2' \rangle}{(2l_2'+1)!! [2(l_2-l_2')+1]!!}$$

$$\times \sum_{l'=l'_{\min},2}^{l_1'+l_2'} (-1)^{l_1'} \langle l_2' m_2' | l_1' m_1' | l' m_2' - m_1' \rangle R_2^{l'} Y_{l'}^{m_2'-m_1'}(\theta_{\vec{R}_2}, \varphi_{\vec{R}_2})$$

$$\times \sum_{l_{12}=l_{12min},2}^{l_1-l_1'+l_2-l_2'} \langle l_2 - l_2' m_2 - m_2' | l_1 - l_1' m_1 - m_1' | l_{12} m_{12} \rangle$$

$$\times \sum_{m_3=-1}^{1} \sum_{m_4=-1}^{1} (-1)^{m_4} c_{u,m_3} c_{v,m_4} \sum_{l''=l''_{\min},2}^{2} \langle 1 m_4 | 1 m_3 | l'' m_4 - m_3 \rangle$$

$$\times \sum_{\lambda=\lambda_{\min},2}^{l''+l_{12}} (-i)^{\lambda} < l_{12} m_{12} | l'' m_3 - m_4 | \lambda \mu > \sum_{j=0}^{\Delta l} \frac{(-2)^j \binom{\Delta l}{j}}{(n_1+n_2+l_1+l_2-j+1)!}$$

$$\times \int_{\alpha=0}^{1} \alpha^{n_{22}} (1-\alpha)^{n_{11}} Y_{\lambda}^{\mu}(\theta_{\vec{v}}, \varphi_{\vec{v}}) \left[\int_{k=0}^{+\infty} k^{n_k} \frac{\hat{k}_v [R_2 \gamma(\alpha,k)]}{[\gamma(\alpha,k)]^{n_{\gamma}}} j_{\lambda}(v k) dk \right] d\alpha, \tag{38}$$

where $\mu = m_{12} - m_3 + m_4$ and $n_k = l_1 - l_1' + l_2 - l_2' + 2$.

The analytical expressions obtained for $\mathcal{I}_3^{(u,v)}$ are similar to those obtained for the three-center nuclear attraction integrals (integrals of zeroth order). The latter were the subject of significant research [21–31]. Our approach is based on the use of extrapolation methods, which led to extremely efficient numerical algorithms for molecular integrals of zeroth order [46,28,31]. In this work, we used successfully the method combining the S and $\bar{D}$ transformations [27,28].

5 Numerical discussion

Table 1 contains values of the semi-infinite integrals involved in $\mathcal{I}_3^{(u,v)}$ (34), and which will be referred to as $\mathcal{I}_3^{(u,v)}(\alpha)$. The values chosen for α are very close to 0 or 1, and they correspond to the regions where the oscillations of the integrands become very strong. Table 2 contains values of the integral $\mathcal{I}_3^{(x,y)}$, Table 3 contains values of the integral $\mathcal{I}_3^{(x,z)}$ and Table 4 contains values of the integral $\mathcal{I}_3^{(y,z)}$.

In all the Tables, the values with the superscript $\natural$ are obtained using the following procedure. First we transformed the semi-infinite spherical Bessel integrals $\mathcal{I}_3^{(u,v)}(\alpha)$ into semi-infinite integrals with the sine function using the S transformation [27]. This reduces considerably the strong oscillations of the integrands. The semi-infinite integrals with the sine function were transformed into infinite series of finite integrals between successive positive zeros of the sine functions and these infinite series were summed to the order N_{sum} in order to obtain values with 15 correct digits.

The values with the superscript $\dagger$ were obtained using the combination of S and $\bar{D}$ transformations of order $n_{S\bar{D}}$ applied to the semi-infinite integrals $\mathcal{I}_3^{(u,v)}(\alpha)$. The recursive algorithm presented in [28] was used to compute the approximations. For more details on this method and the algorithms, we send the readers to [27,28].

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

Table 1 Evaluation of the semi-infinite integrals $\mathcal{I}_3^{(u,v)}(\alpha)$ involved in $\mathcal{I}_3^{(u,v)}$ given by Eq. (34)

α	v	n_γ	n_x	R_1	N_{sum}	$\mathcal{I}_3^{(u,v)}(\alpha)^{\natural}$	$n_{S\bar{D}}$	$\mathcal{I}_3^{(u,v)}(\alpha)^{\dagger}$	Error†
.0024	5/2	3	3	30.0	1481	.293793935102516(−4)	9	.293793935102352(−4)	.16(−16)
.0024	7/2	5	3	30.0	1369	.223021952260607(−3)	10	.223021952260772(−3)	.17(−15)
.0024	9/2	5	4	30.0	1483	.546666143805285(−3)	9	.546666143803639(−3)	.16(−14)
.0024	9/2	7	4	30.0	1308	.547651917256346(−3)	14	.547651917256671(−3)	.32(−15)
.0024	5/2	3	3	60.0	3116	.136624200908388(−5)	7	.136624200931973(−5)	.24(−15)
.0024	7/2	5	3	60.0	2877	.103712814908864(−4)	9	.103712814908869(−4)	.50(−18)
.0024	9/2	5	4	60.0	3119	.118053315515703(−4)	9	.118053315515707(−4)	.39(−18)
.0024	9/2	7	4	60.0	2746	.118266194666102(−4)	9	.118266194666103(−4)	.81(−19)
.9980	5/2	3	3	30.0	1691	.405074503240847(−3)	9	.405074503239350(−3)	.15(−14)
.9980	7/2	5	3	30.0	1496	.954699448316193(−2)	60	.954699448316229(−2)	.36(−15)
.9980	9/2	5	4	30.0	1632	.171102652053185(−1)	58	.171102652053183(−1)	.14(−15)
.9980	9/2	7	4	30.0	1356	.680328636394373(−1)	52	.680328636394371(−1)	.21(−15)
.9980	5/2	3	3	60.0	3304	.253036548695171(−4)	9	.253036548695176(−4)	.50(−18)
.9980	7/2	5	3	60.0	2918	.596368943269386(−3)	10	.596368943269434(−3)	.48(−16)
.9980	9/2	5	4	60.0	3183	.534339371342609(−3)	10	.534339371342691(−3)	.81(−16)
.9980	9/2	7	4	60.0	2638	.212460982641197(−2)	12	.212460982641216(−2)	.19(−15)

$R_2 = 4.0$, $\zeta_1 = 1.0$, $\zeta_2 = 0.5$ and $\lambda = n_k$

Table 2 Evaluation of $\mathcal{I}_3^{(x,y)}$ (38)

n_1	l_1	m_1	n_2	l_2	m_2	$\mathcal{I}_3^{(x,y)\natural}$	$\mathcal{I}_3^{(x,y)\dagger}$	Error†
2	1	−1	2	1	1	−.255465211376434(−4)	−.255465211376433(−4)	.88(−19)
2	1	1	2	1	1	.258940628151295(−4)	.258940628151293(−4)	.18(−18)
3	2	1	2	1	0	.824054485487636(−5)	.824054485487543(−5)	.93(−18)
3	2	1	2	1	1	.786543689818449(−5)	.786543689818427(−5)	.23(−18)
3	2	1	3	2	1	.121557740504221(−5)	.121557740504199(−5)	.22(−18)
3	2	1	3	2	−1	.209900301692709(−5)	.209900301692718(−5)	.85(−19)
3	2	2	3	2	−2	−.123516502840029(−5)	−.123516502840015(−5)	.14(−18)
3	2	2	3	2	1	−.171502843079710(−5)	−.171502843079671(−5)	.39(−18)
3	2	2	3	2	2	−.112511562395839(−5)	−.112511562395827(−5)	.11(−18)
4	2	−1	3	2	1	−.142347567126406(−5)	−.142347567126425(−5)	.19(−18)
4	2	1	3	2	1	.796354507361063(−6)	.796354507360856(−6)	.21(−18)
4	2	−2	3	2	−1	−.106685320260533(−5)	−.106685320260493(−5)	.39(−18)
4	2	2	3	2	2	−.631557439317437(−6)	−.631557439317352(−6)	.85(−19)
4	2	2	4	2	2	−.394449650966507(−6)	−.394449650966452(−6)	.55(−19)
4	3	1	3	2	2	.114006229974806(−6)	.114006229973778(−6)	.10(−17)

$\zeta_1 = 2.0$, $\zeta_2 = 1.0$, $\vec{R}_1 = (12.0, 90^{\mathrm{o}}, 0^{\mathrm{o}})$ and $\vec{R}_2 = (2.0, 90^{\mathrm{o}}, 0^{\mathrm{o}})$ in spherical coordinates

Table 3 Evaluation of $\mathcal{I}_3^{(x,z)}$ (38)

n_1	l_1	m_1	n_2	l_2	m_2	$\mathcal{I}_3^{(x,z)\natural}$	$\mathcal{I}_3^{(x,z)\dagger}$	Error†
2	1	−1	2	1	1	.769304745002413(−4)	.769304745002408(−4)	.51(−18)
2	1	1	2	1	1	−.620498371396542(−4)	−.620498371396534(−4)	.83(−18)
3	2	1	2	1	0	−.146444907098010(−5)	−.146444907098019(−5)	.94(−19)
3	2	1	2	1	1	−.576608712417618(−5)	−.576608712417475(−5)	.14(−17)
3	2	1	3	2	1	.137450124733107(−6)	.137450124735083(−6)	.20(−17)
3	2	1	3	2	−1	−.117106174580659(−6)	−.117106174581176(−6)	.52(−18)
3	2	2	3	2	−2	.287818321675869(−6)	.287818321676003(−6)	.13(−18)
3	2	2	3	2	1	.143900856735976(−6)	.143900856736229(−6)	.25(−18)
3	2	2	3	2	2	−.121032718682734(−5)	−.121032718682770(−5)	.36(−18)
4	2	−1	3	2	1	−.359169492307555(−6)	−.359169492307861(−6)	.31(−18)
4	2	1	3	2	1	.343245699706127(−6)	.343245699707943(−6)	.18(−17)
4	2	−2	3	2	−1	−.165515642442547(−6)	−.165515642442833(−6)	.29(−18)
4	2	2	3	2	2	−.698896446812988(−6)	−.698896446813369(−6)	.38(−18)
4	2	2	4	2	2	−.413598814661039(−6)	−.413598814661309(−6)	.27(−18)
4	3	1	3	2	2	.237743893803876(−6)	.237743893806225(−6)	.23(−17)

$\zeta_1 = 2.0$, $\zeta_2 = 1.0$, $\vec{R}_1 = (12.0, 90^{\mathrm{o}}, 0^{\mathrm{o}})$ and $\vec{R}_2 = (2.0, 90^{\mathrm{o}}, 0^{\mathrm{o}})$ in spherical coordinates

Table 4 Evaluation of $\mathcal{I}_3^{(y,z)}$ (38)

n_1	l_1	m_1	n_2	l_2	m_2	$\mathcal{I}_3^{(y,z)\natural}$	$\mathcal{I}_3^{(y,z)\dagger}$	Error†
2	1	−1	2	1	1	−.664930625197666(−4)	−.664930625197657(−4)	.84(−18)
2	1	1	2	1	1	−.813736998803535(−4)	−.813736998803530(−4)	.45(−18)
3	2	1	2	1	0	−.826812010238081(−6)	−.826812010236493(−6)	.16(−17)
3	2	1	2	1	1	−.560729081999838(−5)	−.560729081999790(−5)	.48(−18)
3	2	1	3	2	1	.118774342744955(−6)	.118774342745402(−6)	.45(−18)
3	2	1	3	2	−1	−.139118292897390(−6)	−.139118292899261(−6)	.19(−17)
3	2	2	3	2	−2	.260356340975781(−6)	.260356340976021(−6)	.24(−18)
3	2	2	3	2	1	.107457460618979(−6)	.107457460618622(−6)	.36(−18)
3	2	2	3	2	2	−.168789647401370(−5)	−.168789647401381(−5)	.11(−18)
4	2	−1	3	2	1	.360298814257210(−6)	.360298814258984(−6)	.18(−17)
4	2	1	3	2	1	.376222606858582(−6)	.376222606858951(−6)	.37(−18)
4	2	−2	3	2	−1	.127944352556904(−6)	.127944352556522(−6)	.38(−18)
4	2	2	3	2	2	−.104273111030148(−5)	−.104273111030157(−5)	.89(−19)
4	2	2	4	2	2	−.582299901671037(−6)	−.582299901671130(−6)	.93(−19)
4	3	1	3	2	2	.406466684088482(−7)	.406466684099736(−7)	.11(−17)

$\zeta_1 = 2.0$, $\zeta_2 = 1.0$, $\vec{R}_1 = (12.0, 90^{\text{o}}, 0^{\text{o}})$ and $\vec{R}_2 = (2.0, 90^{\text{o}}, 0^{\text{o}})$ in spherical coordinates

6 Conclusion

In this paper we showed that the Fourier transformation method 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. Fourier transforms of the operators involved in the aforementioned integrals were derived and with the help of the Rayleigh expansion of the plane wave functions and practical properties of spherical harmonics, analytic expressions for integrals of first order magnetic properties of molecules were obtained. These analytic expressions involve semi-infinite integrals similar to those in the expression of the so-called three-center nuclear attraction integrals over B functions for which we developed highly accurate numerical algorithms based on the combination of S and $\bar{D}$ transformations.

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