Analysis of singular operators in the relativistic calculation of magnetic molecular properties

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In the relativistic theory of magnetic molecular properties which involve the magnetic field of a magnetic nucleus, difficulties associated with the divergence of four-component Dirac spinors in the vicinity of the nucleus need be considered with care. Within the point dipole model of the nucleus, singular operators may be involved. This is the case, for instance, of the relativistic calculation of the nuclear magnetic shielding tensor and indirect spin-spin coupling tensor in the context of Kutzelnigg's minimal coupling approach. We show that matrix elements of the magnetic interaction yield divergent values for every single Fermi contact, spin dipolar, paramagnetic spin orbit, and Kutzelnigg's anisotropic Dirac's δ operator. However, when all terms are added together the divergent results cancel each other and a finite convergent result is obtained. It is concluded that Kutzelnigg's minimal coupling approach can be safely applied in the case of a point dipole model of the nucleus, and numerical results should be equivalent to those of the direct linear response approach for the operator $V=e\boldsymbol{\alpha}\cdot\mathbf{A}$. The importance of the inclusion of the anisotropic Dirac's δ operator is emphasized.

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I. INTRODUCTION

Relativistic effects on molecular magnetic properties can be of great importance in heavy-atom-containing compounds [1]. This is particularly true for properties which depend heavily on the electronic density in the vicinity of the atomic nucleus.

The correct description of such effects depends to a large extent on the proper evaluation of the electron-nucleus magnetic interaction. Both at the four-component level and within quasirelativistic two-component approaches the problem of handling properly such an interaction has subtle difficulties. For instance, in the leading-order elimination of the small component (ESC) approach, relativistic corrections to such an interaction lead to divergent operators [2,3]. Such divergent matrix elements are not involved in the calculation of the nuclear magnetic shielding tensor, and the ESC approximation has proven to be a very good one in this case [4–6]. But such divergent operators make it impossible to apply the same approximation in the case of the indirect spin-spin coupling tensor [2]. Even though spin-orbit effects can be considered, other important scalar relativistic effects cannot be properly handled in this approach. At present only the zeroth order regular approximation (ZORA) and related quasirelativistic approaches have proven to give good results of J couplings [7–10]. However, in some cases *ad hoc* nuclear models were introduced [10]. More recently promising results were obtained within the Douglas-Kroll-Hess decomposition within the point dipole model for the nucleus [11].

At the four-component level, benchmark results of magnetic shieldings and J couplings have been obtained, within linear response (second-order) perturbation theory for the operator $V=e\boldsymbol{\alpha}\cdot\mathbf{A}$ [12–14]. Matrix elements of this operator are well behaved when calculated between Dirac four-component spinors considering a point dipole moment for the nucleus. However, in such an approach the magnetic interaction operator largely couples the small and large components of Dirac spinors and the whole magnetic property is expressed formally as a second-order Rayleigh-Schrödinger perturbation theory (RSPT) energy correction.

In recent work [15], Kutzelnigg introduced a novel approach of "minimal coupling" between the large and small components with several interesting features. A separation into linear and quadratic operators describing the magnetic interaction is obtained. The linear operator closely resembles its nonrelativistic counterpart and does not couple the large and small components of 4-spinors. The quadratic operator has two terms and also closely resembles the nonrelativistic operators. In this way an interesting connection between the relativistic and nonrelativistic results is obtained. It has been argued that this procedure yields a more natural decomposition of paramagnetic and diamagnetic effects in magnetic properties [15]. These operator forms were explicitly applied in recent work by Visscher to obtain the nuclear magnetic shielding tensor [16]. However, a difficulty is found in this case when the point dipole model of the nucleus is considered: Fermi-contact- (FC-) like, paramagnetic-spin-orbit- (PSO-) like, and spin-dipolar- (SD-) like operators are obtained. But the FC operator yields divergent matrix elements for four-component spinors. This fact may introduce difficulties in the numerical evaluation of magnetic properties like the nuclear magnetic shielding and J coupling. The impossibility of its application has been pointed out [17]. Moreover, significant differences were found in numerical values between the total shieldings of the linear response and Kutzelnigg's minimal coupling approach. On the opposite side,

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it has been shown that full agreement between both methods is found at the leading order in $(Z\alpha)^2$ (α: fine structure constant) in the context of the elimination of the small-component formalism [18].

In the present work we present a thorough discussion of the divergent results occurring in the evaluation of the magnetic interaction matrix elements within Kutzelnigg's approach at the four-component level. The need of the inclusion of an extra FC-like operator in agreement with previous work [19] is discussed as well. Despite the appearence of divergent results of individual operators, the overall result is shown to be finite. Explicit formal relations are presented proving the equivalence of the total magnetic properties within different approaches. In particular, an alternative decomposition into first- and second-order RSPT expressions of magnetic properties is obtained on the basis of the Kutzelnigg's transformation. The present analysis could be useful in the search for the mentioned differences in the numerical results of both formalisms found by Visscher in the calculation of the nuclear magnetic shielding tensor. The present theoretical analysis is of general character, and conclusions are in line with recent work by Xiao *et al.* [20].

II. THEORY

A. Nonrelativistic theory

In nonrelativistic theory we can apply the minimal coupling recipe $\left(\mathbf{p}\rightarrow\mathbf{p}+\frac{e}{c}\mathbf{A}\right)$ (where $\mathbf{A}$ is the vector potential) in order to introduce the magnetic interaction to the Schrödinger Hamiltonian

$$H_0=\frac{\mathbf{p}^2}{2m}+V \tag{1}$$

to obtain the corresponding Hamiltonian for an electron within an electromagnetic field:

$$H=\frac{\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)^2}{2m}+V+\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}\quad(e>0), \tag{2}$$

where the last term is added in an *ad-hoc* manner and the Coulomb gauge is assumed. e is the absolute value of the electron charge, m its rest mass, σ the Pauli operator, and $\mathbf{B}$ is the external magnetic field. If we consider the following partition of the Hamiltonian,

$$H_0=\frac{\mathbf{p}^2}{2m}+V,$$

$$H_1=\frac{e}{mc}\mathbf{A}\cdot\mathbf{p}+\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B},$$

$$H_2=\frac{e^2}{2mc^2}\mathbf{A}^2, \tag{3}$$

we can solve the Schrödinger equation applying perturbation theory with the use of intermediate normalization, expanding it in a power series of λ, the perturbation parameter of the field:

$$H=H_0+\lambda H_1+\lambda^2H_2,$$

$$\phi=\phi_0+\lambda\phi_1+\lambda^2\phi_2+\cdots,$$

$$E=E_0+\lambda E_1+\lambda^2E_2+\cdots. \tag{4}$$

First- and second-order magnetic properties are obtained as

$$E_1=\langle\phi_0|H_1|\phi_0\rangle,$$

$$E_2=E_2^d+E_2^p,$$

$$E_2^d=\langle\phi_0|H_2|\phi_0\rangle,$$

$$E_2^p=\mathrm{Re}\langle\phi_0|H_1|\phi_1\rangle, \tag{5}$$

where Re stands for the real part of a complex quantity and ϕ_0 and ϕ_1 are solutions of

$$(H_0-E_0)\phi_0=0,$$

$$(H_0-E_0)\phi_1=-(H_1-E_1)\phi_0. \tag{6}$$

B. Relativistic theory

In relativistic theory, the Dirac Hamiltonian for a particle in an electromagnetic field is

$$D=\beta mc^2+c\boldsymbol{\alpha}\cdot\boldsymbol{\pi}+V, \tag{7}$$

where β and $\boldsymbol{\alpha}$ are the four-component Dirac matrices and $\boldsymbol{\pi}=\mathbf{p}+\frac{e}{c}\mathbf{A}$. Now the separation is

$$D_0=\beta mc^2+c\boldsymbol{\alpha}\cdot\mathbf{p}+V,$$

$$D_1=e\boldsymbol{\alpha}\cdot\mathbf{A} \tag{8}$$

and

$$D=D_0+\lambda D_1,$$

$$\psi=\psi_0+\lambda\psi_1+\cdots,$$

$$W=W_0+\lambda W_1+\lambda^2W_2+\cdots. \tag{9}$$

In order to obtain magnetic properties, the first- and second-order corrections to the energy are

$$W_1=\langle\psi_0|D_1|\psi_0\rangle,$$

$$W_2=\mathrm{Re}\langle\psi_0|D_1|\psi_1\rangle, \tag{10}$$

where the unperturbed and perturbed wave functions fulfill the intermediate normalization condition and are solutions of Eqs. (11):

$$(D_0-W_0)\psi_0=0,$$

$$(D_0-W_0)\psi_1=-(D_1-W_1)\psi_0. \tag{11}$$

Let us observe that magnetic properties which are quadratic in $\mathbf{A}$ can only come from W_2, which is formally a second-order expression. There is no close resemblence between the relativistic and nonrelativistic expressions and the diamagnetic-paramagnetic separation is not evident. In recent work an alternative approach was presented by Kutzelnigg [15] which has several interesting features. It is briefly discussed here. A unitary transformation of the Dirac Hamiltonian yielding a "minimal coupling" of large and small components of a given 4-spinor is introduced:

$$U = \exp\left(\frac{\beta}{2mc^2}\boldsymbol{\alpha}\cdot\mathbf{A}\right). \tag{12}$$

The transformed Dirac Hamiltonian, expanded up to second order in $\mathbf{A}$, is [15]

$$\tilde{D} = D_0 + \beta H_1 + \beta H_2 + \tilde{D}_2, \tag{13}$$

where H_1 and H_2 are the operators defined in Eqs. (3) and $\tilde{D}_2$ is given by

$$\tilde{D}_2 = -\frac{\{D_1,H_1\}}{4mc^2} = -\frac{e^2}{4m^2c^3}\{\boldsymbol{\alpha}\cdot\mathbf{A},\mathbf{A}\cdot\mathbf{p}\}. \tag{14}$$

In this case application of perturbation theory with the intermediate normalization condition yields the system of equations

$$\tilde{D} = D_0 + \lambda\beta H_1 + \lambda^2(\beta H_2 + \tilde{D}_2),$$

$$\tilde{\psi} = \tilde{\psi}_0 + \lambda\tilde{\psi}_1 + \cdots,$$

$$\tilde{W} = \tilde{W}_0 + \lambda\tilde{W}_1 + \lambda^2\tilde{W}_2 + \cdots, \tag{15}$$

and, therefore, first- and second-order corrections to the energy are given by

$$\tilde{W}_2 = \langle\tilde{\psi}_0|\beta H_1|\tilde{\psi}_0\rangle,$$

$$\tilde{W}_2 = \tilde{W}_2^p + \tilde{W}_2^{d1} + \tilde{W}_2^{d2},$$

$$\tilde{W}_2^{d1} = \langle\tilde{\psi}_0|\beta H_2|\tilde{\psi}_0\rangle,$$

$$\tilde{W}_2^{d2} = \langle\tilde{\psi}_0|\tilde{D}_2|\tilde{\psi}_0\rangle,$$

$$\tilde{W}_2^p = \mathrm{Re}\langle\tilde{\psi}|_0\beta H_1|\tilde{\psi}_1\rangle. \tag{16}$$

It is seen that in this case, magnetic properties which are quadratic in $\mathbf{A}$ gathered in $\tilde{W}_2$ are expressed as first- and second-order corrections to the energy in close resemblence with the nonrelativistic counterparts. The connection between this "minimal coupling" formalism and the standard "linear response" formalism at the four-component level can be established considering the transformed wave function upon the action of the unitary operator of Eq. (12). Expansion up to first order (as is required in order to evaluate W_2 and $\tilde{W}_2$) yields the following formal relation between the wave functions of the two formalisms:

$$\tilde{\psi}_0 = \psi_0,$$

$$\tilde{\psi}_1 = \psi_1 + \frac{\beta}{2mc^2}D_1\psi_0. \tag{17}$$

III. FORMAL RELATIONS CONNECTING THE STANDARD "LINEAR RESPONSE" AND MINIMAL COUPLING FORMALISMS

A unitary transformation of the Hamiltonian must yield the same results of magnetic properties, even though their formal appearence may be different, and eventually more suitable for physical interpretation. However, in four-component calculations, this equivalence will only hold if negative energy ("positronic" states) are considered on the same footing as electronic excitations. In order to verify the fulfillment of such a condition it is useful to discuss the formal relations (sum rules) connecting both formalisms. Such a relation is obtained from the unitary transformation, Eq. (12), itself [18]:

$$\begin{aligned}\frac{(W_0^{(n)} - W_0^{(i)})}{2mc^2}\langle\psi_0^{(i)}|\beta D_1|\psi_0^{(n)}\rangle &= \langle\psi_0^{(i)}|\frac{[\beta D_1, D_0]}{2mc^2}|\psi_0^{(n)}\rangle \\ &= \langle\psi_0^{(i)}|\frac{[\beta D_1, c\boldsymbol{\alpha}\cdot\mathbf{p}]}{2mc^2}|\psi_0^{(n)}\rangle \\ &\quad + \langle\psi_0^{(i)}|\frac{[\beta D_1, \beta mc^2]}{2mc^2}|\psi_0^{(n)}\rangle \\ &= \langle\psi_0^{(i)}|\beta H_1|\psi_0^{(n)}\rangle - \langle\psi_0^{(i)}|D_1|\psi_0^{(n)}\rangle,\end{aligned} \tag{18}$$

finally giving:

$$\langle\psi_0^{(i)}|D_1|\psi_0^{(n)}\rangle = \langle\psi_0^{(i)}|\frac{[D_0,\beta D_1]}{2mc^2}|\psi_0^{(n)}\rangle + \langle\psi_0^{(i)}|\beta H_1|\psi_0^{(n)}\rangle, \tag{19}$$

where $\psi_0^{(i)}$ and $\psi_0^{(n)}$ are eigenstates of the unperturbed Hamiltonian and $W_0^{(i)}$ and $W_0^{(n)}$ the corresponding energies.

The energy correction W_2 in the standard linear response approach, Eq. (10), can be explicitly evaluated as the following RSPT expression:

$$W_2^{(i)} = \sum_{n\neq i}\frac{\langle\psi_0^{(n)}|D_1|\psi_0^{(i)}\rangle\langle\psi_0^{(i)}|D_1|\psi_0^{(n)}\rangle}{W_0^{(i)} - W_0^{(n)}}, \tag{20}$$

whereas the corresponding $\tilde{W}_2$ of Kutzelnigg's formalism can be expressed as

$$\begin{aligned}\tilde{W}_2^{(i)} &= \langle\psi_0^{(i)}|\beta H_2 + \tilde{D}_2|\psi_0^{(i)}\rangle \\ &\quad + \sum_{n\neq i}\frac{\langle\psi_0^{(i)}|\beta H_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\beta H_1|\psi_0^{(i)}\rangle}{W_0^{(i)} - W_0^{(n)}}.\end{aligned} \tag{21}$$

The equivalence between both expressions can be proven making use of the result in Eq. (19). This is explicitly shown in Appendix A.

Making use of the result in Eq. (17) it can be shown that yet a third expression of the energy can be found in close connection with Kutzelnigg's transformation. The RSPT expression of the first-order corrected state in Eq. (10) is

$$|\psi_1^{(i)}\rangle = \sum_{n\neq i} |\psi_0^{(n)}\rangle \frac{\langle \psi_0^{(n)}|D_1|\psi_0^{(i)}\rangle}{W_0^{(i)} - W_0^{(n)}}. \tag{22}$$

Introducing the result, Eq. (17), the following is obtained:

$$|\tilde{\psi}_1^{(i)}\rangle = \sum_{n\neq i} |\psi_0^{(n)}\rangle \frac{\langle \psi_0^{(n)}|D_1|\psi_0^{(i)}\rangle}{W_0^{(i)} - W_0^{(n)}} + \frac{\beta}{2mc^2} D_1|\psi_0^{(i)}\rangle. \tag{23}$$

Therefore, $\tilde{W}_2$ in Eq. (16) can be written as

$$\begin{aligned}\tilde{W}_2^{(i)} &= \langle \psi_0^{(i)}|\beta H_2 - \frac{\{D_1,H_1\}}{4mc^2}|\psi_0^{(i)}\rangle + \mathrm{Re}\langle \psi_0^{(i)}|\beta H_1|\tilde{\psi}_1^{(i)}\rangle \\ &= \langle \psi_0^{(i)}|\beta H_2|\psi_0^{(i)}\rangle - \langle \psi_0^{(i)}|\frac{\{D_1,H_1\}}{4mc^2}|\psi_0^{(i)}\rangle \\ &\quad + \mathrm{Re}\langle \psi_0^{(i)}|\frac{\beta H_1 \beta D_1}{2mc^2}|\psi_0^{(i)}\rangle \\ &\quad + \mathrm{Re}\sum_{n\neq i} \frac{\langle \psi_0^{(i)}|\beta H_1|\psi_0^{(n)}\rangle\langle \psi_0^{(n)}|D_1|\psi_0^{(i)}\rangle}{W_0^{(i)} - W_0^{(n)}}.\end{aligned} \tag{24}$$

Taking into account that

$$\mathrm{Re}\langle \psi_0^{(i)}|\frac{\beta H_1 \beta D_1}{2mc^2}|\psi_0^{(i)}\rangle = \langle \psi_0^{(i)}|\frac{\{D_1,H_1\}}{4mc^2}|\psi_0^{(i)}\rangle, \tag{25}$$

we arrive at the final expression:

$$\begin{aligned}\tilde{W}_2 = W_2'^{(i)} &= \langle \psi_0^{(i)}|\beta H_2|\psi_0^{(i)}\rangle \\ &\quad + \mathrm{Re}\sum_{n\neq i} \frac{\langle \psi_0^{(i)}|\beta H_1|\psi_0^{(n)}\rangle\langle \psi_0^{(n)}|D_1|\psi_0^{(i)}\rangle}{W_0^{(i)} - W_0^{(n)}},\end{aligned} \tag{26}$$

which is an alternative expression for a second-order magnetic property. In fact, this expression is coincident to the one obtained by Szmytkowski [21] and by Kutzelnigg [15] in the context of the Gordon-Pyper decomposition [22–24] of the one-particle current density in a relativistic framework. In this expression, the first-order term is closely related to the diamagnetic nonrelativistic expression, but the second-order RSPT expression mixes different operators and, strictly speaking is not related to a first-order correction of the Hamiltonian. For a detailed proof of the equivalence see Appendix A.

IV. ANALYSIS OF DIVERGENCES IN THE CALCULATION OF MAGNETIC PROPERTIES

A. Magnetic field of an atomic nucleus

Magnetic properties which involve the magnetic field of a magnetic atomic nucleus, like the nuclear magnetic shielding or the indirect spin-spin coupling tensors, present particular difficulties. Within the standard linear response approach, matrix elements of the magnetic operator $V=e\boldsymbol{\alpha}\cdot\mathbf{A}$ between four-component Dirac spinors yield finite convergent results within the point dipole model of the nucleus. If Kutzelnigg's minimal coupling approach is followed, the operators in Eq. (13) for a magnetic point dipole contain singularities in the vicinity of the nucleus. In this section the nuclear potential and field of a point dipole nucleus at the origin are derived following the work by Kutzelnigg [25]. The following operators (which must be worked out in the "distribution" sense) are obtained (see Appendix B):

$$\mathbf{A}^{\mu} = \frac{\boldsymbol{\mu}\times\mathbf{r}}{r^3}\theta(r),$$

$$\mathbf{B}^{\mu} = \underbrace{\frac{3(\boldsymbol{\mu}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}} - \boldsymbol{\mu}}{r^3}}_{\mathbf{B}^{\mathrm{SD}}} + \underbrace{\frac{2}{3}\frac{\boldsymbol{\mu}}{r^2}\delta(r)}_{\mathbf{B}^{\mathrm{FC}}} + \underbrace{\frac{1}{3}\frac{\boldsymbol{\mu}}{r^2}\delta(r)}_{\mathbf{B}^{\mathrm{K-FC}}} - \underbrace{\frac{(\boldsymbol{\mu}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}}}{r^2}\delta(r)}_{\mathbf{B}^{\mathrm{K-SD}}}, \tag{27}$$

where

$$\theta(r) = \begin{cases} 1 & \text{for } r>0, \\ 0 & \text{for } r=0, \end{cases} \tag{28}$$

$\boldsymbol{\mu}$ is the nuclear dipole moment, and $\mathbf{r}$ is the electron position with respect to the nucleus.

It is important to remark on the presence of the third and fourth terms in Eq. (27). We will refer to both terms as the "K" term, as the eventual importance of this term in relativistic theory was pointed out in Kutzelnigg's work.

The linear operators of Kutzelnigg's formalism are those of Eqs. (13). The explicit expressions are given below [16]:

$$\beta H_1^{\mu} = \beta \mathbf{H}_1^{\mu}\cdot\boldsymbol{\mu},$$

where

$$\mathbf{H}_1^{\mu} = \mathbf{H}^{\mathrm{PSO}} + \mathbf{H}^{\mathrm{SD}} + \mathbf{H}^{\mathrm{FC}} + \mathbf{H}^{\mathrm{K\text{-}SD}} + \mathbf{H}^{\mathrm{K\text{-}FC}}, \tag{29}$$

with

$$\mathbf{H}^{\mathrm{PSO}} = \left(\frac{e}{mc}\right)\frac{\mathbf{L}}{r^3}\theta(r),$$

$$\mathbf{H}^{\mathrm{SD}} = \left(\frac{e}{mc}\right)\frac{3(\mathbf{S}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{S}}{r^3},$$

$$\mathbf{H}^{\mathrm{FC}} = \left(\frac{e}{mc}\right)\frac{2}{3}\frac{\delta(r)}{r^2}\mathbf{S}, \tag{30}$$

and also the "K" terms are included:

$$\mathbf{H}^{\mathrm{K\text{-}SD}} = -\left(\frac{e}{mc}\right)\frac{(\mathbf{S}\cdot\hat{\mathbf{r}})\hat{\mathbf{r}}}{r^3},$$

$$\mathbf{H}^{\mathrm{K\text{-}FC}} = \left(\frac{e}{mc}\right)\frac{1}{3}\frac{\delta(r)}{r^2}\mathbf{S}, \tag{31}$$

where $\mathbf{S}=\frac{\hbar}{2}\boldsymbol{\sigma}$ is the spin operator. This term combines a δ operator and a traceless second-rank tensor (in the spatial coordinates) dependence and makes no contribution in nonrelativistic theory, as will be shown explicitly.

B. Behavior of four-component Dirac spinors in the vicinity of the nucleus

The behavior of four-component Dirac spinors in the close vicinity of the nucleus has been analyzed in previous work [26,27]. In this section we present a detailed discussion in order to be able to find out the kind of divergences that will occur in the evaluation of matrix elements of Kutzelnigg's formalism. To this end the Dirac Hamiltonian for a particle in the presence of the Coulomb field of all nuclei of a molecule is considered:

$$W^{(n)}\psi^{(n)}(\mathbf{r}) = \left(\beta mc^2 + c\boldsymbol{\alpha}\cdot\mathbf{p} + \sum_K V_K\right)\psi^{(n)}(\mathbf{r}). \tag{32}$$

In the close vicinity of the magnetic nucleus of interest the relative importance of the Coulomb potential of the rest of the molecule is negligibly small and therefore the solutions in this region can be obtained from the following equation:

$$W^{(n)}\psi^{(n)}(\mathbf{r}) \underset{r\to 0}{\to} \left(\beta mc^2 + c\boldsymbol{\alpha}\cdot\mathbf{p} - \frac{Ze^2}{r}\right)\psi^{(n)}(\mathbf{r}), \tag{33}$$

where $Z=Z_N$ is the charge of the nucleus of interest and the eigenvalue $W^{(n)}$ is given by the general problem, Eq. (32). Alternatively, it can be considered that the spectrum of eigenstates of the atomic Dirac equation constitutes a complete basis set to expand any eigengstate of the molecular problem. Therefore, in what follows, we consider the atomic Dirac equation

$$W\psi(\mathbf{r}) = \left(\beta mc^2 + c\boldsymbol{\alpha}\cdot\mathbf{p} - \frac{Ze^2}{r}\right),$$

$$r < a, \quad a \to 0, \tag{34}$$

in the close vicinity of the magnetic atomic nucleus of interest. Eigenstates of the atomic problem are explicitly found in [28,29]. However, in order to discuss the general behavior in the vicinity of the nucleus the following procedure may be followed.

The general structure of the solutions is obtained considering the following operators: total angular momentum J^2, its projection on a reference z axis J_z, the total spin S^2, and the parity operator [28]:

$$\mathcal{P} = \gamma^0\pi = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\pi, \quad \text{with} \quad \pi|\mathbf{r}\rangle = -|\mathbf{r}\rangle \tag{35}$$

to write

$$\psi^k_{jm}(\mathbf{r}) = \begin{pmatrix} f_j(r)\mathcal{Y}^k_{jm}(\hat{r}) \\ \imath g_j(r)\mathcal{Y}^{-k}_{jm}(\hat{r}) \end{pmatrix}, \tag{36}$$

where $\mathcal{Y}^k_{jm}(\hat{r})$ are generalized spherical harmonics:

$$\mathcal{Y}^k_{jm}(\hat{r}) = -\,\mathrm{sgn}(k)\sqrt{\frac{k+\frac{1}{2}-m}{2k+1}}\chi^{(+)}Y_l^{m-1/2}(\hat{r}) + \sqrt{\frac{k+\frac{1}{2}+m}{2k+1}}\chi^{(-)}Y_l^{m+1/2}(\hat{r}), \tag{37}$$

where $k=\pm\left(j+\frac{1}{2}\right)$, $l=j+\frac{1}{2}$ if $k>0$ and $l=j-\frac{1}{2}$ if $k<0$. These solutions satisfy the following conditions:

$$J^2\psi^k_{jm}(\mathbf{r}) = \hbar^2 j(j+1)\psi^k_{jm}(\mathbf{r}),$$

$$J_z\psi^k_{jm}(\mathbf{r}) = \hbar m\psi^k_{jm}(\mathbf{r}),$$

$$P\gamma^0\psi^k_{jm}(\mathbf{r}) = \mathrm{sgn}(k)\psi^k_{jm}(\mathbf{r}). \tag{38}$$

In particular, making use of the relation

$$-\imath\hbar c\boldsymbol{\sigma}\cdot\boldsymbol{\nabla} = -\imath\hbar c\boldsymbol{\sigma}\cdot\hat{r}\frac{\partial}{\partial r} + \imath c\boldsymbol{\sigma}\cdot\hat{r}\frac{\boldsymbol{\sigma}\cdot\mathbf{L}}{r}, \tag{39}$$

the following is obtained:

$$\boldsymbol{\sigma}\cdot\hat{r}\mathcal{Y}^k_{jm}(\hat{r}) = -\mathcal{Y}^{-k}_{jm}(\hat{r}),$$

$$\boldsymbol{\sigma}\cdot\mathbf{L}\mathcal{Y}^k_{jm}(\hat{r}) = -\hbar(k+1)\mathcal{Y}^k_{jm}(\hat{r}). \tag{40}$$

As a consequence, the following equations must be satisfied by the reduced radial functions $f_R(\rho)$ and $g_R(\rho)$:

$$\frac{df_R}{d\rho} + \frac{k}{\rho}f_R - \left(\frac{1}{\epsilon} + \frac{Z\alpha}{\rho}\right)g_R = 0,$$

$$\frac{dg_R}{d\rho} - \frac{k}{\rho}g_R - \left(\epsilon - \frac{Z\alpha}{\rho}\right)f_R = 0, \tag{41}$$

where

$$\rho = \frac{1}{\hbar c}\sqrt{m^2c^4 - W^2}\,r, \quad \epsilon = \sqrt{\frac{mc^2 - W}{mc^2 + W}},$$

$$f_R(\rho) = \rho f(\rho), \quad g_R(\rho) = \rho g(\rho), \tag{42}$$

and $\alpha=e^2/\hbar c$. It is interesting to emphasize that following the present line of reasoning W and ϵ are imposed by the general problem. The general form of the reduced radial functions can be written as [28]:

$$f_R = A_0 P_f(\rho)\rho^\nu,$$

$$g_R = B_0 P_g(\rho)\rho^\nu, \tag{43}$$

where $P_f(\rho)$ and $P_g(\rho)$ stand for series expansions in ρ with the property

$$P_f(0) = 1, \quad P_g(0) = 1. \tag{44}$$

Inserting these forms for the solutions in Eq. (41) the following is found:

$$[A_0P_f(\nu+k) - B_0P_gZ\alpha]\rho^{\nu-1} + \left(A_0\frac{dP_f}{d\rho} - \frac{B_0P_g}{\epsilon}\right)\rho^\nu = 0,$$

$$[B_0P_g(\nu-k)+A_0P_fZ\alpha]\rho^{\nu-1}+\left(B_0\frac{dP_g}{d\rho}-A_0P_f\epsilon\right)\rho^{\nu}=0. \tag{45}$$

Multiplying by $\rho^{1-\nu}$ and setting $\rho=0$ the following equations for A_0 and B_0 are obtained:

$$A_0(\nu+k)-B_0Z\alpha=0,$$
$$B_0(\nu-k)+A_0Z\alpha=0. \tag{46}$$

In order to obtain nonzero solutions, ν must have the value

$$\nu^2-k^2+Z^2\alpha^2=0\Rightarrow\nu_k=\pm\sqrt{k^2-Z^2\alpha^2}. \tag{47}$$

It is seen that the value of ν depends on $|k|=j+\frac{1}{2}$ and the relative values of A_0 and B_0 are independent of the eigenvalue of the corresponding solution. As will be shown later, it is this relative value which plays a fundamental role to analyze the relative contributions of the large and small components to the matrix elements of interest.

Under the condition $Z<118$, only the positive root leads to normalizable solutions, and the following condition for the coefficients is found:

$$\nu_k=\sqrt{k^2-(Z\alpha)^2}. \tag{48}$$

Since

$$\frac{B_0}{A_0}=\frac{\nu_k+k}{Z\alpha}, \tag{49}$$

the general form of a solution can be written as

$$\psi^k_{jm}(\mathbf{r})=r^{\nu_k-1}\begin{pmatrix}P_f\\ -\imath\frac{\nu_k+k}{Z\alpha}P_g\sigma\cdot\hat{r}\end{pmatrix}\mathcal{Y}^k_{jm}(\hat{r}). \tag{50}$$

The complete four-component spinor is left unnormalized, as the normalization constant is not relevant for the present analysis. The behavior of ψ^k_{jm} is divergent in the vicinity of the nucleus in the case $\nu_k-1<0$—i.e., only in the case $|k|=1$.

C. Matrix elements of the magnetic interaction

In this section the evaluation of matrix elements of all operators of Eq. (29) is considered for the cases where divergent results may occur. In the region close to the nucleus the general form of a given matrix element is given by

$$\langle\psi^{k_1}_{j1,m1}|\beta\mathbf{H}^{\mu}_1|\psi^{k_2}_{j_2,m_2}\rangle_{r\le a}=\int_{0^+}^a dr\, r^{\nu_{k_1}+\nu_{k_2}}\Big(\langle\mathcal{Y}^{k_1}_{j_1,m_1}|\mathbf{H}^{\mu}_1|\mathcal{Y}^{k_2}_{j_2,m_2}\rangle-\frac{(\nu_{k_1}+k_1)(\nu_{k_2}+k_2)}{(Z\alpha)^2}\langle\mathcal{Y}^{-k_1}_{j_1,m_1}|\mathbf{H}^{\mu}_1|\mathcal{Y}^{-k_2}_{j_2,m_2}\rangle\Big). \tag{51}$$

For all operators in Eq. (29), divergent results are obtained only for the case $|k_1|=1$ and $|k_2|=1$. In such a case, $j_1=j_2=\frac{1}{2}$, $\nu_{-1}=\nu_1=\sqrt{1-(Z\alpha)^2}\equiv\nu$.

Taking into account that

$$(Z\alpha)^2=1-\nu^2, \tag{52}$$

the only matrix elements to be considered are

$$\langle\psi^{\pm1}_{1/2,m1}|\beta\mathbf{H}^{\mu}_1|\psi^{\pm1}_{1/2,m_2}\rangle_{r\le a}=\int_{0^+}^a dr\, r^{2\nu}\Big(\langle\mathcal{Y}^{\pm1}_{1/2,m_1}|\mathbf{H}^{\mu}_1|\mathcal{Y}^{\pm1}_{1/2,m_2}\rangle+\frac{\nu\pm1}{\nu\mp1}\langle\mathcal{Y}^{\mp1}_{1/2,m_1}|\mathbf{H}^{\mu}_1|\mathcal{Y}^{\mp1}_{1/2,m_2}\rangle\Big), \tag{53}$$

where $\mathbf{H}^{\mu}_1$ is given in (29). Matrix elements mixing states with $k_1=1$ and $k_2=-1$ vanish by symmetry.

The integral of the angular variables can be carried out directly making use of Wigner-Eckart theorem, as each term in $\mathbf{H}^{\mu}_1$ is a first-rank tensor. The detailed calculation is presented in Appendix C. The radial function to be integrated in all cases is one of the following:

$$h(r)=\frac{1}{r^3}\ \text{for the PSO and SD operators},$$
$$h(r)=\frac{\delta(r)}{r^2}\ \text{for the FC and "K" operators}. \tag{54}$$

In order to discuss the appearance of divergent results related to the behavior of the wave functions near the nucleus, the relevant part of the radial function to be considered is $\rho^{\nu-1}$ and the series expansion involved in $P(\rho)$ can be replaced by $P(\rho=0)=1$. The radial integral is analyzed within a sphere of fixed radius a. Therefore the following is obtained:

$$\langle\psi^{\pm1}_{1/2,m1}|\beta T^1_q h(r)|\psi^{\pm1}_{1/2,m_2}\rangle_{r\le a}=\left(\frac{e}{mc}\right)\delta_{m_1,m_2+q}\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\rangle\times\Big(\langle\tfrac{1}{2},\pm1|T^{(1)}|\tfrac{1}{2},\pm1\rangle+\frac{\nu\pm1}{\nu\mp1}\langle\tfrac{1}{2},\mp1|\times T^{(1)}|\tfrac{1}{2},\mp1\rangle\Big)\int_{0^+}^a dr\, r^{2\nu}h(r). \tag{55}$$

Such radial integrals have a divergent behavior of type

$$\int_{0^+}^a dr\, r^{2\nu}h(r)=\begin{cases}-\dfrac{1}{2(\nu-1)}[I(0^+)-I(a)] & \text{if } h(r)=\dfrac{1}{r^3},\\ I(0^+) & \text{if } h(r)=\dfrac{\delta(r)}{r^2},\end{cases} \tag{56}$$

where $I(r)$ is given by:

$$I(r)=r^{2(\nu-1)} \tag{57}$$

and $I(0^+)$ stands for the limit

$$I(0^+)=\lim_{r\to0^+}r^{2(\nu-1)}=\infty. \tag{58}$$

Strictly speaking, the above results express the relative importance of the two types of integrals. It is interesting to remark that all integrals yield divergent results and not only those involving the delta–type operator. The detailed calculation of each term is carried out in Appendix C and the overall result is:

$$\langle \psi^{\pm 1}_{1/2,m_1}|\beta\frac{L^1_q}{r^3}|\psi^{\pm 1}_{1/2,m_2}\rangle_{r\le a} = C_{m_1,q,m_2}\left(-\frac{I(0^+)-I(a)}{\nu\mp 1}\right), \tag{59}$$

$$\langle \psi^{\pm 1}_{1/2,m_1}|\beta\frac{\frac{\hbar}{2}(3(\hat r\cdot\sigma)\hat r-\sigma)^1_q}{r^3}|\psi^{\pm 1}_{1/2,m_2}\rangle_{r\le a} = C_{m_1,q,m_2}\left(-\frac{I(0^+)-I(a)}{\nu\mp 1}\right), \tag{60}$$

$$\langle \psi^{\pm 1}_{1/2,m_1}|\beta\frac{\frac{\hbar}{3}\delta(r)\sigma^1_q}{r^2}|\psi^{\pm 1}_{1/2,m_2}\rangle_{r\le a} = C_{m_1,q,m_2}\left(\frac{2}{3}\frac{\nu+2}{\nu\mp 1}I(0^+)\right), \tag{61}$$

$$\langle \psi^{\pm 1}_{1/2,m_1}|\beta\frac{-\frac{\hbar}{2}\delta(r)(\hat r\cdot\sigma)\hat r^1_q}{r^2}|\psi^{\pm 1}_{1/2,m_2}\rangle_{r\le a} = C_{m_1,q,m_2}\left(-\frac{\nu}{\nu\mp 1}I(0^+)\right), \tag{62}$$

$$\langle \psi^{\pm 1}_{1/2,m_1}|\beta\frac{\frac{\hbar}{6}\delta(r)\sigma^1_q}{r^2}|\psi^{\pm 1}_{1/2,m_2}\rangle_{r\le a} = C_{m_1,q,m_2}\left(\frac{1}{3}\frac{\nu+2}{\nu\mp 1}I(0^+)\right), \tag{63}$$

where

$$C_{m_1,q,m_2} = \left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\left\langle 1,q;\tfrac{1}{2},m_2\middle|\tfrac{1}{2},m_2+q\right\rangle}{\sqrt{3}} \tag{64}$$

and q stands for a given component of the tensor operators of Eq. (29).

As is seen, each separate term FC, PSO, SD, and "K" yields divergent results when evaluated for states with $|k|=1$. The overall matrix element, however, obtained as the sum of all such separate terms leads to a cancellation of the infinite terms. This is readily verified by adding together the coefficients of the separate results in Eqs. (59)–(63):

$$-\frac{1}{\nu\mp 1}-\frac{1}{\nu\mp 1}+\frac{2(\nu+2)}{3(\nu\mp 1)}-\frac{\nu}{\nu\mp 1}+\frac{\nu+2}{3(\nu\mp 1)}=0. \tag{65}$$

It is interesting to remark that in order to obtain such a cancellation, the role played by the extra "K" term is crucial. In recent work by Xiao *et al.* [20], a similar analysis was carried out for $1s_{1/2}$ atomic Dirac spinors. The "K" contribution was taken into account in their "FC(SS)" term.

D. Nuclear magnetic shielding tensor in Kutzelnigg's formalism

The nuclear magnetic shielding tensor can be obtained from the molecular energy in the presence of the magnetic fields of the nucleus and the uniform magnetic field of the spectrometer as

$$\sigma^{\mu}_{ij} = \frac{\partial^2 E}{\partial\mu_i\,\partial B_j}. \tag{66}$$

The operators of the nuclear magnetic field in Kutzelnigg's formalism were discussed in the previous sections. The necessary linear operator associated with the uniform magnetic field is

$$\beta H^B_1 = \beta\mathbf{H}^B_1\cdot\mathbf{B}, \tag{67}$$

where

$$\mathbf{H}^B_1 = \mathbf{H}^{OZ}+\mathbf{H}^{SZ}, \tag{68}$$

with

$$\mathbf{H}^{OZ} = \frac{e}{2mc}\mathbf{L},$$

$$\mathbf{H}^{SZ} = \frac{e}{2mc}2\mathbf{S}, \tag{69}$$

and the necessary bilinear operators in $\boldsymbol{\mu}$ and $\mathbf{B}$ are given by

$$\beta H^{\mu B}_2 = \frac{e^2}{2mc^2}\beta\boldsymbol{\mu}\cdot\frac{1r^2-\mathbf{r}\cdot\mathbf{r}}{r^3}\cdot\mathbf{B} \tag{70}$$

and (see Appendix D for details)

$$\tilde{D}^{\mu B}_2 = -\frac{e^2}{4m^2c^3}\left[\frac{(\mathbf{r}\times\boldsymbol{\alpha})\mathbf{L}+\mathbf{L}(\mathbf{r}\times\boldsymbol{\alpha})}{r^3}-\frac{\imath\hbar}{2}\left(\frac{\mathbf{r}\cdot\boldsymbol{\alpha}-\boldsymbol{\alpha}\cdot\mathbf{r}}{r^3}\right)\right], \tag{71}$$

in agreement with a previous derivation of Visscher [16]. As a consequence, the nuclear magnetic shielding tensor is expressed as

$$\boldsymbol{\sigma}^{\mu}_{\rm kutz} = \langle\tilde{\mathbf{D}}^{\mu B}_2\rangle+\langle\beta\mathbf{H}^{\mu B}_2\rangle+\langle\langle\beta\mathbf{H}^{\mu}_1;\beta\mathbf{H}^B_1\rangle\rangle. \tag{72}$$

Taking into account the discussion of the previous sections, the result of the second-order term is well defined and covergent. The "diamagnetic" contributions of the first two terms yield also finite convergent results. This is readily seen as the dependence of the two operators in the vicinity of the nucleus is $1/r^2$ in the first case and $1/r$ in the second one, and both expressions yield convergent results for Dirac four-component spinors.

E. Discussion

From the discussion in Sec. IV C it is seen that in Kutzelnigg's approach convergent matrix elements are obtained in the case of a point dipole model for the atomic nucleus, despite the appearance of FC-like operators. In fact, all operators yield divergent results. As a consequence, the separation into FC, PSO, SD, and "K" contributions becomes meaningless and only the full matrix element has a definite value. As mentioned above, this result is only obtained if the "K" term is included in the first-order operator. The following comments are worthy to mention regarding such operator. It is neglected in the usual description of the magnetic field of a point dipole nucleus. The reason is that this "distribution" operator may only give nonzero values when it is evaluated for a function with an angular dependence which does not vanish in the limit $r\to 0$. This corresponds to a function which is not continuous at $r=0$. In particular, different values are obtained by approaching $r=0$ from different directions. For all functions which are continuous and differentiable at $r=0$ the "K" term vanishes. This is the reason why it is usually not included in the magnetic field of a point dipole. But in the case of four-component Dirac spinors, the small component of $\psi^{(-)}$ is precisely the kind of function described above: near the atomic nucleus it behaves as $f(r)Y_{1m}(\hat{r})$. The correctness of the "K" term in this case can only be established by verifying that it corresponds to the correct limit of the relativistic theory for a finite nucleus, as was indicated by Kutzelnigg [19].

It is interesting to analyze the non relativistic limit of results in the previous section. In such limit $\nu=1$, and $I(0^+)$ in Eq. (58) is replaced by 1. This means only that all integrals are convergent and the relative values expressed in Eqs. (59)–(63) no longer hold. Only the state with $k=-1$ belongs to the Schrödinger spectrum as only in this case the lower part of the four-component spinor is the "small" component. It is interesting to observe that in such case the "K" term disappears, as it should. To this end we consider the addition of the two factors accompanying the "K" term:

$$-\frac{\nu}{\nu+1}+\frac{\nu+2}{3(\nu+1)}=-\frac{2(\nu-1)}{3(\nu+1)}. \tag{73}$$

It is seen that the result is zero for the non relativistic limit $\nu=1$. The leading order of this contribution has an extra factor of order $(Z\alpha)^2$ compared to the remaining ones. It is therefore shown to yield a contribution at the leading-order relativistic correction of the magnetic interaction matrix element.

V. CONCLUDING REMARKS

In the present work the relation of the standard "linear response" and Kutzelnigg's "minimal coupling" approaches to calculate molecular magnetic properties at the four-component level was analyzed. In particular, the case of properties involving a point dipole model of the atomic nucleus was studied in detail. It was explicitly shown that not only matrix elements of the FC operator, containing a δ distribution, yield divergent results, but also the PSO and SD operators do so when evaluated for four-component Dirac states with $|k|=1$. However, it was explicitly verified that there is a cancellation of such infinities when the "K" term is included and the total magnetic operator is considered together. The overall result is well defined and convergent.

As a consequence of this analysis, it is concluded that there should be full equivalence between the final result of magnetic properties in both formalisms. However, in practical numerical applications such an equivalence could only be found if electronic excitations and electron positron "rotations" are considered on equal footing, in such a way that the "sum rule" expressed in Eq. (19) is fulfilled.

The lack of the "K" term and numerical difficulties associated with the evaluation of matrix elements of the point dipole magnetic nucleus could in part explain differences found in numerical evaluation of the nuclear magnetic shielding tensor in previous work [16]. In order to avoid numerical problems associated with the divergent results in numerical applications with large but finite Gaussian basis sets, it would be very interesting to develop a method allowing one to eliminate such divergences in an *a priori* way. Recent numerical results by Xiao *et al.* [20] are very encouraging in this regard. As a final remark, we would like to point out that the "K" operators yield zero results in the nonrelativistic limit, but yield nonzero values at the leading order in $(Z\alpha)^2$. Therefore, the corresponding effects should be included in quasirelativistic two-component methods.

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APPENDIX A: EQUIVALENCE OF RSPT EXPRESSIONS OF EQS. (20) AND (21)

1. Equivalence of W_2 and $\tilde{W}_2$

The equivalence is proven by inserting the formal relation of Eq. (19) into Eq. (20):

$$\begin{aligned}
W_2^{(i)} &= \sum_{n\neq i}\frac{\langle\psi_0^{(i)}|D_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|D_1|\psi_0^{(i)}\rangle}{W_0^{(i)}-W_0^{(n)}} \\
&= \sum_{n\neq i}\frac{\langle\psi_0^{(i)}|\tilde{D}_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\tilde{D}_1|\psi_0^{(i)}\rangle}{W_0^{(i)}-W_0^{(n)}} \\
&\quad+\sum_{n\neq i}\frac{(W_0^{(i)}-W_0^{(n)})}{2mc^2}\frac{\langle\psi_0^{(i)}|\beta D_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\tilde{D}_1|\psi_0^{(i)}\rangle}{W_0^{(i)}-W_0^{(n)}} \\
&\quad-\sum_{n\neq i}\frac{(W_0^{(i)}-W_0^{(n)})}{2mc^2}\frac{\langle\psi_0^{(i)}|\tilde{D}_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\beta D_1|\psi_0^{(i)}\rangle}{W_0^{(i)}-W_0^{(n)}} \\
&\quad-\sum_{n\neq i}\frac{(W_0^{(i)}-W_0^{(n)})^2}{4m^2c^4}\frac{\langle\psi_0^{(i)}|\beta D_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\beta D_1|\psi_0^{(i)}\rangle}{W_0^{(i)}-W_0^{(n)}} \\
&= \sum_{n\neq i}\frac{\langle\psi_0^{(i)}|\tilde{D}_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\tilde{D}_1|\psi_0^{(i)}\rangle}{W_0^{(i)}-W_0^{(n)}} \\
&\quad+\frac{1}{2mc^2}\sum_{n\neq i}\langle\psi_0^{(i)}|\beta D_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\tilde{D}_1|\psi_0^{(i)}\rangle \\
&\quad-\frac{1}{2mc^2}\sum_{n\neq i}\langle\psi_0^{(i)}|\tilde{D}_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\beta D_1|\psi_0^{(i)}\rangle \\
&\quad-\sum_{n\neq i}\frac{(W_0^{(i)}-W_0^{(n)})}{4m^2c^4}\langle\psi_0^{(i)}|\beta\tilde{D}_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\beta D_1|\psi_0^{(i)}\rangle \\
&= \sum_{n\neq i}\frac{\langle\psi_0^{(i)}|\tilde{D}_1|\psi_0^{(n)}\rangle\langle\psi_0^{(n)}|\tilde{D}_1|\psi_0^{(i)}\rangle}{W_0^{(i)}-W_0^{(n)}}+\frac{\langle\psi_0^{(i)}|[\beta D_1,\tilde{D}_1]|\psi_0^{(i)}\rangle}{2mc^2} \\
&\quad+\frac{\langle\psi_0^{(i)}|[[\beta D_1,D_0],\beta D_1]|\psi_0^{(i)}\rangle}{8m^2c^4}.
\end{aligned}\tag{A1}$$

Taking into account that

$$\frac{[\beta D_1,\tilde{D}_1]}{2mc^2} = -\frac{\{D_1,H_1\}}{2mc^2},$$

$$\begin{aligned}[\beta D_1,D_0] &= [\beta D_1,\beta mc^2] + [\beta D_1,c\boldsymbol{\alpha}\cdot\mathbf{p}]\\ &= -2mc^2 D_1 + \beta\{D_1,c\boldsymbol{\alpha}\cdot\mathbf{p}\},\end{aligned}$$

$$\begin{aligned}\frac{[[\beta D_1,D_0],\beta D_1]}{8m^2c^4} &= \beta\frac{D_1^2}{2mc^2} + \frac{[\beta\{D_1,c\boldsymbol{\alpha}\cdot\mathbf{p}\},\beta D_1]}{8m^2c^4}\\ &= \beta H_2 + \frac{\{D_1,H_1\}}{4mc^2},\end{aligned} \tag{A2}$$

the result of Eq. (21) is obtained.

APPENDIX B: MAGNETIC FIELD DISTRIBUTION OF A POINT MAGNETIC DIPOLE

The magnetic field is obtained from the vector potential of Eq. (27):

$$\boldsymbol{\nabla}\times\left[\boldsymbol{\mu}\times\left(\frac{\mathbf{r}}{r^3}\theta(r)\right)\right] = \boldsymbol{\mu}\cdot\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{r}}{r^3}\theta(r)\right) - (\boldsymbol{\mu}\cdot\boldsymbol{\nabla})\left(\frac{\mathbf{r}}{r^3}\theta(r)\right). \tag{B1}$$

Taking into account that

$$\boldsymbol{\nabla} f = \hat{r}\partial_r f + \frac{\hat{\theta}}{r}\partial_\theta f + \frac{\hat{\phi}}{r}\sin(\theta)\partial_\phi,$$

$$\boldsymbol{\nabla}\cdot\mathbf{F} = \frac{1}{r^2}\partial_r r^2 F_r + \frac{1}{r}\sin(\theta)\partial_\theta\sin(\theta)F_\theta + \frac{\partial\phi F_\phi}{r\sin(\theta)},$$

$$\boldsymbol{\mu} = \mu[\hat{r}(\hat{r}\cdot\hat{z}) + \hat{\theta}(\hat{\theta}\cdot\hat{z})] = \mu\cos(\theta)\hat{r} - \mu\sin(\theta)\hat{\theta}, \tag{B2}$$

the following is obtained:

$$\begin{aligned}&\boldsymbol{\mu}\cdot\boldsymbol{\nabla}\cdot\left(\frac{\mathbf{r}}{r^3}\theta(r)\right) - (\boldsymbol{\mu}\cdot\boldsymbol{\nabla})\left(\frac{\mathbf{r}}{r^3}\theta(r)\right)\\ &= \boldsymbol{\mu}\frac{\delta(r)}{r^2} - \left(\mu\cos(\theta)\partial_r - \mu\frac{\sin(\theta)}{r}\partial_\theta\right)\left(\frac{\hat{r}}{r^2}\theta(r)\right)\\ &= \boldsymbol{\mu}\frac{\delta(r)}{r^2} - \mu\cos(\theta)\hat{r}\left(\frac{\delta(r)r - 2\theta(r)}{r^3}\right) + \mu\sin(\theta)\hat{r}\frac{\theta(r)}{r^3}\\ &= \boldsymbol{\mu}\frac{\delta(r)}{r^2} - \frac{\boldsymbol{\mu}\cdot\hat{r}}{r^2}\delta(r) + 3\boldsymbol{\mu}\cdot\hat{r}\frac{\theta(r)}{r^3} - \boldsymbol{\mu}\cdot\hat{r}\frac{\theta(r)}{r^3}\\ &+ \mu\sin(\theta)\hat{r}\frac{\theta(r)}{r^3},\end{aligned} \tag{B3}$$

where the FC, SD, PSO, and "K" terms are readily recognized.

APPENDIX C: MATRIX ELEMENTS OF THE NUCLEAR MAGNETIC INTERACTION

We consider the vector operators:

$$\begin{aligned}T_{\text{pso}} &= \mathbf{L},\\ T_{\text{sd}} &= \frac{\hbar}{2}[3(\hat{r}\cdot\sigma)\hat{\mathbf{r}} - \boldsymbol{\sigma}],\\ T_{\text{fc}} &= \frac{\hbar}{3}\boldsymbol{\sigma},\\ T_{\text{k-sd}} &= -\frac{\hbar}{2}(\hat{r}\cdot\sigma)\hat{\mathbf{r}},\\ \mathbf{T}_{\text{k-fc}} &= \frac{\hbar}{6}\boldsymbol{\sigma}.\end{aligned} \tag{C1}$$

Taking into account Eq. (37),

$$\begin{aligned}\mathcal{Y}^{1}_{1/2,+1/2}(\hat{r}) &= -\sqrt{\tfrac{1}{3}}\chi^{(+)}Y_1^0(\hat{r}) + \sqrt{\tfrac{2}{3}}\chi^{(-)}Y_1^1(\hat{r}),\\ \mathcal{Y}^{1}_{1/2,-1/2}(\hat{r}) &= -\sqrt{\tfrac{2}{3}}\chi^{(+)}Y_1^{-1}(\hat{r}) + \sqrt{\tfrac{1}{3}}\chi^{(-)}Y_1^0(\hat{r}),\\ \mathcal{Y}^{-1}_{1/2,+1/2}(\hat{r}) &= \chi^{(+)}Y_0^0(\hat{r}),\\ \mathcal{Y}^{-1}_{1/2,-1/2}(\hat{r}) &= \chi^{(-)}Y_0^0(\hat{r}),\end{aligned} \tag{C2}$$

the "reduced" matrix elements of a rank-1 tensor operator $\left\langle\frac{1}{2},\pm1\middle|T^{(1)}\middle|\frac{1}{2},\pm1\right\rangle$ satisfy the relation, according to the Wigner-Eckart theorem,

$$\begin{aligned}\langle\mathcal{Y}^{\pm1}_{1/2,1/2}|T^1_0|\mathcal{Y}^{\pm1}_{1/2,1/2}\rangle &= \left\langle 1,0;\tfrac{1}{2},\tfrac{1}{2}\middle|\tfrac{1}{2},\tfrac{1}{2}\right\rangle\left\langle\tfrac{1}{2},\pm1\middle|T^{(1)}\middle|\tfrac{1}{2},\pm1\right\rangle\\ &= \sqrt{\tfrac{1}{3}}\left\langle\tfrac{1}{2},\pm1\middle|T^{(1)}\middle|\tfrac{1}{2},\pm1\right\rangle,\end{aligned} \tag{C3}$$

and therefore, the following rule can be applied:

$$\left\langle\tfrac{1}{2},\pm1\middle|T^{(1)}\middle|\tfrac{1}{2},\pm1\right\rangle = \sqrt{3}\langle\mathcal{Y}^{\pm1}_{1/2,1/2}|T^1_0|\mathcal{Y}^{\pm1}_{1/2,1/2}\rangle. \tag{C4}$$

We consider separately each operator of Eq. (C1).

1. $\left\langle\psi^{\pm1}_{1/2,m_1}\middle|\beta\frac{L_q^1}{r^3}\middle|\psi^{\pm1}_{1/2,m_2}\right\rangle_{r\le a}$

From

$$\langle\mathcal{Y}^{+1}_{1/2,1/2}|L^1_0|\mathcal{Y}^{+1}_{1/2,1/2}\rangle = \frac{1}{3}\langle Y_1^0|L_z|Y_1^0\rangle + \frac{2}{3}\langle Y_1^1|L_z|Y_1^1\rangle = \frac{2}{3}\hbar, \tag{C5a}$$

$$\langle\mathcal{Y}^{-1}_{1/2,1/2}|L^1_0|\mathcal{Y}^{-1}_{1/2,1/2}\rangle = \langle Y_1^0|L_z|Y_1^0\rangle = 0, \tag{C5b}$$

the following is obtained:

$$\left\langle\tfrac{1}{2},\pm1\middle|T^{(1)}_{\text{pso}}\middle|\tfrac{1}{2},\pm1\right\rangle = \frac{1\pm1}{\sqrt{3}}\hbar \tag{C6}$$

and, therefore, according to Eq. (55),

$$\langle \psi^{+1}_{1/2,m_1}|\beta\frac{L^1_q}{r^3}|\psi^{+1}_{1/2,m_2}\rangle_{r\le a}$$
$$=\left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle\frac{2}{\sqrt{3}}\left(-\frac{I(0^+)-I(a)}{2(\nu-1)}\right)$$
$$=\left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle}{\sqrt{3}}\left(-\frac{I(0^+)-I(a)}{\nu-1}\right), \tag{C7a}$$

$$\langle \psi^{-1}_{1/2,m_1}|\beta\frac{L^1_q}{r^3}|\psi^{-1}_{1/2,m_2}\rangle_{r\le a}$$
$$=\left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle\frac{\frac{\nu-1}{\nu+1}2}{\sqrt{3}}$$
$$\times\left(-\frac{I(0^+)-I(a)}{2(\nu-1)}\right)$$
$$=\left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle}{\sqrt{3}}\left(-\frac{I(0^+)-I(a)}{\nu+1}\right). \tag{C7b}$$

2. $\left\langle \psi^{\pm1}_{1/2,m_1}\middle|\beta\frac{\frac{\hbar}{2}(3(\hat{r}\cdot\sigma)\hat{r}-\sigma)^1_q}{r^3}\middle|\psi^{\pm1}_{1/2,m_2}\right\rangle_{r\le a}$

Making use of Eq. (40),

$$\langle \mathcal{Y}^{+1}_{1/2,1/2}|\frac{\hbar}{2}(3(\hat{r}\cdot\sigma)\hat{r}-\sigma)^1_0|\mathcal{Y}^{+1}_{1/2,1/2}\rangle$$
$$=-\frac{\hbar}{2}3\langle \mathcal{Y}^{+1}_{1/2,1/2}|\cos(\theta)|\mathcal{Y}^{-1}_{1/2,1/2}\rangle-\frac{\hbar}{2}\langle \mathcal{Y}^{+1}_{1/2,1/2}|\sigma_z|\mathcal{Y}^{+1}_{1/2,1/2}\rangle$$
$$=\frac{\hbar}{2}\sqrt{3}\langle Y^1_0|\cos(\theta)|Y^0_0\rangle-\frac{\hbar}{6}\langle\chi^{(+)}|\sigma_z|\chi^{(+)}\rangle-\frac{\hbar}{3}\langle\chi^{(-)}|\sigma_z|\chi^{(-)}\rangle$$
$$=\frac{\hbar}{2}\left(\sqrt{4\pi}\langle Y^1_0|Y^1_0|Y^0_0\rangle+\frac{1}{3}\right)=\frac{2}{3}\hbar, \tag{C8a}$$

$$\langle \mathcal{Y}^{-1}_{1/2,1/2}|\frac{\hbar}{2}[3(\hat{r}\cdot\sigma)\hat{r}-\sigma]^1_0|\mathcal{Y}^{-1}_{1/2,1/2}\rangle$$
$$=-\frac{\hbar}{2}3\langle \mathcal{Y}^{-1}_{1/2,1/2}|\cos(\theta)|\mathcal{Y}^{+1}_{1/2,1/2}\rangle-\frac{\hbar}{2}\langle \mathcal{Y}^{-1}_{1/2,1/2}|\sigma_z|\mathcal{Y}^{-1}_{1/2,1/2}\rangle$$
$$=\frac{\hbar}{2}\sqrt{3}\langle Y^0_0|\cos(\theta)|Y^1_0\rangle-\frac{\hbar}{2}\langle\chi^{(+)}|\sigma_z|\chi^{(+)}\rangle$$
$$=\frac{\hbar}{2}(\sqrt{4\pi}\langle Y^0_0|Y^1_0|Y^1_0\rangle-1)=0, \tag{C8b}$$

and the following holds:

$$\left\langle\tfrac{1}{2},\pm1\middle|T^{(1)}_{\mathrm{sd}}\middle|\tfrac{1}{2},\pm1\right\rangle=\frac{1\pm1}{\sqrt{3}}\hbar, \tag{C9}$$

and making use of Eq. (55) it is obtained that

$$\langle \psi^{+1}_{1/2,m_1}|\beta\frac{\frac{\hbar}{2}(3(\hat{r}\cdot\sigma)\hat{r}-\sigma)^1_q}{r^3}|\psi^{+1}_{1/2,m_2}\rangle_{r\le a}$$
$$=\left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle}{\sqrt{3}}\left(-\frac{I(0^+)-I(a)}{\nu-1}\right), \tag{C10a}$$

$$\langle \psi^{-1}_{1/2,m_1}|\beta\frac{\frac{\hbar}{2}(3(\hat{r}\cdot\sigma)\hat{r}-\sigma)^1_q}{r^3}|\psi^{-1}_{1/2,m_2}\rangle_{r\le a}$$
$$=\left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle}{\sqrt{3}}\left(-\frac{I(0^+)-I(a)}{\nu+1}\right). \tag{C10b}$$

3. $\left\langle \psi^{\pm1}_{1/2,m_1}\middle|\beta\frac{\frac{\hbar}{3}\delta(r)\sigma^1_q}{r^2}\middle|\psi^{\pm1}_{1/2,m_2}\right\rangle_{r\le a}$

Considering

$$\langle \mathcal{Y}^{+1}_{1/2,1/2}|\frac{\hbar}{3}\sigma^1_0|\mathcal{Y}^{+1}_{1/2,1/2}\rangle=\frac{\hbar}{9}\langle\chi^{(+)}|\sigma_z|\chi^{(+)}\rangle+\frac{2\hbar}{9}\langle\chi^{(-)}|\sigma_z|\chi^{(-)}\rangle=-\frac{\hbar}{9}, \tag{C11a}$$

$$\langle \mathcal{Y}^{-1}_{1/2,1/2}|\frac{\hbar}{3}\sigma^1_0|\mathcal{Y}^{-1}_{1/2,1/2}\rangle=\frac{\hbar}{3}\langle\chi^{(+)}|\sigma_z|\chi^{(+)}\rangle=\frac{\hbar}{6}, \tag{C11b}$$

the following is found:

$$\left\langle\tfrac{1}{2},\pm1\middle|T^{(1)}_{\mathrm{fc}}\middle|\tfrac{1}{2},\pm1\right\rangle=\frac{1}{\sqrt{3}}\begin{cases}-\dfrac{\hbar}{3}\\ \hbar\end{cases}, \tag{C12}$$

and, according to Eq. (55),

$$\langle \psi^{+1}_{1/2,m_1}|\beta\frac{\frac{\hbar}{3}\delta(r)\sigma^1_q}{r^2}|\psi^{+1}_{1/2,m_2}\rangle_{r\le a}$$
$$=\left(\frac{e}{mc}\right)\delta_{m_1,m_2+q}\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle$$
$$\times\left(\frac{-\hbar}{3\sqrt{3}}+\frac{\nu+1}{\nu-1}\frac{\hbar}{\sqrt{3}}\right)I(0^+)$$
$$=\left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\left\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\right\rangle}{\sqrt{3}}\left(\frac{2}{3}\frac{\nu+2}{\nu-1}I(0^+)\right), \tag{C13a}$$

$$\langle \psi^{-1}_{1/2,m_1} | \beta \frac{\frac{\hbar}{3}\delta(r)\sigma^1_q}{r^2} | \psi^{-1}_{1/2,m_2} \rangle_{r\le a}$$

$$= \left(\frac{e}{mc}\right)\delta_{m_1,m_2+q}\langle 1,q;\tfrac{1}{2},m_2|\tfrac{1}{2},m_2+q\rangle \times\left(\frac{\hbar}{\sqrt{3}} - \frac{\nu-1}{\nu+1}\frac{\hbar}{3\sqrt{3}}\right)I(0^+)$$

$$= \left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\langle 1,q;\frac{1}{2},m_2|\frac{1}{2},m_2+q\rangle}{\sqrt{3}}\left(\frac{2}{3}\frac{\nu+2}{\nu+1}I(0^+)\right). \tag{C13b}$$

4. $\left\langle \psi^{\pm 1}_{1/2,m_1} \middle| \beta \frac{-\frac{\hbar}{2}\delta(r)(\hat{r}\cdot\sigma)\hat{r}^1_q}{r^2} \middle| \psi^{\pm 1}_{1/2,m_2} \right\rangle_{r\le a}$

According to Eq. (40),

$$\langle \mathcal{Y}^{+1}_{1/2,1/2}| - \frac{\hbar}{2}(\hat{r}\cdot\sigma)\hat{r}^1_0|\mathcal{Y}^{+1}_{1/2,1/2}\rangle = \frac{\hbar}{2}\langle \mathcal{Y}^{+1}_{1/2,1/2}|\cos(\theta)|\mathcal{Y}^{-1}_{1/2,1/2}\rangle = -\frac{\hbar}{2\sqrt{3}}\langle Y^1_0|\cos(\theta)|Y^0_0\rangle = -\frac{\hbar}{6}\sqrt{4\pi}\langle Y^1_0|Y^1_0|Y^0_0\rangle = -\frac{\hbar}{6}, \tag{C14a}$$

$$\langle \mathcal{Y}^{-1}_{1/2,1/2}| - \frac{\hbar}{2}(\hat{r}\cdot\sigma)\hat{r}^1_0|\mathcal{Y}^{-1}_{1/2,1/2}\rangle = \frac{\hbar}{2}\langle \mathcal{Y}^{-1}_{1/2,1/2}|\cos(\theta)|\mathcal{Y}^{+1}_{1/2,1/2}\rangle = -\frac{\hbar}{2\sqrt{3}}\langle Y^0_0|\cos(\theta)|Y^1_0\rangle = -\frac{\hbar}{6}\sqrt{4\pi}\langle Y^0_0|Y^1_0|Y^1_0\rangle += -\frac{\hbar}{6}, \tag{C14b}$$

and the following holds:

$$\langle \tfrac{1}{2},\pm 1|T^{(1)}_{\text{k-sd}}|\tfrac{1}{2},\pm 1\rangle = -\frac{1}{\sqrt{3}}\frac{\hbar}{2}. \tag{C15}$$

And from Eq. (55) it follows that

$$\langle \psi^{+1}_{1/2,m_1} | \beta \frac{-\frac{\hbar}{2}\delta(r)(\hat{r}\cdot\sigma)\hat{r}^1_q}{r^2} | \psi^{+1}_{1/2,m_2} \rangle_{r\le a}$$

$$= \left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\langle 1,q;\frac{1}{2},m_2|\frac{1}{2},m_2+q\rangle}{\sqrt{3}}\left(1+\frac{\nu+1}{\nu-1}\right)\times\left(\frac{-I(0^+)}{2}\right)$$

$$= \left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\langle 1,q;\frac{1}{2},m_2|\frac{1}{2},m_2+q\rangle}{\sqrt{3}}\left(-\frac{\nu}{\nu-1}I(0^+)\right) \tag{C16a}$$

$$\langle \psi^{-1}_{1/2,m_1} | \beta \frac{-\frac{\hbar}{2}\delta(r)(\hat{r}\cdot\sigma)\hat{r}^1_q}{r^2} | \psi^{-1}_{1/2,m_2} \rangle_{r\le a}$$

$$= \left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\langle 1,q;\frac{1}{2},m_2|\frac{1}{2},m_2+q\rangle}{\sqrt{3}}\left(1+\frac{\nu-1}{\nu+1}\right)\times\left(-\frac{I(0^+)}{2}\right)$$

$$= \left(\frac{e\hbar}{mc}\right)\delta_{m_1,m_2+q}\frac{\langle 1,q;\frac{1}{2},m_2|\frac{1}{2},m_2+q\rangle}{\sqrt{3}}\times\left(-\frac{\nu}{\nu+1}I(0^+)\right). \tag{C16b}$$

5. $\left\langle \psi^{\pm 1}_{1/2,m_1} \middle| \beta \frac{\frac{\hbar}{6}\delta(r)\sigma^1_q}{r^2} \middle| \psi^{\pm 1}_{1/2,m_2} \right\rangle_{r\le a}$

This is the same matrix element as

$$\langle \psi^{\pm 1}_{1/2,m_1} | \beta \frac{\frac{\hbar}{3}\delta(r)\sigma^1_q}{r^2} | \psi^{\pm 1}_{1/2,m_2} \rangle_{r\le a}$$

with a factor of $\frac{1}{2}$.

APPENDIX D: EXPLICIT EXPRESSION OF OPERATOR $\tilde{D}^{\mu B}_2$

The anticommutator of Eq. (14) is explicitly evaluated retaining terms bilinear in $\boldsymbol{\mu}$ and $\mathbf{B}$. The Einstein convention of summation over repeated cartesian indices is applied to write

$$\tilde{D}^{\mu B}_2 = -\frac{e^2}{4m^2c^3}\{\alpha_i A_i, A_j p_j\}$$
$$= -\frac{e^2}{4m^2c^3}(\{\alpha_i A^\mu_i, A^B_j p_j\} + \{\alpha_j A^B_j, A^\mu_i p_i\})$$
$$= -\frac{e^2}{4m^2c^3}(\alpha_i A^\mu_i A^B_j p_j + A^B_j p_j \alpha_i A^\mu_i + \alpha_j A^B_j A^\mu_i p_i + A^\mu_i p_i \alpha_j A^B_j)$$
$$= -\frac{e^2}{4m^2c^3}(2\alpha_i A^\mu_i A^B_j p_j + [A^B_j p_j, \alpha_i A^\mu_i] + [\alpha_j A^B_j, A^\mu_i p_i] + 2A^\mu_i p_i \alpha_j A^B_j). \tag{D1}$$

Each term is considered separately. The gauge origin of the uniform magnetic field is set at the nucleus position:

$$
\begin{aligned}
[A_j^B p_j, \alpha_i A_i^\mu] + [\alpha_j A_j^B, A_i^\mu p_i] &= A_j^B [p_j, \alpha_i A_i^\mu] + [A_j^B, \alpha_i A_i^\mu] p_j + \alpha_j [A_j^B, A_i^\mu p_i] + [\alpha_j, A_i^\mu p_i] A_j^B \\
&= A_j^B \alpha_i [p_j, A_i^\mu] + \alpha_j A_i^\mu [A_j^B, p_i] \\
&= A_j^B \alpha_i \epsilon_{ilm} \mu_l \left[p_j, \frac{r_m}{r^3} \theta(r) \right] + \alpha_j A_i^\mu \frac{1}{2} \epsilon_{jpq} B_p [r_q, p_i] \\
&= A_j^B \alpha_i \epsilon_{ilm} \mu_l (-\imath\hbar) \left(\partial_j \frac{r_m}{r^3} \theta(r) \right) + \alpha_j A_i^\mu \frac{1}{2} \epsilon_{jpq} B_p (\imath\hbar) \delta_{qi} \\
&= (-\imath\hbar) A_j^B \alpha_i \epsilon_{ilm} \mu_l \left[\frac{r_m}{r^3} \frac{r_j}{r} \delta(r) + \theta(r) \left(\frac{\delta_{jm}}{r^3} - 3 \frac{r_j r_m}{r^5} \right) \right] + \frac{\imath\hbar}{2} \alpha_j A_i^\mu \epsilon_{jpi} B_p \\
&= -\imath\hbar \epsilon_{jpq} \frac{1}{2} B_p \epsilon_{ilm} \mu_l \left[\frac{r_m r_j r_q \alpha_i}{r^4} \delta(r) + \theta(r) \left(\frac{\delta_{jm} r_q \alpha_i}{r^3} - 3 \frac{r_j r_m r_q \alpha_i}{r^5} \right) \right] + \frac{\imath\hbar}{2} \alpha_j A_i^\mu \epsilon_{jpi} B_p \\
&= -\imath\hbar \epsilon_{jpq} \frac{1}{2} B_p r_q \alpha_i \epsilon_{ilm} \mu_l \theta(r) \frac{\delta_{jm}}{r^3} + \frac{\imath\hbar}{2} \alpha_j \epsilon_{ilm} \frac{\mu_l r_m}{r^3} \epsilon_{jpi} B_p = \mu_l \left[-\frac{\imath\hbar}{2r^3} (\epsilon_{jpq} r_q \alpha_i \epsilon_{ilj} - \alpha_j \epsilon_{ilm} r_m \epsilon_{jpi}) \right] B_p \\
&= \mu_l \left[-\frac{\imath\hbar}{2r^3} (r_l \alpha_p + \delta_{lp} r_i \alpha_i - \alpha_l r_p - \delta_{lp} \alpha_j r_j) \right] B_p = \boldsymbol{\mu} \cdot \left[-\frac{\imath\hbar}{2r^3} (\mathbf{r}\boldsymbol{\alpha} - \boldsymbol{\alpha}\mathbf{r}) \right] \cdot \mathbf{B}, \qquad \text{(D2)}
\end{aligned}
$$

$$
\begin{aligned}
2\alpha_i A_i^\mu A_j^B p_j + 2A_i^\mu p_i \alpha_j A_j^B &= 2\left(\boldsymbol{\alpha} \cdot \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3} \right) [(\mathbf{B} \times \mathbf{r}) \cdot \mathbf{p}] + 2\left(\mathbf{p} \cdot \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3} \right) [\boldsymbol{\alpha} \cdot (\mathbf{B} \times \mathbf{r})] \\
&= 2\left(\boldsymbol{\mu} \cdot \frac{\mathbf{r} \times \boldsymbol{\alpha}}{r^3} \right) (\mathbf{L} \cdot \mathbf{B}) + \left(\boldsymbol{\mu} \cdot \frac{\mathbf{L}}{r^3} \right) [\mathbf{B} \cdot (\mathbf{r} \times \boldsymbol{\alpha})] \\
&= \boldsymbol{\mu} \cdot \left(\frac{(\mathbf{r} \times \boldsymbol{\alpha})\mathbf{L} + \mathbf{L}(\mathbf{r} \times \boldsymbol{\alpha})}{r^3} \right) \cdot \mathbf{B}. \qquad \text{(D3)}
\end{aligned}
$$

Therefore,

$$
\tilde{D}_2^{\mu B} = -\frac{e^2}{4m^2c^3} \left[\frac{(\mathbf{r} \times \boldsymbol{\alpha})\mathbf{L} + \mathbf{L}(\mathbf{r} \times \boldsymbol{\alpha})}{r^3} - \frac{\imath\hbar}{2} \left(\frac{\mathbf{r}\boldsymbol{\alpha} - \boldsymbol{\alpha}\mathbf{r}}{r^3} \right) \right], \qquad \text{(D4)}
$$

which is an alternative expression to that of Ref. [16].

[1] See, e.g., *Calculation of NMR and EPR Parameters: Theory and Applications*, edited by M. Kaupp, M. Bühl, and V. G. Malkin (Wiley-VCH, Weinheim, 2004).

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