Electric and magnetic dipole shielding constants for the ground state of the relativistic hydrogen-like atom: Application of the Sturmian expansion of the generalized Dirac–Coulomb Green function

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Abstract

The Sturmian expansion of the generalized Dirac–Coulomb Green function [R. Szmytkowski, J. Phys. B 30 (1997) 825; erratum 30 (1997) 2747] is exploited to derive closed-form expressions for electric (σ_{E}) and magnetic (σ_{M}) dipole shielding constants for the ground state of the relativistic hydrogen-like atom with a point-like and spinless nucleus of charge Ze. It is found that $\sigma_{\mathrm{E}} = Z^{-1}$ (as it should be) and

$$\sigma_{\mathrm{M}} = -(2Z\alpha^2/27)(4\gamma_1^3 + 6\gamma_1^2 - 7\gamma_1 - 12)/[\gamma_1(\gamma_1+1)(2\gamma_1-1)],$$

where $\gamma_1 = \sqrt{1-(Z\alpha)^2}$ (α is the fine-structure constant). This expression for σ_{M} agrees with earlier findings of several other authors, obtained with the use of other analytical techniques, and is elementary compared to an alternative one presented recently by Cheng *et al.* [J. Chem. Phys. 130 (2009) 144102], which involves an infinite series of ratios of the Euler's gamma functions.

Key words: Electric nuclear shielding; magnetic nuclear shielding; Dirac one-electron atom; Dirac–Coulomb Green function; Sturmian functions

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1 Introduction

In the series of papers published by our group over the period of past several years, it has been shown that the Sturmian expansion of the generalized (or reduced) Dirac–Coulomb Green function (GDCGF), found in Ref. [1], may be used as a convenient tool in perturbation-theory calculations of some electromagnetic properties of relativistic one-electron atoms. In particular, closed-form expressions, in terms of the generalized hypergeometric function ${}_3F_2$ with the unit argument, have been derived for the ground-state static dipole magnetizability [2], the polarizability [3] and the Stark-induced magnetic anapole moment [4] for the system.

Recently, Cheng *et al.* [5] have reported the use of the GDCGF Sturmian expansion technique of Ref. [1] for the purpose to find the magnetic dipole shielding constant σ_{M} for the Dirac one-electron atom in its ground state. Absolutely no details of calculations have been provided in Ref. [5]; only the final expression for σ_{M} has been given therein as a sum of two contributions, one being

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elementary and the second one having a form of an infinite series of ratios of the Euler's gamma functions. A literature search shows that calculations of σ_{M} for the same system were carried out before by several research groups and published in Refs. [6–11] (none of those works has been referenced in Ref. [5]). An expression for σ_{M} arrived at in Refs. [9–11] (a corresponding formula given in Refs. [6–8] contains a misprint, cf. Sec. 3 below) appears to be elementary compared to the one in Ref. [5]. This prompts one to inquire whether the GDCGF Sturmian expansion technique is practically capable to provide the same simple representation of σ_{M} as the one given in Refs. [9–11] (and, after a due correction is made, also in Refs. [6–8]). In the present paper, we answer this question affirmatively.

When preparing this report, we have decided not to focus only on the dipole magnetic shielding constant σ_{M} for the Dirac one-electron atom in the ground state, but to present at first in Sec. 2 details of calculations of the electric dipole shielding constant σ_{E} for the same system. The value of the latter quantity is known exactly to be Z^{-1} [13], where Z is the nuclear charge in the units of e. This fact makes the evaluation of σ_{E} an ideal test of correctness and robustness of any analytical technique, including the present one. We believe the material of Sec. 2 is highly instructive, as it shows how certain infinite series encountered in calculations based on the GDCGF Sturmian expansion technique may be summed to closed elementary forms. The practical knowledge gained in that way is then successfully exploited in calculations of σ_{M} reported in Sec. 3.

A small part of the material of Sec. 3 has been presented in an unpublished comment [12] on Ref. [5].

2 The electric dipole shielding constant

Consider a Dirac one-electron atom with an infinitely heavy, point-like and spinless nucleus of charge Ze. In the presence of a weak, static, uniform electric field $\boldsymbol{E}_{\mathrm{ext}}$, an electronic wave function of a ground quasi-bound state is, to the first order in the perturbing field, approximated by

$$\Psi(\boldsymbol{r}) \simeq \Psi^{(0)}(\boldsymbol{r}) + \Psi^{(1)}(\boldsymbol{r}). \tag{2.1}$$

Here, $\Psi^{(0)}(\boldsymbol{r})$ is the ground-state wave function of an isolated atom and is given by

$$\Psi^{(0)}(\boldsymbol{r}) = a_{1/2}^{(0)}\Psi_{1/2}^{(0)}(\boldsymbol{r}) + a_{-1/2}^{(0)}\Psi_{-1/2}^{(0)}(\boldsymbol{r}), \tag{2.2}$$

where

$$|a_{1/2}^{(0)}|^2 + |a_{-1/2}^{(0)}|^2 = 1 \tag{2.3}$$

(otherwise the coefficients $a_{\pm 1/2}^{(0)}$ are arbitrary),

$$\Psi_{\mu}^{(0)}(\boldsymbol{r}) = \frac{1}{r}\begin{pmatrix} P^{(0)}(r)\Omega_{-1\mu}(\boldsymbol{n}_r) \\ \mathrm{i}Q^{(0)}(r)\Omega_{1\mu}(\boldsymbol{n}_r) \end{pmatrix} \qquad (\mu = \pm\tfrac{1}{2}), \tag{2.4}$$

with

$$P^{(0)}(r) = -\sqrt{\frac{Z}{a_0}\frac{1+\gamma_1}{\Gamma(2\gamma_1+1)}}\left(\frac{2Zr}{a_0}\right)^{\gamma_1}\exp(-Zr/a_0), \tag{2.5}$$

$$Q^{(0)}(r) = \sqrt{\frac{Z}{a_0}\frac{1-\gamma_1}{\Gamma(2\gamma_1+1)}}\left(\frac{2Zr}{a_0}\right)^{\gamma_1}\exp(-Zr/a_0), \tag{2.6}$$

and with $\Omega_{\kappa\mu}(\boldsymbol{n}_r)$, ($\boldsymbol{n}_r = \boldsymbol{r}/r$), being the orthonormal spherical spinors defined as in Ref. [14]. The second term on the right-hand side of Eq. (2.1), $\Psi^{(1)}(\boldsymbol{r})$, is the first-order perturbation-theory correction to $\Psi^{(0)}(\boldsymbol{r})$ given by

$$\Psi^{(1)}(\boldsymbol{r}) = -e\boldsymbol{E}_{\mathrm{ext}} \cdot \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \bar{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')\boldsymbol{r}'\Psi^{(0)}(\boldsymbol{r}'), \tag{2.7}$$

with $\bar{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')$ being the generalized Dirac–Coulomb Green function associated with the ground-state hydrogenic energy level $\mathcal{E}^{(0)} = mc^2\gamma_1$.

The symbol γ_κ, appearing in Eqs. (2.5), (2.6), and also in later considerations, is standardly defined as

$$\gamma_\kappa = \sqrt{\kappa^2 - (Z\alpha)^2}, \tag{2.8}$$

where α is the Sommerfeld's fine-structure constant. Moreover, as usual, a_0 denotes the Bohr radius.

The electric field produced at the point $\boldsymbol{r}$ by the atomic electron, the latter being in the state characterized by the wave function $\Psi(\boldsymbol{r})$, is given by

$$\boldsymbol{E}(\boldsymbol{r}) = \frac{1}{4\pi\epsilon_0} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \rho_{\mathrm{e}}(\boldsymbol{r}') \frac{\boldsymbol{r} - \boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}'|^3}, \tag{2.9}$$

where

$$\rho_{\mathrm{e}}(\boldsymbol{r}) = -e\Psi^\dagger(\boldsymbol{r})\Psi(\boldsymbol{r}) \tag{2.10}$$

is the smeared electronic charge density distribution. Hence, at the point $\boldsymbol{r} = \boldsymbol{0}$, where the nucleus is located, the field is

$$\boldsymbol{E}(\boldsymbol{0}) = -\frac{1}{4\pi\epsilon_0} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \boldsymbol{r}' \frac{\rho_{\mathrm{e}}(\boldsymbol{r}')}{r'^{\,3}}. \tag{2.11}$$

Now, if $\Psi(\boldsymbol{r})$ is approximated as in Eq. (2.1), we have

$$\rho_{\mathrm{e}}(\boldsymbol{r}) \simeq \rho_{\mathrm{e}}^{(0)}(\boldsymbol{r}) + \rho_{\mathrm{e}}^{(1)}(\boldsymbol{r}), \tag{2.12}$$

where

$$\rho_{\mathrm{e}}^{(0)}(\boldsymbol{r}) = -e\Psi^{(0)\dagger}(\boldsymbol{r})\Psi^{(0)}(\boldsymbol{r}) \tag{2.13}$$

and

$$\rho_{\mathrm{e}}^{(1)}(\boldsymbol{r}) = -2e\,\mathrm{Re}[\Psi^{(0)\dagger}(\boldsymbol{r})\Psi^{(1)}(\boldsymbol{r})]. \tag{2.14}$$

Consequently, $\boldsymbol{E}(\boldsymbol{0})$ is approximately given by

$$\boldsymbol{E}(\boldsymbol{0}) \simeq \boldsymbol{E}^{(0)}(\boldsymbol{0}) + \boldsymbol{E}^{(1)}(\boldsymbol{0}), \tag{2.15}$$

with

$$\boldsymbol{E}^{(0)}(\boldsymbol{0}) = \frac{e}{4\pi\epsilon_0} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \boldsymbol{r}' \frac{\Psi^{(0)\dagger}(\boldsymbol{r}')\Psi^{(0)}(\boldsymbol{r}')}{r'^{\,3}} \tag{2.16}$$

and

$$\boldsymbol{E}^{(1)}(\boldsymbol{0}) = \frac{2e}{4\pi\epsilon_0}\,\mathrm{Re} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \boldsymbol{r}' \frac{\Psi^{(0)\dagger}(\boldsymbol{r}')\Psi^{(1)}(\boldsymbol{r}')}{r'^{\,3}}. \tag{2.17}$$

It may be easily shown that, because of parity reasons, the field component at $\boldsymbol{r} = \boldsymbol{0}$ due to the unperturbed electronic distribution, $\boldsymbol{E}^{(0)}(\boldsymbol{0})$, vanishes.

In turn, using the expression (2.7) for $\Psi^{(1)}(\boldsymbol{r})$, we find that the first-order field correction $\boldsymbol{E}^{(1)}(\boldsymbol{0})$ may be written in the form

$$\boldsymbol{E}^{(1)}(\boldsymbol{0}) = -\boldsymbol{\Sigma}_{\mathrm{E}} \cdot \boldsymbol{E}_{\mathrm{ext}}, \tag{2.18}$$

where $\boldsymbol{\Sigma}_{\mathrm{E}}$ is the electric dipole shielding tensor given by

$$\boldsymbol{\Sigma}_{\mathrm{E}} = \frac{2e^2}{4\pi\epsilon_0}\,\mathrm{Re} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \Psi^{(0)\dagger}(\boldsymbol{r}) \frac{\boldsymbol{r}}{r^3} \bar{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')\boldsymbol{r}'\Psi^{(0)}(\boldsymbol{r}'). \tag{2.19}$$

To evaluate $\boldsymbol{\Sigma}_{\mathrm{E}}$, we rewrite Eq. (2.19) in the form

$$\boldsymbol{\Sigma}_{\mathrm{E}} = \frac{2e^2}{4\pi\epsilon_0}\,\mathrm{Re} \sum_{n,n'=-1}^{+1} \boldsymbol{e}_n \boldsymbol{e}_{n'}^* \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \Psi^{(0)\dagger}(\boldsymbol{r}) r^{-2} \boldsymbol{e}_n^* \cdot \boldsymbol{n}_r \bar{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}') r' \boldsymbol{e}_{n'} \cdot \boldsymbol{n}_r' \Psi^{(0)}(\boldsymbol{r}'), \tag{2.20}$$

where $\boldsymbol{e}_n$, with $n = 0, \pm 1$, are the unit vectors of the cyclic basis, related to the Cartesian unit vectors through

$$\boldsymbol{e}_0 = \boldsymbol{e}_z, \qquad \boldsymbol{e}_{\pm 1} = \mp \frac{1}{\sqrt{2}}(\boldsymbol{e}_x \pm \mathrm{i}\boldsymbol{e}_y). \tag{2.21}$$

In the next step, we substitute $\Psi^{(0)}(\boldsymbol{r})$, as given by Eqs. (2.2) and (2.4), and the multipole expansion of the generalized Dirac–Coulomb Green function, which is

$$\begin{aligned}\bar{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}') &= \frac{4\pi\epsilon_0}{e^2} \sum_{\substack{K=-\infty \\ (K\neq 0)}}^{\infty} \sum_{M=-|K|+1/2}^{|K|-1/2} \frac{1}{rr'} \\ &\times \begin{pmatrix} \bar{g}^{(0)}_{K,(++)}(r,r')\Omega_{KM}(\boldsymbol{n}_r)\Omega^{\dagger}_{KM}(\boldsymbol{n}'_r) & -\mathrm{i}\bar{g}^{(0)}_{K,(+-)}(r,r')\Omega_{KM}(\boldsymbol{n}_r)\Omega^{\dagger}_{-KM}(\boldsymbol{n}'_r) \\ \mathrm{i}\bar{g}^{(0)}_{K,(-+)}(r,r')\Omega_{-KM}(\boldsymbol{n}_r)\Omega^{\dagger}_{KM}(\boldsymbol{n}'_r) & \bar{g}^{(0)}_{K,(--)}(r,r')\Omega_{-KM}(\boldsymbol{n}_r)\Omega^{\dagger}_{-KM}(\boldsymbol{n}'_r) \end{pmatrix},\end{aligned} \tag{2.22}$$

into Eq. (2.20). After the angular integrals appearing in the resulting series representation of $\boldsymbol{\Sigma}_{\mathrm{E}}$ are evaluated with the aid of the following identities obeyed by the spherical spinors [14]:

$$\begin{aligned}\boldsymbol{e}_0 \cdot \boldsymbol{n}_r \, \Omega_{\kappa\mu}(\boldsymbol{n}_r) &= -\frac{2\mu}{4\kappa^2 - 1}\Omega_{-\kappa\mu}(\boldsymbol{n}_r) + \frac{\sqrt{(\kappa + \frac{1}{2})^2 - \mu^2}}{|2\kappa + 1|}\Omega_{\kappa+1,\mu}(\boldsymbol{n}_r) \\ &\quad + \frac{\sqrt{(\kappa - \frac{1}{2})^2 - \mu^2}}{|2\kappa - 1|}\Omega_{\kappa-1,\mu}(\boldsymbol{n}_r),\end{aligned} \tag{2.23}$$

$$\begin{aligned}\boldsymbol{e}_{\pm 1} \cdot \boldsymbol{n}_r \, \Omega_{\kappa\mu}(\boldsymbol{n}_r) &= \pm\sqrt{2}\frac{\sqrt{\kappa^2 - (\mu \pm \frac{1}{2})^2}}{4\kappa^2 - 1}\Omega_{-\kappa,\mu\pm 1}(\boldsymbol{n}_r) \\ &\quad + \frac{\sqrt{(\kappa \pm \mu + \frac{1}{2})(\kappa \pm \mu + \frac{3}{2})}}{\sqrt{2}(2\kappa + 1)}\Omega_{\kappa+1,\mu\pm 1}(\boldsymbol{n}_r) \\ &\quad - \frac{\sqrt{(\kappa \mp \mu - \frac{1}{2})(\kappa \mp \mu - \frac{3}{2})}}{\sqrt{2}(2\kappa - 1)}\Omega_{\kappa-1,\mu\pm 1}(\boldsymbol{n}_r),\end{aligned} \tag{2.24}$$

we arrive at the conclusion that for arbitrary (up to the normalization constraint (2.3)) values of the coefficients $a^{(0)}_{\pm 1/2}$ the electric shielding tensor for the hydrogenic ground state is a multiple of the unit dyad,

$$\boldsymbol{\Sigma}_{\mathrm{E}} = \sigma_{\mathrm{E}} \mathsf{I}, \tag{2.25}$$

and that the only contributions to the shielding constant σ_{E} come from the terms with $K = +1$ and $K = -2$. One has

$$\sigma_{\mathrm{E}} = \sigma_{\mathrm{E},1} + \sigma_{\mathrm{E},-2}, \tag{2.26}$$

where

$$\sigma_{\mathrm{E},1} = \frac{2}{9}\int_0^{\infty} \mathrm{d}r \int_0^{\infty} \mathrm{d}r' \begin{pmatrix} P^{(0)}(r) & Q^{(0)}(r) \end{pmatrix} r^{-2} \bar{\mathsf{G}}^{(0)}_{1}(r,r') r' \begin{pmatrix} P^{(0)}(r') \\ Q^{(0)}(r') \end{pmatrix} \tag{2.27}$$

and

$$\sigma_{\mathrm{E},-2} = \frac{4}{9}\int_0^{\infty} \mathrm{d}r \int_0^{\infty} \mathrm{d}r' \begin{pmatrix} P^{(0)}(r) & Q^{(0)}(r) \end{pmatrix} r^{-2} \bar{\mathsf{G}}^{(0)}_{-2}(r,r') r' \begin{pmatrix} P^{(0)}(r') \\ Q^{(0)}(r') \end{pmatrix}, \tag{2.28}$$

with

$$\bar{\mathsf{G}}^{(0)}_{K}(r,r') = \begin{pmatrix} \bar{g}^{(0)}{}_{K,(++)}(r,r') & \bar{g}^{(0)}{}_{K,(+-)}(r,r') \\ \bar{g}^{(0)}{}_{K,(-+)}(r,r') & \bar{g}^{(0)}{}_{K,(--)}(r,r') \end{pmatrix} \tag{2.29}$$

being the radial generalized Dirac–Coulomb Green function associated with the hydrogenic ground-state energy level.

To evaluate the integrals in Eqs. (2.27) and (2.28), we shall exploit the following separable expansion of $\bar{\mathsf{G}}_K^{(0)}(r,r')$:

$$\bar{\mathsf{G}}_K^{(0)}(r,r') = \sum_{n=-\infty}^{\infty} \frac{1}{\mu_{nK}^{(0)}-1} \left(\begin{array}{c} S_{nK}^{(0)}(r) \\ T_{nK}^{(0)}(r) \end{array} \right) \left(\begin{array}{cc} \mu_{nK}^{(0)} S_{nK}^{(0)}(r') & T_{nK}^{(0)}(r') \end{array} \right) \qquad (K \neq -1), \tag{2.30}$$

which is a corollary from the theory of the Dirac–Coulomb Sturmian functions [1]. Here

$$\begin{aligned} S_{nK}^{(0)}(r) &= \sqrt{\frac{(1+\gamma_1)(|n|+2\gamma_K)|n|!}{2ZN_{nK}(N_{nK}-K)\Gamma(|n|+2\gamma_K)}} \\ &\quad \times \left(\frac{2Zr}{a_0}\right)^{\gamma_K} \mathrm{e}^{-Zr/a_0} \left[L_{|n|-1}^{(2\gamma_K)}\left(\frac{2Zr}{a_0}\right) + \frac{K-N_{nK}}{|n|+2\gamma_K} L_{|n|}^{(2\gamma_K)}\left(\frac{2Zr}{a_0}\right) \right] \end{aligned} \tag{2.31}$$

and

$$\begin{aligned} T_{nK}^{(0)}(r) &= \sqrt{\frac{(1-\gamma_1)(|n|+2\gamma_K)|n|!}{2ZN_{nK}(N_{nK}-K)\Gamma(|n|+2\gamma_K)}} \\ &\quad \times \left(\frac{2Zr}{a_0}\right)^{\gamma_K} \mathrm{e}^{-Zr/a_0} \left[L_{|n|-1}^{(2\gamma_K)}\left(\frac{2Zr}{a_0}\right) - \frac{K-N_{nK}}{|n|+2\gamma_K} L_{|n|}^{(2\gamma_K)}\left(\frac{2Zr}{a_0}\right) \right] \end{aligned} \tag{2.32}$$

(with $L_n^{(\alpha)}(\rho)$ denoting the generalized Laguerre polynomials [15]; we define $L_{-1}^{(\alpha)}(\rho) \equiv 0$) are the radial Dirac–Coulomb Sturmian functions associated with the hydrogenic ground-state energy level, and

$$\mu_{nK}^{(0)} = \frac{|n|+\gamma_K+N_{nK}}{\gamma_1+1}, \tag{2.33}$$

where

$$N_{nK} = \pm\sqrt{(|n|+\gamma_K)^2+(Z\alpha)^2} = \pm\sqrt{|n|^2+2|n|\gamma_K+K^2} \tag{2.34}$$

is the 'apparent principal quantum number' (notice that it may assume positive as well as negative values!). The following sign convention applies to the definition (2.34): the plus sign should be chosen for $n>0$ and the minus one for $n<0$; for $n=0$ one chooses the plus sign if $K<0$ and the minus sign if $K>0$.

At first, we attack the double integral in the expression for $\sigma_{\mathrm{E},1}$. Inserting Eqs. (2.5), (2.6) and (2.30)–(2.33) into the right-hand side of Eq. (2.27), taking the two resulting separated integrals with the aid of the known formula [16, Eq. (7.414.11)]

$$\int_0^\infty \mathrm{d}\rho\, \rho^\beta \mathrm{e}^{-\rho} L_n^{(\alpha)}(\rho) = \frac{\Gamma(\beta+1)\Gamma(n+\alpha-\beta)}{n!\Gamma(\alpha-\beta)} = (-)^n \frac{\Gamma(\beta+1)\Gamma(\beta-\alpha+1)}{n!\Gamma(\beta-\alpha-n+1)} \qquad [\mathrm{Re}(\beta)>-1] \tag{2.35}$$

and employing Eq. (2.34), we obtain $\sigma_{\mathrm{E},1}$ in the form of the following finite sum:

$$\begin{aligned} \sigma_{\mathrm{E},1} &= \frac{2}{9Z}(\gamma_1+1)^2(2\gamma_1+1)\Gamma(2\gamma_1-1) \\ &\quad \times \sum_{n=-2}^{2} (-)^n \frac{(N_{n1}-1)(|n|+N_{n1}+1)(|n|-\gamma_1 N_{n1}-\gamma_1+1)}{N_{n1}(2-|n|)!\Gamma(|n|+2\gamma_1+1)(|n|+N_{n1}-1)}. \end{aligned} \tag{2.36}$$

Using again Eq. (2.34), after some algebra, the right-hand side of Eq. (2.36) simplifies considerably, yielding

$$\sigma_{\mathrm{E},1} = \frac{2\gamma_1+1}{9Z}. \tag{2.37}$$

As one of the two separated integrals evaluated above converges at its lower integration limit provided $\gamma_1 > 1/2$, we have the following constraint on the nuclear charge:

$$Z < \alpha^{-1}\frac{\sqrt{3}}{2} \simeq 118.67. \tag{2.38}$$

Evaluation of the double integral on the right-hand side of Eq. (2.28) appears to be much more cumbersome. Proceeding initially as in the case discussed above, employing Eq. (2.34) and the trivial but useful identity

$$\gamma_2^2 = \gamma_1^2 + 3, \tag{2.39}$$

with much labor we obtain

$$\begin{aligned}\sigma_{\mathrm{E},-2} &= \frac{1}{2Z}\frac{(\gamma_1+1)\Gamma(\gamma_2+\gamma_1-1)\Gamma(\gamma_2+\gamma_1+2)}{\Gamma(\gamma_2-\gamma_1-1)\Gamma(\gamma_2-\gamma_1+2)\Gamma(2\gamma_1+1)} \\ &\quad\times\sum_{n=-\infty}^{\infty}\frac{\Gamma(|n|+\gamma_2-\gamma_1+1)\Gamma(|n|+\gamma_2-\gamma_1-2)}{|n|!\Gamma(|n|+2\gamma_2+1)}\frac{N_{n,-2}+2}{N_{n,-2}} \\ &\quad\times\frac{(|n|+\gamma_2+\gamma_1+1-\gamma_1 N_{n,-2})[(\gamma_1-1)(2\gamma_1+5)-(2\gamma_1-1)(|n|+\gamma_2+N_{n,-2})]}{|n|+\gamma_2-\gamma_1-1+N_{n,-2}}.\end{aligned} \tag{2.40}$$

Collecting together those terms in the above series which correspond to the same absolute value of n, again with the use of Eqs. (2.34) and (2.39), we arrive at

$$\begin{aligned}\sigma_{\mathrm{E},-2} &= -\frac{4}{9Z}\frac{(\gamma_1+1)\Gamma(\gamma_2+\gamma_1-1)\Gamma(\gamma_2+\gamma_1+2)}{\Gamma(\gamma_2-\gamma_1-1)\Gamma(\gamma_2-\gamma_1+2)\Gamma(2\gamma_1+1)} \\ &\quad\times\sum_{n=0}^{\infty}\frac{\Gamma(n+\gamma_2-\gamma_1-2)\Gamma(n+\gamma_2-\gamma_1)}{n!\Gamma(n+2\gamma_2+1)} \\ &\quad\times\big[3(\gamma_1-1)(n+\gamma_2-\gamma_1-2)(n+\gamma_2-\gamma_1)+(2\gamma_1^2+2\gamma_1-3)(n+\gamma_2-\gamma_1)-3(\gamma_1-2)\big].\end{aligned} \tag{2.41}$$

The series in Eq. (2.41) does not terminate. Nevertheless, we shall show that $\sigma_{\mathrm{E},-2}$ may be expressed in the form which is as elementary as the one in the case of $\sigma_{\mathrm{E},1}$. To this end, we invoke the relationship

$$\sum_{n=0}^{\infty}\frac{\Gamma(n+a_1)\Gamma(n+a_2)}{\Gamma(n+b)}\frac{z^n}{n!} = \frac{\Gamma(a_1)\Gamma(a_2)}{\Gamma(b)}\,{}_2F_1\left(\begin{array}{c}a_1,a_2\\ b\end{array};z\right) \qquad (|z|\leqslant 1), \tag{2.42}$$

where ${}_2F_1$ is the hypergeometric function. Transforming Eq. (2.41) with the aid of the above formula results in

$$\begin{aligned}\sigma_{\mathrm{E},-2} &= -\frac{4}{9Z}\frac{(\gamma_1+1)\Gamma(\gamma_2+\gamma_1-1)\Gamma(\gamma_2+\gamma_1+2)}{(\gamma_2-\gamma_1-2)(\gamma_2-\gamma_1)(\gamma_2-\gamma_1+1)\Gamma(2\gamma_1+1)\Gamma(2\gamma_2+1)} \\ &\quad\times\Bigg[3(\gamma_1-1)(\gamma_2-\gamma_1-2)(\gamma_2-\gamma_1)\,{}_2F_1\left(\begin{array}{c}\gamma_2-\gamma_1-1,\gamma_2-\gamma_1+1\\ 2\gamma_2+1\end{array};1\right) \\ &\quad+(2\gamma_1^2+2\gamma_1-3)(\gamma_2-\gamma_1)\,{}_2F_1\left(\begin{array}{c}\gamma_2-\gamma_1-2,\gamma_2-\gamma_1+1\\ 2\gamma_2+1\end{array};1\right) \\ &\quad-3(\gamma_1-2)\,{}_2F_1\left(\begin{array}{c}\gamma_2-\gamma_1-2,\gamma_2-\gamma_1\\ 2\gamma_2+1\end{array};1\right)\Bigg].\end{aligned} \tag{2.43}$$

Now, we owe to Gauss the following identity [15]:

$${}_2F_1\left(\begin{array}{c}a_1,a_2\\ b\end{array};1\right) = \frac{\Gamma(b)\Gamma(b-a_1-a_2)}{\Gamma(b-a_1)\Gamma(b-a_2)} \qquad [\mathrm{Re}(b-a_1-a_2)>0]. \tag{2.44}$$

Applying it to the three ${}_2F_1$ functions appearing in Eq. (2.43), we find

$$ {}_2F_1\left(\begin{matrix}\gamma_2-\gamma_1-1,\gamma_2-\gamma_1+1\\ 2\gamma_2+1\end{matrix};1\right)=\frac{\Gamma(2\gamma_1+1)\Gamma(2\gamma_2+1)}{\Gamma(\gamma_2+\gamma_1)\Gamma(\gamma_2+\gamma_1+2)}, \tag{2.45} $$

$$ {}_2F_1\left(\begin{matrix}\gamma_2-\gamma_1-2,\gamma_2-\gamma_1+1\\ 2\gamma_2+1\end{matrix};1\right)=\frac{\Gamma(2\gamma_1+2)\Gamma(2\gamma_2+1)}{\Gamma(\gamma_2+\gamma_1)\Gamma(\gamma_2+\gamma_1+3)} \tag{2.46} $$

and

$$ {}_2F_1\left(\begin{matrix}\gamma_2-\gamma_1-2,\gamma_2-\gamma_1\\ 2\gamma_2+1\end{matrix};1\right)=\frac{\Gamma(2\gamma_1+3)\Gamma(2\gamma_2+1)}{\Gamma(\gamma_2+\gamma_1+1)\Gamma(\gamma_2+\gamma_1+3)}. \tag{2.47} $$

Plugging Eqs. (2.45)–(2.47) into Eq. (2.43), after some further simplifications based on the use of the relation (2.39), we arrive at the afore-announced elementary representation of the $K=-2$ component of the shielding constant:

$$ \sigma_{\mathrm{E},-2}=-\frac{2(\gamma_1-4)}{9Z}. \tag{2.48} $$

Insertion of $\sigma_{\mathrm{E},1}$ and $\sigma_{\mathrm{E},-2}$ as given in Eqs. (2.37) and (2.48), respectively, into Eq. (2.26) leads us to the conclusion that the electric dipole shielding constant for the Dirac hydrogenic atom in its ground state is

$$ \sigma_{\mathrm{E}}=Z^{-1}, \tag{2.49} $$

as it should be.

In the nonrelativistic limit

$$ \gamma_1\simeq 1-\frac{1}{2}(Z\alpha)^2, \tag{2.50} $$

so that one has

$$ \sigma_{\mathrm{E},1}\simeq\frac{1}{3Z}\left[1-\frac{1}{3}(Z\alpha)^2\right] \tag{2.51} $$

and

$$ \sigma_{\mathrm{E},-2}\simeq\frac{2}{3Z}\left[1+\frac{1}{6}(Z\alpha)^2\right]. \tag{2.52} $$

3 The magnetic dipole shielding constant

We proceed to the evaluation of the magnetic dipole shielding constant. The model of the hydrogen-like atom we shall adopt for this purpose is the same as in the preceding section.

In a weak, constant, uniform magnetic field $\boldsymbol{B}_{\mathrm{ext}}$, the atomic ground energy level $\mathcal{E}^{(0)}$ splits into two, their energies being given, to the first order in $\boldsymbol{B}_{\mathrm{ext}}$, by

$$ \mathcal{E}_\mu\simeq\mathcal{E}^{(0)}+\mathcal{E}_\mu^{(1)}\qquad(\mu=\pm\tfrac{1}{2}), \tag{3.1} $$

with

$$ \mathcal{E}_\mu^{(1)}=\operatorname{sgn}(\mu)\frac{2\gamma_1+1}{3}\mu_{\mathrm{B}}B_{\mathrm{ext}}, \tag{3.2} $$

where μ_B is the Bohr magneton. The corresponding wave functions, to the same approximation order, are

$$ \Psi_\mu(\boldsymbol{r})\simeq\Psi_\mu^{(0)}(\boldsymbol{r})+\Psi_\mu^{(1)}(\boldsymbol{r})\qquad(\mu=\pm\tfrac{1}{2}), \tag{3.3} $$

with $\Psi_\mu^{(0)}(\boldsymbol{r})$ given by Eq. (2.4) (the space quantization axis being chosen along the external magnetic field direction) and with

$$ \Psi_\mu^{(1)}(\boldsymbol{r})=-\frac{1}{2}ec\boldsymbol{B}_{\mathrm{ext}}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\,\bar{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')(\boldsymbol{r}'\times\boldsymbol{\alpha})\Psi_\mu^{(0)}(\boldsymbol{r}'). \tag{3.4} $$

Here, $\boldsymbol{\alpha}$ is the Dirac 4×4 vector matrix given standardly by

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{pmatrix}, \tag{3.5}$$

where $\boldsymbol{\sigma}$ is the vector composed of the Pauli matrices.

According to the Dirac theory, there is an electric current with density

$$\boldsymbol{j}_{\mu}(\boldsymbol{r}) = -ec\Psi_{\mu}^{\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\Psi_{\mu}(\boldsymbol{r}) \tag{3.6}$$

associated with the electron being in the state $\Psi_{\mu}(\boldsymbol{r})$. Using the Biot–Savart law, we find that at the point $\boldsymbol{r}$ the magnetic field due to the current distribution $\boldsymbol{j}_{\mu}(\boldsymbol{r}')$ is

$$\boldsymbol{B}_{\mu}(\boldsymbol{r}) = \frac{\mu_0}{4\pi} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \boldsymbol{j}_{\mu}(\boldsymbol{r}') \times \frac{\boldsymbol{r} - \boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}'|^3}. \tag{3.7}$$

In the particular case when the observation point is located at the nucleus, i.e., at $\boldsymbol{r} = \mathbf{0}$, the above expression simplifies to

$$\boldsymbol{B}_{\mu}(\mathbf{0}) = \frac{\mu_0}{4\pi} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \frac{\boldsymbol{r}' \times \boldsymbol{j}_{\mu}(\boldsymbol{r}')}{r'^{\,3}}. \tag{3.8}$$

If, as we have assumed above, the electronic wave function $\Psi_{\mu}(\boldsymbol{r})$ is known to the first order in the perturbing field $\boldsymbol{B}_{\mathrm{ext}}$, the current $\boldsymbol{j}_{\mu}(\boldsymbol{r})$ may be approximated as

$$\boldsymbol{j}_{\mu}(\boldsymbol{r}) \simeq \boldsymbol{j}_{\mu}^{(0)}(\boldsymbol{r}) + \boldsymbol{j}_{\mu}^{(1)}(\boldsymbol{r}), \tag{3.9}$$

with

$$\boldsymbol{j}_{\mu}^{(0)}(\boldsymbol{r}) = -ec\Psi_{\mu}^{(0)\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\Psi_{\mu}^{(0)}(\boldsymbol{r}) \tag{3.10}$$

and

$$\boldsymbol{j}_{\mu}^{(1)}(\boldsymbol{r}) = -2ec\,\mathrm{Re}[\Psi_{\mu}^{(0)\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\Psi_{\mu}^{(1)}(\boldsymbol{r})]. \tag{3.11}$$

Consequently, for the magnetic field at the nucleus location we have

$$\boldsymbol{B}_{\mu}(\mathbf{0}) \simeq \boldsymbol{B}_{\mu}^{(0)}(\mathbf{0}) + \boldsymbol{B}_{\mu}^{(1)}(\mathbf{0}), \tag{3.12}$$

with

$$\boldsymbol{B}_{\mu}^{(0)}(\mathbf{0}) = -ec\,\frac{\mu_0}{4\pi} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \frac{\Psi_{\mu}^{(0)\dagger}(\boldsymbol{r}')\boldsymbol{r}' \times \boldsymbol{\alpha}\Psi_{\mu}^{(0)}(\boldsymbol{r}')}{r'^{\,3}} \tag{3.13}$$

and

$$\boldsymbol{B}_{\mu}^{(1)}(\mathbf{0}) = -2ec\,\frac{\mu_0}{4\pi}\,\mathrm{Re} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \frac{\Psi_{\mu}^{(0)\dagger}(\boldsymbol{r}')\boldsymbol{r}' \times \boldsymbol{\alpha}\Psi_{\mu}^{(1)}(\boldsymbol{r}')}{r'^{\,3}}. \tag{3.14}$$

If Eq. (3.13) is rewritten in the form

$$\boldsymbol{B}_{\mu}^{(0)}(\mathbf{0}) = -ec\,\frac{\mu_0}{4\pi} \sum_{n=-1}^{1} \boldsymbol{e}_n^{*} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \frac{\Psi_{\mu}^{(0)\dagger}(\boldsymbol{r}')r'\boldsymbol{e}_n \cdot (\boldsymbol{n}_r' \times \boldsymbol{\alpha})\Psi_{\mu}^{(0)}(\boldsymbol{r}')}{r'^{\,3}}, \tag{3.15}$$

using Eqs. (2.4)–(2.6) and the spherical spinor identities [14]

$$\begin{aligned} \boldsymbol{e}_0 \cdot (\boldsymbol{n}_r \times \boldsymbol{\sigma})\,\Omega_{\kappa\mu}(\boldsymbol{n}_r) \quad = \quad & \mathrm{i}\frac{4\mu\kappa}{4\kappa^2 - 1}\Omega_{-\kappa\mu}(\boldsymbol{n}_r) + \mathrm{i}\frac{\sqrt{(\kappa + \frac{1}{2})^2 - \mu^2}}{|2\kappa + 1|}\Omega_{\kappa+1,\mu}(\boldsymbol{n}_r) \\ & - \mathrm{i}\frac{\sqrt{(\kappa - \frac{1}{2})^2 - \mu^2}}{|2\kappa - 1|}\Omega_{\kappa-1,\mu}(\boldsymbol{n}_r), \end{aligned} \tag{3.16}$$

$$
\begin{aligned}
\boldsymbol{e}_{\pm 1} \cdot (\boldsymbol{n}_r \times \boldsymbol{\sigma})\, \Omega_{\kappa\mu}(\boldsymbol{n}_r) \quad = \quad & \mp \mathrm{i} 2\sqrt{2}\kappa \frac{\sqrt{\kappa^2 - (\mu \pm \frac{1}{2})^2}}{4\kappa^2 - 1} \Omega_{-\kappa,\mu\pm 1}(\boldsymbol{n}_r) \\
& + \mathrm{i} \frac{\sqrt{(\kappa \pm \mu + \frac{1}{2})(\kappa \pm \mu + \frac{3}{2})}}{\sqrt{2}(2\kappa + 1)} \Omega_{\kappa+1,\mu\pm 1}(\boldsymbol{n}_r) \\
& + \mathrm{i} \frac{\sqrt{(\kappa \mp \mu - \frac{1}{2})(\kappa \mp \mu - \frac{3}{2})}}{\sqrt{2}(2\kappa - 1)} \Omega_{\kappa-1,\mu\pm 1}(\boldsymbol{n}_r),
\end{aligned} \tag{3.17}
$$

with no difficulty one finds that

$$
\boldsymbol{B}_{\mu}^{(0)}(\mathbf{0}) = \mathrm{sgn}(-\mu) \frac{8}{3\gamma_1(2\gamma_1 - 1)} b_0 \boldsymbol{n}_{\mathrm{ext}}, \tag{3.18}
$$

where

$$
b_0 = \frac{\mu_0}{4\pi} \frac{\mu_{\mathrm{B}}}{a_0^3} \tag{3.19}
$$

is the atomic unit of the magnetic field induction, while $\boldsymbol{n}_{\mathrm{ext}}$ is the unit vector along $\boldsymbol{B}_{\mathrm{ext}}$. The radial integral

$$
\int_0^\infty \mathrm{d}r\, r^{-2} P^{(0)}(r) Q^{(0)}(r),
$$

encountered in the course of evaluation of $\boldsymbol{B}_{\mu}^{(0)}(\mathbf{0})$, converges at its lower limit provided $\gamma_1 > 1/2$, which constrains the nuclear charge as in Eq. (2.38).

To evaluate the first order approximation to the magnetic field induced at the nucleus, we plug Eq. (3.4) into Eq. (3.14). This gives

$$
\boldsymbol{B}_{\mu}^{(1)}(\mathbf{0}) = -\boldsymbol{\Sigma}_{\mathrm{M},\mu} \cdot \boldsymbol{B}_{\mathrm{ext}}, \tag{3.20}
$$

where

$$
\boldsymbol{\Sigma}_{\mathrm{M},\mu} = -\frac{e^2}{4\pi\epsilon_0} \mathrm{Re} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \Psi_{\mu}^{(0)\dagger}(\boldsymbol{r}) \frac{\boldsymbol{r} \times \boldsymbol{\alpha}}{r^3} \bar{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}') \boldsymbol{r}' \times \boldsymbol{\alpha} \Psi_{\mu}^{(0)}(\boldsymbol{r}') \tag{3.21}
$$

is the magnetic dipole shielding tensor. Rewriting Eq. (3.21) in the form

$$
\boldsymbol{\Sigma}_{\mathrm{M},\mu} = -\frac{e^2}{4\pi\epsilon_0} \mathrm{Re} \sum_{n,n'=-1}^{+1} \boldsymbol{e}_n \boldsymbol{e}_{n'}^* \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \Psi_{\mu}^{(0)\dagger}(\boldsymbol{r}) r^{-2} \boldsymbol{e}_n^* \cdot (\boldsymbol{n}_r \times \boldsymbol{\alpha}) \bar{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}') r' \boldsymbol{e}_{n'} \cdot (\boldsymbol{n}_r' \times \boldsymbol{\alpha}) \Psi_{\mu}^{(0)}(\boldsymbol{r}'), \tag{3.22}
$$

inserting the multipole representation (2.22) of the generalized Dirac–Coulomb Green function into Eq. (3.22) and using the relations (3.16) and (3.17) to carry out integrations over the angles of the vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$, after some labor we discover that, like its electric counterpart, the tensor $\boldsymbol{\Sigma}_{\mathrm{M},\mu}$ is a multiple of the unit dyad:

$$
\boldsymbol{\Sigma}_{\mathrm{M},\mu} = \sigma_{\mathrm{M}} \mathsf{I}. \tag{3.23}
$$

As the notation used indicates, the factor σ_{M}, being the magnetic shielding constant for the system under study, is independent of the angular momentum projection quantum number μ; it is given by the sum

$$
\sigma_{\mathrm{M}} = \sigma_{\mathrm{M},-1} + \sigma_{\mathrm{M},2}, \tag{3.24}
$$

where

$$
\sigma_{\mathrm{M},-1} = -\frac{4}{9} \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}r' \begin{pmatrix} Q^{(0)}(r) & P^{(0)}(r) \end{pmatrix} r^{-2} \bar{\mathsf{G}}_{-1}^{(0)}(r, r') r' \begin{pmatrix} Q^{(0)}(r') \\ P^{(0)}(r') \end{pmatrix} \tag{3.25}
$$

and

$$
\sigma_{\mathrm{M},2} = -\frac{2}{9} \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}r' \begin{pmatrix} Q^{(0)}(r) & P^{(0)}(r) \end{pmatrix} r^{-2} \bar{\mathsf{G}}_{2}^{(0)}(r, r') r' \begin{pmatrix} Q^{(0)}(r') \\ P^{(0)}(r') \end{pmatrix}. \tag{3.26}
$$

The Sturmian expansion of $\bar{\mathsf{G}}_K^{(0)}(r,r')$ given in Eq. (2.30) is inapplicable in the case of $K=-1$ and thus it cannot be used for the purpose of evaluation of the double integral in Eq. (3.25). The valid Sturmian representation of $\bar{\mathsf{G}}_{-1}^{(0)}(r,r')$ which we employ for that purpose is [1]

$$
\begin{aligned}
\bar{\mathsf{G}}_{-1}^{(0)}(r,r') &= \sum_{\substack{n=-\infty \\ (n\neq 0)}}^{\infty} \frac{1}{\mu_{n,-1}^{(0)}-1} \begin{pmatrix} S_{n,-1}^{(0)}(r) \\ T_{n,-1}^{(0)}(r) \end{pmatrix} \begin{pmatrix} \mu_{n,-1}^{(0)} S_{n,-1}^{(0)}(r') & T_{n,-1}^{(0)}(r') \end{pmatrix} \\
&\quad + \left(\gamma_1 - \tfrac{1}{2}\right) \begin{pmatrix} S_{0,-1}^{(0)}(r) \\ T_{0,-1}^{(0)}(r) \end{pmatrix} \begin{pmatrix} S_{0,-1}^{(0)}(r') & T_{0,-1}^{(0)}(r') \end{pmatrix} \\
&\quad + \begin{pmatrix} I^{(0)}(r) \\ K^{(0)}(r) \end{pmatrix} \begin{pmatrix} S_{0,-1}^{(0)}(r') & T_{0,-1}^{(0)}(r') \end{pmatrix} \\
&\quad + \begin{pmatrix} S_{0,-1}^{(0)}(r) \\ T_{0,-1}^{(0)}(r) \end{pmatrix} \begin{pmatrix} J^{(0)}(r') & K^{(0)}(r') \end{pmatrix},
\end{aligned} \tag{3.27}
$$

where

$$
I^{(0)}(r) = \left(\gamma_1 - \tfrac{1}{2}\right) S_{0,-1}^{(0)}(r) + \gamma_1 \left(\frac{1+\gamma_1}{\alpha} \frac{r}{a_0} + Z\alpha \right) T_{0,-1}^{(0)}(r), \tag{3.28}
$$

$$
\begin{aligned}
J^{(0)}(r) &= I^{(0)}(r) + S_{0,-1}^{(0)}(r) \\
&= \left(\gamma_1 + \tfrac{1}{2}\right) S_{0,-1}^{(0)}(r) + \gamma_1 \left(\frac{1+\gamma_1}{\alpha} \frac{r}{a_0} + Z\alpha \right) T_{0,-1}^{(0)}(r)
\end{aligned} \tag{3.29}
$$

and

$$
K^{(0)}(r) = \gamma_1 \left(\frac{1-\gamma_1}{\alpha} \frac{r}{a_0} - Z\alpha \right) S_{0,-1}^{(0)}(r) - \left(\gamma_1 - \tfrac{1}{2}\right) T_{0,-1}^{(0)}(r). \tag{3.30}
$$

Exploiting Eqs. (2.5), (2.6) and (2.31)–(2.35), we find that

$$
\begin{aligned}
\sigma_{\mathrm{M},-1} &= -\frac{8Z\alpha^2}{9}(\gamma_1+1)(2\gamma_1+1)\Gamma(2\gamma_1-1) \\
&\quad \times \sum_{\substack{n=-2 \\ (n\neq 0)}}^{+2} (-)^n \frac{N_{n,-1}+1}{N_{n,-1}} \frac{|n|+1}{(2-|n|)!\Gamma(|n|+2\gamma_1+1)(|n|+N_{n,-1}-1)} \\
&\quad - \frac{2Z\alpha^2}{9}\frac{2\gamma_1+1}{\gamma_1} - \frac{2Z\alpha^2}{9}\frac{2\gamma_1+1}{2\gamma_1-1} + \frac{2Z\alpha^2}{9}\frac{2\gamma_1+1}{\gamma_1},
\end{aligned} \tag{3.31}
$$

terms on the right-hand side being ordered in correspondence with Eq. (3.27). The first of them is readily found to be $8Z\alpha^2/[9\gamma_1(2\gamma_1-1)]$, so that $\sigma_{\mathrm{M},-1}$ is

$$
\sigma_{\mathrm{M},-1} = -\frac{2Z\alpha^2}{9}\frac{2\gamma_1^2+\gamma_1-4}{\gamma_1(2\gamma_1-1)}. \tag{3.32}
$$

To calculate $\sigma_{\mathrm{M},2}$ from Eq. (3.26), we use $\bar{\mathsf{G}}_2^{(0)}(r,r')$ in the form (2.30). Applying Eqs. (2.5), (2.6), (2.31)–(2.35) and (2.39), we arrive at

$$
\begin{aligned}
\sigma_{\mathrm{M},2} &= \frac{2Z\alpha^2}{9}\frac{\Gamma(\gamma_2+\gamma_1-1)\Gamma(\gamma_2+\gamma_1+2)}{\Gamma(\gamma_2-\gamma_1-1)\Gamma(\gamma_2-\gamma_1+2)\Gamma(2\gamma_1+1)} \\
&\quad \times \sum_{n=-\infty}^{\infty} \frac{\Gamma(|n|+\gamma_2-\gamma_1-2)\Gamma(|n|+\gamma_2-\gamma_1+2)}{|n|!\Gamma(|n|+2\gamma_2+1)} \frac{N_{n2}-2}{N_{n2}} \\
&\quad \times \frac{3|n|+3\gamma_2+\gamma_1+1+3N_{n2}}{|n|+\gamma_2-\gamma_1-1+N_{n2}}.
\end{aligned} \tag{3.33}
$$

The simplification is achieved after one collects terms with the same absolute value of n. This gives

$$\sigma_{\mathrm{M},2} = \frac{2Z\alpha^2}{9} \frac{\Gamma(\gamma_2+\gamma_1-1)\Gamma(\gamma_2+\gamma_1+2)}{\Gamma(\gamma_2-\gamma_1-1)\Gamma(\gamma_2-\gamma_1+2)\Gamma(2\gamma_1+1)} \sum_{n=0}^{\infty} \frac{\Gamma(n+\gamma_2-\gamma_1-1)\Gamma(n+\gamma_2-\gamma_1+2)}{n!\Gamma(n+2\gamma_2+1)(n+\gamma_2-\gamma_1)}, \tag{3.34}$$

which is the final expression for $\sigma_{\mathrm{M},2}$ provided in Ref. [5]. We shall show that, similarly to the series in Eq. (2.41), the one in Eq. (3.34) may be also summed to a closed elementary form. To this end, we rewrite the latter equation as

$$\begin{aligned} \sigma_{\mathrm{M},2} \;&=\; \frac{2Z\alpha^2}{9} \frac{\Gamma(\gamma_2+\gamma_1-1)\Gamma(\gamma_2+\gamma_1+2)}{\Gamma(\gamma_2-\gamma_1-1)\Gamma(\gamma_2-\gamma_1+2)\Gamma(2\gamma_1+1)} \\ &\quad\times \left[\sum_{n=0}^{\infty} \frac{\Gamma(n+\gamma_2-\gamma_1-1)\Gamma(n+\gamma_2-\gamma_1)}{n!\Gamma(n+2\gamma_2+1)} \right. \\ &\quad\left. + \sum_{n=0}^{\infty} \frac{\Gamma(n+\gamma_2-\gamma_1-1)\Gamma(n+\gamma_2-\gamma_1+1)}{n!\Gamma(n+2\gamma_2+1)} \right] \end{aligned} \tag{3.35}$$

and further, after use is made of Eq. (2.42), as

$$\begin{aligned} \sigma_{\mathrm{M},2} \;&=\; \frac{2Z\alpha^2}{9} \frac{\Gamma(\gamma_2+\gamma_1-1)\Gamma(\gamma_2+\gamma_1+2)}{(\gamma_2-\gamma_1)(\gamma_2-\gamma_1+1)\Gamma(2\gamma_1+1)\Gamma(2\gamma_2+1)} \\ &\quad\times \left[{}_2F_1\left(\begin{matrix} \gamma_2-\gamma_1-1, \gamma_2-\gamma_1 \\ 2\gamma_2+1 \end{matrix} ;1 \right) + (\gamma_2-\gamma_1)\, {}_2F_1\left(\begin{matrix} \gamma_2-\gamma_1-1, \gamma_2-\gamma_1+1 \\ 2\gamma_2+1 \end{matrix} ;1 \right) \right]. \end{aligned} \tag{3.36}$$

According to Eq. (2.44), the first of the two ${}_2F_1$ functions appearing above is

$${}_2F_1\left(\begin{matrix} \gamma_2-\gamma_1-1, \gamma_2-\gamma_1 \\ 2\gamma_2+1 \end{matrix} ;1 \right) = \frac{\Gamma(2\gamma_1+2)\Gamma(2\gamma_2+1)}{\Gamma(\gamma_2+\gamma_1+1)\Gamma(\gamma_2+\gamma_1+2)}, \tag{3.37}$$

while the second one has been already encountered in the course of evaluation of $\sigma_{\mathrm{E},-2}$ and is given by Eq. (2.45). Hence, once Eqs. (2.45) and (3.37) are inserted into Eq. (3.36), we eventually arrive at the following simple representation of $\sigma_{\mathrm{M},2}$:

$$\sigma_{\mathrm{M},2} = \frac{2Z\alpha^2}{27} \frac{\gamma_1+2}{\gamma_1+1}. \tag{3.38}$$

From the expressions for the components $\sigma_{\mathrm{M},-1}$ and $\sigma_{\mathrm{M},2}$ of σ_{M}, displayed in Eqs. (3.32) and (3.38), we deduce that the total magnetic shielding constant for the hydrogen-like atom in its ground state is

$$\sigma_{\mathrm{M}} = -\frac{2Z\alpha^2}{27} \frac{4\gamma_1^3+6\gamma_1^2-7\gamma_1-12}{\gamma_1(\gamma_1+1)(2\gamma_1-1)}, \tag{3.39}$$

in agreement with the findings of Moore [9], Pyper and Zhang [10] and also of Ivanov *et al.* [11] (after one takes into account that the latter authors define σ_{M} with the opposite sign). The expression for σ_{M} given by Zapryagaev *et al.* in Refs. [6–8] becomes equivalent to the one in Eq. (3.39) after in the denominator of the former one replaces λ_2 by λ_1, the latter quantity being identical with our γ_1.

In the nonrelativistic limit one has

$$\sigma_{\mathrm{M},-1} \simeq \frac{2Z\alpha^2}{9} \left[1+4(Z\alpha)^2\right] \tag{3.40}$$

and

$$\sigma_{\mathrm{M},2} \simeq \frac{Z\alpha^2}{9} \left[1+\frac{1}{12}(Z\alpha)^2\right], \tag{3.41}$$

and also

$$\sigma_{\mathrm{M}} \simeq \frac{Z\alpha^2}{3} \left[1+\frac{97}{36}(Z\alpha)^2\right]. \tag{3.42}$$

4 Conclusions

In this paper, we have proved that the analytical technique based on the Sturmian expansion of the generalized Dirac–Coulomb Green function enables one to arrive at the same simple closed-form representations of the electric (σ_{E}) and magnetic (σ_{M}) dipole shielding constants for the Dirac one-electron atom in its ground state as have been given previously by several other authors. We find this encouraging in the perspective of our planned, mathematically much more challenging, application of the same calculational technique to the evaluation of σ_{M} for an *arbitrary* state of that atom. Accomplishment of this task would be undoubtly worthy of effort since although results for some particular excited states are known (cf., e.g., Ref. [9–11]), in the most general case, to the best of our knowledge, calculations of σ_{M} have never been carried out.

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