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Magnetizability of the relativistic hydrogen-like atom: application of the Sturmian expansion of the first-order Dirac–Coulomb Green function

Radosław Szmytkowski

Atomic Physics Division, Department of Atomic Physics and Luminescence, Faculty of Applied Physics and Mathematics, Technical University of Gdańsk, Narutowicza 11/12, PL 80–952 Gdańsk, Poland

E-mail: radek@mif.pg.gda.pl

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Abstract
The Sturmian expansion of the first-order Dirac–Coulomb Green function (Szmytkowski R 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 825) is employed to derive an analytical formula for the magnetizability of the relativistic hydrogen-like atom in the ground state. The Gordon decomposition of the magnetizability is carried out, allowing one to identify its diamagnetic and paramagnetic parts.

1. Introduction

Within the framework of non-relativistic Schrödinger–Pauli wave mechanics, one shows that the magnetizability of a one-electron system in a state described by a two-component function $\psi^{(0)}(\boldsymbol{r})$ is

$$\chi_{\mathrm{nr}} = \chi_{\mathrm{nr,d}} + \chi_{\mathrm{nr,p}} \tag{1.1}$$

where

$$\chi_{\mathrm{nr,d}} = -\tfrac{1}{4}\alpha^2 a_0 \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \psi^{(0)\dagger}(\boldsymbol{r})(\boldsymbol{n}_z \times \boldsymbol{r})^2 \psi^{(0)}(\boldsymbol{r}) \tag{1.2}$$

and

$$\chi_{\mathrm{nr,p}} = \tfrac{1}{2}\alpha^4 a_0^3 mc^2 \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}} + \boldsymbol{\sigma})\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}}' + \boldsymbol{\sigma})\psi^{(0)}(\boldsymbol{r}') \tag{1.3}$$

are so-called diamagnetic (or Langevin–Larmor) and paramagnetic (or Van Vleck) contributions to χ_{nr}, respectively [1]. Here $\alpha = e^2/(4\pi\epsilon_0)c\hbar$ and $a_0 = (4\pi\epsilon_0)\hbar^2/me^2$ denote the Sommerfeld fine-structure constant and the Bohr radius, respectively, $\boldsymbol{n}_z$ is a unit vector along the z-axis (coinciding with the angular momenta quantization axis) of the Cartesian coordinate system,

$$\hat{\mathbf{\Lambda}} = -\mathrm{i}\boldsymbol{r} \times \boldsymbol{\nabla} \tag{1.4}$$

$\boldsymbol{\sigma}$ is a vector composed of Pauli matrices and $\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')$ is a generalized Green function associated with an energy level to which the function $\psi^{(0)}(\boldsymbol{r})$ belongs.

Evaluating the integrals (1.2) and (1.3) for the ground state of a non-relativistic hydrogen-like atom with an infinitely heavy point-like and spinless nucleus of charge Ze, one easily finds that

$$\chi_{\mathrm{nr,d}} = -\frac{1}{2}\frac{\alpha^2 a_0^3}{Z^2} \qquad \chi_{\mathrm{nr,p}} = 0 \tag{1.5}$$

hence, the well known result

$$\chi_{\mathrm{nr}} = -\frac{1}{2}\frac{\alpha^2 a_0^3}{Z^2} \tag{1.6}$$

follows.

The validity of the formula (1.6) is restricted to low-Z hydrogen-like atoms. For multiply charged one-electron atoms this expression should be replaced by its generalization obtained within the framework of the relativistic Dirac wave mechanics. Such a relativistic formula for χ was derived independently by Granovskii and Nechet [2], who used an integral representation of radial components of the *first*-order Dirac–Coulomb Green function, and by Manakov *et al* [3] (cf also [4–7]), who used a Sturmian expansion of the *second*-order Dirac–Coulomb Green function.

In this paper we show that the magnetizability of the relativistic hydrogen-like atom may be conveniently and easily derived, in a way alternative to those presented in [2, 3], by using a Sturmian expansion of the *first*-order Dirac–Coulomb Green function found by us some time ago [8,9]. We tabulate magnetizabilities for hydrogen-like atoms with $1 \leqslant Z \leqslant 137$, providing in this way reference data for future calculations taking into account the finite mass and size of the nucleus, its spin as well as QED effects. Finally, following ideas of Pyper [10–14] and the author [15], we carry out the Gordon decomposition of the total magnetizability, providing a quantitative answer to the question concerning the influence of relativity on the magnitudes of dia- and paramagnetic contributions to χ.

2. A relativistic hydrogen-like atom in a weak static uniform magnetic field

The energy eigenvalue problem for bound states of a relativistic hydrogen-like atom, with an infinitely heavy, spinless and point-like nucleus of charge $+Ze$, placed in a static uniform magnetic field of induction $\boldsymbol{B}$ (directed along the z axis of a Cartesian coordinate system), is constituted by the Dirac equation

$$\left[c\boldsymbol{\alpha} \cdot [-\mathrm{i}\hbar\boldsymbol{\nabla} + e\boldsymbol{A}(\boldsymbol{r})] + \beta mc^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} - E\right]\psi(\boldsymbol{r}) = 0 \tag{2.1}$$

(here $\boldsymbol{\alpha}$ and β are the standard 4×4 Dirac matrices [16]) supplemented by the boundary conditions

$$r\psi(\boldsymbol{r}) \xrightarrow{r\to 0} 0 \qquad r\psi(\boldsymbol{r}) \xrightarrow{r\to\infty} 0. \tag{2.2}$$

In a symmetric gauge, adopted in this work, the vector potential $\boldsymbol{A}(\boldsymbol{r})$ is

$$\boldsymbol{A}(\boldsymbol{r}) = \tfrac{1}{2}\boldsymbol{B} \times \boldsymbol{r}. \tag{2.3}$$

Henceforth we shall assume that the magnetic field is sufficiently weak so that the electron–field interaction operator

$$\hat{H}^{(1)} = ec\boldsymbol{\alpha} \cdot \boldsymbol{A}(\boldsymbol{r}) \tag{2.4}$$

may be considered as a small perturbation of the zeroth-order Hamiltonian describing an isolated atom. The zeroth-order bound state eigenproblem is given by the Dirac–Coulomb equation

$$\left[-\mathrm{i}c\hbar\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + \beta mc^2 - \frac{Ze^2}{(4\pi\epsilon_0)r} - E^{(0)}\right]\psi^{(0)}(\boldsymbol{r}) = 0 \tag{2.5}$$

supplemented by the boundary conditions

$$r\psi^{(0)}(\boldsymbol{r}) \xrightarrow{r\to 0} 0 \qquad r\psi^{(0)}(\boldsymbol{r}) \xrightarrow{r\to\infty} 0. \tag{2.6}$$

In the rest of the work we shall restrict ourselves to the case when the unperturbed state of the atom is the ground state. Then one has

$$E^{(0)} = mc^2\gamma_1 \tag{2.7}$$

where

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

The eigenvalue $E^{(0)}$ is doubly degenerate. Two orthonormal eigenfunctions to the problem (2.5) and (2.6) associated with $E^{(0)}$ are, for instance,

$$\psi_M^{(0)}(\boldsymbol{r}) = \frac{1}{r}\begin{pmatrix} P^{(0)}(r)\,\Omega_{-1M}(\boldsymbol{n}_r) \\ \mathrm{i}Q^{(0)}(r)\,\Omega_{+1M}(\boldsymbol{n}_r) \end{pmatrix} \tag{2.9}$$

with $M = \pm 1/2$. Here

$$\Omega_{\kappa\mu}(\boldsymbol{n}_r) = \begin{pmatrix} -\mathrm{sgn}(\kappa)\sqrt{\frac{\kappa+\frac{1}{2}-\mu}{2\kappa+1}}\,Y_{l,\mu-1/2}(\boldsymbol{n}_r) \\ \sqrt{\frac{\kappa+\frac{1}{2}+\mu}{2\kappa+1}}\,Y_{l,\mu+1/2}(\boldsymbol{n}_r) \end{pmatrix} \tag{2.10}$$

with

$$l = |\kappa + \tfrac{1}{2}| - \tfrac{1}{2} = \begin{cases} -\kappa - 1 & \text{for } \kappa < 0 \\ \kappa & \text{for } \kappa > 0 \end{cases} \tag{2.11}$$

and $\boldsymbol{n}_r = \boldsymbol{r}/r$, is a spherical spinor while the radial functions are

$$P^{(0)}(r) = -\sqrt{\frac{Z}{a_0}\frac{1+\gamma_1}{\Gamma(2\gamma_1+1)}}\left(\frac{2Zr}{a_0}\right)^{\gamma_1}\exp(-Zr/a_0) \tag{2.12}$$

$$Q^{(0)}(r) = \sqrt{\frac{Z}{a_0}\frac{1-\gamma_1}{\Gamma(2\gamma_1+1)}}\left(\frac{2Zr}{a_0}\right)^{\gamma_1}\exp(-Zr/a_0). \tag{2.13}$$

The functions (2.9) are eigenfunctions, associated with the eigenvalues $M\hbar$, of the projection $\hat{J}_z$ of the total angular momentum on the magnetic field direction.

Since both the Hamiltonian of an isolated atom and the perturbing operator $\hat{H}^{(1)}$ commute with the operator $\hat{J}_z$, the perturbation does not mix states associated with different eigenvalues of $\hat{J}_z$. Consequently, the perturbation-adjusted zeroth-order eigenfunctions are those in equation (2.9).

It follows from the above considerations that we may seek approximate solutions to the eigenproblem (2.1) and (2.2) in the form

$$\psi_M(\boldsymbol{r}) \simeq \psi_M^{(0)}(\boldsymbol{r}) + \psi_M^{(1)}(\boldsymbol{r}) \qquad E_M \simeq E^{(0)} + E_M^{(1)}. \tag{2.14}$$

The corrections $\psi_M^{(1)}(\boldsymbol{r})$ and $E_M^{(1)}$, which, by assumption, are small quantities of the first order in $B = |\boldsymbol{B}|$, are solutions to the inhomogeneous problem

$$\left[-\mathrm{i}c\hbar\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}+\beta mc^2-\frac{Ze^2}{(4\pi\epsilon_0)r}-E^{(0)}\right]\psi_M^{(1)}(\boldsymbol{r}) = -\left[\frac{1}{2}ec\boldsymbol{B}\cdot(\boldsymbol{r}\times\boldsymbol{\alpha})-E_M^{(1)}\right]\psi_M^{(0)}(\boldsymbol{r}) \tag{2.15}$$

$$r\psi_M^{(1)}(\boldsymbol{r}) \xrightarrow{r\to 0} 0 \qquad r\psi_M^{(1)}(\boldsymbol{r}) \xrightarrow{r\to\infty} 0. \tag{2.16}$$

Henceforth, we shall assume that

$$\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}\;\psi_M^{(0)\dagger}(\boldsymbol{r})\psi_{M'}^{(1)}(\boldsymbol{r}) = 0. \tag{2.17}$$

In the standard way, from equation (2.15) we obtain

$$E_M^{(1)} = \tfrac{1}{2}ec\boldsymbol{B}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}\;\psi_M^{(0)\dagger}(\boldsymbol{r})(\boldsymbol{r}\times\boldsymbol{\alpha})\psi_M^{(0)}(\boldsymbol{r}) \tag{2.18}$$

and

$$\psi_M^{(1)}(\boldsymbol{r}) = -\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\;\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')\left[\tfrac{1}{2}ec\boldsymbol{B}\cdot(\boldsymbol{r}'\times\boldsymbol{\alpha})-E_M^{(1)}\right]\psi_M^{(0)}(\boldsymbol{r}') \tag{2.19}$$

where $\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')$ is the *generalized* Dirac–Coulomb Green function for the energy level $E^{(0)}$. It is a solution to the inhomogeneous differential equation ($\boldsymbol{r}'$ fixed)

$$\begin{aligned}&\left[-\mathrm{i}c\hbar\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}+\beta mc^2-\frac{Ze^2}{(4\pi\epsilon_0)r}-E^{(0)}\right]\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')\\&\qquad = \mathcal{I}\,\delta^3(\boldsymbol{r}-\boldsymbol{r}')-\psi_{-1/2}^{(0)}(\boldsymbol{r})\psi_{-1/2}^{(0)\dagger}(\boldsymbol{r}')-\psi_{1/2}^{(0)}(\boldsymbol{r})\psi_{1/2}^{(0)\dagger}(\boldsymbol{r}')\\&\qquad (-mc^2 < E < +mc^2)\end{aligned} \tag{2.20}$$

(here $\mathcal{I}$ is the unit 4×4 matrix) with the boundary conditions

$$r\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}') \xrightarrow{r\to 0} 0 \qquad r\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}') \xrightarrow{r\to\infty} 0 \tag{2.21}$$

and obeys the additional orthogonality constraints

$$\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\;\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')\psi_M^{(0)}(\boldsymbol{r}') = 0. \tag{2.22}$$

The latter constraints imply that equation (2.15) may be simplified to

$$\psi_M^{(1)}(\boldsymbol{r}) = -\tfrac{1}{2}ec\boldsymbol{B}\cdot\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\;\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')(\boldsymbol{r}'\times\boldsymbol{\alpha})\psi_M^{(0)}(\boldsymbol{r}'). \tag{2.23}$$

For the sake of later use in section 4, it is convenient to transform equation (2.23) to an alternative form. To this end, we rewrite equation (2.5) as

$$\psi_M^{(0)}(\boldsymbol{r}) = \frac{\mathrm{i}\hbar}{mc}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}\psi_M^{(0)}(\boldsymbol{r})+\frac{E^{(0)}-V_{\mathrm{c}}(r)}{mc^2}\beta\psi_M^{(0)}(\boldsymbol{r}) \tag{2.24}$$

and equation (2.20) as

$$\begin{aligned}\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}') &= \frac{\mathrm{i}\hbar}{mc}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')+\frac{E^{(0)}-V_{\mathrm{c}}(r)}{mc^2}\beta\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}')+\frac{1}{mc^2}\beta\delta^3(\boldsymbol{r}-\boldsymbol{r}')\\&\quad -\frac{1}{mc^2}\sum_{M'=\pm 1/2}\beta\psi_{M'}^{(0)}(\boldsymbol{r})\psi_{M'}^{(0)\dagger}(\boldsymbol{r}')\end{aligned} \tag{2.25}$$

where, for brevity, $V_c(r)$ stands for the Coulomb potential. On interchanging the variables $\boldsymbol{r}$ and $\boldsymbol{r}'$ in equation (2.25), performing the matrix Hermitean conjugation of the resulting equation and utilizing the well known property

$$\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}') = \mathcal{G}^{(0)\dagger}(\boldsymbol{r}', \boldsymbol{r}) \tag{2.26}$$

we find

$$\begin{aligned}\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}') = &-\frac{\mathrm{i}\hbar}{mc}\nabla'\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}') \cdot \boldsymbol{\alpha}\beta + \frac{E^{(0)} - V_c(r')}{mc^2}\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')\beta \\ &+ \frac{1}{mc^2}\beta\delta^3(\boldsymbol{r}' - \boldsymbol{r}) - \frac{1}{mc^2}\sum_{M'=\pm 1/2}\psi_{M'}^{(0)}(\boldsymbol{r})\psi_{M'}^{(0)\dagger}(\boldsymbol{r}')\beta.\end{aligned} \tag{2.27}$$

Rewriting then equation (2.23) in the form

$$\begin{aligned}\psi_M^{(1)}(\boldsymbol{r}) = &-\tfrac{1}{4}ec\boldsymbol{B} \cdot \int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\,\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')(\boldsymbol{r}' \times \boldsymbol{\alpha})\psi_M^{(0)}(\boldsymbol{r}') \\ &- \tfrac{1}{4}ec\boldsymbol{B} \cdot \int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\,\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')(\boldsymbol{r}' \times \boldsymbol{\alpha})\psi_M^{(0)}(\boldsymbol{r}')\end{aligned} \tag{2.28}$$

substituting equations (2.24) and (2.27) into the first and the second integrals on the right-hand side of equation (2.28), respectively, after some rearrangements we arrive at

$$\begin{aligned}\psi_M^{(1)}(\boldsymbol{r}) = &-\frac{e\hbar B}{2m}\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\,\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}}' + \boldsymbol{\Sigma})\beta\psi_M^{(0)}(\boldsymbol{r}') + \frac{eB}{4mc}\boldsymbol{n}_z \cdot (\boldsymbol{r} \times \boldsymbol{\alpha})\beta\psi_M^{(0)}(\boldsymbol{r}) \\ &- \frac{eB}{4mc}\psi_M^{(0)}(\boldsymbol{r})\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\,\psi_M^{(0)\dagger}(\boldsymbol{r}')\boldsymbol{n}_z \cdot (\boldsymbol{r}' \times \boldsymbol{\alpha})\beta\psi_M^{(0)}(\boldsymbol{r}').\end{aligned} \tag{2.29}$$

Henceforth, for brevity, we shall omit the subscript M at $\psi_M^{(0)}(\boldsymbol{r})$ and $\psi_M^{(1)}(\boldsymbol{r})$, keeping in mind, however, that $M = \pm 1/2$.

3. Magnetizability

The atomic magnetizability χ is defined through the relationship

$$\chi = \frac{\mu_0}{4\pi}\frac{\boldsymbol{m}^{(1)} \cdot \boldsymbol{B}}{B^2} \tag{3.1}$$

where μ_0 is the permeability of vacuum and

$$\boldsymbol{m}^{(1)} = \tfrac{1}{2}\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}\,\boldsymbol{r} \times \boldsymbol{j}^{(1)}(\boldsymbol{r}) \tag{3.2}$$

is an *induced* magnetic dipole moment of the atom in the perturbed state $\psi(\boldsymbol{r})$. In equation (3.2) $\boldsymbol{j}^{(1)}(\boldsymbol{r})$ is a first-order contribution to an induced current density in the perturbed state $\psi(\boldsymbol{r})$ and is given by

$$\boldsymbol{j}^{(1)}(\boldsymbol{r}) = -ec\psi^{(1)\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi^{(0)}(\boldsymbol{r}) - ec\psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi^{(1)}(\boldsymbol{r}). \tag{3.3}$$

On substituting equation (3.3) into (3.2), after integrating by parts and making use of the boundary conditions obeyed by $\psi^{(0)}(\boldsymbol{r})$ and $\psi^{(1)}(\boldsymbol{r})$ at infinity, we obtain

$$\boldsymbol{m}^{(1)} = -ec\,\mathrm{Re}\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}\,\psi^{(0)\dagger}(\boldsymbol{r})(\boldsymbol{r} \times \boldsymbol{\alpha})\psi^{(1)}(\boldsymbol{r}) \tag{3.4}$$

hence, on utilizing equation (2.23) and the relation $\epsilon_0 = 1/\mu_0 c^2$, we arrive at

$$\chi = \frac{\alpha^2 a_0 mc^2}{2}\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\,\psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{n}_z \cdot (\boldsymbol{r} \times \boldsymbol{\alpha})\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')\boldsymbol{n}_z \cdot (\boldsymbol{r}' \times \boldsymbol{\alpha})\psi^{(0)}(\boldsymbol{r}'). \tag{3.5}$$

We have omitted the symbol Re since the double integral in equation (3.5) is evidently real.

To evaluate the double integral in equation (3.5), we utilize the following partial wave expansion:

$$\mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{\alpha^2 a_0 m c^2} \sum_{\substack{\kappa=-\infty \\ (\kappa\neq 0)}}^{\infty} \sum_{m=-|\kappa|+\frac{1}{2}}^{|\kappa|-\frac{1}{2}} \frac{1}{rr'} \times \begin{pmatrix} g^{(0)}_{(++)\kappa}(r,r')\Omega_{\kappa m}(\boldsymbol{n}_r)\Omega^{\dagger}_{\kappa m}(\boldsymbol{n}'_r) & -\mathrm{i}g^{(0)}_{(+-)\kappa}(r,r')\Omega_{\kappa m}(\boldsymbol{n}_r)\Omega^{\dagger}_{-\kappa m}(\boldsymbol{n}'_r) \\ \mathrm{i}g^{(0)}_{(-+)\kappa}(r,r')\Omega_{-\kappa m}(\boldsymbol{n}_r)\Omega^{\dagger}_{\kappa m}(\boldsymbol{n}'_r) & g^{(0)}_{(--)\kappa}(r,r')\Omega_{-\kappa m}(\boldsymbol{n}_r)\Omega^{\dagger}_{-\kappa m}(\boldsymbol{n}'_r) \end{pmatrix} \tag{3.6}$$

of the generalized Dirac–Coulomb Green function. Employing the relation

$$\boldsymbol{n}_z \cdot (\boldsymbol{n}_r \times \boldsymbol{\sigma})\Omega_{\kappa\mu}(\boldsymbol{n}_r) = \mathrm{i}\frac{4\mu\kappa}{4\kappa^2-1}\Omega_{-\kappa\mu}(\boldsymbol{n}_r) + \mathrm{i}\frac{\sqrt{(\kappa+\frac{1}{2})^2-\mu^2}}{|2\kappa+1|}\Omega_{\kappa+1,\mu}(\boldsymbol{n}_r) - \mathrm{i}\frac{\sqrt{(\kappa-\frac{1}{2})^2-\mu^2}}{|2\kappa-1|}\Omega_{\kappa-1,\mu}(\boldsymbol{n}_r) \tag{3.7}$$

reduces equation (3.5) to the form

$$\chi = \chi_{-1} + \chi_{+2} \tag{3.8}$$

where

$$\chi_{-1} = \tfrac{2}{9}\int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}r'\, rr' \left(Q^{(0)}(r) \quad P^{(0)}(r) \right) \mathsf{G}^{(0)}_{-1}(r,r') \begin{pmatrix} Q^{(0)}(r') \\ P^{(0)}(r') \end{pmatrix} \tag{3.9}$$

$$\chi_{+2} = \tfrac{1}{9}\int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}r'\, rr' \left(Q^{(0)}(r) \quad P^{(0)}(r) \right) \mathsf{G}^{(0)}_{+2}(r,r') \begin{pmatrix} Q^{(0)}(r') \\ P^{(0)}(r') \end{pmatrix}. \tag{3.10}$$

The 2×2 real and symmetric matrix

$$\mathsf{G}^{(0)}_{\kappa}(r,r') = \begin{pmatrix} g^{(0)}_{(++)\kappa}(r,r') & g^{(0)}_{(+-)\kappa}(r,r') \\ g^{(0)}_{(-+)\kappa}(r,r') & g^{(0)}_{(--)\kappa}(r,r') \end{pmatrix} \tag{3.11}$$

appearing in equations (3.9) and (3.10) is a generalized radial Dirac–Coulomb Green function associated with the ground state energy (2.7) and with the set of $2|\kappa|$ partial waves belonging to the combined parity and total angular momentum quantum number κ. The Sturmian expansions of $\mathsf{G}^{(0)}_{-1}(r,r')$ and $\mathsf{G}^{(0)}_{+2}(r,r')$ follow from the general formulae for $\mathsf{G}^{(0)}_{\kappa}(r,r')$ found in [8]. These expansions are

$$\begin{aligned}\mathsf{G}^{(0)}_{-1}(r,r') = {} & \sum_{\substack{n=-\infty \\ (n\neq 0)}}^{\infty} \frac{1}{\mu^{(0)}_{n,-1}-1} \begin{pmatrix} S^{(0)}_{n,-1}(r) \\ T^{(0)}_{n,-1}(r) \end{pmatrix} \left(\mu^{(0)}_{n,-1}S^{(0)}_{n,-1}(r') \quad T^{(0)}_{n,-1}(r') \right) \\ & + (\gamma_1 - \tfrac{1}{2}) \begin{pmatrix} S^{(0)}_{0,-1}(r) \\ T^{(0)}_{0,-1}(r) \end{pmatrix} \left(S^{(0)}_{0,-1}(r') \quad T^{(0)}_{0,-1}(r') \right) \\ & + \begin{pmatrix} I^{(0)}(r) \\ K^{(0)}(r) \end{pmatrix} \left(S^{(0)}_{0,-1}(r') \quad T^{(0)}_{0,-1}(r') \right) \\ & + \begin{pmatrix} S^{(0)}_{0,-1}(r) \\ T^{(0)}_{0,-1}(r) \end{pmatrix} \left(J^{(0)}(r') \quad K^{(0)}(r') \right)\end{aligned} \tag{3.12}$$

where

$$I^{(0)}(r) = \left(\gamma_1 - \tfrac{1}{2}\right) S^{(0)}_{0,-1}(r) + \gamma_1 \left(\frac{1+\gamma_1}{\alpha}\frac{r}{a_0} + \alpha Z \right) T^{(0)}_{0,-1}(r) \tag{3.13}$$

$$J^{(0)}(r) = I^{(0)}(r) + S^{(0)}_{0,-1}(r) = (\gamma_1 + \tfrac{1}{2}) S^{(0)}_{0,-1}(r) + \gamma_1 \left(\frac{1+\gamma_1}{\alpha}\frac{r}{a_0} + \alpha Z \right) T^{(0)}_{0,-1}(r) \tag{3.14}$$

$$K^{(0)}(r) = \gamma_1 \left(\frac{1-\gamma_1}{\alpha}\frac{r}{a_0} - \alpha Z \right) S^{(0)}_{0,-1}(r) - (\gamma_1 - \tfrac{1}{2}) T^{(0)}_{0,-1}(r) \tag{3.15}$$

and

$$\mathsf{G}_{+2}^{(0)}(r,r') = \sum_{n=-\infty}^{\infty} \frac{1}{\mu_{n,+2}^{(0)}-1} \begin{pmatrix} S_{n,+2}^{(0)}(r) \\ T_{n,+2}^{(0)}(r) \end{pmatrix} \left(\mu_{n,+2}^{(0)} S_{n,+2}^{(0)}(r') \quad T_{n,+2}^{(0)}(r') \right) \tag{3.16}$$

respectively. Here

$$\mu_{n\kappa}^{(0)} = \frac{|n| + \gamma_\kappa + N_{n\kappa}}{\gamma_1 + 1} \tag{3.17}$$

$$S_{n\kappa}^{(0)}(r) = \sqrt{\frac{(1+\gamma_1)(|n|+2\gamma_\kappa)|n|!}{2ZN_{n\kappa}(N_{n\kappa}-\kappa)\Gamma(|n|+2\gamma_\kappa)}} \times \left(\frac{2Zr}{a_0}\right)^{\gamma_\kappa} \mathrm{e}^{-Zr/a_0} \left[L_{|n|-1}^{(2\gamma_\kappa)}\left(\frac{2Zr}{a_0}\right) + \frac{\kappa - N_{n\kappa}}{|n|+2\gamma_\kappa} L_{|n|}^{(2\gamma_\kappa)}\left(\frac{2Zr}{a_0}\right) \right] \tag{3.18}$$

$$T_{n\kappa}^{(0)}(r) = \sqrt{\frac{(1-\gamma_1)(|n|+2\gamma_\kappa)|n|!}{2ZN_{n\kappa}(N_{n\kappa}-\kappa)\Gamma(|n|+2\gamma_\kappa)}} \times \left(\frac{2Zr}{a_0}\right)^{\gamma_\kappa} \mathrm{e}^{-Zr/a_0} \left[L_{|n|-1}^{(2\gamma_\kappa)}\left(\frac{2Zr}{a_0}\right) - \frac{\kappa - N_{n\kappa}}{|n|+2\gamma_\kappa} L_{|n|}^{(2\gamma_\kappa)}\left(\frac{2Zr}{a_0}\right) \right] \tag{3.19}$$

(with $L_n^{(\alpha)}(\rho)$ denoting the generalized Laguerre polynomials [17]) are the radial Dirac–Coulomb Sturmians and

$$N_{n\kappa} = \pm\sqrt{(|n|+\gamma_\kappa)^2 + (\alpha Z)^2} = \pm\sqrt{|n|^2 + 2|n|\gamma_\kappa + \kappa^2} \tag{3.20}$$

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 (3.20): 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 $\kappa < 0$ and the minus sign if $\kappa > 0$.

The radial integrals in equations (3.9) and (3.10) are easily evaluated after making use of the Sturmian expansions (3.12) and (3.16) and the integral formula

$$\int_0^\infty \mathrm{d}\rho\, \rho^\gamma \mathrm{e}^{-\rho} L_n^{(\alpha)}(\rho) = \frac{\Gamma(\gamma+1)\Gamma(n+\alpha-\gamma)}{n!\Gamma(\alpha-\gamma)}. \tag{3.21}$$

In the case of $\kappa = -1$, one arrives at the following simple expression for χ_{-1}:

$$\chi_{-1} = -\frac{\alpha^2 a_0^3}{Z^2} \frac{(\gamma_1+1)(4\gamma_1^2-1)}{18}. \tag{3.22}$$

In turn, in the case of $\kappa = +2$, on collecting terms with the same values of $|n|$, one finds

$$\chi_{+2} = -\frac{\alpha^2 a_0^3}{Z^2} \frac{1}{72\Gamma(2\gamma_1+1)} \frac{\Gamma^2(\gamma_1+\gamma_2+2)}{\Gamma^2(\gamma_2-\gamma_1-1)} \sum_{n=0}^{\infty} \frac{\Gamma^2(n+\gamma_2-\gamma_1-1)}{n!\Gamma(n+2\gamma_2+1)(n+\gamma_2-\gamma_1)} \tag{3.23}$$

or, equivalently,

$$\chi_{+2} = -\frac{\alpha^2 a_0^3}{Z^2} \frac{\Gamma^2(\gamma_1+\gamma_2+2)}{72(\gamma_2-\gamma_1)\Gamma(2\gamma_1+1)\Gamma(2\gamma_2+1)} \times {}_3F_2(\gamma_2-\gamma_1-1, \gamma_2-\gamma_1-1, \gamma_2-\gamma_1; 2\gamma_2+1, \gamma_2-\gamma_1+1; 1) \tag{3.24}$$

where ${}_3F_2$ is a generalized hypergeometric function. Consequently, we have

$$\chi = \frac{\alpha^2 a_0^3}{Z^2} \left[-\frac{(\gamma_1+1)(4\gamma_1^2-1)}{18} - \frac{\Gamma^2(\gamma_1+\gamma_2+2)}{72(\gamma_2-\gamma_1)\Gamma(2\gamma_1+1)\Gamma(2\gamma_2+1)} \times {}_3F_2(\gamma_2-\gamma_1-1, \gamma_2-\gamma_1-1, \gamma_2-\gamma_1; 2\gamma_2+1, \gamma_2-\gamma_1+1; 1) \right] \tag{3.25}$$

that agrees with earlier findings of Granovskii and Nechet [2] and Manakov *et al* [3–6] (see also [7]). In the non-relativistic limit

$$\gamma_1 \stackrel{c\to\infty}{\longrightarrow} 1 \qquad \gamma_2 \stackrel{c\to\infty}{\longrightarrow} 2 \tag{3.26}$$

and the generalized hypergeometric series reduces to unity, hence one finds

$$\chi \stackrel{c\to\infty}{\longrightarrow} -\frac{1}{2}\frac{\alpha^2 a_0^3}{Z^2} \tag{3.27}$$

which agrees with the non-relativistic formula (1.6).

Numerical values of χ for $1 \leqslant Z \leqslant 137$, computed from equation (3.25), are presented in table 1. The number of terms necessary to include in the series ${}_3F_2$ in order to achieve convergence to the number of figures quoted varied from 1 for $Z = 1$ and 17 for $Z = 80$ to 272 for $Z = 137$. In table 2 numerical values of the ratio χ/χ_{nr} are presented for selected values of Z.

It is interesting to notice that while for the non-relativistic atom the magnetizability is always negative, in the relativistic case there is a critical value of Z, Z_{c}, such that for $Z < Z_{\mathrm{c}}$ the magnetizability is negative, i.e. the induced magnetic moment is anti-parallel to the perturbing field, and for $Z \geqslant Z_{\mathrm{c}}$ the magnetizability is positive, implying the parallel orientation of the induced magnetic moment and the external magnetic field. We have found $Z_{\mathrm{c}} = 130$ which differs from the result $Z_{\mathrm{c}} = 118$ predicted, with the same assumptions about the atomic nucleus, by Manakov *et al* [3,6] (the origin of this difference is unclear to us). The dependence of Z_{c} on a particular nuclear model adopted might be worth investigating in future.

4. Dia- and paramagnetic contributions to the magnetizability

The partitioning of the magnetizability χ into diamagnetic (χ_{d}) and paramagnetic (χ_{p}) components has its origin in the analogous partitioning of the induced current density $\boldsymbol{j}^{(1)}(\boldsymbol{r})$:

$$\boldsymbol{j}^{(1)}(\boldsymbol{r}) = \boldsymbol{j}_{\mathrm{d}}^{(1)}(\boldsymbol{r}) + \boldsymbol{j}_{\mathrm{p}}^{(1)}(\boldsymbol{r}). \tag{4.1}$$

Indeed, on combining equations (3.2) and (4.1), for the induced magnetic dipole moment one finds

$$\boldsymbol{m}^{(1)} = \boldsymbol{m}_{\mathrm{d}}^{(1)} + \boldsymbol{m}_{\mathrm{p}}^{(1)} \tag{4.2}$$

where

$$\boldsymbol{m}_{\mathrm{d}}^{(1)} = \tfrac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \boldsymbol{r} \times \boldsymbol{j}_{\mathrm{d}}^{(1)}(\boldsymbol{r}) \qquad \boldsymbol{m}_{\mathrm{p}}^{(1)} = \tfrac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \boldsymbol{r} \times \boldsymbol{j}_{\mathrm{p}}^{(1)}(\boldsymbol{r}) \tag{4.3}$$

and, consequently,

$$\chi = \chi_{\mathrm{d}} + \chi_{\mathrm{p}} \tag{4.4}$$

with

$$\chi_{\mathrm{d}} = \frac{\mu_0}{4\pi}\frac{\boldsymbol{m}_{\mathrm{d}}^{(1)} \cdot \boldsymbol{B}}{B^2} \qquad \chi_{\mathrm{p}} = \frac{\mu_0}{4\pi}\frac{\boldsymbol{m}_{\mathrm{p}}^{(1)} \cdot \boldsymbol{B}}{B^2}. \tag{4.5}$$

We shall find $\boldsymbol{j}_{\mathrm{d}}^{(1)}(\boldsymbol{r})$ and $\boldsymbol{j}_{\mathrm{p}}^{(1)}(\boldsymbol{r})$ with the aid of the Gordon decomposition of the induced current density $\boldsymbol{j}^{(1)}(\boldsymbol{r})$. To carry out this decomposition, we rewrite the expressions

$$\boldsymbol{j}(\boldsymbol{r}) = -ec\psi^{\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi(\boldsymbol{r}) \qquad \boldsymbol{j}^{(0)}(\boldsymbol{r}) = -ec\psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi^{(0)}(\boldsymbol{r}) \tag{4.6}$$

for the current densities in the states $\psi(\boldsymbol{r})$ and $\psi^{(0)}(\boldsymbol{r})$, respectively, in the following ways:

$$\boldsymbol{j}(\boldsymbol{r}) = -\tfrac{1}{2}ec\psi^{\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi(\boldsymbol{r}) - \tfrac{1}{2}ec\psi^{\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi(\boldsymbol{r}) \tag{4.7}$$

$$\boldsymbol{j}^{(0)}(\boldsymbol{r}) = -\tfrac{1}{2}ec\psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi^{(0)}(\boldsymbol{r}) - \tfrac{1}{2}ec\psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{\alpha}\psi^{(0)}(\boldsymbol{r}) \tag{4.8}$$

and transform the Dirac equations (2.1) and (2.5) to the forms

Table 1. Magnetizabilities for ground states of relativistic hydrogen-like atoms with infinitely heavy point-like and spinless nuclei. The number in brackets following the entries is the power of 10 by which the entry is to be multiplied. The value of the inverse of the fine structure constant used was $\alpha^{-1} = 137.035\,9895$.

Z	χ ($\alpha^2 a_0^3$)	Z	χ ($\alpha^2 a_0^3$)	Z	χ ($\alpha^2 a_0^3$)
1	−4.999 644 99(−1)	47	−1.914 539 71(−4)	93	−2.485 920 59(−5)
2	−1.249 645 00(−1)	48	−1.821 478 16(−4)	94	−2.369 686 43(−5)
3	−5.552 005 71(−2)	49	−1.734 078 23(−4)	95	−2.257 393 95(−5)
4	−3.121 450 34(−2)	50	−1.651 892 08(−4)	96	−2.148 885 59(−5)
5	−1.996 450 58(−2)	51	−1.574 515 34(−4)	97	−2.044 012 02(−5)
6	−1.385 339 77(−2)	52	−1.501 582 13(−4)	98	−1.942 631 68(−5)
7	−1.016 859 40(−2)	53	−1.432 760 80(−4)	99	−1.844 610 31(−5)
8	−7.777 016 37(−3)	54	−1.367 750 10(−4)	100	−1.749 820 52(−5)
9	−6.137 360 47(−3)	55	−1.306 275 91(−4)	101	−1.658 141 41(−5)
10	−4.964 526 10(−3)	56	−1.248 088 40(−4)	102	−1.569 458 20(−5)
11	−4.096 763 18(−3)	57	−1.192 959 45(−4)	103	−1.483 661 86(−5)
12	−3.436 760 22(−3)	58	−1.140 680 43(−4)	104	−1.400 648 86(−5)
13	−2.923 124 64(−3)	59	−1.091 060 26(−4)	105	−1.320 320 82(−5)
14	−2.515 572 48(−3)	60	−1.043 923 65(−4)	106	−1.242 584 25(−5)
15	−2.186 782 15(−3)	61	−9.991 095 68(−5)	107	−1.167 350 32(−5)
16	−1.917 693 33(−3)	62	−9.564 698 55(−5)	108	−1.094 534 61(−5)
17	−1.694 681 08(−3)	63	−9.158 680 35(−5)	109	−1.024 056 90(−5)
18	−1.507 796 65(−3)	64	−8.771 782 14(−5)	110	−9.558 409 71(−6)
19	−1.349 638 37(−3)	65	−8.402 841 10(−5)	111	−8.898 144 14(−6)
20	−1.214 607 41(−3)	66	−8.050 781 90(−5)	112	−8.259 084 78(−6)
21	−1.098 405 40(−3)	67	−7.714 608 94(−5)	113	−7.640 579 12(−6)
22	−9.976 881 05(−4)	68	−7.393 399 31(−5)	114	−7.042 008 26(−6)
23	−9.098 220 90(−4)	69	−7.086 296 57(−5)	115	−6.462 785 74(−6)
24	−8.327 108 68(−4)	70	−6.792 505 09(−5)	116	−5.902 356 48(−6)
25	−7.646 686 76(−4)	71	−6.511 284 93(−5)	117	−5.360 195 88(−6)
26	−7.043 275 68(−4)	72	−6.241 947 23(−5)	118	−4.835 809 08(−6)
27	−6.505 681 35(−4)	73	−5.983 850 10(−5)	119	−4.328 730 47(−6)
28	−6.024 672 23(−4)	74	−5.736 394 75(−5)	120	−3.838 523 33(−6)
29	−5.592 580 46(−4)	75	−5.499 022 16(−5)	121	−3.364 779 77(−6)
30	−5.202 994 50(−4)	76	−5.271 209 88(−5)	122	−2.907 120 94(−6)
31	−4.850 519 93(−4)	77	−5.052 469 28(−5)	123	−2.465 197 58(−6)
32	−4.530 591 84(−4)	78	−4.842 342 91(−5)	124	−2.038 691 03(−6)
33	−4.239 326 31(−4)	79	−4.640 402 17(−5)	125	−1.627 314 80(−6)
34	−3.973 402 06(−4)	80	−4.446 245 19(−5)	126	−1.230 816 88(−6)
35	−3.729 965 40(−4)	81	−4.259 494 83(−5)	127	−8.489 831 40(−7)
36	−3.506 553 41(−4)	82	−4.079 796 87(−5)	128	−4.816 421 51(−7)
37	−3.301 031 43(−4)	83	−3.906 818 45(−5)	129	−1.286 722 16(−7)
38	−3.111 541 93(−4)	84	−3.740 246 46(−5)	130	+2.099 882 73(−7)
39	−2.936 462 44(−4)	85	−3.579 786 21(−5)	131	+5.343 250 95(−7)
40	−2.774 370 73(−4)	86	−3.425 160 16(−5)	132	+8.442 232 33(−7)
41	−2.624 015 88(−4)	87	−3.276 106 74(−5)	133	+1.139 424 82(−6)
42	−2.484 294 08(−4)	88	−3.132 379 26(−5)	134	+1.419 452 03(−6)
43	−2.354 228 39(−4)	89	−2.993 744 93(−5)	135	+1.683 446 33(−6)
44	−2.232 951 60(−4)	90	−2.859 983 95(−5)	136	+1.929 755 29(−6)
45	−2.119 691 77(−4)	91	−2.730 888 66(−5)	137	+2.154 585 33(−6)
46	−2.013 759 95(−4)	92	−2.606 262 77(−5)		

Table 2. Ratios of relativistic to non-relativistic magnetizabilities for ground states of hydrogen-like atoms with infinitely heavy point-like and spinless nuclei.

Z	χ/χ_{nr}	Z	χ/χ_{nr}	Z	χ/χ_{nr}
1	+0.999 929	60	+0.751 625	120	+0.110 549
10	+0.992 905	70	+0.665 665	129	+0.004 282
20	+0.971 686	80	+0.569 119	130	−0.007 098
30	+0.936 539	90	+0.463 317	137	−0.080 879
40	+0.887 799	100	+0.349 964		
50	+0.825 946	110	+0.231 314		

$$\psi(\boldsymbol{r}) = \frac{\mathrm{i}\hbar}{mc}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}\psi(\boldsymbol{r}) - \frac{e}{mc}\beta\boldsymbol{\alpha}\cdot\boldsymbol{A}(\boldsymbol{r})\psi(\boldsymbol{r}) + \frac{E - V_{\mathrm{c}}(r)}{mc^2}\beta\psi(\boldsymbol{r}) \tag{4.9}$$

$$\psi^{(0)}(\boldsymbol{r}) = \frac{\mathrm{i}\hbar}{mc}\beta\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}\psi^{(0)}(\boldsymbol{r}) + \frac{E^{(0)} - V_{\mathrm{c}}(r)}{mc^2}\beta\psi^{(0)}(\boldsymbol{r}) \tag{4.10}$$

where $V_{\mathrm{c}}(r)$ stands for the Coulomb potential. On substituting the expressions (4.9) and (4.10) into the first terms on the right-hand sides of equations (4.7) and (4.8) and their Hermitian conjugates to the second terms, after some matrix algebra we obtain [18, 19]

$$\boldsymbol{j}(\boldsymbol{r}) = -\frac{e\hbar}{m}\mathrm{Im}\,[\psi^{\dagger}(\boldsymbol{r})\beta\boldsymbol{\nabla}\psi(\boldsymbol{r})] - \frac{e\hbar}{2m}\boldsymbol{\nabla}\times[\psi^{\dagger}(\boldsymbol{r})\beta\boldsymbol{\Sigma}\psi(\boldsymbol{r})] - \frac{e^2}{m}\psi^{\dagger}(\boldsymbol{r})\beta\boldsymbol{A}(\boldsymbol{r})\psi(\boldsymbol{r}) \tag{4.11}$$

$$\boldsymbol{j}^{(0)}(\boldsymbol{r}) = -\frac{e\hbar}{m}\mathrm{Im}\,[\psi^{(0)\dagger}(\boldsymbol{r})\beta\boldsymbol{\nabla}\psi^{(0)}(\boldsymbol{r})] - \frac{e\hbar}{2m}\boldsymbol{\nabla}\times[\psi^{(0)\dagger}(\boldsymbol{r})\beta\boldsymbol{\Sigma}\psi^{(0)}(\boldsymbol{r})] \tag{4.12}$$

where the 4×4 vector matrix $\boldsymbol{\Sigma}$ is

$$\boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}. \tag{4.13}$$

Subtracting equation (4.12) from (4.11), making use of the first of equations (2.14) and neglecting second-order terms, we arrive at equation (4.1) in which

$$\boldsymbol{j}_{\mathrm{d}}^{(1)}(\boldsymbol{r}) = -\frac{e^2}{m}\psi^{(0)\dagger}(\boldsymbol{r})\beta\boldsymbol{A}(\boldsymbol{r})\psi^{(0)}(\boldsymbol{r}) \tag{4.14}$$

$$\begin{aligned}\boldsymbol{j}_{\mathrm{p}}^{(1)}(\boldsymbol{r}) = &-\frac{e\hbar}{m}\mathrm{Im}\,[\psi^{(0)\dagger}(\boldsymbol{r})\beta\boldsymbol{\nabla}\psi^{(1)}(\boldsymbol{r}) + \psi^{(1)\dagger}(\boldsymbol{r})\beta\boldsymbol{\nabla}\psi^{(0)}(\boldsymbol{r})] \\ &-\frac{e\hbar}{m}\boldsymbol{\nabla}\times\mathrm{Re}\,[\psi^{(0)\dagger}(\boldsymbol{r})\beta\boldsymbol{\Sigma}\psi^{(1)}(\boldsymbol{r})]\end{aligned} \tag{4.15}$$

are the sought induced dia- and paramagnetic current densities, respectively.

The explicit expression for the induced diamagnetic moment $\boldsymbol{m}_{\mathrm{d}}^{(1)}$ is immediately obtained on substituting equation (4.14) into the first of equations (4.3) and making use of equation (2.3). This yields

$$\boldsymbol{m}_{\mathrm{d}}^{(1)} = -\frac{e^2B}{4m}\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}\;\psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{r}\times(\boldsymbol{n}_z\times\boldsymbol{r})\beta\psi^{(0)}(\boldsymbol{r}). \tag{4.16}$$

From the first of equations (4.5) and from (4.16) we obtain

$$\chi_{\mathrm{d}} = -\tfrac{1}{4}\alpha^2 a_0\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}\;\psi^{(0)\dagger}(\boldsymbol{r})(\boldsymbol{n}_z\times\boldsymbol{r})^2\beta\psi^{(0)}(\boldsymbol{r}) \tag{4.17}$$

(cf equation (1.2)). The integration over angular variables is straightforward and reduces equation (4.17) to the form

$$\chi_{\mathrm{d}} = -\tfrac{1}{6}\alpha^2 a_0\int_0^{\infty}\mathrm{d}r\,r^2[P^{(0)}(r)P^{(0)}(r) - Q^{(0)}(r)Q^{(0)}(r)]. \tag{4.18}$$

The remaining radial integration is also trivial and yields the final result for the diamagnetic contribution to χ:

$$\chi_{\mathrm{d}} = -\frac{\alpha^2 a_0^3}{Z^2} \frac{\gamma_1(\gamma_1+1)(2\gamma_1+1)}{12}. \tag{4.19}$$

Similarly, substituting equation (4.15) into the second of equations (4.3), making use of the identity

$$\int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \boldsymbol{r} \times [\boldsymbol{\nabla} \times \boldsymbol{F}(\boldsymbol{r})] = 2\int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \boldsymbol{F}(\boldsymbol{r}) \qquad (r^2\boldsymbol{F}(\boldsymbol{r}) \xrightarrow{r\to\infty} 0) \tag{4.20}$$

after some manipulations, for the paramagnetic moment $\boldsymbol{m}_{\mathrm{p}}^{(1)}$ we find

$$\boldsymbol{m}_{\mathrm{p}}^{(1)} = -\frac{e\hbar}{m}\mathrm{Re} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \psi^{(0)\dagger}(\boldsymbol{r})\beta(\hat{\boldsymbol{\Lambda}} + \boldsymbol{\Sigma})\psi^{(1)}(\boldsymbol{r}). \tag{4.21}$$

Substituting here equation (2.29) and the result into the second of equations (4.5), we obtain

$$\chi_{\mathrm{p}} = \chi_{\mathrm{p}}' + \chi_{\mathrm{p}}'' + \chi_{\mathrm{p}}''' \tag{4.22}$$

with the contributions given by

$$\chi_{\mathrm{p}}' = \tfrac{1}{2}\alpha^4 a_0^3 mc^2 \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}} + \boldsymbol{\Sigma}) \times \beta \mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}')\beta \boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}}' + \boldsymbol{\Sigma})\psi^{(0)}(\boldsymbol{r}') \tag{4.23}$$

$$\chi_{\mathrm{p}}'' = \tfrac{1}{4}\alpha^3 a_0^2\, \mathrm{Re} \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}} + \boldsymbol{\Sigma})\boldsymbol{n}_z \cdot (\boldsymbol{r} \times \boldsymbol{\alpha})\psi^{(0)}(\boldsymbol{r}) \tag{4.24}$$

$$\chi_{\mathrm{p}}''' = \tfrac{1}{4}\alpha^3 a_0^2\, \mathrm{Re} \left\{ \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}\, \psi^{(0)\dagger}(\boldsymbol{r})\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}} + \boldsymbol{\Sigma})\beta\psi^{(0)}(\boldsymbol{r}) \times \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \psi^{(0)\dagger}(\boldsymbol{r}')\boldsymbol{n}_z \cdot (\boldsymbol{r}' \times \boldsymbol{\alpha})\beta\psi^{(0)}(\boldsymbol{r}') \right\}. \tag{4.25}$$

Since the operators $\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}} + \boldsymbol{\Sigma})$ and $\boldsymbol{n}_z \cdot (\boldsymbol{r} \times \boldsymbol{\alpha})\beta$ are, respectively, Hermitean and anti-Hermitean with respect to the volume scalar product, the expression in curly brackets on the right-hand side of equation (4.25) is purely imaginary. Consequently, χ_{p}''' vanishes and

$$\chi_{\mathrm{p}} = \chi_{\mathrm{p}}' + \chi_{\mathrm{p}}''. \tag{4.26}$$

It is interesting to notice that in the relativistic theory the paramagnetic contribution to χ is the sum of two terms. The first one, χ_{p}', is an analogue of the non-relativistic expression (1.3) while the second one, χ_{p}'', is an additional contribution of a purely relativistic origin.

On making use of the partial wave expansion (3.6) and the relation

$$\boldsymbol{n}_z \cdot (\hat{\boldsymbol{\Lambda}} + \boldsymbol{\sigma})\Omega_{\kappa\mu}(\boldsymbol{n}_r) = \frac{2\mu\kappa}{2\kappa+1}\Omega_{\kappa\mu}(\boldsymbol{n}_r) - \frac{\sqrt{(\kappa+\frac{1}{2})^2 - \mu^2}}{|2\kappa+1|}\Omega_{-\kappa-1,\mu}(\boldsymbol{n}_r) \tag{4.27}$$

the contribution χ_{p}' is found to be

$$\chi_{\mathrm{p}}' = \chi_{\mathrm{p},-1}' + \chi_{\mathrm{p},+2}' \tag{4.28}$$

where

$$\chi_{\mathrm{p},-1}' = \tfrac{1}{2}\alpha^2 a_0^2 \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}r' \begin{pmatrix} P^{(0)}(r) & -\frac{1}{3}Q^{(0)}(r) \end{pmatrix} \mathsf{G}_{-1}^{(0)}(r, r') \begin{pmatrix} P^{(0)}(r') \\ -\frac{1}{3}Q^{(0)}(r') \end{pmatrix} \tag{4.29}$$

and

Table 3. Relative dia- and paramagnetic contributions to magnetizabilities for ground states of relativistic hydrogen-like atoms with infinitely heavy point-like and spinless nuclei. The number in brackets following the entries is the power of 10 by which the entry is to be multiplied.

Z	χ_{d}/χ	χ'_{p}/χ	χ''_{p}/χ	χ_{p}/χ
1	+1.00(+0)	+7.99(−12)	−1.33(−5)	−1.33(−5)
10	+1.00(+0)	+8.05(−8)	−1.34(−3)	−1.34(−3)
20	+1.01(+0)	+1.32(−6)	−5.44(−3)	−5.44(−3)
30	+1.01(+0)	+6.91(−6)	−1.26(−2)	−1.26(−2)
40	+1.02(+0)	+2.30(−5)	−2.33(−2)	−2.33(−2)
50	+1.04(+0)	+6.03(−5)	−3.84(−2)	−3.84(−2)
60	+1.06(+0)	+1.37(−4)	−5.95(−2)	−5.93(−2)
70	+1.09(+0)	+2.86(−4)	−8.88(−2)	−8.85(−2)
80	+1.13(+0)	+5.69(−4)	−1.31(−1)	−1.30(−1)
90	+1.19(+0)	+1.11(−3)	−1.95(−1)	−1.93(−1)
100	+1.30(+0)	+2.23(−3)	−3.00(−1)	−2.98(−1)
110	+1.50(+0)	+4.87(−3)	−5.09(−1)	−5.04(−1)
120	+2.12(+0)	+1.41(−2)	−1.28(+0)	−1.26(+0)
129	+2.94(+1)	+4.67(−1)	−2.89(+1)	−2.84(+1)
130	−1.60(+1)	−2.89(−1)	+1.73(+1)	+1.70(+1)
137	−5.05(−2)	−2.65(−2)	+1.08(+0)	+1.05(+0)

$$\chi'_{\mathrm{p},+2} = \tfrac{1}{9}\alpha^2 a_0^2 \int_0^\infty \mathrm{d}r \int_0^\infty \mathrm{d}r' \,\left(0 \quad Q^{(0)}(r)\right) \mathsf{G}^{(0)}_{+2}(r,r') \begin{pmatrix} 0 \\ Q^{(0)}(r') \end{pmatrix}. \tag{4.30}$$

The radial integrals in equations (4.29) and (4.30) are easily evaluated with the aid of the Sturmian expansions (3.12) and (3.16) and the integral formula (3.21), yielding

$$\chi'_{\mathrm{p},-1} = 0 \tag{4.31}$$

and

$$\chi'_{\mathrm{p},+2} = \frac{\alpha^2 a_0^3}{Z^2}\left[\frac{(\gamma_1+1)^2(2\gamma_1+1)}{72} - \frac{\Gamma^2(\gamma_1+\gamma_2+2)}{72(\gamma_2-\gamma_1)\Gamma(2\gamma_1+1)\Gamma(2\gamma_2+1)} \times {}_3F_2(\gamma_2-\gamma_1-1, \gamma_2-\gamma_1-1, \gamma_2-\gamma_1; 2\gamma_2+1, \gamma_2-\gamma_1+1; 1)\right] \tag{4.32}$$

respectively. In turn, on utilizing the relations (3.7) and (4.27), equation (4.24) may be transformed to the form

$$\chi''_{\mathrm{p}} = -\tfrac{1}{6}\alpha^3 a_0^2 \int_0^\infty \mathrm{d}r\, r\, P^{(0)}(r) Q^{(0)}(r) \tag{4.33}$$

which, after performing the radial integration, yields

$$\chi''_{\mathrm{p}} = \frac{\alpha^2 a_0^3}{Z^2}\frac{(1-\gamma_1^2)(2\gamma_1+1)}{24}. \tag{4.34}$$

Hence, on combining equations (4.26), (4.28), (4.31), (4.32) and (4.34), for the paramagnetic contribution to χ we finally obtain

$$\chi_{\mathrm{p}} = \frac{\alpha^2 a_0^3}{Z^2}\left[\frac{(\gamma_1+1)(2\gamma_1+1)(2-\gamma_1)}{36} - \frac{\Gamma^2(\gamma_1+\gamma_2+2)}{72(\gamma_2-\gamma_1)\Gamma(2\gamma_1+1)\Gamma(2\gamma_2+1)} \times {}_3F_2(\gamma_2-\gamma_1-1, \gamma_2-\gamma_1-1, \gamma_2-\gamma_1; 2\gamma_2+1, \gamma_2-\gamma_1+1; 1)\right]. \tag{4.35}$$

From equations (4.18) and (4.35) it is seen that, as might be expected, the sum $\chi_{\mathrm{d}} + \chi_{\mathrm{p}}$ coincides with the expression (3.25). Moreover, in the non-relativistic limit, from equations (4.18) and (4.35) one infers

$$\chi_{\mathrm{d}} \stackrel{c\to\infty}{\longrightarrow} -\frac{1}{2}\frac{\alpha^2 a_0^3}{Z^2} \qquad \chi_{\mathrm{p}} \stackrel{c\to\infty}{\longrightarrow} 0 \tag{4.36}$$

which agrees with equation (1.5).

In table 3 relative dia- and paramagnetic contributions to magnetizabilities for selected hydrogen-like atoms are compared. It is seen that always $|\chi_{\mathrm{p}}'| \ll |\chi_{\mathrm{p}}''|$ and that χ_{p}' tends to reduce the contribution of χ_{p} to χ. Moreover, in agreement with the qualitative results already deduced by us from table 1, for $Z < 130$ the diamagnetic contribution χ_{d} dominates over the paramagnetic one χ_{p}, while for $Z \geqslant 130$ the opposite situation occurs.

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