Relativistic, QED, and nuclear mass effects in the magnetic shielding of ^{3}He

Adam Rudziński, Mariusz Puchalski,* and Krzysztof Pachucki†

Institute of Theoretical Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

(Dated: June 9, 2009)

Abstract

The magnetic shielding σ of ^{3}He is studied. The complete relativistic corrections of order $O(\alpha^2)$, leading QED corrections of order $O(\alpha^3\,\ln\alpha)$, and finite nuclear mass effects of order $O(m/m_{\rm N})$ are calculated with high numerical precision. The resulting theoretical predictions for $\sigma = 59.967\,43(10)\cdot 10^{-6}$ are the most accurate to date among all elements and support the use of ^{3}He as a NMR standard.

*mpuchals@fuw.edu.pl

†krp@fuw.edu.pl

I. INTRODUCTION

The coupling of the nuclear magnetic moment $\vec{\mu}$ to an external magnetic field $\vec{B}$ in closed shell atoms is shielded by electrons and thus is slightly smaller in comparison to the free nucleus [1, 2]. This shielding is described by the dimensionless constant σ

$$H = -\vec{\mu}\cdot\vec{B}\,(1-\sigma)\,. \tag{1}$$

For a specified atom σ is a function of the fine structure constant α and depends also on the electron-nucleus mass ratio. Since this ratio is very small, (for ^{3}He it is about $1.8\cdot 10^{-4}$), σ can be expanded in a power series in $m/m_{\rm N}$. We demonstrate in this work that the leading term in the mass ratio is numericaly significant, amounting for ^{3}He to $-3.7\cdot 10^{-4}\,\sigma$, which is 42% of the relativistic correction. Regarding dependence on α, as long as the nuclear charge Z is sufficiently small, say $Z\leq 10$, the expansion in α is also well convergent. We have therefore for σ a double series expansion

$$\sigma = \sigma\Big(\alpha, \frac{m}{m_{\rm N}}\Big) = \alpha^2\,\sigma^{(2)} + \alpha^4\,\sigma^{(4)} + \alpha^5\,\sigma^{(5)} + \alpha^2\,\frac{m}{m_{\rm N}}\sigma^{(2,1)} + \ldots \tag{2}$$

The first term of this expansion, $\sigma^{(2)}$, is obtained from the Ramsey nonrelativistic theory [1] of the magnetic shielding and for atomic systems takes the very simple form shown in Eq. (11). The derivation of the next coefficient $\sigma^{(4)}$ was considered in a series of works by Vaara and collaborators [3]. They expressed $\sigma^{(4)}$ in terms of the first, second, and third order expectation values of certain operators with the nonrelativistic wave function. Numerical evaluations of $\sigma^{(4)}$ were performed for various elements, but somehow not for ^{3}He, for example by Ruud *et al.* [4]. These calculations were not complete, in the sense that the authors omitted some terms which correspond to Q_5, Q_8, Q_{11} from our Table I, all of them come from the Breit interaction (the second term in Eq. (7)). These terms are small, but nevertheless important for the estimation of theoretical uncertainties. Moreover, the inclusion of the exact electron g-factor instead of the factor 2 by the authors of Ref. [3], in our opinion, is incorrect, as we explain in Sec. III, devoted to QED effects. In general, the relativistic correction $\sigma^{(4)}$ can be obtained from the Breit-Pauli Hamiltonian in Eq. (5), in a very similar way to $\sigma^{(2)}$. In this work, apart from evaluation of the complete $\sigma^{(4)}$ and $\sigma^{(2,1)}$, we present the calculation of the leading logarithmic QED correction $\sigma^{(5)}$, which has a numerical value of about $10^{-5}\,\sigma$. Finally we consider further improvement of theoretical predictions for ^{3}He and the other light atomic systems.

II. RELATIVISTIC CORRECTION

The relativistic correction $\sigma^{(4)}$ can be derived from the generalized Breit-Pauli Hamiltonian, which in addition to relativistic corrections includes coupling to the external magnetic field [7]. In our case, this field consists of the magnetic field $\vec{A}_I$ coming from the magnetic moment of the nucleus

$$\vec{A}_I = \frac{1}{4\,\pi}\,\vec{\mu}\times\frac{\vec{r}}{r^3}\,, \tag{3}$$

and of the homogenous external magnetic field $\vec{A}_E$

$$\vec{A}_E = \frac{1}{2}\,\vec{B}\times\vec{r}. \tag{4}$$

This Breit-Pauli Hamiltonian in natural units with the external magnetic field $\vec{A}$ and with g being the electron g-factor is [7]

$$\begin{aligned}
H_{BP} &= \sum_a H_a + \sum_{a>b,b} H_{ab}\,, && (5)\\
H_a &= \frac{\vec{\pi}_a^2}{2\,m} - \frac{Z\,\alpha}{r_a} - \frac{\vec{\pi}_a^4}{8\,m^3} - \frac{e}{2\,m}\,g\,\vec{s}_a\cdot\vec{B}_a - \frac{e^2}{8\,m^3}\,\vec{B}_a^2 + \frac{\pi\,Z\,\alpha}{2\,m^2}\,\delta(\vec{r}_a)\\
&\quad +\frac{e}{8\,m^3}\Big[2\,\{\vec{\pi}_a^2\,,\,\vec{s}_a\cdot\vec{B}_a\} + (g-2)\,\big\{\vec{\pi}_a\cdot\vec{B}_a\,,\,\vec{\pi}_a\cdot\vec{s}_a\big\}\Big] && (6)\\
H_{ab} &= \frac{e^2}{4\,\pi}\bigg\{\frac{1}{r_{ab}} - \frac{1}{2\,m^2}\,\pi_a^i\left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right)\pi_b^j + \frac{\pi}{m^2}\,\delta(\vec{r}_{ab})\\
&\quad +\frac{g^2}{4\,m^2}\,\frac{s_a^i\,s_b^j}{r_{ab}^3}\left(\delta^{ij} - 3\,\frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^2}\right) + \frac{1}{2\,m^2\,r_{ab}^3}\Big[g\,\vec{s}_a\cdot\vec{r}_{ab}\times\vec{\pi}_b\\
&\quad -g\,\vec{s}_b\cdot\vec{r}_{ab}\times\vec{\pi}_a + (g-1)\,\vec{s}_b\cdot\vec{r}_{ab}\times\vec{\pi}_b - (g-1)\,\vec{s}_a\cdot\vec{r}_{ab}\times\vec{\pi}_a\Big)\Big]\bigg\}\,. && (7)
\end{aligned}$$

where $\vec{\pi} = \vec{p} - e\,\vec{A}$, and H_{BP} in the above includes dependence on the electron g-factor only for spin dependent terms. For the derivation of $\sigma^{(4)}$ we set $g = 2$ and separate H_{BP} into parts: the leading interaction with the external field, no external field $H_{BP}\big|_{\vec{A}_E=\vec{A}_I=0}$, linear in the homogenous field $\delta_{\vec{A}_E}H_{BP}\big|_{\vec{A}_I=0}$, linear in the nuclear magnetic field $\delta_{\vec{A}_I}H_{BP}\big|_{\vec{A}_E=0}$, and bilinear in the homogenous and the nuclear magnetic fields $\delta_{\vec{A}_E,\vec{A}_I}H_{BP}$.

$$\begin{aligned}
H_{BP} &= \frac{e^2}{m}\,\vec{A}_E\cdot\vec{A}_I - \frac{e}{2\,m}\,\sum_a(\vec{L}_a + 2\,\vec{s}_a)\cdot\vec{B}\\
&\quad +H_{BP}\big|_{\vec{A}_E=\vec{A}_I=0} + \delta_{\vec{A}_E}H_{BP}\big|_{\vec{A}_I=0} + \delta_{\vec{A}_I}H_{BP}\big|_{\vec{A}_E=0} + \delta_{\vec{A}_E,\vec{A}_I}H_{BP} && (8)
\end{aligned}$$

Corrections to the energy, which are bilinear in magnetic fields, can be represented in terms of the leading contribution $E^{(2)}$ and the relativistic correction $E^{(4)}$,

$$E^{(2)} = \frac{e^2}{m}\,\langle \vec{A}_E\cdot\vec{A}_I\rangle \tag{9}$$

$$\begin{aligned}E^{(4)} &= 2\left\langle \frac{e^2}{m}\,\vec{A}_E\cdot\vec{A}_I\frac{1}{(E-H)'}\,H_{BP}\big|_{\vec{A}_E=\vec{A}_I=0}\right\rangle\\ &+2\left\langle \delta_{\vec{A}_E}H_{BP}\big|_{\vec{A}_I=0}\,\frac{1}{(E-H)'}\,\delta_{\vec{A}_I}H_{BP}\big|_{\vec{A}_E=0}\right\rangle\\ &+\langle\delta_{\vec{A}_E,\vec{A}_I}H_{BP}\rangle\,.\end{aligned} \tag{10}$$

Because of the spherical symmetry of closed shell atoms, perturbations due to $-\frac{e}{2\,m}\sum_a(\vec{L}_a+2\,\vec{s}_a)\cdot\vec{B}$ vanish, which is a significant simplification over molecular systems. Thus, in the leading order the shielding constant σ takes the form

$$\sigma^{(2)} = \frac{1}{3}\sum_a\left\langle\frac{1}{r_a}\right\rangle, \tag{11}$$

while relativistic corrections are

$$\sigma^{(4)} = \sigma^{(4)}_1+\sigma^{(4)}_{2A}+\sigma^{(4)}_{2B}+\sigma^{(4)}_{2C}+\sigma^{(4)}_3 \tag{12}$$

$$\sigma^{(4)}_1 = \frac{2}{3}\left\langle\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\frac{1}{(E-H)'}\left[\sum_a\left(\frac{\pi\,Z}{2}\,\delta(\vec{r}_a)-\frac{p_a^4}{8}\right)+\pi\,\delta(\vec{r})-\frac{1}{2}\,p_1^i\left(\frac{\delta^{ij}}{r}+\frac{r^i\,r^j}{r^2}\right)p_2^j\right]\right\rangle \tag{13}$$

$$\sigma^{(4)}_{2A} = -\frac{2}{9}\left\langle\pi\left[\delta(\vec{r}_1)-\delta(\vec{r}_2)\right]\frac{1}{(E-H)}\left[3\,p_1^2-3\,p_2^2-\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{\vec{r}\cdot(\vec{r}_1+\vec{r}_2)}{r^3}\right]\right\rangle \tag{14}$$

$$\begin{aligned}\sigma^{(4)}_{2B} &= -\frac{1}{6}\left\langle\left(\frac{\vec{r}_1\times\vec{p}_1}{r_1^3}+\frac{\vec{r}_2\times\vec{p}_2}{r_2^3}\right)\frac{1}{(E-H)}\right.\\ &\left.\left[\vec{r}_1\times\vec{p}_1\,p_1^2+\vec{r}_2\times\vec{p}_2\,p_2^2+\frac{1}{r}\,\vec{r}_1\times\vec{p}_2+\frac{1}{r}\,\vec{r}_2\times\vec{p}_1-\vec{r}_1\times\vec{r}_2\,\frac{\vec{r}}{r^3}\cdot(\vec{p}_1+\vec{p}_2)\right]\right\rangle\end{aligned} \tag{15}$$

$$\sigma^{(4)}_{2C} = -\frac{1}{8}\left\langle\left(\frac{r_1^i\,r_1^j}{r_1^5}-\frac{r_2^i\,r_2^j}{r_2^5}\right)^{(2)}\frac{1}{(E-H)}\left(Z\,\frac{r_1^i\,r_1^j}{r_1^3}-Z\,\frac{r_2^i\,r_2^j}{r_2^3}+\frac{r^i}{r^3}\,(r_1^j+r_2^j)\right)^{(2)}\right\rangle \tag{16}$$

$$\begin{aligned}\sigma^{(4)}_3 &= \frac{1}{12}\left\langle\left(\frac{1}{r_1^3}+\frac{1}{r_2^3}\right)\left(\frac{\vec{r}\cdot\vec{r}_1\,\vec{r}\cdot\vec{r}_2}{r^3}-3\,\frac{\vec{r}_1\cdot\vec{r}_2}{r}\right)\right\rangle\\ &-\frac{1}{6}\sum_a\left\langle\frac{1}{r_a}\,p_a^2+\frac{(\vec{r}_a\times\vec{p}_a)^2}{r_a^3}+4\,\pi\,\delta(\vec{r}_a)\right\rangle\end{aligned} \tag{17}$$

where $\vec{r}\equiv\vec{r}_1-\vec{r}_2$, $(p^i\,q^i)^{(2)} = p^i\,q^j/2+p^j\,q^i/2-\delta^{ij}\,\vec{p}\cdot\vec{q}/3$, and $1/(E-H)'$ is the reduced Green function (the reference state is subtracted out). We have split these relativistic corrections into first order terms $\sigma^{(4)}_3$, the second order terms with intermediate singlet ^1S- $\sigma^{(4)}_1$, triplet ^3S- $\sigma^{(4)}_{2A}$, singlet $^1P^e$- $\sigma^{(4)}_{2B}$, and triplet ^3D- $\sigma^{(4)}_{2C}$. These terms form a complete relativistic correction of order $O(\alpha^4)$ and their numerical calculations are described in Sec. V.

III. QED EFFECTS

The next order correction $O(\alpha^5)$ comes from QED effects. They contribute by F_i electromagnetic formfactors [13], the magnetic susceptibility and the so called Bethe logarithms. The slope of $F_1'(0)$ and $F_2(0) = (g-2)/2$ are known analytically at one-loop order [13]. However, $F_1'(0)$ is infrared divergent and this divergence cancels out with the uv divergence from the low-energy contribution in a similar way as for the Lamb shift in hydrogen [13]. The contribution from $F_2(0)$ is encoded by the g-factor in the Breit-Pauli Hamiltonian H_{BP}, Eqs. (5-7). We note that the g-factor enters relativistic corrections with different coefficients, which is not in accordance with Ref. [4]. The radiative corrections to the magnetic susceptibility have not yet been evaluated, but their calculation can be performed along the lines of Ref. [15]. Finally the Bethe logarithmic contribution, as for the Lamb shift, is probably the most difficult part of the numerical evaluation and can be obtained probably only for simple systems. However, the total QED correction can easily be estimated on the basis of the leading logarithmic contribution, which is derived below.

The leading logarithmic correction to σ can be obtained in the same way as with the Lamb shift. One considers 2-electron self interaction in the magnetic field due to low-energy photons ($m = 1$)

$$E_L = e^2 \int^{\epsilon} \frac{d^3k}{(2\,\pi)^3\,2\,k} \left(\delta^{ij} - \frac{k^i\,k^j}{k^2}\right) \left\langle\phi\middle|(\pi_1^i + \pi_2^i)\,\frac{1}{E-H-k}\,(\pi_1^j + \pi_2^j)\middle|\phi\right\rangle \tag{18}$$

where ϕ is the eigenstate of the nonrelativistic Hamiltonian H in the magnetic field, with energy E. The logarithmic part is

$$\begin{aligned} E_{\rm Log} &= \frac{\alpha}{3\,\pi}\,\ln\bigl[(Z\,\alpha)^{-2}\bigr]\,\langle\phi|[\vec\pi_1 + \vec\pi_2\,,\,[H-E\,,\,\vec\pi_1+\vec\pi_2]]|\phi\rangle \\ &= \frac{\alpha}{3\,\pi}\,\ln\bigl[(Z\,\alpha)^{-2}\bigr]\,\sum_a\left\langle\phi\middle|4\,\pi\,Z\,\alpha\,\delta(\vec r_a) + 2\,e^2\,B_a^2 + \frac{e}{2}\,\{\vec\pi_a\,,\,\nabla_a\times\vec B_a\}\middle|\phi\right\rangle \end{aligned} \tag{19}$$

The resulting logarithmic contribution to the shielding constant in order α^5 is

$$\begin{aligned} \sigma^{(5)} &= \frac{8\,Z}{9}\,\ln\bigl[(Z\,\alpha)^{-2}\bigr]\left\langle\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\frac{1}{(E-H)'}\,\bigl[\delta(\vec r_1)+\delta(\vec r_2)\bigr]\right\rangle \\ &\quad+\frac{20}{9}\,\ln\bigl[(Z\,\alpha)^{-2}\bigr]\,\langle\delta(\vec r_1)+\delta(\vec r_2)\rangle \\ &\quad+\frac{28}{9}\,\ln\alpha\left\langle\delta(\vec r)\,\frac{1}{(E-H)'}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right\rangle \end{aligned} \tag{20}$$

where we have added a small second order $\ln\alpha$ term, which comes from the two-electron Lamb shift [10], and thus Eq. (20) is a complete logarithmic contribution.

IV. NUCLEAR MASS CORRECTIONS

Effects coming from the finite nuclear mass are usually, if not always, neglected. Here we use the result derived in our previous work [6], namely the leading correction $\sigma^{(2,1)}$ is given by

$$\begin{aligned}\sigma^{(2,1)} &= \frac{1}{3}\left\langle\sum_a \frac{1}{r_a}\,\frac{1}{(E-H)'}\,p_N^2\right\rangle + \frac{1}{3}\,\frac{(1-g_N)}{Z\,g_N}\,\langle p_N^2\rangle \\ &+\frac{1}{3}\left\langle\left(\vec{r}_1\times\vec{p}_2+\vec{r}_2\times\vec{p}_1\right)\frac{1}{(E-H)}\sum_a\frac{\vec{r}_a}{r_a^3}\times\vec{p}_a\right\rangle\end{aligned} \tag{21}$$

where $\vec{p}_N = -\sum_a \vec{p}_a$, and

$$g_{\rm N} = \frac{m_{\rm N}}{Z\,m_{\rm p}}\,\frac{\mu}{\mu_{\rm n}}\,\frac{1}{I}, \tag{22}$$

where $\mu_{\rm n}$ is the nuclear magneton, I is the nuclear spin, and m_p is the proton mass. The definition of the nuclear g-factor assumed here is different from the standard one by the use of the actual charge e_N and the mass m_N of the corresponding particle, namely the coupling of the spin to the magnetic field is $-e_N\,g_N/(2\,m_N)\,\vec{I}\cdot\vec{B}$. The numerical value of g_N obtained from the known spin $I = 1/2$, nuclear charge $Z = 2$, magnetic moment $\mu = -2.127\ 625\ 2(1)\,\mu_{\rm n}$, and the mass ratio $m_{\rm N}/m_{\rm p} = 2.993\ 152\ 671\ 3(26)$ is presented in the caption of Table II, while the numerical evaluation of $\sigma^{(2,1)}$ is performed in Sec. V. Our result is not in agreement with the work on Neronov and Barzakh in [8], which based on earlier results of Hegstrom in [9].

V. NUMERICAL CALCULATIONS

The numerical calculations are performed with the use of explicitly correlated exponential functions, which for the S-state have the form

$$\phi(r_1,r_2,r) = \sum_{i=1}^{\mathcal{N}} v_i[e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r} \pm (r_1\leftrightarrow r_2)], \tag{23}$$

where α_i, β_i and γ_i are generated randomly with conditions:

$$\begin{aligned}&A_1<\alpha_i<A_2,\quad \beta_i+\gamma_i>\varepsilon,\\ &B_1<\beta_i<B_2,\quad \alpha_i+\gamma_i>\varepsilon,\\ &C_1<\gamma_i<C_2,\quad \alpha_i+\beta_i>\varepsilon.\end{aligned} \tag{24}$$

with ε approximately equal to $\sqrt{2\,m\,(E_{\rm He^+}-E_{\rm He})}$. In order to obtain a more accurate wave function, following Korobov [11], we use double set of the form (24). Parameters A_i, B_i, C_i are determined by minimization of the nonrelativistic energy. The linear coefficients v_i in Eq. (23) are obtained from a solution of the generalized eigenvalue problem with the length of the basis set $\mathcal{N} = 100, 300, 600, 900, 1200, 1500$ using extended precision arithmetic. As a result we obtain the following nonrelativistic energy in au

$$E_0(1^1S_0) = -2.903\,724\,377\,034\,119\,593(5), \tag{25}$$

in agreement with the even more accurate result of Korobov [11] and of Drake in [12]. The calculation of matrix elements of the nonrelativistic Hamiltonian are performed with the use of a simple formula for the master integral:

$$\frac{1}{16\,\pi^2}\int d^3r_1\int d^3r_2\,\frac{e^{-\alpha r_1-\beta r_2-\gamma r}}{r_1\,r_2\,r} = \frac{1}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}. \tag{26}$$

Integrals with any additional powers of r_i in the numerator can be obtained by differentiation with respect to the corresponding parameter α, β or γ. Matrix elements of relativistic corrections involve inverse powers of r_1, r_2, r, and these can be obtained by integration with respect to the corresponding parameter. In fact, all matrix elements involved in relativistic, QED and the finite nuclear mass corrections can be expressed in terms of rational, logarithmic and dilogarithmic functions in α, β, and γ. Considering numerical convergence, first order matrix elements can be calculated accurately using even short, i.e. $\mathcal{N} = 300$ expansion of the nonrelativistic wave function. The calculation of the second order corrections $Q_{6-13,15-16}$ is more complicated. The inversion of the operator $E-H$ is performed in a basis set of even parity functions with $l = 0, 1, 2$ of the form in Eq. (23) and

$$\vec{\phi}(r_1,r_2,r) = \sum_k v_k\,\vec{r}_1\times\vec{r}_2\,[e^{-\alpha_k r_1-\beta_k r_2-\gamma_k r} - (r_1\leftrightarrow r_2)]\,, \tag{27}$$

$$\begin{aligned}\phi^{ij}(r_1,r_2,r) &= \sum_k v_k\,[(r_1^i\,r_1^j - r_1^2\,\delta^{ij}/3)\,e^{-\alpha_k r_1-\beta_k r_2-\gamma_k r} - (r_1\leftrightarrow r_2)]\\ &\quad+\sum_l v_l\,(r^i\,r^j - r^2\,\delta^{ij}/3)\,[e^{-\alpha_l r_1-\beta_l r_2-\gamma_l r} - (r_1\leftrightarrow r_2)]\end{aligned} \tag{28}$$

The values of parameters A_i, B_i and C_i are obtained by minimization of the appropriate functional, which is the symmetric second order matrix element with the operator standing on the right hand side of the corresponding Q_i in Table I. This explicitly correlated exponential basis set allows us to obtain precise matrix elements of all Q_i operators, and the numerical results are presented in Table I. Some of these matrix elements have already been presented in [12], and results in Table I are in agreement with them.

TABLE I: Expectation values of operators entering σ, all digits are significant, $\vec r=\vec r_1-\vec r_2$, and $1/(E-H)$ is the nonrelativistic Green function.

$Q_1=$	$\frac{1}{r_1}+\frac{1}{r_2}$	3.376 633 601
$Q_2=$	$\frac{1}{r_1}\,p_1^2+\frac{1}{r_2}\,p_2^2$	33.677 743
$Q_3=$	$\frac{(\vec r_1\times\vec p_1)^2}{r_1^3}+\frac{(\vec r_2\times\vec p_2)^2}{r_2^3}$	0.073 109
$Q_4=$	$\delta(\vec r_1)+\delta(\vec r_2)$	3.620 859
$Q_5=$	$\left(\frac{1}{r_1^3}+\frac{1}{r_2^3}\right)\left(\frac{\vec r\cdot\vec r_1\,\vec r\cdot\vec r_2}{r^3}-3\frac{\vec r_1\cdot\vec r_2}{r}\right)$	−3.435 251
$Q_6=$	$[\delta(\vec r_1)+\delta(\vec r_2)]\,\frac{1}{(E-H)'}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$	−3.025 857
$Q_7=$	$(p_1^4+p_2^4)\,\frac{1}{(E-H)'}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$	−118.140 232
$Q_8=$	$p_1^i\left(\frac{\delta^{ij}}{r}+\frac{r^i\,r^j}{r^3}\right)p_2^j\,\frac{1}{(E-H)'}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$	−0.208 449
$Q_9=$	$\delta(\vec r)\,\frac{1}{(E-H)'}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$	−0.112 964
$Q_{10}=$	$(p_1^2\,\vec r_1\times\vec p_1+p_2^2\,\vec r_2\times\vec p_2)\,\frac{1}{E-H}\left(\frac{\vec r_1\times\vec p_1}{r_1^3}+\frac{\vec r_2\times\vec p_2}{r_2^3}\right)$	−0.041 690
$Q_{11}=$	$\left[\frac{1}{r}\,(\vec r_2\times\vec p_1+\vec r_1\times\vec p_2)-\vec r_1\times\vec r_2\,\frac{\vec r}{r^3}\cdot(\vec p_1+\vec p_2)\right]\frac{1}{E-H}\left(\frac{\vec r_1\times\vec p_1}{r_1^3}+\frac{\vec r_2\times\vec p_2}{r_2^3}\right)$	0.037 546
$Q_{12}=$	$\left(\frac{r_1^i\,r_1^j}{r_1^5}-\frac{r_2^i\,r_2^j}{r_2^5}\right)^{(2)}\frac{1}{E-H}\left(Z\,\frac{r_1^i\,r_1^j}{r_1^3}-Z\,\frac{r_2^ir_2^j}{r_2^3}+\frac{r^i\,(r_1^j+r_2^j)}{r^3}\right)^{(2)}$	−6.838 1(4)
$Q_{13}=$	$[\delta(\vec r_1)-\delta(\vec r_2)]\,\frac{1}{E-H}\left(3\,p_1^2-3\,p_2^2-\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{r_1^2-r_2^2}{r^3}\right)$	−39.921 269
$Q_{14}=$	$(\vec p_1+\vec p_2)^2$	6.125 588
$Q_{15}=$	$(\vec p_1+\vec p_2)^2\,\frac{1}{(E-H)'}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$	−3.504 997
$Q_{16}=$	$(\vec r_1\times\vec p_2+\vec r_2\times\vec p_1)\,\frac{1}{E-H}\left(\frac{\vec r_1\times\vec p_1}{r_1^3}+\frac{\vec r_2\times\vec p_2}{r_2^3}\right)$	0.078 743

VI. RESULTS

All corrections to the shielding constant σ can be expressed in terms of Q_i values and results are presented in Table II. All of them are accurate to all digits shown, nevertheless the uncertainty is different from 0, due to the neglect of the non logarithmic part of $\sigma^{(5)}$ which we estimate, on the basis of the helium Lamb shift, to be about 20%. The relativistic correction $\sigma^{(4)}$ is relatively large, namely 10^{-3} of the nonrelativistic one, and is dominated by the second order contribution from the triplet S states. QED corrections are non negligible, 1% of the relativistic contribution, while the finite nuclear mass corrections are very significant, about 42% of the relativistic contribution and of the opposite sign. Except for neglected QED contributions, in our opinion, no other correction including the finite nuclear size, may alter the result at the 0.1 ppb level.

TABLE II: Contribution to the shielding constant. Physical constants are taken from [14]: $\alpha^{-1} = 137.035\ 999\ 679(94), g_{\rm N} = -6.368\ 307\ 2, m_{\rm N}/m = 5\ 495.885\ 276\ 5(52)$. Uncertainty of σ is set to 20% of $\sigma^{(5)}$ contribution

operator	expectation value	contribution to $\sigma \times 10^6$
$\sigma^{(2)} = \frac{1}{3}\,Q_1$	1.125 544 534	59.936 770
$\sigma^{(4)}_1 = \frac{\pi Z}{3}\,Q_6 - \frac{1}{12}\,Q_7 - \frac{1}{3}\,Q_8 + \frac{2\pi}{3}\,Q_9$	3.340 6	
$\sigma^{(4)}_{2A} = -\frac{2\pi}{9}\,Q_{13}$	27.870 3	
$\sigma^{(4)}_{2B} = -\frac{1}{6}\,Q_{10} - \frac{1}{6}\,Q_{11}$	0.000 7	
$\sigma^{(4)}_{2C} = -\frac{1}{8}\,Q_{12}$	0.854 8	
$\sigma^{(4)}_3 = -\frac{1}{6}\,Q_2 - \frac{1}{6}\,Q_3 - \frac{2\pi}{3}\,Q_4 + \frac{1}{12}\,Q_5$	−13.494 9	
$\sigma^{(4)} = \sigma^{(4)}_1 + \sigma^{(4)}_{2A} + \sigma^{(4)}_{2B} + \sigma^{(4)}_{2C} + \sigma^{(4)}_3$	18.571 4	0.052 663
$\sigma^{(5)} = \ln\big[(Z\,\alpha)^{-2}\big]\left(\frac{8\,Z}{9}\,Q_6 + \frac{20}{9}\,Q_4\right) + \frac{28}{9}\,\ln\alpha\,Q_9$	24.277 0	0.000 502
$\sigma^{(2,1)} = \frac{1}{3}\left(\frac{1-g_{\rm N}}{Z g_{\rm N}}\,Q_{14} + Q_{15} + Q_{16}\right)$	−2.323 3	−0.022 511
$\sigma = \alpha^2\,\sigma^{(2)} + \alpha^4\,\sigma^{(4)} + \alpha^5\,\sigma^{(5)} + \alpha^2\,\frac{m}{m_{\rm N}}\,\sigma^{(2,1)}$		59.967 43(10)

VII. SUMMARY

We have obtained relativistic, QED and finite nuclear mass corrections to the magnetic shielding constant in ^{3}He with the uncertainty of 0.1 ppb, which is caused by neglected QED corrections. While our nonrelativistic result is in perfect agreement with the previous one by Drake in [12], the relativistic correction $0.052\,663$ is in the moderate agreement with result by Vaara and Pyykkö in Ref. [5] 0.04, which is obtained as the difference between DF LR and HF values in their Table I. We think therefore, that our calculation needs more accurate confirmation, since we have not been able to test individual relativistic corrections. However, under the assumption that the present calculation is correct, the shielding factor for ^{3}He is now known with the highest accuracy of any atom, which supports its use as a NMR standard. Moreover, the theoretical accuracy can be further improved by the complete calculation of the QED effects, which for He is certainly possible. Regarding calculations for other light atoms and molecules, we are not convinced that the commonly used Gaussian functions can be applied for the accurate evaluation of second order matrix elements, especially for Q_7, Q_{12} and Q_{13}. It is likely that the use of linear terms, which improve the cusp condition of the nonrelativistic wave function, will be necessary in order to obtain numerical result with predictable uncertainty. If this can be achieved, it will open a window for high accuracy determination of nuclear magnetic moments. Since the NMR frequencies can be measured very accurately, as that in ^{3}He, with respect to the proton in tetramethylsilane (TMS) [16], the magnetic moment of helion can be related to the accurately measured proton magnetic moment [14].

Acknowledgments

This work was supported by NIST through Precision Measurement Grant PMG 60NANB7D6153.

---

[1] N.F. Ramsey, Phys. Rev. **78**, 699 (1950).

[2] T. Helgaker, M. Jaszuński and K. Ruud, Chem. Rev. **99**, 293 (1999).

[3] P. Maninen, K. Ruud, P. Lantto, and J. Vaarra, J. Chem. Phys. **122**, 114107 (2005); erratum **124**, 149901 (2006) and references therein.

[4] M. Jaszuński and K. Ruud, Mol. Phys. **104**, 2139 (2006) and references therein.

[5] J. Vaara and P. Pyykkö, J. Chem. Phys. **118**, 2973 (2003).

[6] K. Pachucki, Phys. Rev. A **78**, 012504 (2008).

[7] K. Pachucki, Phys. Rev. A **69**, 052502 (2004).

[8] Yu.I. Neronov and A.E. Barzakh, Zh. Eksp. Teor. Fis. **75**, 1521 (1978) [JETP **48**, 769 (1978)].

[9] R.A. Hegstrom, Phys. Rev. A **7**, 451 (1973).

[10] J.R. Sapirstein, *Quantum Electrodynamics*, in Handbook of Atomic, Molecular, and Optical Physics, by G.W.F. Drake, Springer (2005).

[11] V. Korobov, Phys. Rev. A **61**, 064503 (2000), Phys. Rev. A **66**, 024501 (2002).

[12] G.W.F. Drake, *High Precision Calculations for Helium*. in Handbook of Atomic, Molecular, and Optical Physics, by G.W.F. Drake, Springer (2005).

[13] C. Itzykson and J. B. Zuber, *Quantum Field Theory*, McGraw–Hill, New York (1990).

[14] P. J. Mohr, B. N. Taylor, and David B. Newell, Rev. Mod. Phys. **80**, 633 (2008).

[15] K. Pachucki, A. Czarnecki, U.D. Jentschura, and V.A. Yerokhin, Phys. Rev. A **72**, 022108 (2005).

[16] K. Jackowski, M. Jaszuński. B. Kamieński, and M. Wilczek, J. Mag. Res. **193**, 147 (2008).