Relativistic treatment of the diamagnetic susceptibility of helium

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We report theoretical calculations of the diamagnetic susceptibility χ_0 of helium atom. We determined the complete relativistic correction to χ_0 of the order of α^4, where α is the fine-structure constant, by including all α^4 terms originating from the Dirac and Breit equations for a helium atom in a static magnetic field. Finite-nuclear-mass corrections to χ_0 were also evaluated. To obtain very accurate results and reliable uncertainty estimates we used a sequence of explicitly correlated basis sets of fully optimized Slater geminals. We found that $\chi_0 = -2.119\,070(34) \times 10^{-5}\ a_0^3$ and $\chi_0 = -2.119\,365(34) \times 10^{-5}\ a_0^3$ for ^{4}He and ^{3}He isotopes, respectively, where a_0 is the Bohr radius and the uncertainties shown in the parentheses are due entirely to the very conservative estimate of the neglected QED corrections of the order of α^5. Our results are compared with the available experimental data and with previous, incomplete theoretical determinations of the α^4 contributions to the diamagnetic susceptibility of helium.

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I. INTRODUCTION

For closed-shell atoms the static diamagnetic susceptibility χ_0 can be defined as the second derivative of the energy E with respect to the strength $B = |\mathbf{B}|$ of the uniform external magnetic field $\mathbf{B}$, in the limit of $B \to 0$,

$$\chi_0 = -\left.\frac{\partial^2 E}{\partial B^2}\right|_{B=0}. \tag{1}$$

In general, the magnetic susceptibility is dependent on the frequency of the oscillating magnetic field. However, as for closed-shall atoms the frequency-dependent terms appear only in the order of α^5 [1,2] or are quadratic in the electron-to-nucleus mass ratio [3] and, consequently, very small, thus we consider only static magnetic fields. Our interest in this quantity is motivated primarily by recent advances in metrology [4–7]. In particular, in the refractive-index gas thermometry [8–11], measurements of the refractive index n of a gas are used to determine its density ρ. If the equation of state is known, for instance, in the form of the virial expansion, the measurement of n provides a possibility to find the gas pressure p. Alternatively, the thermodynamic temperature of a gas can be determined by knowing its refractive index and pressure. The fundamental relation linking the refractive index and the gas density is the Lorentz-Lorenz formula [12,13]:

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}(\alpha_\mathrm{d} + \chi)\rho, \tag{2}$$

where α_d is the electric dipole polarizability of the gas particles. Formally, this expression is valid only for small densities, but generalizations involving higher powers of ρ with an extended range of applicability are well-known [4].

In most realizations of the refractive-index gas thermometry, helium is used as a medium gas [9]. Currently, the most reliable sources of fundamental microscopic properties of helium are *ab initio* calculations. For example, the electric dipole polarizability α_d is known from theory with relative accuracy of 10^{-7} [14–18]. In the foreseeable future, we expect the present accuracy level for α_d to be entirely sufficient from the experimental point of view. However, the same cannot be said about the magnetic susceptibility. On one hand, this quantity is roughly 5 orders of magnitude smaller than α_d and hence does not have to be determined as accurately. On the other hand, the most recent calculations of χ_0 by Bruch and Weinhold [19,20] for helium differ from the experimental results of Barter *et al.* [21] by roughly 7%. While the current consensus is that such a large discrepancy is most likely due to errors in the measurements, some problems on the theoretical side remain. As pointed out by Pachucki [22], the relativistic correction to χ_0 calculated by Bruch and Weinhold is incomplete and misses several terms originating from the magnetic-field dependence of the Dirac equation and the Breit interaction. As the magnitude of these terms is yet unknown, it is impossible to rigorously determine the uncertainty of the calculated χ_0.

This situation is not satisfactory from the point of view of modern metrological applications. Additionally, refractive-index gas thermometry measurements using neon and argon as medium gases have been proposed and argued to offer several advantages over helium [11]. Unfortunately, the magnetic susceptibility of neon and, especially, argon is not known with sufficient accuracy. This prompted us to undertake systematic theoretical calculations of the static magnetic susceptibility

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of light noble gases: Helium, neon, and argon. Our results for ^{4}He and ^{3}He are reported in the present paper, while the magnetic susceptibilities of neon and argon will be considered in a subsequent publication.

Throughout most this work, we use the standard cgs system of units employed, for instance, in the book of Bethe and Salpeter [23]. In these units, employed also in the experimental work, the magnetic susceptibility has the dimension of the volume and is expressed in cm^3/mol. In order to present the intermediate and final results of our calculations, it is convenient to use the atomic units (a.u.), where the electron mass m_e, the charge e, and the Planck constant $\hbar$ are assumed to be equal to 1. The atomic unit of the magnetic susceptibility is then a_0^3, where a_0 is the Bohr radius, $a_0 = 0.529\,177\,211 \times 10^{-8}$ cm. The conversion relation between the cgs and the atomic units is cm^3/mol $= 11.205\,873\,1\, a_0^3$. For the speed of light in vacuum we adopt the value $c = \alpha^{-1} = 137.035\,999$ a.u. The masses of the α particle and the ^{3}He nucleus used by us are 7 294.299 54 and 5 495.885 28 a.u., respectively.

II. THEORY

A. Leading-order contribution

Consider a helium atom in its electronic ground state ^1S. We temporarily neglect the nuclear motion and treat the nucleus as a stationary classical charge with infinite mass. Let us denote the nonrelativistic electronic Hamiltonian in the absence of external fields by $\hat{H}_0$. The total Hamiltonian $\hat{H}$ in the magnetic field $\mathbf{B}$ reads then [23] as

$$\hat{H} = \hat{H}_0 + \frac{e}{mc}\mathbf{B}\cdot\mathbf{S} + \frac{e}{mc}\mathbf{B}\cdot\mathbf{L} + \frac{e^2}{8mc^2}[(\mathbf{B}\times\mathbf{r}_1)^2 + (\mathbf{B}\times\mathbf{r}_2)^2], \tag{3}$$

where $\mathbf{S}$ and $\mathbf{L}$ are the total spin and angular momentum operators, respectively. The origin of the coordinate system is placed at the atomic nucleus, and $\mathbf{r}_i$, $i = 1$ and 2, denotes coordinates of the ith electron with respect to the origin. In the nonrelativistic theory the terms linear in $\mathbf{B}$ bring no contribution to the magnetic susceptibility of the ^1S state. The quadratic, diamagnetic term gives [23,24]

$$\chi_0^{(0)} = -\frac{e^2}{6mc^2}\langle\psi_0|r_1^2 + r_2^2|\psi_0\rangle, \tag{4}$$

where ψ_0 is the ground-state wave function. This is the dominant contribution to the magnetic susceptibility of helium. The leading corrections to $\chi_0^{(0)}$ computed in this work are either of the order of α^4 (referred to as the relativistic corrections) or are proportional to the electron-to-nucleus mass ratio.

B. Finite-nuclear-mass corrections

Finite-nuclear-mass (FNM) corrections to the magnetic susceptibility of helium were derived by Bruch and Weinhold [19]; see also the erratum correcting a small numerical error [20]. For the helium atom at rest, the complete correction of the order m_e/m_N, where m_N is the mass of the nucleus, comprises three contributions,

$$\chi_0^{\mathrm{FNM}} = \delta\chi_0^{\mathrm{ms}} + \delta\chi_0^{\mathrm{PZW}} + \delta\chi_0^{\mathrm{mp}}. \tag{5}$$

The first is the reduced-mass scaling term [19]

$$\delta\chi_0^{\mathrm{ms}} = 3\frac{m}{m_N}\chi_0^{(0)}, \tag{6}$$

while the second results from the application of the Power-Zienau-Wooley (PZW) transformation to eliminate the dependence of the vector potential on the center-of-mass position [19,25],

$$\delta\chi_0^{\mathrm{PZW}} = -\frac{e^2}{3m_N c^2}\langle\psi_0|\mathbf{r}_1\cdot\mathbf{r}_2|\psi_0\rangle. \tag{7}$$

The third term is the correction due to the conventional mass-polarization term in the Hamiltonian resulting from the separation of the center-of-mass motion,

$$\delta\chi_0^{\mathrm{mp}} = -\frac{e^2}{3mc^2}\langle\psi_0|(r_1^2 + r_2^2)\mathcal{R}_0\, H_{\mathrm{mp}}|\psi_0\rangle, \tag{8}$$

where $\mathcal{R}_0 = (E_0 - Q\hat{H}_0)^{-1}Q$, with $Q = 1 - |\psi_0\rangle\langle\psi_0|$ being the ground-state reduced resolvent of H_0, and $H_{\mathrm{mp}} = \mathbf{p}_1\cdot\mathbf{p}_2/m_N$ is the mass-polarization perturbation. Equations (6) and (7) are special cases of the equations derived by Pachucki and Yerokhin [25] for many-electron atoms. Bruch and Weinhold [19] considered also a small temperature-dependent correction, denoted as $\delta\chi_0^{\mathrm{BO}}$, resulting from the center-of-mass motion of the atom and derived an order-of-magnitude estimation of its value. The significance of this correction is discussed in Sec. IV.

C. Relativistic corrections

Relativistic corrections to the magnetic susceptibility can be divided into three groups. The first group originates from the Foldy-Wouthuysen transformation of the Dirac Hamiltonian in the presence of a homogeneous external magnetic field. The transformed Hamiltonian contains several magnetic-field-dependent terms, see Eq. (14) in Ref. [26], that are not included in Eq. (3). There are two terms linear in the magnetic-field vector $\mathbf{B}$ which can give a contribution of the order of α^6 (and also a small frequency dependence of χ_0) and, therefore, are beyond the scope of the present work. Equation (14) of Ref. [26] contains also four diamagnetic terms quadratic in $\mathbf{B}$ that read as follows:

$$\hat{A}^{(0)} = \frac{e^2}{4m^3c^4}[\{\mathbf{l}_1\cdot\mathbf{B},\ \mathbf{s}_1\cdot\mathbf{B}\} + \{\mathbf{l}_2\cdot\mathbf{B},\ \mathbf{s}_2\cdot\mathbf{B}\}], \tag{9}$$

$$\hat{A}^{(1)} = -\frac{e^2}{8m^3c^4}[(\mathbf{l}_1\cdot\mathbf{B})^2 + (\mathbf{l}_2\cdot\mathbf{B})^2], \tag{10}$$

$$\hat{A}^{(2)} = -\frac{e^2}{32m^3c^4}\big[\big\{(\mathbf{B}\times\mathbf{r}_1)^2, \mathbf{p}_1^2\big\} + \big\{(\mathbf{B}\times\mathbf{r}_2)^2, \mathbf{p}_2^2\big\}\big], \tag{11}$$

$$\hat{A}^{(3)} = -\frac{e^2\hbar^2}{4m^3c^4}B^2, \tag{12}$$

where $\mathbf{p}_i$ and $\mathbf{l}_i = \mathbf{r}_i\times\mathbf{p}_i$ are the momentum and angular momentum operators, respectively, of the ith electron. The curly brackets in the above formulas denote the anticommutators. Note the additional factor of 2 included in Eq. (12) compared to the value given in Eq. (14) of Ref. [26]. This change is due to the fact that Eq. (14) in Ref. [26] applies to one electron only while we are considering a two-electron system. For singlet states, $\hat{A}^{(0)}$ gives no α^4 contribution to χ_0, since its

expectation value vanishes under spin integration. By differentiating the expectation values of the operators $\hat{A}^{(1)}$, $\hat{A}^{(2)}$, and $\hat{A}^{(3)}$ with respect to B and setting the magnetic-field strength equal to zero, one obtains consecutively three corrections to the static magnetic susceptibility:

$$\delta\chi_0^{(1)} = \frac{e^2}{12m^3c^4}\,\langle\psi_0|l_1^2 + l_2^2|\psi_0\rangle, \tag{13}$$

$$\delta\chi_0^{(2)} = \frac{e^2}{12m^3c^4}\,\langle\psi_0|r_1^2p_1^2 + r_2^2p_2^2|\psi_0\rangle, \tag{14}$$

$$\delta\chi_0^{(3)} = \frac{e^2\hbar^2}{2m^3c^4}. \tag{15}$$

The second group of relativistic contributions originates from the Breit correction to the electron-electron interaction. The explicit form of the Breit-Pauli Hamiltonian in the presence of homogeneous electric and magnetic fields has been given in Ref. [26], see Eq. (17) of this reference. Similarly as for the Dirac Hamiltonian, it contains several linear and quadratic magnetic-field-dependent terms. However, all terms linear in $\mathbf{B}$ give contributions to χ_0 that are of the order of $1/c^6$ and hence are neglected in the present work. The spin-dependent quadratic terms vanish for singlet states upon the spin integration. All spin-independent quadratic terms in the Breit-Pauli Hamiltonian, which can give an α^4 contribution to χ_0, originate from the orbit-orbit interaction

$$\hat{H}_{\rm oo} = -\frac{e^2}{2m^2c^2}\left[\frac{\boldsymbol{\pi}_1\cdot\boldsymbol{\pi}_2}{r_{12}} + \frac{(\boldsymbol{\pi}_1\cdot\mathbf{r}_{12})(\mathbf{r}_{12}\cdot\boldsymbol{\pi}_2)}{r_{12}^3}\right], \tag{16}$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and $\boldsymbol{\pi}_i = \mathbf{p}_1 + e\,(\mathbf{B}\times\mathbf{r}_i)/2c$. From Eq. (16) we obtain two diamagnetic terms quadratic in the magnetic-field vector, namely,

$$\hat{A}^{(4)} = -\frac{e^4}{8m^2c^4}\,\frac{(\mathbf{B}\times\mathbf{r}_1)\cdot(\mathbf{B}\times\mathbf{r}_2)}{r_{12}}, \tag{17}$$

$$\hat{A}^{(5)} = -\frac{e^4}{8m^2c^4}\,\frac{[(\mathbf{B}\times\mathbf{r}_1)\cdot\mathbf{r}_{12}][(\mathbf{B}\times\mathbf{r}_2)\cdot\mathbf{r}_{12}]}{r_{12}^3}. \tag{18}$$

Differentiation with respect to B leads to the following two corrections:

$$\delta\chi_0^{(4)} = \frac{e^4}{6m^2c^4}\,\langle\psi_0|\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_{12}}|\psi_0\rangle, \tag{19}$$

$$\delta\chi_0^{(5)} = \frac{e^4}{12m^2c^4}\,\langle\psi_0|\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_{12}} - \frac{(\mathbf{r}_1\cdot\mathbf{r}_{12})(\mathbf{r}_2\cdot\mathbf{r}_{12})}{r_{12}^3}|\psi_0\rangle. \tag{20}$$

Derivations of Eqs. (19) and (20) are given in the Appendix.

Finally, the third group of contributions to the magnetic susceptibility originates from relativistic corrections to the electronic wave function. Using the standard perturbation theory one derives the following general formula:

$$\delta\chi_0^{\rm BP} = -\frac{e^2}{3mc^2}\,\langle\psi_0|\big(r_1^2 + r_2^2\big)\mathcal{R}_0\,\hat{H}_{\rm BP}|\psi_0\rangle, \tag{21}$$

where $\mathcal{R}_0$ is the resolvent defined in the same way as in Eq. (8), and $\hat{H}_{\rm BP}$ is the relativistic part of the Breit-Pauli Hamiltonian in the absence of the external electric and magnetic fields. When acting on singlet states this Hamiltonian can be assumed to comprise the following four terms [23]:

$$\hat{H}_{\rm BP} = \hat{P}_4 + \hat{D}_1 + \hat{D}_2 + \hat{B}, \tag{22}$$

$$\hat{P}_4 = -\frac{1}{8m^3c^2}\big(p_1^4 + p_2^4\big), \tag{23}$$

$$\hat{D}_1 = \frac{\pi e^2\hbar^2}{m^2c^2}[\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)], \tag{24}$$

$$\hat{D}_2 = \frac{\pi e^2\hbar^2}{m^2c^2}\,\delta(\mathbf{r}_{12}), \tag{25}$$

$$\hat{B} = -\frac{e^2}{2m^2c^2}\left[\frac{\mathbf{p}_1\cdot\mathbf{p}_2}{r_{12}} - \frac{(\mathbf{p}_1\cdot\mathbf{r}_{12})(\mathbf{p}_2\cdot\mathbf{r}_{12})}{r_{12}^3}\right], \tag{26}$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac distribution. The terms in Eqs. (23)–(26) are usually referred to as, consecutively, the mass-velocity, one-electron Darwin, two-electron Darwin, and orbit-orbit interaction (or Breit) operators. For further convenience, we split the $\delta\chi_0^{\rm BP}$ correction into the components related to the individual operators in Eqs. (23)–(26),

$$\delta\chi_0^{\rm BP} = \delta\chi_0^{\rm P_4} + \delta\chi_0^{\rm D_1} + \delta\chi_0^{\rm D_2} + \delta\chi_0^{\rm B}. \tag{27}$$

In summary, the total relativistic correction to the static diamagnetic susceptibility, evaluated in the present work, comprises nine terms:

$$\delta\chi_0^{\rm rel} = \sum_{i=1}^{5}\delta\chi_0^{(i)} + \delta\chi_0^{\rm P_4} + \delta\chi_0^{\rm D_1} + \delta\chi_0^{\rm D_2} + \delta\chi_0^{\rm B}. \tag{28}$$

In the work of Bruch and Weinhold [19], only the last four terms in Eq. (28) were considered and all the remaining ones were neglected.

D. Quantum electrodynamics correction

The leading corrections to χ_0 which have not been considered thus far originate from quantum electrodynamics (QED). These corrections are of the order of α^5 (in fact of the order of $\alpha^5\ln\alpha$) and take account of two physical phenomena: Vacuum polarization and electron self-energy. The QED formulas for these corrections can be derived along similar lines as for the nuclear magnetic shielding constants [1,2,27] and implemented numerically for helium in a way largely parallel to that presented in Ref. [28]. The resulting computations would inevitably be extremely complicated as they would require calculations of new forms of the so-called Bethe logarithms, including their magnetic-field dependence [28]. This would represent a massive computational task far beyond the scope of the present work.

However, one can easily perform a crude, order-of-magnitude assessment of the QED effects and obtain a conservative estimate of the uncertainty of χ_0 computed by us that can be useful in metrological applications. From the formal perturbation theory expressions, one can naively expect that QED corrections should be by a factor of the order of $\alpha\ln\alpha$ smaller than the relativistic corrections determined in the present work.

However, it would be overly optimistic to scale the total relativistic correction to χ_0 by $\alpha\ln\alpha$. In fact, there is a considerable cancellation between various relativistic contributions, making the total correction significantly smaller than the individual contributions. It is impossible to guarantee that a similar cancellation persists also for the QED corrections.

In fact, in the case of QED corrections to the energy [29–34] and other properties [3,17,35], it has been observed that this is frequently the case. The QED effects are only several times smaller than the relativistic corrections in such cases, rather than by a factor close to $\alpha \ln \alpha \approx 0.036$.

To account for this phenomena, we settle on the worst-case scenario. Namely, instead of scaling the total relativistic correction by a factor of $\alpha \ln \alpha$, we chose the relativistic correction which is the largest in magnitude and perform similar scaling. Multiplying the relativistic kinetic-energy correction $\delta\chi_0^{\mathrm{P}_4}$ by $\alpha \ln \alpha$, we find that the leading QED correction to χ_0 can be roughly estimated as $0.000\,034 \times 10^{-5}\, a_0^3$. This value most likely overestimates the QED effects, and so we view our estimate of the uncertainty of χ_0 as rather conservative.

III. COMPUTATIONAL DETAILS AND NUMERICAL RESULTS

To evaluate all quantities necessary for the determination of the magnetic susceptibility of helium, we follow closely the numerical approach applied in our recent calculations of electric polarizability [18]. The ground-state wave function of the helium atom is represented as a linear combination of Slater geminals, namely,

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = (1 + \mathcal{P}_{12}) \sum_{i=1}^{N} c_i\, e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}}, \tag{29}$$

where the $\mathcal{P}_{12}$ operator interchanges coordinates of $\mathbf{r}_1$ and $\mathbf{r}_2$. The linear coefficients c_i and the nonlinear parameters α_i, β_i, and γ_i are fully optimized to minimize the nonrelativistic energy of helium. For a given set of basis functions, defined by the nonlinear parameters α_i, β_i, and γ_i, the coefficients c_i were obtained using the Rayleigh-Ritz method. The standard linear algebra and minimization algorithms implemented in the HSL Mathematical Software Library [36] were applied and quadruple precision arithmetics was used to enhance the numerical stability. In particular, matrix factorizations and solutions of corresponding systems of equations were performed employing the DAG-based parallel Cholesky method with the OpenMP interface for shared-memory multiprocessing. Full optimization of the nonlinear parameters was carried out by applying two subroutines, i.e., VA13, the. Broyden–Fletcher–Goldfarb–Shanno (BFGS) variable metric method when values of the derivatives with respect to the variables were used, and VA24, the conjugate directions method when these derivatives were not employed. Using two different optimization procedures allowed us to avoid the situation of optimization getting stuck in one of the local minima and also accelerated the convergence of the whole optimization procedure.

The advantage of the exponential basis set (29) is the correct functional form near the interparticle coalescence points (the Kato's cusp), both the electron-electron and electron-nucleus types. This enables us to determine highly accurate wave functions with a relatively compact basis. In order to estimate the uncertainty of the results, we performed all calculations with a sequence of basis sets with $N = 128$, 256, and 512 functions. With the largest basis set, the nonrelativistic energy is accurate to 17 significant digits as compared to the benchmark value of Ref. [37]. This accuracy guarantees that numerical uncertainties of all computed quantities are negligible in comparison with errors resulting from omission of higher-order corrections (both in α and m/m_N).

TABLE I. Expectation values of various operators for the ground state of the helium atom computed with the largest basis set of $N = 512$ functions. The results are given in atomic units. In the parentheses we show the estimated uncertainty of the last digit.

Operator	Expectation value
H_0	−2.903 724 377 034 119 59(1)
$r_1^2 + r_2^2$	2.386 965 990 037 9(1)
$l_1^2 + l_2^2$	0.018 970 526 333(1)
$r_1^2\, p_1^2 + r_2^2\, p_2^2$	−0.139 689 120 125(1)
$\mathbf{r}_1 \cdot \mathbf{r}_2$	−0.064 736 661 397 785(1)
$\mathbf{r}_1 \cdot \mathbf{r}_2\; r_{12}^{-1}$	0.059 280 414 991 545(2)
$\mathbf{r}_1 \cdot \mathbf{r}_2\; r_{12}^{-1} - (\mathbf{r}_{12} \cdot \mathbf{r}_1)\, r_{12}^{-3} (\mathbf{r}_{12} \cdot \mathbf{r}_2)$	0.212 506 954 000(1)

In Table I we present expectation values of all operators required to calculate the diamagnetic susceptibility of helium, taking into account the finite-nuclear-mass and relativistic corrections considered in Secs. II B and II C, respectively. The error of each quantity is estimated conservatively as half of the difference between the results obtained with $N = 256$ and $N = 512$ basis sets.

In order to evaluate the mass-polarization correction (8), as well as the relativistic Breit-Pauli correction (21), one has to compute the following first-order response function:

$$\psi_1 = -\mathcal{R}_0\big(r_1^2 + r_2^2\big)\psi_0. \tag{30}$$

Once the response function ψ_1 is known, all these corrections can be rewritten in a form that permits their stable numerical evaluation. In order to obtain ψ_1 we first note that it obeys the equation

$$(QH - E_0)\psi_1 = Q\big(r_1^2 + r_2^2\big)\psi_0 \tag{31}$$

and hence can be found by minimization of the following Hylleraas functional:

$$\mathcal{F}[\widetilde{\psi}] = \langle\widetilde{\psi}|(H_0 - E_0 - E_0 P_0)|\widetilde{\psi}\rangle + 2\,\langle\widetilde{\psi}|Q\big(r_1^2 + r_2^2\big)|\psi_0\rangle, \tag{32}$$

where $P_0 = |\,\psi_0\rangle\langle\psi_0|$, with respect to all parameters appearing in the trial wave function $\widetilde{\psi}$. Since the operator $r_1^2 + r_2^2$ is spherically symmetric, the trial function $\widetilde{\psi}$ can also be represented by the expansion of the form of Eq. (29). However, the size of the basis employed in the calculation of ψ_1 had to be twice as large as that employed for ψ_0. This basis was generated in the following way. The first part of the basis set, comprising N functions, has the same nonlinear parameters α_i, β_i, and γ_i as found for the ground state. This part of the basis is not the subject of further optimization; i.e., the nonlinear parameters α_i, β_i, and γ_i for $i \leqslant N$ are fixed and only the expansion coefficients c_i are calculated anew. This approach guarantees accurate fulfillment of the orthogonality condition $\langle\psi_1|\psi_0\rangle = 0$, resulting from the presence of the Q projection in the definition of the resolvent. The second part of the basis for $\widetilde{\psi}$, also comprising N functions, includes functions with nonlinear parameters optimized by minimizing the functional

TABLE II. The matrix elements $\langle\psi_0|(r_1^2+r_2^2)\mathcal{R}_0 X|\psi_0\rangle$ for several operators X required in this work obtained with the largest basis set of $N = 512$ functions. The results are given in atomic units. The estimated uncertainty of the last digit is shown in parentheses.

X	Matrix element
$p_1^4 + p_2^4$	−80.298 613(2)
$\pi[\delta^3(\mathbf{r}_1) + \delta^3(\mathbf{r}_2)]$	−7.918 414 9(1)
$\pi\,\delta^3(\mathbf{r}_{12})$	−0.547 997 8(1)
$\mathbf{p}_1 r_{12}^{-1}\mathbf{p}_2 + (\mathbf{p}_1\cdot\mathbf{r}_{12})r_{12}^{-3}(\mathbf{r}_{12}\cdot\mathbf{p}_2)$	0.420 214 859 4(2)
$\mathbf{p}_1\cdot\mathbf{p}_2$	−0.179 805 762 988 59(3)

of Eq. (32). In Table II we show the numerical results of the second-order matrix elements obtained for the ground state of the helium atom using the largest basis set $N = 512$. The error estimation is performed in the same way as for the data given in Table I.

IV. DISCUSSION AND CONCLUSIONS

In Table III we present contributions to the diamagnetic susceptibility of the ^{3}He and ^{4}He atoms based on numerical values from Tables I and II. Our results for ^{3}He are compared with the previous results of Bruch and Weinhold from Ref. [19]. We found a good agreement among all individual contributions computed in Ref. [19], including both the $\chi_0^{\rm FNM}$ and the $\delta\chi_0^{\rm BP}$ corrections. However, the remaining relativistic contributions derived in the present work, namely, $\delta\chi_0^{(i)}$, $i = 1,\ldots,5$, were not considered in Ref. [19]. Most of these corrections turned out to be small, with the exception of $\delta\chi_0^{(3)}$, which is of the same order of magnitude as the dominant $\delta\chi_0^{\rm BP}$ term. Because of that, the total relativistic correction reported in Ref. [19] is underestimated by a factor of about one-third in comparison to our data. Note that in Ref. [19], the mass polarization correction $\delta\chi_0^{\rm mp}$ was treated together with $\delta\chi_0^{\rm BP}$ rather than with $\chi_0^{\rm FNM}$, as in our work, which would be more appropriate considering the scaling of both terms with the nuclear mass. Overall, the present numerical results are of high numerical accuracy. The errors of our calculations, rigorously estimated, are negligible in comparison with neglected higher-order order terms in α and in m_e/m_N.

In Ref. [19], Bruch and Weinhold considered also the effect on χ_0 due to the the center-of-mass motion, referred to by them as $\delta\chi_0^{\rm BO}$. Using two different approximate perturbation theory procedures they derived two order-of-magnitude estimations of $\delta\chi_0^{\rm BO}$ that can be expressed by the formula

$$\delta\chi_0^{\rm BO} \approx f\frac{E_{\rm cm}}{m_N c^2}a_0^3, \tag{33}$$

where $E_{\rm cm}$ is the center-of-mass kinetic energy of the atom and f is a dimensionless parameter close to 1.5. This temperature-dependent correction is proportional to the ratio of the translational energy $E_{\rm cm} = \frac{3}{2}kT$ to the rest mass of the atom and turns out to be several orders of magnitude smaller than $\chi_0^{\rm FNM}$—4 orders for the liquid helium temperature of $T \approx 20$ K and 3 orders for the average temperature $T \approx 296$ K of the gas-phase measurements [21]. Therefore, even the large relative error in the determination of $\delta\chi_0^{\rm BO}$ would not be relevant for metrology applications.

TABLE III. Contributions to the diamagnetic susceptibility of the ^{3}He and ^{4}He atoms given in the units of $10^{-5}a_0^3$. The numbers in parentheses are the uncertainties of the last digit; when no uncertainty estimate is shown, the last digit is accurate. The uncertainties of the data from Ref. [19] were not estimated by the authors and hence are not shown.

Contribution	^{4}He	^{3}He	^{3}He, Refs. [19,20]
$\chi_0^{(0)}$	−2.118 486 203 037 9(1)		
	Finite-nuclear-mass correction, $\chi_0^{\rm FNM}$		
$\delta\chi_0^{\rm ms}$	−0.000 871 291 146 3	−0.001 156 403 069 7	−0.001 16
$\delta\chi_0^{\rm PZW}$	0.000 015 753 465 6	0.000 020 908 459 8	0.000 020 92[a]
$\delta\chi_0^{\rm mp}$	−0.000 043 755 174 2	−0.000 058 073 145 8	−0.000 058 1
Total $\chi_0^{\rm FNM}$	−0.000 899 21	−0.001 193 49	−0.001 20[b]
	Relativistic correction, $\delta\chi_0^{\rm rel}$		
$\delta\chi_0^{(1)}$	0.000 000 448 290		n/a
$\delta\chi_0^{(2)}$	−0.000 003 300 978		n/a
$\delta\chi_0^{(3)}$	0.000 141 785 338		n/a
$\delta\chi_0^{(4)}$	0.000 002 801 697		n/a
$\delta\chi_0^{(5)}$	0.000 005 021 728		n/a
$\sum_i \delta\chi_0^{(i)}$	0.000 146 756 076		n/a
$\delta\chi_0^{\rm P_4}$	0.000 948 763 83(2)		0.000 95
$\delta\chi_0^{\rm D_1} + \delta\chi_0^{\rm D_2}$	−0.000 800 275 46(1)		−0.000 802
$\delta\chi_0^{\rm B}$	0.000 019 860 10		0.000 019 8
$\delta\chi_0^{\rm BP}$	0.000 168 348 47(3)		0.000 162 8
Total $\delta\chi_0^{\rm rel}$	0.000 315 104 55(2)		0.000 162 8
$\chi_0 = \chi_0^{(0)} + \chi_0^{\rm FNM} + \delta\chi_0^{\rm rel}$	−2.119 070(34)	−2.119 365(34)	−2.119 52

[a]The original value from Ref. [19] adjusted by a factor 4 as noted in Ref. [20].
[b]Based on values from Ref. [19].

A more serious problem is the omission of the QED corrections in the present work. From the discussion in Sec. II D, it is clear that the final uncertainty of the magnetic susceptibility comes from the crude estimation of the QED correction, and our final recommended value of χ_0 for ^{4}He, used in the last row Table III, is $0.000\,034 \times 10^{-5}\, a_0^3$. Further improvements in the accuracy of χ_0 for helium would require more rigorous determination of the QED contributions.

Let us also compare our results with the available experimental data. From the gas-phase experiments performed by Barter *et al.* [21], we have the value $\chi_0 = -2.26(8) \times 10^{-5}\, a_0^3$ for ^{4}He. Therefore, we find a roughly 2σ disagreement with the theoretical result $\chi_0 = -2.119\,106(34) \times 10^{-5}\, a_0^3$ determined by us. The reason for this disagreement is not clear. On the experimental side, another measurement of the magnetic susceptibility was performed in the liquid phase for the ^{3}He isotope [38–40]. To add to the confusion, the experimental results in the liquid phase and the gas phase also do not agree, with a deviation of about 6%. Moreover, the liquid-phase–gas-phase discrepancy is inconsistent with theoretical estimates of Bruch and Weinhold [41], supported by calculations of Komasa [42], who argued that the interaction-induced increment to the diamagnetic susceptibility of liquid helium is below 1%.

While the possible sources of error on the experimental side cannot be elucidated in the present work, it is worth discussing the possible sources of the discrepancy resulting from inaccurate calculations or incomplete theory. First, we believe that such large deviations cannot be explained by numerical errors or artifacts such as basis-set incompleteness, etc., in our computations. This is partly due to the mature state of the technology used for accurate calculations for two-electron systems. Additionally, there is a very good agreement between our numerical results and the data of Bruch and Weinhold, in all cases where the latter are available. Similarly, we find it extremely unlikely that the QED effects bring such a large contribution to the magnetic susceptibility. This would imply a catastrophic failure of the convergence of the QED energy in powers of α, resulting in the QED effects being about 3 orders of magnitude larger than the α^2 relativistic correction. Such a phenomenon would be unprecedented and would contradict the current knowledge about the accuracy of QED for a light system like the helium atom [34,43].

Several other sources of error in theoretical calculations of χ_0 have been discussed, such as the approximate treatment of the temperature dependence of χ_0 (represented by the $\delta\chi_0^{\mathrm{BO}}$ term) or the density dependence of χ_0 considered by Bruch and Weinhold [41]. In all cases, these effects cannot explain the observed discrepancy. It is worth mentioning that the magnetic susceptibility exhibits also a frequency dependence, an effect completely neglected in the present work. However, the frequency dependence of χ_0 originates solely from high-order contributions of the order of $1/m_N^2$ or $1/c^6$ and higher, and hence is entirely negligible within the present accuracy requirements.

To conclude, we have reported state-of-the-art theoretical calculations of the static diamagnetic susceptibility of ^{3}He and ^{4}He in the ^1S electronic ground state. We have evaluated the complete relativistic correction to χ_0 of the order of α^4, including terms originating from the magnetic-field-dependent Dirac equation and the Breit interaction. The correction due to the finite nuclear mass has also been evaluated. The main source of error in our calculations is the omission of the QED effects which were crudely and very conservatively estimated. Our theoretical results disagree with both the gas-phase and the liquid-phase measurements of the magnetic susceptibility. The reason for this disagreement is not known; possible sources of error on the theoretical side were discussed. A new independent measurement may shed light on this problem and help to resolve the discrepancy.

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APPENDIX

Here we give the derivation of Eqs. (19) and (20). Let us first consider the $\delta\chi_0^{(4)}$ correction of Eq. (19). Using the vector identity

$$(\mathbf{a}\times\mathbf{b})\cdot(\mathbf{c}\times\mathbf{d}) = (\mathbf{a}\cdot\mathbf{c})(\mathbf{b}\cdot\mathbf{d}) - (\mathbf{a}\cdot\mathbf{d})(\mathbf{b}\cdot\mathbf{c}), \tag{A1}$$

the operator in the numerator in Eq. (17) can be written as

$$(\mathbf{B}\times\mathbf{r}_1)\cdot(\mathbf{B}\times\mathbf{r}_2) = B^2\,\mathbf{r}_1\cdot\mathbf{r}_2 - (\mathbf{B}\cdot\mathbf{r}_1)(\mathbf{B}\cdot\mathbf{r}_2). \tag{A2}$$

It is not difficult to see that the expectation value of the second term on the right-hand side of Eq. (A2), when evaluated with a spherically symmetric wave function, is the same as the expectation value of the operator $-\frac{1}{3}B^2\,\mathbf{r}_1\cdot\mathbf{r}_2$. This allows us to write

$$\langle\psi_0|\frac{(\mathbf{B}\times\mathbf{r}_1)\cdot(\mathbf{B}\times\mathbf{r}_2)}{r_{12}}|\psi_0\rangle = \frac{2}{3}B^2\,\langle\psi_0|\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_{12}}|\psi_0\rangle. \tag{A3}$$

Double differentiation with respect to B generates an additional factor of 2 which finally leads to Eq. (19).

The derivation of Eq. (20) is somewhat more complicated. First, by expanding the vector and scalar products appearing in Eq. (18) we obtain

$$\begin{aligned}&[(\mathbf{B}\times\mathbf{r}_1)\cdot\mathbf{r}_{12}][(\mathbf{B}\times\mathbf{r}_2)\cdot\mathbf{r}_{12}]\\ &\quad= [\mathbf{B}\cdot(\mathbf{r}_1\times\mathbf{r}_{12})][\mathbf{B}\cdot(\mathbf{r}_2\times\mathbf{r}_{12})]\\ &\quad= \tfrac{1}{3}B^2\,(\mathbf{r}_1\times\mathbf{r}_{12})\cdot(\mathbf{r}_2\times\mathbf{r}_{12}) + \cdots,\end{aligned} \tag{A4}$$

where the dots indicate several terms that give zero when evaluated with a spherically symmetric wave function. Using Eq. (A1) again, one obtains

$$\begin{aligned}&\frac{1}{3}B^2\langle\psi_0|\frac{(\mathbf{r}_1\times\mathbf{r}_{12})\cdot(\mathbf{r}_2\times\mathbf{r}_{12})}{r_{12}^3}|\psi_0\rangle\\ &\quad= \frac{1}{3}B^2\langle\psi_0|\frac{r_{12}^2(\mathbf{r}_1\cdot\mathbf{r}_2) - (\mathbf{r}_1\cdot\mathbf{r}_{12})(\mathbf{r}_2\cdot\mathbf{r}_{12})}{r_{12}^3}|\psi_0\rangle.\end{aligned} \tag{A5}$$

Differentiation with respect to the external magnetic field leads to Eq. (20). Note that the term explicitly written on the rightmost side in Eq. (A4) can also be expressed as $\frac{1}{3}B^2\,(\mathbf{r}_1 \times \mathbf{r}_2)\cdot(\mathbf{r}_1 \times \mathbf{r}_2)$. Thus, in view of Eq. (A1), the right-hand side of Eq. (A5) can be written in a formally somewhat simpler form:

$$\frac{1}{3}B^2\langle\psi_0|\frac{r_1^2 r_2^2 - (\mathbf{r}_1\cdot\mathbf{r}_2)^2}{r_{12}^3}|\psi_0\rangle. \tag{A6}$$

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