PHYSICAL REVIEW A **109**, 012820 (2024)

Diamagnetic susceptibility of neon and argon including leading relativistic effects

Michał Lesiuk [*] and Bogumił Jeziorski
Faculty of Chemistry, University of Warsaw Pasteura 1, 02-093 Warsaw, Poland

(Received 19 November 2023; accepted 4 January 2024; published 29 January 2024)

We report theoretical calculations of the static diamagnetic susceptibility, χ_0 of neon and argon atoms. The calculations were performed using a hierarchy coupled-cluster methods combined with application of both the Gaussian and Slater orbital basis sets. We included the complete relativistic correction of order of α^4, where α is the fine-structure constant, and obtained an estimate of the quantum electrodynamics contributions. The finite nuclear mass and size corrections were also considered but were found to be small. The final results are $\chi_0 = -8.4786(7) \times 10^{-5} a_0^3$ for the neon atom and $\chi_0 = -22.9545(32) \times 10^{-5} a_0^3$ for the argon atom, where a_0 is the Bohr radius. The uncertainties in the last digits, shown in the parentheses, are primarily due to the errors in the nonrelativistic electronic wave function, as well as to the neglected quantum electrodynamics corrections.

DOI: 10.1103/PhysRevA.109.012820

I. INTRODUCTION

In an earlier paper [1], we reported an accurate calculation of the static magnetic susceptibility χ_0 of the helium atom taking into account the complete set of relativistic corrections as well as the finite-nuclear-mass effects. The magnetic susceptibility is a fundamental property of atoms and molecules that enables us to determine their leading-order response (for closed-shell systems) to the applied external magnetic field. Moreover, this quantity is an important ingredient of the Lorentz-Lorenz formula [2,3], which relates the refractive index n of an atomic gas to its density ρ. The latter can be determined experimentally by measuring the resonance frequencies of a quasispherical cavity under vacuum and when the cavity is filled with a working gas. Such measurements form the basis of the refractive-index gas thermometry (RIGT) [4–7], a novel experimental technique in the field of metrology [8–11]. Knowing the resonance frequencies in vacuum $f(0)$ and at some pressure p of the gas $f(p)$ measured at a constant temperature, the refractive index is calculated as

$$n = \frac{f(0)}{f(p)\,(1-\kappa_{\text{eff}}\,p)}, \tag{1}$$

where κ_{eff} is an effective parameter, characteristic for a given apparatus, that accounts for the compression of the cavity as the pressure is increased. It is worth pointing out that this parameter is not affected by the composition of the working gas, which opens up a window for an alternative experimental setup for RIGT measurements, as discussed by Schmidt *et al.* [12]. In this variant, two independent measurements are performed with two different working gases, such as helium and argon. The results are then combined to eliminate κ_{eff} parameter entirely, thereby removing the uncertainty related to the compressibility of the cavity (see Ref. [5]).

In the current realizations of the RIGT experimental setup, helium is the preferred working gas. This is justified by the accuracy of the theoretical data available for this system, in particular the polarizability [13–16], magnetic susceptibility [1,17,18], density virial coefficients [19,20], and dielectric or refractivity virial coefficients [21–24]. However, the main disadvantage of helium is its small polarizability, making the RIGT measurements sensitive to small perturbations caused by inaccurate frequency or resonator compressibility determinations and gas purity. The latter problem is especially troublesome as the most common impurity—water vapor—is roughly 2 orders of magnitude more polarizable than helium. For this reason, using other elements, in particular neon or argon, as the working gas has been suggested (see Ref. [5] and references therein). Neon and argon have macroscopic properties similar to those of helium, but their polarizabilities are roughly a factor of 2 and 8 larger, respectively. This helps to reduce the sensitivity of RIGT measurements to impurities and to further improve their accuracy.

Despite the aforementioned advantages of neon and argon as the working gas, knowledge of the fundamental properties of these atoms is still incomplete. For example, their polarizabilities were only recently calculated from first principles with high accuracy [25–27]. The magnetic susceptibilities χ_0 of neon and argon are currently known with an estimated error of several percent, which is not satisfactory from the experimental point of view. In this work we report theoretical determination of χ_0 for neon and argon following the theoretical framework introduced in our earlier paper [1]. For brevity, we refer to this work as paper I in the following. We compute the complete set of relativistic contributions to χ_0 (of the order of α^4, where α is the fine-structure constant) and consider several other corrections due to finite nuclear mass and size and quantum electrodynamics (QED) effects.

Atomic units are used throughout the present work, i.e., $\hbar = m_e = e = 1$, where m_e and e are the electron mass and charge, respectively. We adopt the following values [28] for the fundamental physical constants: fine-structure constant

---

[*] m.lesiuk@uw.edu.pl

$\alpha = 1/137.035\,999$, Bohr radius $a_0 = 0.529\,177\,210$ Å, and Avogadro's number $N_A = 6.022\,140\,76 \times 10^{23}$. The conversion factor between cm^3/mol, frequently used in the literature for χ_0, and atomic units is $1\,\mathrm{cm}^3/\mathrm{mol} = 11.205\,872$ a.u.

II. THEORY

For closed-shell atoms the diamagnetic susceptibility χ_0 is 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 $B \to 0$,

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

In general, the magnetic susceptibility is dependent on the frequency of the oscillating magnetic field. However, for closed-shell atoms the frequency-dependent terms appear only on the order of α^5 and higher [29,30] or are quadratic in the electron-to-nucleus mass ratio; see the discussion in Ref. [25]. As a result, the frequency contribution to χ_0 is expected to be tiny, and in this work we consider only static magnetic fields.

For closed-shell singlet electronic states, the dominant contribution (of the order α^2) to χ_0 is given by the formula [31]

$$\chi_0^{(0)} = -\frac{\alpha^2}{6}\left\langle \sum_i r_i^2 \right\rangle, \tag{3}$$

where the summation index i runs over all electrons in the system, $r_i = |\mathbf{r}_i|$ are the electron-nuclear distances, $\mathbf{r}_i$ are the spatial coordinates of the ith electron, and, finally, $\langle X \rangle$ is shorthand notation for the expectation value of an arbitrary operator X with the nonrelativistic ground-state electronic wave function, Ψ_0.

The relativistic corrections to χ_0 of the order α^4 can be divided into three groups. The first group comes from relativistic corrections to the electronic Hamiltonian resulting from Foldy-Woythausen expansion of the magnetic-field-dependent Dirac equation in powers of α^2 [32]. In paper I we identified three corrections of this type which make a diamagnetic contribution to χ_0 and do not vanish after spin integration in a closed-shell system. They are given by the formulas

$$\delta\chi_0^{(1)} = \frac{\alpha^4}{12}\left\langle \sum_i l_i^2 \right\rangle, \tag{4}$$

$$\delta\chi_0^{(2)} = -\frac{\alpha^4}{12}\left\langle \sum_i r_i^2\, \nabla_i^2 \right\rangle, \tag{5}$$

$$\delta\chi_0^{(3)} = \frac{\alpha^4}{4} N_e, \tag{6}$$

where l_i^2 is the square of the total electronic angular momentum operator for the ith electron and N_e denotes the number of electrons in the atom. These equations are equivalent to the formulas presented previously for the helium atom [see Eqs. (13)–(15)], and changes in the prefactors result solely from the use of atomic units here.

The second group of corrections originates from the Breit contribution to the electron-electron interaction. There are two corrections in this group, namely,

$$\delta\chi_0^{(4)} = \frac{\alpha^4}{6}\left\langle \sum_{i<j} \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_{ij}} \right\rangle, \tag{7}$$

$$\delta\chi_0^{(5)} = \frac{\alpha^4}{12}\left\langle \sum_{i<j} \frac{\mathbf{r}_i \cdot \mathbf{r}_j}{r_{ij}} - \frac{(\mathbf{r}_i \cdot \mathbf{r}_{ij})(\mathbf{r}_j \cdot \mathbf{r}_{ij})}{r_{ij}^3} \right\rangle, \tag{8}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and r_{ij} is the electron-electron distance.

Finally, the third group of corrections takes into account the relativistic corrections to the electronic wave function. Let us recall the standard form of the Breit-Pauli Hamiltonian [31]

$$\hat{H}_{\mathrm{BP}} = \hat{P}_4 + \hat{D}_1 + \hat{D}_2 + \hat{B}, \tag{9}$$

where the above operators are defined as

$$\hat{P}_4 = -\frac{\alpha^2}{8}\sum_i \nabla_i^4, \tag{10}$$

$$\hat{D}_1 = \alpha^2 \frac{\pi Z}{2} \sum_i \delta(\mathbf{r}_{ia}), \tag{11}$$

$$\hat{D}_2 = \alpha^2 \pi \sum_{i>j} \delta(\mathbf{r}_{ij}), \tag{12}$$

$$\hat{B} = \frac{\alpha^2}{2}\sum_{i>j}\left[\frac{\nabla_i \cdot \nabla_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_j)\nabla_i}{r_{ij}^3} \right] \tag{13}$$

and Z is the nuclear charge. Following the usual convention, we refer to these operators as the mass-velocity (MV), one-electron Darwin (D1), two-electron Darwin (D2), and orbit-orbit operators, respectively. Every operator $\hat{X} = \hat{P}_4, \hat{D}_1, \hat{D}_2, \hat{B}$ appearing in the Breit-Pauli Hamiltonian gives an additional correction to the magnetic susceptibility of the following general form:

$$\delta\chi_0^{\mathrm{X}} = -\frac{\alpha^2}{3}\langle \Psi_0 | \left(\sum_i r_i^2 \right) \frac{Q}{\hat{H} - E_0} \hat{X} | \Psi_0 \rangle, \tag{14}$$

where $\hat{H}$ is the nonrelativistic electronic Hamiltonian, E_0 is the ground-state electronic energy, and $Q = 1 - |\Psi_0\rangle\langle\Psi_0|$ denotes projection onto the subspace orthogonal to Ψ_0.

It is worth pointing out that besides the relativistic contributions to χ_0, there are some minor corrections that account for the effects beyond the clamped-nucleus Born-Oppenheimer approximation: the finite-nuclear-size (FNS) and finite-nuclear-mass (FNM) corrections. They are considered in subsequent sections.

III. COMPUTATIONAL DETAILS

Calculation of the corrections listed in the previous section is a nontrivial problem, and in many cases there are no programs available that can perform this task. In these cases, we developed and implemented the necessary formalism specifically for the purposes of this project. In this section we provide the details of our calculations and specify the level of theory used to determine each contribution.

In the present work, two types of basis sets were employed in the calculations: Gaussian-type orbitals (GTOs) [33] and Slater-type orbitals (STOs) [34,35]. The choice of the basis-set type used in the calculation of specific quantities was dictated by limitations of the available computer programs and by the accuracy required in the final results. In general, the available GTOs for neon and argon are larger than the corresponding STOs. Indeed, GTOs for neon up to the bewildering tredecuple-zeta (13Z) quality are available from the recent work of Hellmann [26]. For argon, GTOs up to nonuple-zeta (9Z) were optimized by us for calculations of the polarizability [27]. In comparison, STOs only up to 7Z quality were reported for neon and argon [25]. Therefore, we use GTOs for the calculation of $\chi_0^{(0)}$, for which the accuracy requirements are the most stringent. Three program packages were used in these calculations: DALTON [36], CFOUR [37] and MRCC [38], as detailed in the subsequent section. Additionally, GTOs were used for the calculation of the $\delta\chi_0^{\mathrm{MV}}$ and $\delta\chi_0^{\mathrm{D1}}$ corrections; here we exploit the fact that such calculations can be performed with the DALTON package without any modifications. Finally, GTOs were employed in the determination of the $\delta\chi_0^{\mathrm{D2}}$ and $\delta\chi_0^{\mathrm{B}}$ contributions, which required us to write a dedicated in-house program. The necessary orbit-orbit and two-electron Darwin integrals within GTOs were exported from the DALTON package. To the best of our knowledge, a general implementation of the orbit-orbit integrals within STOs is not available publicly.

The calculation of the remaining corrections, that is, $\delta\chi_0^{(1)}$, $\delta\chi_0^{(2)}$, $\delta\chi_0^{(4)}$, and $\delta\chi_0^{(5)}$, was accomplished within the STOs. This choice is motivated by the fact that these corrections are not large and hence do not have to be determined as accurately. At the same time, we found that calculation of matrix elements corresponding to the operators appearing in Eqs. (7) and (8) is actually simpler within STOs than GTOs (for atomic systems), which negates the main technical advantage of GTOs. In fact, the calculation of two-electron integrals within STOs with the interaction operators

$$K_1(\mathbf{r}_1,\mathbf{r}_2)=\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_{12}}, \tag{15}$$

$$K_2(\mathbf{r}_1,\mathbf{r}_2)=\frac{(\mathbf{r}_1\cdot\mathbf{r}_{12})(\mathbf{r}_2\cdot\mathbf{r}_{12})}{r_{12}^3} \tag{16}$$

is a straightforward generalization of the formalism from Refs. [39,40], provided that partial-wave expansions (PWEs) of these operators are available. Therefore, we seek the following PWE:

$$K_i(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l=0}^{\infty} f_l^{(i)}(r_<,r_>)\,P_l(\cos\gamma) \tag{17}$$

for $i=1,2$, where $r_<=\min(r_1,r_2)$, $r_>=\max(r_1,r_2)$, and γ is the angle between vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. To derive the necessary expressions we first recall PWEs for the Coulomb potential and for the interelectronic distance:

$$\frac{1}{r_{12}}=\sum_{l=0}^{\infty}\frac{r_<^l}{r_>^{l+1}}P_l(\cos\gamma),$$
$$r_{12}=\sum_{l=0}^{\infty}\left[\frac{1}{2l+3}\frac{r_<^{l+2}}{r_>^{l+1}}-\frac{1}{2l-1}\frac{r_<^{l}}{r_>^{l-1}}\right]P_l(\cos\gamma). \tag{18}$$

With these formulas at hand, the PWE for the first operator is obtained straightforwardly if we additionally exploit the law of cosines to eliminate $\mathbf{r}_1\cdot\mathbf{r}_2$:

$$\begin{aligned}K_1(\mathbf{r}_1,\mathbf{r}_2)&=\frac{r_1^2+r_2^2}{2r_{12}}-\frac{1}{2}r_{12}\\&=\sum_{l=0}^{\infty}\left[\frac{l+1}{2l+3}\frac{r_<^{l+2}}{r_>^{l+1}}+\frac{l}{2l-1}\frac{r_<^{l}}{r_>^{l-1}}\right]P_l(\cos\gamma).\end{aligned} \tag{19}$$

The manipulations are somewhat more involved for the second operator. First, we recall the PWE for r_{12}^{-3} which can be obtained as a special case of a more general formalism introduced by Sack [41]:

$$r_{12}^{-3}=\frac{1}{r_>^2-r_<^2}\sum_{l=0}^{\infty}(2l+1)\frac{r_<^l}{r_>^{l+1}}P_l(\cos\gamma), \tag{20}$$

After some algebra necessary to eliminate the vector quantities we find

$$\begin{aligned}K_2(\mathbf{r}_1,\mathbf{r}_2)&=\frac{\left(r_1^2-r_2^2\right)^2}{4r_{12}^3}-\frac{1}{4}r_{12}\\&=\sum_{l=0}^{\infty}\left[\frac{l^2}{2l-1}\frac{r_<^{l}}{r_>^{l-1}}-\frac{(l+1)^2}{2l+3}\frac{r_<^{l+2}}{r_>^{l+1}}\right]P_l(\cos\gamma).\end{aligned} \tag{21}$$

By inserting the PWE for $K_i(\mathbf{r}_1,\mathbf{r}_2)$ into the corresponding two-electron integrals within the STO, the infinite summation over l truncates, and integration over all angles can be expressed through 3-j symbols. The remaining radial integrals are simple linear combinations of the integrals encountered for the standard $1/r_{12}$ and r_{12} operators, and hence, no additional classes of basic integrals need to be implemented. In all calculations involving STOs, a locally modified version of the GAMESS package developed in Ref. [42] was employed.

The calculation of one-electron integrals required to evaluate $\delta\chi_0^{(1)}$ and $\delta\chi_0^{(2)}$ is equally simple within GTOs and STOs, and hence, the choice of the latter was made for consistency.

IV. NUMERICAL RESULTS

A. The leading $\chi_0^{(0)}$ contribution

The $\chi_0^{(0)}$ contribution to the magnetic susceptibility is dominant, and hence, it has to be determined highly accurately. For this purpose we employ the doubly augmented GTO, abbreviated as dXZ in the following, combined with a hierarchy of coupled-cluster (CC) methods [43,44] which converge to the exact solution of the electronic Schrödinger equation. The composition of the GTO basis sets and the number of functions are provided explicitly in Table I.

The expectation value $\langle\sum_i r_i^2\rangle$ entering $\chi_0^{(0)}$ is denoted by the symbol $\langle r^2\rangle$ in the following. This quantity is split into several components calculated at different levels of theory:

$$\begin{aligned}\langle r^2\rangle=\langle r^2\rangle_{\mathrm{HF}}+\delta\langle r^2\rangle_{\mathrm{SD(T)}}+\delta\langle r^2\rangle_{\mathrm{T}}\\+\delta\langle r^2\rangle_{\mathrm{Q}}+\delta\langle r^2\rangle_{\mathrm{P}},\end{aligned} \tag{22}$$

TABLE I. The composition of the dXZ GTO basis sets used in the present work, taken from Ref. [26] for neon and Ref. [25] for argon. A common set of $33s26p$ (neon) and $36s29p$ (argon) functions is used for all X (not included below). The total number of functions in each basis is given in parentheses

	Composition (excluding sp)	
X	Ne	Ar
2	$3d$ (126)	$4d$ (143)
3	$5d3f$ (157)	$6d4f$ (181)
4	$7d5f3g$ (208)	$8d6f4g$ (241)
5	$8d6f4g3h$ (262)	$10d8f6g4h$ (327)
6	$10d8f6g4h3i$ (354)	$11d10f8g6h4i$ (438)
7	$11d10f8g6h4i3k$ (471)	$12d11f10g8h6i4k$ (576)
8	$12d11f10g8h6i4k3l$ (615)	$13d12f11g10h8i6k3l$ (726)
9	$13d12f11g10h8i6k4l3m$ (788)	$14d13f12g11h9i7k5l3m$ (877)

where $\langle r^2\rangle_{\mathrm{HF}}$ is the Hartree-Fock contribution and the remaining components $\delta\langle r^2\rangle_{\mathrm{X}}$ are corrections accounting for electron correlation effects obtained with the method X. For example, $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ is a correction to the Hartree-Fock result calculated using the coupled-cluster with single, double, and perturbative triple excitations CCSD(T) method [45], $\delta\langle r^2\rangle_{\mathrm{Q}}$ is the difference between the CCSDTQ (coupled-cluster with single, double, triple, and quadruple excitations) [46,47] and CCSDT (coupled-cluster with single, double, and triple excitations) [48,49] methods and so on. The correction $\delta\langle r^2\rangle_{\mathrm{P}}$ was obtained using the CCSDTQP (coupled-cluster with single, double, triple, quadruple, and pentuple excitations) model [50,51]. Based on a set of preliminary calculations using CCSDTQPH (coupled-cluster with single, double, triple, quadruple, pentuple, and sextuple excitations) [52] and full-configuration-interaction methods in small basis sets, we found that the contributions of CC excitations higher than pentuple are negligible. In the calculations reported in this section, we employed the DALTON program for the determination of the $\langle r^2\rangle_{\mathrm{HF}}$ and $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ contributions, the CFOUR program for the $\delta\langle r^2\rangle_{\mathrm{T}}$ correction, and the MRCC program for the $\delta\langle r^2\rangle_{\mathrm{Q}}$ and $\delta\langle r^2\rangle_{\mathrm{P}}$ corrections.

The Hartree-Fock contribution $\langle r^2\rangle_{\mathrm{HF}}$ is straightforward to calculate accurately using GTOs, but even more accurate results are available in the literature from purely numerical HF computations based on the B-spline expansion method. The following values were extracted from Ref. [53]:

$$\begin{aligned} &\text{He:}\quad \langle r^2\rangle_{\mathrm{HF}} = 2.369\,66,\\ &\text{Ne:}\quad \langle r^2\rangle_{\mathrm{HF}} = 9.371\,84,\\ &\text{Ar:}\quad \langle r^2\rangle_{\mathrm{HF}} = 26.034\,4. \end{aligned} \tag{23}$$

The values given above are accurate to all digits shown, and hence, the uncertainty of the $\langle r^2\rangle_{\mathrm{HF}}$ contribution is negligible. As a by-product of subsequent calculations, we obtained $\langle r^2\rangle_{\mathrm{HF}}$ contributions within GTOs for all atoms. Near-perfect agreement was obtained with the data given in Eq. (23), differing only in the last digit in the case of neon and argon.

The next large contribution to $\chi_0^{(0)}$ comes from the CCSD(T) level of theory, denoted $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$. We do not adopt a frozen-core approximation in these calculations, and hence, all electrons were correlated at this stage. In Table II we report the results of the calculations of the $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ contribution.

To eliminate the remaining basis-set incompleteness error, extrapolation towards the complete basis set (CBS) limit is required. To this end, we employ the formalism based on the Riemann ζ function [54]. Let us assume that the quantity of interest $\mathcal{O}$ was calculated with two consecutive basis sets (X and $X-1$) and the results are denoted by the symbols $\mathcal{O}_X$ and $\mathcal{O}_{X-1}$, respectively. The CBS limit $\mathcal{O}_\infty$ is then determined from the formula

$$\mathcal{O}_\infty = \mathcal{O}_X + X^4\left[\zeta(4) - \sum_{l=1}^{X} l^{-4}\right](\mathcal{O}_X - \mathcal{O}_{X-1}), \tag{24}$$

where $\zeta(s) = \sum_{n=1}^{\infty} n^{-s}$ is the Riemann ζ function and $\zeta(4) = \pi^4/90$. This extrapolation scheme will be used for estimating CBS limits of all quantities considered in this work, unless extrapolation is deemed unnecessary. The determined CBS limits of the $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ contributions are given in Table II. Clearly, the increments resulting from the extrapolation are sizable and necessary to ascertain the reliability of the final data. To illustrate this, in Fig. 1 we plot the calculated $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ corrections as a function of the parameter X. Additionally, we include the extrapolated results from basis-set pairs $(X, X-1)$. The uncertainty of the extrapolation, represented in Fig. 1 by horizontal dashed lines, is estimated as the difference between the CBS limits obtained with the two largest basis-set pairs (for example, $X = 9, 8$ and $X = 8, 7$ for neon and argon). One can see that the extrapolation is

TABLE II. The correction $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ obtained within the dacXZ basis-set family (all electrons are correlated). In the case of helium, the $d2Z$ and $d9Z$ basis sets are not available in the literature.

	$\delta\langle r^2\rangle_{\mathrm{SD(T)}}$		
X	He	Ne	Ar
2		0.254 9	0.173 6
3	0.022 53	0.229 0	0.033 0
4	0.019 26	0.206 7	−0.059 7
5	0.018 19	0.197 8	−0.085 2
6	0.017 77	0.194 3	−0.096 4
7	0.017 58	0.192 5	−0.102 0
8	0.017 48	0.191 5	−0.104 7
9		0.190 8	−0.106 7
∞	0.017 27(9)	0.189 1(4)	−0.111 7(23)

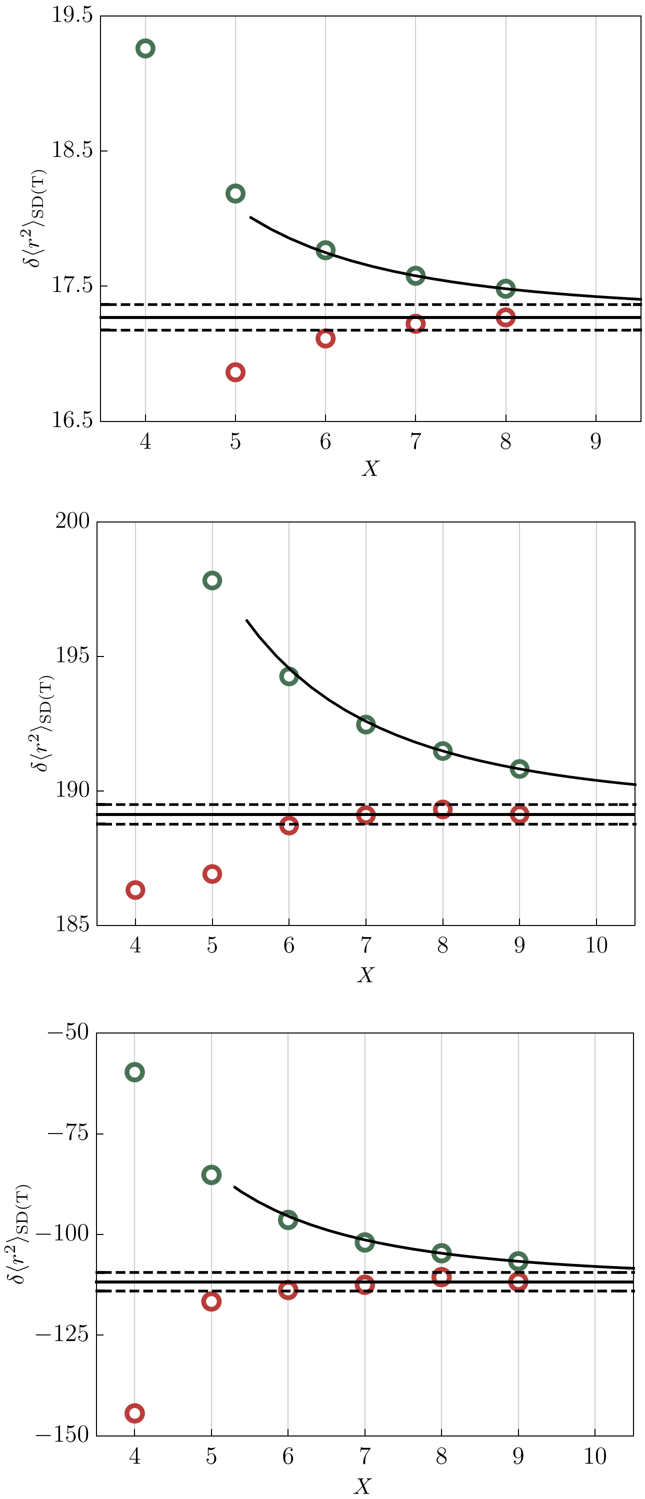

FIG. 1. The corrections $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ for helium (top panel), neon (middle panel), and argon (bottom panel) atoms. Raw results obtained within dacXZ basis sets are represented by green points, while the values obtained by extrapolation from $(X, X-1)$ basis-set pairs are given in red. The solid horizontal lines denote the best estimate obtained for $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$, and the dashed horizontal lines represent the estimated error bars. For comparison, a curve $a + b/X^3$ obtained by fitting the results from the largest two basis sets is also plotted.

TABLE III. Corrections to $\langle r^2\rangle$ accounting for higher-order coupled-cluster excitations for the neon atom (all electrons are correlated). For clarity, the results were multiplied by a constant factor of 10^3.

X	$\delta\langle r^2\rangle_{\mathrm{T}} \times 10^3$	$\delta\langle r^2\rangle_{\mathrm{Q}} \times 10^3$	$\delta\langle r^2\rangle_{\mathrm{P}} \times 10^3$
2	−0.268	−0.333	−0.328
3	−0.726	0.002	−0.103
4	−1.068	0.104	
5	−1.219		
6	−1.287		
∞	−1.39(2)	0.19(4)	0.03(6)

remarkably stable with respect to X. In particular, for neon and argon the last four extrapolated values already fall within the estimated error bars. This gives us confidence that the final value of $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ is not accidental and is supported by ample numerical evidence.

As an additional test, we analyze the data obtained for the helium atom and compare with the results reported in paper I. The latter are significantly more accurate and can be treated as a reference. By adding the $\langle r^2\rangle_{\mathrm{HF}}$ contribution from Eq. (23) and the extrapolated $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ correction given in Table II, we obtain $\langle r^2\rangle = 2.38\,693(9)$. This compares favorably with the corresponding result from paper I, $\langle r^2\rangle = 2.38\,697$, differing only at the last digit. Moreover, the difference is smaller by a factor of 2 than the determined error bars, suggesting that our uncertainty-estimation scheme is quite conservative. Moreover, it is worth pointing out that without extrapolation, i.e., by taking the $\delta\langle r^2\rangle_{\mathrm{SD(T)}}$ correction obtained within the largest basis set available in Table II, we obtain $\langle r^2\rangle = 2.387\,14$. The error of this quantity with respect to the reference data from paper I is more than 4 times larger than of the recommended extrapolated results. This shows that the adopted extrapolation scheme is reliable and enables us to drastically reduce the residual basis-set completeness error.

Next, we move to the determination of corrections to $\delta\langle r^2\rangle$ accounting for higher-order coupled-cluster excitations. In the case of argon, these corrections were determined in our recent paper [27], and despite significant effort, we did not manage to improve upon these results in a meaningful way. Therefore, we adopt the following values for argon:

$$\begin{aligned}\delta\langle r^2\rangle_{\mathrm{T}} &= -0.0020(4),\\ \delta\langle r^2\rangle_{\mathrm{Q}} &= 0.0032(12),\\ \delta\langle r^2\rangle_{\mathrm{P}} &= -0.0012(2).\end{aligned} \tag{25}$$

As one can see, these corrections accidentally nearly cancel out.

For neon, we carried out a different set of calculations of the corrections accounting for higher-order coupled-cluster excitations. The results are reported in Table III. In the case of the $\delta\langle r^2\rangle_{\mathrm{T}}$ contribution we managed to carry out calculations within Gaussian basis sets up to $X = 6$. Therefore, we apply the same extrapolation and error-estimation protocol as for the lower-order contributions. Unfortunately, the calculations of the $\delta\langle r^2\rangle_{\mathrm{Q}}$ and $\delta\langle r^2\rangle_{\mathrm{P}}$ corrections are feasible only within basis sets $X = 2, 3, 4$ and $X = 2, 3$, respectively. Due to the relatively small size of these basis sets, the results are not as reliable as the lower-level corrections. To account for this, the extrapolation is still performed using formula (24), but the error is estimated as half of the difference between the extrapolated value and the result in the largest basis set available (see Table III).

B. Relativistic corrections from the Dirac equation

In this section, we consider relativistic corrections to the magnetic susceptibility that originate from the expansion of the Dirac Hamiltonian, $\delta\chi_0^{(1)}$ and $\delta\chi_0^{(2)}$, defined in Eqs. (4) and (5). The remaining correction $\delta\chi_0^{(3)}$ is trivial to evaluate. Technically, the simplest way of evaluating $\delta\chi_0^{(1)}$ and $\delta\chi_0^{(2)}$ is the finite-difference approach based on the Hellmann-Feynman theorem:

$$\langle \mathcal{O} \rangle = \partial_\lambda \big|_{\lambda=0} \langle H + \lambda \mathcal{O} \rangle \approx \frac{\langle H + \lambda_0 \mathcal{O} \rangle - \langle H - \lambda_0 \mathcal{O} \rangle}{2\lambda_0}, \tag{26}$$

where λ_0 is a suitably chosen small constant. The calculations were carried out at the all-electron CCSD(T) level of theory within STOs, denoted by the abbreviation STOXZ, where X is the maximum angular momentum present in the basis. The STOs were adopted from Ref. [25] and include both the diffuse and core-valence functions.

In order to calculate the corrections $\delta\chi_0^{(i)}$, $i = 1, \ldots, 5$, using the finite-difference method, the operators in Eqs. (4)–(8) multiplied by the constant $\pm\lambda_0$ are added to the electronic Hamiltonian. The atomic energies evaluated with the modified Hamiltonians are used to extract the expectation values according to Eq. (26). This is straightforward in the case of all operators except $\sum_i r_i^2 \nabla_i^2$, which is not Hermitian and hence is incompatible with the usual form of the electronic Hamiltonian. However, any operator can be written as a sum of Hermitian and anti-Hermitian operators as $\mathcal{O} = \frac{1}{2}(\mathcal{O} + \mathcal{O}^\dagger) + \frac{1}{2}(\mathcal{O} - \mathcal{O}^\dagger)$. Since expectation values of an anti-Hermitian operator on an electronic wave function vanish, it is sufficient to calculate only the expectation value of $\frac{1}{2}(\mathcal{O} + \mathcal{O}^\dagger)$, which is straightforward. Several values of the displacement λ_0 were tested in preliminary calculations, but negligible differences were observed for λ_0 within the range 10^{-3}–10^{-5}, and hence, the midpoint of this interval, $\lambda_0 = 10^{-4}$, was used in all subsequent calculations. In general, the approximation (26) results in negligible errors in comparison to, e.g., basis-set incompleteness.

In Tables IV and V we report the results of the calculations of the expectation values $\langle \sum_i l_i^2 \rangle$ and $\langle \sum_i r_i^2 \nabla_i^2 \rangle$, respectively. These operators are closely related to the kinetic energy operator and converge to the CBS limit at the same rate as the kinetic energy (and hence the total energy by virtue of the virial theorem). Therefore, we extrapolated the results towards the CBS using formula (24), and the uncertainty was estimated in the same way as in Sec. IV A. Finally, we point out that the reference results obtained in our previous work for helium, $\langle \sum_i l_i^2 \rangle = 0.018\,970\,526$ and $\langle \sum_i r_i^2 \nabla_i^2 \rangle = -0.139\,689\,120$, agree with the values determined here (see Tables IV and V) within the estimated error bars of the latter.

The last correction, $\delta\chi_0^{(3)}$, depends only on the number of electrons in the system and is trivial to evaluate. We attach no uncertainty to this contribution.

TABLE IV. Expectation values $\langle \sum_i l_i^2 \rangle$ obtained within the STOXZ basis-set family at the CCSD(T) level of theory (all electrons are correlated).

	$\langle \sum_i l_i^2 \rangle$		
X	He	Ne	Ar
2	0.018 375	12.092 8	24.444 5
3	0.018 740	12.135 7	24.635 2
4	0.018 860	12.153 1	24.715 7
5	0.018 913	12.157 9	24.732 9
6	0.018 934	12.160 0	24.739 3
∞	0.018 967(3)	12.163 2(7)	24.749 2(50)

C. Relativistic corrections from the Breit interaction

Relativistic corrections originating from the Breit interaction, Eqs. (7) and (8), are somewhat more complicated than the contributions from the Dirac equation because they involve two-electron operators. However, calculating the corresponding matrix elements within the STO is manageable, as discussed in Sec. III. Fortunately, both operators present in Eqs. (7) and (8) are purely real and multiplicative and hence Hermitian. Therefore, expectation values appearing in $\delta\chi_0^{(4)}$ and $\delta\chi_0^{(5)}$ can be calculated using the finite-difference approach in a way analogous to that in Sec. IV B.

In Tables VI and VII we report the results of the calculations of the expectation values required in the $\delta\chi_0^{(4)}$ and $\delta\chi_0^{(5)}$ corrections, respectively. The computations were performed at the all-electron CCSD(T) level of theory. We adopt the same extrapolation and uncertainty-estimation strategy as for the corrections originating from the Dirac equation (see Sec. IV B). For helium, the results agree perfectly with the reference data from paper I.

D. Relativistic corrections to the electronic wave function

Relativistic corrections to the electronic wave function lead to additional contributions to the magnetic susceptibility, given by general formula (14). Evaluation of these corrections requires some additional approximations. First, according to the results for helium from paper I, the contribution of the two-electron Darwin operator $\delta\chi_0^{D_2}$ is tiny. Note that this quantity involves the two-electron Dirac δ distribution, which is sensitive only to the regions of the wave function where

TABLE V. Expectation values $\langle \sum_i r_i^2 \nabla_i^2 \rangle$ obtained within the STOXZ basis-set family at the CCSD(T) level of theory (all electrons are correlated).

	$\langle \sum_i r_i^2 \nabla_i^2 \rangle$		
X	He	Ne	Ar
2	−0.140 616	13.892 8	38.130 6
3	−0.139 979	13.961 3	38.405 2
4	−0.139 884	13.986 7	38.530 1
5	−0.139 915	13.994 3	38.561 5
6	−0.139 838	13.998 0	38.574 2
∞	−0.139 7(2)	14.003 6(2)	38.593 9(63)

TABLE VI. Expectation values present in the $\delta\chi_0^{(4)}$ correction [see Eq. (7)] obtained within the STOXZ basis-set family at the CCSD(T) level of theory (all electrons are correlated)

	$\langle\sum_{i<j} r_{ij}^{-1}\,\mathbf{r}_i\cdot\mathbf{r}_j\rangle$		
X	He	Ne	Ar
2	0.060 31	1.928 6	6.772 4
3	0.059 73	1.851 4	6.467 1
4	0.059 52	1.823 7	6.353 5
5	0.059 43	1.815 8	6.325 2
6	0.059 37	1.812 3	6.314 1
∞	0.059 29(3)	1.807 0(9)	6.296 8(64)

the electrons collide. This regime is governed by Kato's cusp condition, which is universal and does not depend on the system [55]. Therefore, we argue that $\delta\chi_0^{\mathrm{D}_2}$ is also small for neon and argon and neglect this correction from further considerations. It is worth pointing out that a similar phenomenon was observed in calculations of the polarizability of noble-gas atoms.

The corrections $\delta\chi_0^{\mathrm{D}_1}$ and $\delta\chi_0^{\mathrm{P}_4}$ are the dominant relativistic corrections of this type and need to be calculated accurately. For this purpose we employ the (orbital unrelaxed) linear response coupled-cluster theory based on the CC3 (coupled-cluster with single, double, and approximate triple excitations) wave function as implemented in the DALTON program. The corrections are obtained from the symmetric form of the polarization propagator at zero frequency as

$$\delta\chi_0^{\mathrm{X}} = \frac{\alpha^2}{6}\langle\langle X; r^2\rangle\rangle_{\omega=0}, \tag{27}$$

where r^2 is shorthand notation for $\sum_i r_i^2$ and X is either the D_1 or P_4 operator. The results obtained within the same GTO as used in the $\delta\chi_0^0$ calculations are given in Tables VIII and IX. The extrapolation towards the CBS limit and estimation of the uncertainty are performed according to the same protocol as for the previous contributions considered in Secs. IV B and IV C.

Finally, we consider the orbit-orbit correction to the magnetic susceptibility $\delta\chi_0^{\mathrm{B}}$. Taking into account the results for the helium atom reported in paper I, we expect this correction to be relatively minor. Therefore, it does not have to be computed as accurately as the contributions described in the previous paragraph. For simplicity, we adopt the Hartree-Fock approximation in the calculation of $\delta\chi_0^{\mathrm{B}}$. The ground-state wave function is represented by a single Slater determinant, while the first-order response function $(\hat{H}-E_0)^{-1}Q(\sum_i r_i^2)|\Psi_0\rangle$ is expanded into a linear combination of singly excited determinants. Contributions from higher-order excitations vanish due to Slater-Condon rules as $\sum_i r_i^2$ is a sum of one-electron operators.

TABLE VII. Expectation values present in the $\delta\chi_0^{(5)}$ correction [see Eq. (8)] obtained within the STOXZ basis-set family at the CCSD(T) level of theory (all electrons are correlated).

	$\langle\sum_{i<j} r_{ij}^{-1}(\mathbf{r}_i\cdot\mathbf{r}_j) - r_{ij}^{-3}(\mathbf{r}_i\cdot\mathbf{r}_{ij})(\mathbf{r}_j\cdot\mathbf{r}_{ij})\rangle$		
X	He	Ne	Ar
2	0.212 9	7.416 8	22.048 7
3	0.212 8	7.373 3	21.895 1
4	0.212 7	7.360 1	21.849 4
5	0.212 6	7.355 9	21.837 4
6	0.212 6	7.353 9	21.832 5
∞	0.212 5(1)	7.350 9(2)	21.824 8(22)

TABLE VIII. The correction $-\langle(\sum_i r_i^2)(H-E_0)^{-1}Q\hat{D}_1\rangle$ obtained within the da$X$Z basis-set family using the linear-response CC3 theory (all electrons are correlated). The data were multiplied by a factor of 10^3 for clarity.

	$-\langle(\sum_i r_i^2)(H-E_0)^{-1}Q\hat{D}_1\rangle\times 10^3$		
X	He	Ne	Ar
2		0.488 8	−0.331 3
3	−0.421 5	0.485 6	−0.437 6
4	−0.421 4	0.456 0	−0.725 7
5	−0.421 4	0.447 5	−0.800 5
6	−0.421 4	0.443 6	−0.830 6
7	−0.421 4	0.441 6	−0.843 9
8	−0.421 4	0.440 4	
∞	−0.421 4(1)	0.437 8(2)	−0.869 0(83)

The adoption of the Hartree-Fock wave function for Ψ_0 enables a significant truncation of the basis set used in the calculations. To expand the Hartree-Fock orbitals only basis-set functions with angular momenta $l=0,1$ (s and p) are needed. Additionally, since the operator r_i^2 is spherically symmetric, the same basis is sufficient also for the first-order response function. To saturate the results with respect to basis-set size, we used a large GTO comprising $33s26p$ and $40s40p$ functions for neon and argon, respectively. The calculations were carried out using a program written specifically for this purpose, and all necessary basic integrals were imported from a locally modified version of the DALTON package. We obtained

$$\begin{aligned}\text{Ne:}\quad \delta\chi_0^{\mathrm{B}} &= 0.00028(14),\\ \text{Ar:}\quad \delta\chi_0^{\mathrm{B}} &= 0.0010(5),\end{aligned} \tag{28}$$

TABLE IX. The correction $-\langle(\sum_i r_i^2)(H-E_0)^{-1}Q\hat{P}_4\rangle$ obtained within the da$X$Z basis-set family using the linear-response CC3 theory (all electrons are correlated). The data were multiplied by a factor of 10^3 for clarity.

	$-\langle(\sum_i r_i^2)(H-E_0)^{-1}Q\hat{P}_4\rangle\times 10^3$		
X	He	Ne	Ar
2		2.786	29.46
3	0.530 4	2.800	29.34
4	0.531 8	2.852	29.65
5	0.532 4	2.872	29.74
6	0.532 7	2.880	29.78
7	0.532 9	2.885	29.80
8	0.533 1	2.888	
∞	0.533 4(1)	2.893(5)	29.83(2)

where we adopted a large (50%) uncertainty estimate to account for all approximations involved in the calculations.

E. Estimation of higher-order QED contributions

Besides the relativistic corrections to the magnetic susceptibility of the order of α^4, one has to consider higher-order corrections originating from QED. Rigorous calculation of these corrections is a formidable task beyond the scope of the present work. However, we can estimate the magnitude of the QED effects like in paper I, namely, by taking the relativistic correction which is the largest in magnitude and scaling it by a factor of $-\alpha \ln(\alpha) \approx 0.036$. Both for neon and argon, the largest relativistic correction (in absolute terms) is $\delta\chi_0^{\rm P4}$. By scaling its value by $-\alpha \ln(\alpha)$ we obtain the following estimates of the QED effects:

$$\begin{aligned} &\text{Ne:} \quad \delta\chi_0^{\rm QED} = 0.0002(2), \\ &\text{Ar:} \quad \delta\chi_0^{\rm QED} = 0.0019(19), \end{aligned} \tag{29}$$

where we have attached a very large (100%) uncertainty to the resulting values.

F. Estimation of the finite-nuclear-mass and -size corrections

Finally, let us discuss the FNS and FNM corrections to the magnetic susceptibility. In order to estimate the former, we carried out calculations of the $\chi_0^{(0)}$ contribution using the Gaussian finite-nuclear model and compared the results with the same results obtained with the point nucleus. Following the recommendations of Visscher and Dyall [56], we used a simple nuclear charge distribution in the form

$$\rho(r) = \rho_0\, e^{-\xi r^2}, \quad \rho_0 = Z\left(\frac{\xi}{\pi}\right)^{3/2} \quad \xi = \frac{3}{2\langle r_c^2\rangle}, \tag{30}$$

where $\langle r_c^2\rangle$ is the averaged square of the nuclear charge radius, which can be calculated for an isotope with atomic mass number A from the empirical formula $\langle r_c^2\rangle = (0.836A^{1/9} + 0.570)$ fm. The advantage of the Gaussian charge model is the fact that the corresponding electron-nucleus interaction potential is given by the simple expression

$$V(r) = -\frac{Z}{r}\mathrm{erf}(\sqrt{\xi}r), \tag{31}$$

where $\mathrm{erf}(x)$ is the error function. This form of the potential is trivial to incorporate into the standard quantum-chemical programs operating within Gaussian basis sets, and the necessary integrals are available in the LIBINT library [57]. For simplicity, we applied the Gaussian nuclear model in the Hartree-Fock calculations of $\chi_0^{(0)}$. By comparing the results with analogous results obtained with the point nucleus, we found that the FNS effects are of the order of 1 ppm for argon and even less for neon. Therefore, they can be safely neglected in the present work.

The finite-nuclear-mass effects are also small for neon and argon. Even for ^{4}He, these effects are not large, constituting about 4×10^{-4} of the total value of χ_0 (see paper I). For neon and argon, the FNM effects are expected to be smaller (on a relative basis) because they are dependent on the inverse of the nuclear mass. To estimate the magnitude of these corrections, we consider the dominant correction, i.e., the reduced-mass scaling term, which is given by the formula

$$\delta\chi_0^{\rm FNM} \approx \frac{3}{m_N}\,\chi_0^{(0)}, \tag{32}$$

where m_N is the nuclear mass. For the most abundant isotopes, i.e., ^{20}Ne and ^{40}Ar, the mass-scaling corrections amounts to roughly -7×10^{-4} and -9×10^{-4}, respectively. Therefore, FNM effects become important for Ne and Ar only if relative accuracy levels better than 1×10^{-4} are desired. Nonetheless, we include the $\delta\chi_0^{\rm FNM}$ correction in our final results and assign a large 50% uncertainty to the corrections evaluated using Eq. (32) in order to account for the missing terms (see paper I).

TABLE X. Final results of the calculations of the static magnetic susceptibility χ_0 of neon and argon. For clarity, all terms are multiplied by a constant factor of 10^5.

	Ne	Ar
$\chi_0^{\rm HF}$	−8.317 7	−23.106 1
$\delta\chi_0^{\rm SD(T)}$	−0.167 8(4)	0.099 1(20)
$\delta\chi_0^{\rm T}$	0.001 2(1)	0.001 8(4)
$\delta\chi_0^{\rm Q}$	−0.000 2(1)	−0.002 8(11)
$\delta\chi_0^{\rm P}$	−0.000 0(1)	0.001 1(2)
Contributions from the Dirac equation		
$\delta\chi_0^{(1)}$	0.000 3(1)	0.000 6(1)
$\delta\chi_0^{(2)}$	−0.000 3(1)	−0.000 9(1)
$\delta\chi_0^{(3)}$	0.000 7	0.001 3
Contributions from the Breit interaction		
$\delta\chi_0^{(4)}$	0.000 1(1)	0.000 3(1)
$\delta\chi_0^{(5)}$	0.000 2(1)	0.000 5(1)
Relativistic corrections to the wave function		
$\delta\chi_0^{\rm D1}$	0.000 8(1)	−0.001 5(1)
$\delta\chi_0^{\rm P4}$	0.005 1(1)	0.052 9(1)
$\delta\chi_0^{\rm D2}$	neglected	neglected
$\delta\chi_0^{\rm B}$	−0.000 5(2)	−0.001 8(9)
Other corrections		
$\delta\chi_0^{\rm QED}$	0.000 2(2)	0.001 9(19)
$\delta\chi_0^{\rm FNM}$	−0.000 7(3)	−0.000 9(4)
$\delta\chi_0^{\rm FMS}$	neglected	neglected
Total		
χ_0	−8.478 6(7)	−22.954 5(32)

The small magnitude of the FNM and FNS corrections is straightforward to explain by noting that the dominant contribution to the magnetic susceptibility, namely, $\chi_0^{(0)}$, involves the operator $\sum_i r_i^2$. This operator vanishes at the nuclear site and hence is relatively insensitive to minor changes in the electronic wave function in the vicinity of the nucleus resulting from FNM and FNS corrections.

V. SUMMARY AND DISCUSSION

In Table X we gather all contributions to the magnetic susceptibility of neon and argon considered in this work, together with their respective uncertainties. The final values of χ_0 are obtained as a sum of these contributions; the overall error is calculated by adding squares of the uncertainties in the individual components and taking the square root. This approach is justified by the standard-error-propagation formulas under

TABLE XI. Comparison with other theoretical and experimental literature values for the static magnetic susceptibility of neon and argon. The error estimation is not present in cases where it was not provided by the original authors. All values are given in atomic units.

	χ_0	
Ref.	Neon	Argon
Experimental values		
Havens [65]	$-8.574(9) \times 10^{-5}$	$-2.15(2) \times 10^{-4}$
Mann [66]	$-7.56(20) \times 10^{-5}$	$-2.19(2) \times 10^{-4}$
Barter *et al.* [67]	$-7.80(16) \times 10^{-4}$	$-2.16(2) \times 10^{-4}$[a]
		$-2.16(15) \times 10^{-5}$[b]
Theoretical values		
Yoshizawa and Hada [68]	-8.27×10^{-5}	-2.22×10^{-4}
Ruud *et al.* [69], Jaszuński *et al.* [70]	-8.48×10^{-5}	-2.31×10^{-4}
Reinsch and Meyer [71]	-8.57×10^{-5}	-2.32×10^{-4}
Levy and Perdew [72], Desclaux [73]	-8.31×10^{-5}	-2.30×10^{-4}
Lesiuk and Jeziorski [25,27]	$-8.484(19) \times 10^{-5}$	$-2.30(2) \times 10^{-4}$
This work	$-8.4786(7) \times 10^{-5}$	$-2.29548(32) \times 10^{-4}$

[a] Original error estimate from Ref. [67].

[b] Revised error estimate proposed in Ref. [7].

the assumption that the uncertainties are not correlated in the statistical sense.

The final results determined in this work are $\chi_0 = -8.4786(7) \times 10^{-5}$ and $\chi_0 = -22.9545(32) \times 10^{-5}$ for neon and argon atoms, respectively. The relative uncertainty of both quantities is of the order of 1 part per 10 000. In the case of neon, the total uncertainty is dominated by the $\delta\chi_0^{\mathrm{SD(T)}}$ contribution, amounting to more than 50% of the overall error. It is possible that the accuracy of this component can be improved in the future by using even larger Gaussian basis sets in the calculations and/or adopting a different extrapolation scheme. However, to reduce the total uncertainty by an order of magnitude, two other contributions, namely, $\delta\chi_0^{\mathrm{B}}$ and $\delta\chi_0^{\mathrm{QED}}$, have to be determined more accurately. In the case of $\delta\chi_0^{\mathrm{B}}$ this would require treatment with the inclusion of the electron correlation. Fortunately, the correlation contribution to $\delta\chi_0^{\mathrm{B}}$ appears to be small, so low-level methods such as second-order Møller-Plesset [58] or CC2 [59] may be entirely sufficient, avoiding technical complications of higher-order methods. To improve the relative accuracy by an order of magnitude, finite-nuclear-mass effects must also be determined for neon. Finite-nuclear-size contributions are negligible up to 1 ppm uncertainty level.

The dominant sources of uncertainty are similar for argon but are somewhat larger in magnitude. In particular, due to larger nuclear charge, the errors resulting from $\delta\chi_0^{\mathrm{B}}$, $\delta\chi_0^{\mathrm{QED}}$, and $\delta\chi_0^{\mathrm{SD(T)}}$ are comparable in magnitude. Therefore, further improvements in accuracy would require a more rigorous treatment of the $\delta\chi_0^{\mathrm{QED}}$ contribution. For both neon and argon, there is an additional source of uncertainty from the $\delta\chi_0^{\mathrm{T}}$, $\delta\chi_0^{\mathrm{Q}}$, and $\delta\chi_0^{\mathrm{P}}$ corrections. However, these contributions cancel to a significant degree, so their impact on the overall accuracy is not expected to be large.

This analysis leads to the conclusion that it is worthwhile to derive and evaluate the complete $\delta\chi_0^{\mathrm{QED}}$ correction for all noble-gas atoms, as it constitutes the main source of uncertainty that cannot be reduced by, e.g., using a larger basis set. While determination of the QED corrections to the energy is now possible [19,27,42,60–64], that is not the case for atomic and molecular properties such as polarizability or magnetic susceptibility. In fact, the required theoretical framework has not been developed yet, and that would require considerable progress beyond the current state of the art.

In Table XI we compare our results with the available theoretical and experimental data. The previous theoretical determinations are in rough agreement with our data but are significantly less accurate. However, the present results are in disagreement with the experimental data of Barter *et al.* [67]. In the case of argon, the value given by Barter *et al.* [67] is an average of three previous measurements (used to calibrate the apparatus) and does not count as an independent experimental determination. It was suggested [7] that the experimental uncertainty for argon has to be increased to about 7%. After this revision, theory and experiment agree for argon, but for neon a large discrepancy remains. Somewhat unexpectedly, for neon good agreement is obtained with older experimental data by Havens [65]. The reasons for the observed disagreement with the work of Barter *et al.* [67] are not known definitively. In paper I we discussed possible sources of the discrepancy in the case of helium, and similar conclusions apply to neon and argon. In short, physical effects neglected in our calculations are most likely orders of magnitude too small to explain such a large discrepancy. We uphold our conviction that new and independent measurements of the magnetizability of the noble gases are needed to resolve this issue.

To sum up, we have reported state-of-the-art calculations of the static magnetic susceptibilities of neon and argon. The results appear to be the most accurate available in the literature. They will be useful, for example, in refractive-index gas-thermometry measurements or as a benchmark for other theoretical methods.

ACKNOWLEDGMENTS

We thank M. Przybytek (UW) for providing several types of integrals required in the relativistic calculations. This project (QuantumPascal Project No. 18SIB04) has received funding from the EMPIR program cofinanced by the participating states and from the European Union's Horizon 2020 research and innovation program. The authors also acknowledge support from the National Science Center, Poland, within Project No. 2017/27/B/ST4/02739. We gratefully acknowledge Poland's high-performance infrastructure PLGrid (HPC Centers: ACK Cyfronet AGH, PCSS, CI TASK, WCSS) for providing computer facilities and support within Computational Grant No. PLG/2023/016599.

---

[1] M. Puchalski, M. Lesiuk, and B. Jeziorski, Phys. Rev. A **108**, 042812 (2023).
[2] H. A. Lorentz, Ann. Phys. (Berlin, Ger.) **245**, 641 (1880).
[3] L. Lorenz, Ann. Phys. (Berlin, Ger.) **247**, 70 (1880).
[4] B. Gao, L. Pitre, E. Luo, M. Plimmer, P. Lin, J. Zhang, X. Feng, Y. Chen, and F. Sparasci, Measurement **103**, 258 (2017).
[5] P. M. Rourke, C. Gaiser, B. Gao, D. M. Ripa, M. R. Moldover, L. Pitre, and R. J. Underwood, Metrologia **56**, 032001 (2019).
[6] D. M. Ripa, D. Imbraguglio, C. Gaiser, P. Steur, D. Giraudi, M. Fogliati, M. Bertinetti, G. Lopardo, R. Dematteis, and R. Gavioso, Metrologia **58**, 025008 (2021).
[7] P. M. Rourke, J. Phys. Chem. Ref. Data **50**, 033104 (2021).
[8] K. Jousten *et al.*, Metrologia **54**, S146 (2017).
[9] C. Gaiser and B. Fellmuth, Phys. Rev. Lett. **120**, 123203 (2018).
[10] C. Gaiser, B. Fellmuth, and W. Sabuga, Nat. Phys. **16**, 177 (2020).
[11] C. Gaiser, B. Fellmuth, and W. Sabuga, Ann. Phys. (Berlin, Ger.) **534**, 2200336 (2022).
[12] J. W. Schmidt, R. M. Gavioso, E. F. May, and M. R. Moldover, Phys. Rev. Lett. **98**, 254504 (2007).
[13] K. Pachucki and J. Sapirstein, Phys. Rev. A **63**, 012504 (2000).
[14] G. Łach, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. **92**, 233001 (2004).
[15] M. Puchalski, K. Piszczatowski, J. Komasa, B. Jeziorski, and K. Szalewicz, Phys. Rev. A **93**, 032515 (2016).
[16] M. Puchalski, K. Szalewicz, M. Lesiuk, and B. Jeziorski, Phys. Rev. A **101**, 022505 (2020).
[17] L. W. Bruch and F. Weinhold, J. Chem. Phys. **117**, 3243 (2002).
[18] L. W. Bruch and F. Weinhold, J. Chem. Phys. **119**, 638 (2003).
[19] W. Cencek, M. Przybytek, J. Komasa, J. B. Mehl, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **136**, 224303 (2012).
[20] P. Czachorowski, M. Przybytek, M. Lesiuk, M. Puchalski, and B. Jeziorski, Phys. Rev. A **102**, 042810 (2020).
[21] A. Rizzo, C. Hättig, B. Fernández, and H. Koch, J. Chem. Phys. **117**, 2609 (2002).
[22] W. Cencek, J. Komasa, and K. Szalewicz, J. Chem. Phys. **135**, 014301 (2011).
[23] B. Song and Q.-Y. Luo, Metrologia **57**, 025007 (2020).
[24] G. Garberoglio, A. H. Harvey, and B. Jeziorski, J. Chem. Phys. **155**, 234103 (2021).
[25] M. Lesiuk, M. Przybytek, and B. Jeziorski, Phys. Rev. A **102**, 052816 (2020).
[26] R. Hellmann, Phys. Rev. A **105**, 022809 (2022).
[27] M. Lesiuk and B. Jeziorski, Phys. Rev. A **107**, 042805 (2023).
[28] E. Tiesinga, P. J. Mohr, D. B. Newell, and B. N. Taylor, The 2018 CODATA recommended values of the fundamental physical constants, 2018, http://physics.nist.gov/constants.
[29] V. A. Yerokhin, K. Pachucki, Z. Harman, and C. H. Keitel, Phys. Rev. Lett. **107**, 043004 (2011).
[30] V. A. Yerokhin, K. Pachucki, Z. Harman, and C. H. Keitel, Phys. Rev. A **85**, 022512 (2012).
[31] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two- Electron Systems* (Springer, Berlin, 1975).
[32] K. Pachucki, Phys. Rev. A **78**, 012504 (2008).
[33] P. M. W. Gill, in *Molecular integrals Over Gaussian Basis Functions*, edited by J. R. Sabin and M. C. Zerner, Advances in Quantum Chemistry Vol. 25 (Academic Press, 1994), pp. 141–205.
[34] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[35] J. C. Slater, Phys. Rev. **42**, 33 (1932).
[36] K. Aidas *et al.*, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **4**, 269 (2014).
[37] J. F. Stanton, J. Gauss, L. Cheng, M. E. Harding, D. A. Matthews, and P. G. Szalay, CFOUR (Coupled-Cluster techniques for Computational Chemistry), a quantum-chemical program package, with contributions from A. A. Auer *et al.*, and the integral packages MOLECULE, PROPS, and ABACUS and ECP routines, http://www.cfour.de.
[38] M. Kállay, P. R. Nagy, D. Mester, Z. Rolik, G. Samu, J. Csontos, J. Csóka, P. B. Szabó, L. Gyevi-Nagy, B. Hégely, I. Ladjánszki, L. Szegedy, B. Ladóczki, K. Petrov, M. Farkas, P. D. Mezei, and A. Ganyecz, J. Chem. Phys. **152**, 074107 (2020).
[39] M. Lesiuk and R. Moszynski, Phys. Rev. E **90**, 063318 (2014).
[40] M. Lesiuk and R. Moszynski, Phys. Rev. E **90**, 063319 (2014).
[41] R. Sack, J. Math. Phys. **5**, 245 (1964).
[42] M. Lesiuk, M. Przybytek, M. Musiał, B. Jeziorski, and R. Moszynski, Phys. Rev. A **91**, 012510 (2015).
[43] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).
[44] T. D. Crawford and H. F. Schaefer III, Rev. Comput. Chem. **14**, 33 (2007).
[45] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[46] S. A. Kucharski and R. J. Bartlett, Theor. Chim. Acta **80**, 387 (1991).
[47] S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **97**, 4282 (1992).
[48] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987).
[49] G. E. Scuseria and H. F. Schaefer, Chem. Phys. Lett. **152**, 382 (1988).
[50] M. Musiał, S. A. Kucharski, and R. J. Bartlett, Chem. Phys. Lett. **320**, 542 (2000).
[51] M. Musiał, S. Kucharski, and R. Bartlett, J. Chem. Phys. **116**, 4382 (2002).
[52] M. Kállay and P. R. Surján, J. Chem. Phys. **115**, 2945 (2001).
[53] S. L. Saito, At. Data Nucl. Data Tables **95**, 836 (2009).
[54] M. Lesiuk and B. Jeziorski, J. Chem. Theory Comput. **15**, 5398 (2019).
[55] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
[56] L. Visscher and K. G. Dyall, At. Data Nucl. Data Tables **67**, 207 (1997).

[57] E. F. Valeev, LIBINT, a library for the evaluation of molecular integrals of many-body operators over gaussian functions, version 2.8.0, http://libint.valeyev.net/.

[58] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[59] O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **243**, 409 (1995).

[60] K. Pachucki, Phys. Rev. A **74**, 022512 (2006).

[61] K. Piszczatowski, G. Łach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, J. Chem. Theory Comput. **5**, 3039 (2009).

[62] J. G. Balcerzak, M. Lesiuk, and R. Moszynski, Phys. Rev. A **96**, 052510 (2017).

[63] M. Lesiuk, M. Przybytek, J. G. Balcerzak, M. Musiał, and R. Moszynski, J. Chem. Theory Comput. **15**, 2470 (2019).

[64] M. Lesiuk and J. Lang, Phys. Rev. A **108**, 042817 (2023).

[65] G. G. Havens, Phys. Rev. **43**, 992 (1933).

[66] K. E. Mann, Z. Phys. **98**, 548 (1936).

[67] C. Barter, R. Meisenheimer, and D. Stevenson, J. Phys. Chem. **64**, 1312 (1960).

[68] T. Yoshizawa and M. Hada, J. Comp. Chem. **30**, 2550 (2009).

[69] K. Ruud, H. Skaane, T. Helgaker, K. L. Bak, and P. Joergensen, J. Am. Chem. Soc. **116**, 10135 (1994).

[70] M. Jaszuński, P. Jørgensen, and A. Rizzo, Theor. Chim. Acta **90**, 291 (1995).

[71] E.-A. Reinsch and W. Meyer, Phys. Rev. A **14**, 915 (1976).

[72] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).

[73] J. Desclaux, At. Data Nucl. Data Tables **12**, 311 (1973).