


First-principles calculation of the frequency-dependent dipole polarizability of argonMichał Lesiuk^{*} and Bogumił Jeziorski[†]*Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland* (Received 29 January 2023; accepted 27 March 2023; published 10 April 2023)

In this work we report state-of-the-art theoretical calculations of the dipole polarizability of the argon atom. Frequency dependence of the polarizability is taken into account by means of the dispersion coefficients (Cauchy coefficients), which is sufficient for experimentally relevant wavelengths below the first resonant frequency. In the proposed theoretical framework, all known physical effects including the relativistic, quantum electrodynamics, finite nuclear mass, and finite nuclear size corrections are accounted for. We obtained $\alpha_0 = 11.0775(19)$ for the static polarizability and $\alpha_2 = 27.976(15)$ and $\alpha_4 = 95.02(11)$ for the second and fourth dispersion coefficients, respectively. The result obtained for the static polarizability agrees (within the estimated uncertainty) with the most recent experimental data [C. Gaiser and B. Fellmuth, *Phys. Rev. Lett.* **120**, 123203 (2018)] but is less accurate. The dispersion coefficients determined in this work appear to be the most accurate in the literature, improving by more than an order of magnitude upon previous estimates. By combining the experimentally determined value of the static polarizability with the dispersion coefficients from our calculations, the polarizability of argon can be calculated with accuracy of around 10 ppm for wavelengths above roughly 450 nm. This result is important from the point of view of quantum metrology, especially for a new pressure standard based on thermophysical properties of gaseous argon. Additionally, in this work we calculate the static magnetic susceptibility of argon, which relates the refractive index of dilute argon gas with its pressure. While our results for this quantity are less accurate than in the case of the polarizability, they can provide, via the Lorenz-Lorentz formula, the best available theoretical estimate of the refractive index of argon.

DOI: [10.1103/PhysRevA.107.042805](https://doi.org/10.1103/PhysRevA.107.042805)**I. INTRODUCTION**

The electric dipole polarizability $\alpha(\omega)$ is an intrinsic microscopic property of atomic and molecular systems describing their response to an external electric field oscillating with frequency ω . Focusing on dilute gases of noble atoms, the polarizability appears in the fundamental Clausius-Mossotti equation

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{4\pi}{3} \alpha \rho, \quad (1)$$

which relates the relative electric permittivity ϵ_r of an atomic gas with the density of the gas, ρ . We can further express the gas density through the ideal gas formula $p = kT\rho$, where k is the Boltzmann constant. After some rearrangements we arrive at the relation

$$p = \frac{3}{4\pi} \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{kT}{\alpha}, \quad (2)$$

which is the basis for the new primary gas-pressure standard established in 2020 [1,2]. Indeed, according to the recent revisions of the fundamental constants [3–5], the Boltzmann constant k has a fixed predefined value. Therefore, by measuring the temperature and electric permittivity of a gas [1,6–9], the macroscopic pressure p can be found, as long as the atomic polarizability is known. By progressive improvements

to the experimental setup and accuracy of the polarizability determined from theory, the new pressure standard is competitive with the best mechanical pressure measurements, as illustrated with the recent stress test [2].

The aforementioned pressure standard uses helium as the medium gas. This choice is justified, among other things, by high accuracy of theoretical predictions that can be obtained for this relatively simple two-electron atom [10–18]. However, the disadvantage of helium is its relatively small polarizability, which makes this setup sensitive to impurities, requires high-quality materials free of contaminants, etc. A natural way to avoid these problems is to replace helium by a heavier noble atom such as neon or argon. As both of them are significantly more polarizable than helium, the sensitivity problems are marginalized. Unfortunately, as the electronic structure of neon and argon is much more complicated, it is impossible to maintain the same accuracy of theoretical predictions. In fact, while the polarizability of helium can be calculated from first principles [18] with relative accuracy of about 10^{-7} , which is entirely sufficient from the point of view of metrology, the same is not true for neon and argon. Two recent papers [19,20] devoted to the theoretical calculation of the polarizability of neon were the first studies where all known relevant physical effects were systematically included. Despite significant effort and an immense amount of computational time, the best theoretical estimate still has an uncertainty about five times larger than the experiment [21] in the case of the static polarizability. However, the theoretically derived frequency dependence of the polarizability, which is more difficult to get experimentally, is a useful supplement for the measurements [22].

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In comparison with neon and, especially, helium, the best available theoretical results for argon lag behind in terms of accuracy. The most reliable theoretical data for the polarizability reported by Lupinetti and Thakkar [23] and by Pałowski *et al.* [24] can be estimated to have uncertainties of several parts per thousand. This is insufficient for the purposes of metrology, and hence in the present work we report state-of-the-art *ab initio* calculations in order to improve the current state of theory. We employ a sequence of coupled-cluster (CC) methods [25,26] that converge to the exact solution of the nonrelativistic clamped-nuclei Schrödinger equation, combined with a large basis set up to nonuple-zeta quality. This enables reliable extrapolation to the complete basis set limit and estimation of the residual error, which is particularly important in applications to metrology. Equally importantly, in the theoretical framework we include all known physical effects, including relativistic, quantum electrodynamics (QED), finite nuclear mass, and finite nuclear size contributions.

The static polarizability of argon measured by Gaiser and Fellmuth [21] is accurate to about 2 parts per million (ppm). Within the current state of the theory, it is unreasonable to expect that a comparable accuracy can be achieved from first principles. However, this is not the goal of the present work; comparison with the experimental data for the static polarizability will be used primarily to verify that the adopted theoretical framework is adequate. We shall also focus on determination of the so-called dispersion coefficients (defined further in the text) which describe the frequency dependence of the polarizability and are much more difficult to determine experimentally. However, by combining the experimental result for the static polarizability with the frequency dependence derived from theory, a high level of accuracy can be obtained for the dynamic polarizability at experimentally relevant frequencies.

Besides the polarizability, in the present work we consider the static magnetic susceptibility of argon atom, χ_0 . It is defined as the second derivative of the energy (with sign reversed) with respect to the strength of the external magnetic field. The importance of the magnetic susceptibility is motivated by the Lorentz-Lorenz formula

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}(\alpha + \chi_0)\rho, \quad (3)$$

which relates the refractive index, n , of a gas with its density, ρ . The magnetic susceptibility of argon is several orders of magnitude smaller than the polarizability. Therefore, the value of χ_0 may be determined less accurately without a significant impact on the accuracy of n . This allows us to neglect the frequency dependence of the magnetic susceptibility and consider only its static value. Additionally, we neglect several minor corrections in our theoretical framework which are included in case of polarizability.

Unless explicitly stated otherwise, atomic units (a.u.) are used throughout. Following the CODATA recommendations [27], we adopt the following values of the fundamental physical constants: speed of light in vacuum, $c = 137.035999084$, atomic mass unit, $1 \text{ Da} = 1822.888486209(53)$, and Bohr radius, $a_0 = 0.529177210903 \text{ \AA}$. We consider only the most naturally abundant (99.6%) stable isotope ^{40}Ar with atomic mass 39.962383 Da . Most of the available experimental data

related to the molar polarizability of argon are reported in the literature in units of cm^3/mol . To express such quantities in the atomic units we use the conversion factor $1 \text{ cm}^3/\text{mol} = 11.205872 a_0^3$.

II. BASIS SET PREPARATION

The family of correlation-consistent [28] Gaussian basis sets for argon, usually abbreviated as cc-pVXZ, was optimized by Dunning and collaborators [29–32] up to the sextuple-zeta level of quality. Moreover, additional sets of diffuse and core-valence augmenting functions are also available in the literature. Unfortunately, the standard cc-pVXZ basis sets are not adequate for the purposes of the present work, because of considerable irregularities in the convergence pattern of the results to the complete basis set limit. While for total energies these irregularities were negligible, a significant deterioration was observed for atomic polarizabilities, which are the main focus herein. It is worth pointing out that the quality of the results reported in this work depends significantly on the reliability of the extrapolation procedure used to eliminate the residual basis set incompleteness error. The presence of the aforementioned irregularities precludes a robust extrapolation and complicates the error estimation. Therefore, we have decided to optimize a family of Gaussian basis sets for argon that matches the specific requirements of this work.

In the design of the basis sets we follow the general principles of correlation consistency introduced by Dunning [28]. First, we optimized a large set of s - and p -type Gaussian functions to variationally minimize the Hartree-Fock energy of argon. Note that at this level of theory functions with angular momentum $l \geq 2$ do not contribute to the ground-state energy. The number of s - and p -type functions was increased progressively and the exponents of the Gaussian-type orbitals (GTO) were constrained to form a geometric sequence

$$\zeta_{ln} = \alpha_l \beta_l^n \quad \text{or} \quad \log \zeta_{ln} = \log \alpha_l + n \log \beta_l, \quad (4)$$

where $n = 0, 1, \dots$, and α_l and β_l are subject to the optimization. Starting with a small number of functions taken from the cc-pVDZ basis set, the size of the basis was increased by one function at a time, followed by reoptimization of the α_l and β_l parameters. We finally settled for the basis set of size $34s27p$, which leads to the accuracy of about $0.3 \mu\text{H}$ (nine significant digits in the energy) in comparison with the numerical Hartree-Fock results of Cinal [33], which are assumed to be exact for the present purposes.

At some stages of the calculations we shall require an even more accurate basis for the Hartree-Fock calculations. However, extending the geometric sequence (4) further leads to progressive accumulation of numerical noise due to the increasing linear dependencies. It is hence difficult to use the formula (4) for basis sets with more than about 30–40 functions. To circumvent this problem we used a generalization of Eq. (4), namely,

$$\log \zeta_{ln} = \log \alpha_l + n \log \beta_l + n^2 \log \gamma_l + n^3 \log \delta_l, \quad (5)$$

where γ_l and δ_l are additional variational parameters. Employing this formula, we optimized a $37s37p$ basis for Hartree-Fock calculations, which is the smallest basis that

reaches the accuracy of a few nH (11 significant digits in the energy). No significant numerical issues were encountered for this basis.

The next step of the basis set optimization is the addition of polarization functions necessary to recover the electronic correlation effects. At this stage it is customary to contract the *sp* part of the basis optimized in order to reduce the size of the basis. We follow this protocol; however, in some calculations we will use uncontracted basis sets when explicitly stated. The contraction coefficients were obtained from expansion coefficients of the Hartree-Fock orbitals within a given basis. The polarization functions were added according to the correlation consistency principle, i.e., the double-zeta basis contains a single *d* polarization function, triple-zeta—two *d* and one *f*, quadruple-zeta—three *d*, two *f*, and one *g*, etc. At each expansion stage, additional *s* and *p* functions were added by taking from the contraction the functions with the lowest exponents.

The exponents of the polarization functions follow the sequence defined by Eq. (4), and the parameters α_l and β_l were optimized to minimize the frozen-core (eight active electrons) MP2 correlation energy. While in the literature it is common to use the configuration interaction with the single and double excitations (CISD) method for basis set optimization, it is not feasible for the basis sets required in this work. This is due to the high cost of CISD calculations in comparison with MP2. The parameters α_l and β_l were optimized in turn using Powell's method until the convergence to within 10^{-11} H in the MP2 energy was obtained. The largest basis set considered is of nonuple-zeta quality and includes basis set functions up to $l = 9$. The optimizations were performed using the Dalton program package [34] combined with an external program written especially for this purpose. Note that to carry out calculations with such high angular momentum, it is necessary to modify the source code of the Dalton package before compilation. Details of how to perform the necessary changes can be obtained from the authors upon request. The composition and exponents of the optimized Gaussian basis sets are given in the Supplemental Material [35]. For brevity, we refer to the basis sets simply as XZ , $X = 2, \dots, 9$ here. Note that the parameter X coincides with the highest angular momentum present in the basis set.

The polarizability is sensitive, to a much larger degree than the energy, to the accuracy of the long-range tail of the atomic density. Therefore, in our calculations it is necessary to augment the Gaussian basis with additional functions with low exponents. In this work the exponents are not optimized but are generated from the formula (4) by setting $n = -1, -2, \dots$. In this way, we generated singly augmented (adding $n = -1$ up to $l \leq X$), doubly augmented ($n = -1, -2$ up to $l \leq X$), and triply augmented ($n = -1, -2, -3$ up to $l \leq X$) basis sets, which are denoted aXZ , $daXZ$, and $taXZ$. Preliminary calculations shown that further augmentation of the basis leads to only a tiny improvement of the results, which does not justify the corresponding increase of the computational costs.

Finally, in the optimization of the XZ basis sets we kept ten inner core orbitals of the argon atom inactive. While their influence on the results is much smaller than of the valence shells, it is still nonnegligible from the point of view of the

adopted accuracy standards. To take the contribution of the core orbitals into account, the basis sets must be extended with a set of functions with high exponents (tight functions). Fortunately, we found that the cc-pCVXZ basis sets available in the literature [29,32] which were optimized to take the core-valence effects into account do not suffer from the irregularities we encountered in reproduction of the valence contributions. Therefore, we simply use the optimized tight functions from the standard cc-pCVXZ basis sets in combination with the remaining functions from the XZ family. We denote this extended core-valence basis set as cXZ and their augmented counterparts as $acXZ$, $dacXZ$, etc.

III. OVERVIEW OF THE THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

The main goal of the present work is to theoretically determine the polarizability of the argon atom, denoted $\alpha(\omega)$, including all known physical effects that bring a significant contribution. The atomic polarizability depends on the frequency ω of the external electromagnetic field that the atom is subjected to. We are interested in a range of wavelengths above (roughly) 450 nm, which covers operating wavelengths of most of the practically used gas lasers based on noble gases. After conversion to the atomic units, this gives the interval $0 \leq \omega \lesssim 0.1$. As the supremum of this interval is significantly lower than the first resonance frequency of the argon atom (equal to about $\omega_{\text{res}} \approx 0.42$ [36]) we can use the power expansion:

$$\alpha(\omega) = \alpha_0 + \alpha_2 \omega^2 + \alpha_4 \omega^4 + \dots \quad (6)$$

The first term of the above formula, α_0 , is usually called the static polarizability, while the quantities α_2 , α_4 , etc., are the dispersion coefficients (or Cauchy coefficients).

The static polarizability of the argon atom has recently been determined experimentally by Gaiser and Fellmuth [21] using the dielectric-constant gas thermometry. They obtained the relative accuracy of about 2 parts per million (ppm). Within the current state of the theory, it is unlikely that any calculations can deliver a similar accuracy level. In fact, among noble gases, only for helium does the quality of theoretical predictions match (or even surpass) that of the experiments, but this is feasible only because of a relatively simple electronic structure of two-electron systems. Already for neon, in the most accurate theoretical calculations performed thus far [19,20], the uncertainty estimates are several times larger than of the experimental results. Instead, we will test and validate our theoretical model by comparing with the experimental data for α_0 .

Our focus in this work is placed on the dispersion coefficients. These quantities cannot be determined experimentally at present as accurately as the static polarizability. Therefore, in applications where the frequency dependence of the polarizability is necessary, theoretical results for the dispersion coefficients can supplement the experimental α_0 . Therefore, let us estimate the accuracy level required in α_n to achieve the accuracy of about 10 ppm for wavelengths above (roughly) 450 nm. Such an accuracy level is acceptable from the point of view of metrology. Considering the worst-case scenario of $\omega \approx 0.1$, the value of α_2 must be determined with relative

accuracy of about $\times 10^{-3}$, while α_4 by about 10%. The higher-order dispersion coefficients, α_n , $n \geq 6$, can be neglected. In this analysis, we assumed that all α_n , $n = 0, 2, 4$, are of a similar magnitude. In practice, α_2 is larger than α_0 by roughly a factor of two, and hence the relative accuracy of around 5×10^{-4} is needed. The value of α_4 is about eight times larger than α_0 , thus it has to be determined with an accuracy of about 1%. One can also expect that the value of α_6 is significantly larger than α_0 , and it may contribute for short wavelengths. Therefore, in this work we additionally determine the value of α_6 with an accuracy goal of 10%.

Regarding the magnetic susceptibility, its value is by a factor of around 2×10^{-5} smaller than the polarizability. Taking into account that a simple sum of the two quantities is relevant from the point of view of Eq. (3), it is sufficient to determine χ with an accuracy of about 10%. Provided that this level of accuracy can be reached, the sum $\alpha_0 + \chi_0$ would have the uncertainty comparable with the experiment of Gaiser and Fellmuth [21] for α_0 . This allows us to adopt several approximations in determination of the magnetic susceptibility. First, we neglect the frequency dependence; its influence is expected to be around 1% within the relevant frequency range. Second, we omit all corrections which contribute to less than 1% in the case of the static polarizability. This eliminates the relativistic, QED, and several other minor corrections. We hence focus on accurate determination of the nonrelativistic value, which is much more straightforward and sufficient for all practical purposes.

The calculations reported in this work are based primarily on the coupled-cluster hierarchy of methods. For calculations using the Hartree-Fock, CCSD [37,38], CCSD(T) [39], and CC3 [40] methods (including the relativistic effects), we employed the DALTON program package [34] with the aforementioned modifications of the source code to enable calculations with high angular momentum functions. For CCSDT [41,42] calculations and computations of the finite nuclear mass corrections we used the C FOUR program [43], interfaced with the MRCC package [44]. The latter code is used for all higher-order CC methods (CCSDTQ [45–48], CCSDTQP [49,50], and higher [51–53]). In all calculations we use tight thresholds for the convergence of the CC iterations and of the response function solver (10^{-9} in the norm of the residual vector). Purely spherical Gaussian basis sets are used throughout this work. The orbital-unrelaxed variant of the CC response theory is employed in all calculations.

IV. NONRELATIVISTIC POLARIZABILITY

The dominant contribution to the polarizability of argon comes from the nonrelativistic clamped-nucleus approximation. Therefore, this contribution must be calculated with high precision, and we adopt a composite scheme based on the CC theory for this purpose.

A. Mean-field contribution

The first contribution to the polarizability and dispersion coefficients, denoted by the symbol α_n^{HF} , comes from the (restricted closed-shell) Hartree-Fock method and was calculated using the standard coupled-perturbed response theory.

We used the large $37s37p$ basis set described in the preceding section, augmented with three sets of diffuse functions, giving a $40s40p$ set in total. Note that at the Hartree-Fock level only s and p functions are needed to expand the ground-state orbitals, but d functions are additionally needed for the calculation of the polarizability. Therefore, a set of $40d$ functions was added to the basis with the same exponents as for the p functions. Within the complete $40s40p40d$ basis we obtain the following values of the polarizability and dispersion coefficients at the Hartree-Fock level of theory:

$$\begin{aligned}\alpha_0^{\text{HF}} &= 11.4726(1), \\ \alpha_2^{\text{HF}} &= 25.6162(1), \\ \alpha_4^{\text{HF}} &= 78.9658(2), \\ \alpha_6^{\text{HF}} &= 297.775(6).\end{aligned}\tag{7}$$

We assessed the accuracy of the results by randomly removing one or two functions of each angular momentum from the basis and recomputing the polarizability with the reduced set (bootstrapping). In all cases, we observed deviations at the level of 1–2 ppm, which is negligible in the present context.

B. Valence correlation contribution

The second contribution to the polarizability, denoted $\Delta\alpha_n^{\text{SD}}$, was obtained at the frozen-core CCSD level of theory (eight active valence electrons). Here we use the optimized XZ basis sets, $X = 2, \dots, 9$ (fully uncontracted variants) and their counterparts augmented with diffuse functions. In Table I we present results of the calculations. As is well known, the results converge rather slowly (asymptotically as X^{-3}) with respect to the basis set size, which is a consequence of the nonanalytic behavior of the exact wave function at the coalescence points of the electrons (the cusp condition). To eliminate the residual basis set incompleteness error, we perform extrapolation to the complete basis set (CBS) limit using the recently proposed formalism based on the Riemann ζ function [54]. Application of this scheme is straightforward provided that results obtained with two consecutive basis sets (X and $X - 1$) are available. Let us denote the quantity of interest \mathcal{O} obtained with the basis set X by \mathcal{O}_X . The CBS limit \mathcal{O}_∞ is then estimated from the formula [54]

$$\mathcal{O}_\infty = \mathcal{O}_X + X^4 \left[\zeta(4) - \sum_{l=1}^X l^{-4} \right] (\mathcal{O}_X - \mathcal{O}_{X-1}), \tag{8}$$

where $\zeta(s) = \sum_{n=1}^{\infty} n^{-s}$ is the Riemann ζ function and hence $\zeta(4) = \frac{\pi^4}{90}$. Throughout this work, this extrapolation formula is used for all components of the static polarizability and the dispersion coefficients. Note that the CBS limit estimated from Eq. (8) is still formally dependent on the variable X , and by observing the progression of the extrapolated values from a series of basis sets one can estimate the uncertainty of the predictions. To illustrate this, in Fig. 1 we provide extrapolated values of the $\Delta\alpha_n^{\text{SD}}$ contributions, $n = 0, 2, 4$, as a function of the X parameter that defines the size of the basis set. The extrapolated values converge quickly to the vicinity of the limiting value; for basis sets $X \geq 7$ the differences are minor. It is reasonable to estimate that the extrapolation error is

TABLE I. Linear-response frozen-core CCSD contribution to the static polarizability and dispersion coefficients, $\Delta\alpha_n^{\text{SD}}$, of the argon atom calculated using the augmented XZ basis sets. In the last row we provide results extrapolated to the complete basis set limit according to Eq. (8) and the corresponding error estimate.

X	Singly augmented			Doubly augmented			Triply augmented		
	$\Delta\alpha_0^{\text{SD}}$	$\Delta\alpha_2^{\text{SD}}$	$\Delta\alpha_4^{\text{SD}}$	$\Delta\alpha_0^{\text{SD}}$	$\Delta\alpha_2^{\text{SD}}$	$\Delta\alpha_4^{\text{SD}}$	$\Delta\alpha_0^{\text{SD}}$	$\Delta\alpha_2^{\text{SD}}$	$\Delta\alpha_4^{\text{SD}}$
2	-0.4025	1.4828	13.4945	-0.3166	2.3074	17.3982	-0.2635	2.8722	20.7742
3	-0.2775	2.3570	15.8547	-0.2184	2.8555	18.8666	-0.2162	2.8822	19.0202
4	-0.3270	2.0304	13.1597	-0.3115	2.2346	14.7719	-0.3117	2.2346	14.7754
5	-0.3412	1.9645	12.6164	-0.3320	2.0923	13.7132	-0.3321	2.0923	13.7155
6	-0.3507	1.9142	12.2765	-0.3447	2.0147	13.2029	-0.3447	2.0146	13.2055
7	-0.3551	1.8991	12.2270	-0.3512	1.9711	12.9275	-0.3512	1.9712	12.9318
8	-0.3582	1.8847	12.1634	-0.3552	1.9429	12.7499	-0.3552	1.9432	12.7569
9	-0.3605	1.8689	12.0687	-0.3577	1.9246	12.6333	-0.3577	1.9252	12.6462
∞	-0.3665(32)	1.8290(476)	11.8286(944)	-0.3642(4)	1.8781(48)	12.3376(401)	-0.3642(4)	1.8797(32)	12.3654(99)

equal to the difference between the CBS limits obtained with $X = 9, 8$ and $X = 8, 7$ basis set pairs. However, to make this error estimate more conservative, we additionally multiply it by a factor of two. The shaded areas plotted in Fig. 1 represent the error bars obtained in this way.

While the bulk of the basis set incompleteness error, addressed in the previous paragraph, stems from truncation with respect to the angular momentum, the secondary source of error is related to the augmentation with diffuse functions. Fortunately, the results converge rapidly with increasing augmentation level, as evident from Table I. The single augmentation level is not satisfactory with the present accuracy standards, but the differences between the results obtained as doubly and triply augmented basis sets are minor. This is especially true for the static polarizability, where the estimated CBS limits are essentially indistinguishable. However, for the dispersion coefficients we observe a small discrepancy between the CBS limits obtained with daXZ and taXZ basis sets, signaling that the adopted extrapolation scheme (8) does not fully resolve this problem. To eliminate this issue, we assume that the results converge exponentially with respect to the augmentation levels. The CBS limits obtained with aXZ, daXZ, and taXZ are fitted with the functional form

$$\Delta\alpha_n^{\text{SD}} = A_n + B_n e^{-C_n m}, \quad (9)$$

where m is the augmentation level. By extrapolating to the limit $m \rightarrow \infty$ we obtain the final estimates of the frozen-core CCSD contribution to the polarizability and dispersion coefficients:

$$\begin{aligned} \Delta\alpha_0^{\text{SD}} &= -0.3642(4), \\ \Delta\alpha_2^{\text{SD}} &= 1.8797(32), \\ \Delta\alpha_4^{\text{SD}} &= 12.3670(99), \\ \Delta\alpha_6^{\text{SD}} &= 67.906(26). \end{aligned} \quad (10)$$

For the sake of brevity, in the above discussion we have not considered the quantity $\Delta\alpha_6^{\text{SD}}$ explicitly. However, the value given above has been obtained using exactly the same protocol as for the lower-order coefficients.

The next contribution to the polarizability and dispersion coefficients is due to coupled-cluster triple excitations within the frozen-core approximation. We split this contribution into two parts. The first (dominant) part is calculated at the CC3 level of theory, denoted $\Delta\alpha_n^{\text{CC3}}$ here, while the second (presumably minor) is the difference between the CC3 and full CCSDT results, that is,

$$\Delta\alpha_n^{\text{T}} = \Delta\alpha_n^{\text{CCSDT}} - \Delta\alpha_n^{\text{CC3}}. \quad (11)$$

The reason for adopting this two-step approach is the fact that the CC3 calculations are significantly less computationally expensive than the full CCSDT. Moreover, the CC3 method

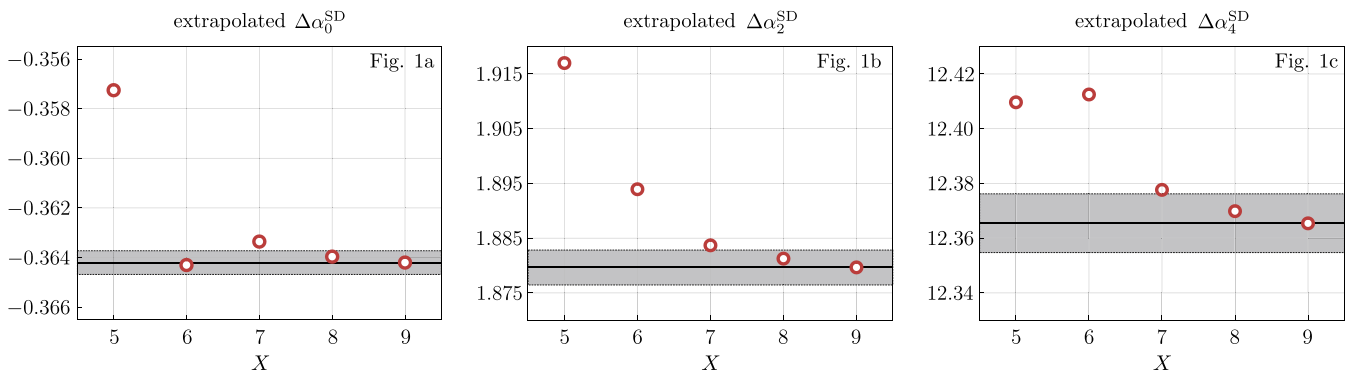


FIG. 1. Extrapolation of the $\Delta\alpha_n^{\text{SD}}$ contributions to the complete basis set limit using the formula (8). The solid horizontal line denotes the best estimate of the corresponding quantity (see text for details), and the shaded area represents the respective error bars.

TABLE II. Comparison of the $\Delta\alpha_n^{\text{CC3}}$ coefficients obtained by fitting and from the direct calculation (da4Z basis set). The fitting procedure includes even powers of ω up to the tenth order.

Quantity	Direct	Fitting
$\Delta\alpha_0^{\text{CC3}}$	-0.0250	-0.0250
$\Delta\alpha_2^{\text{CC3}}$	0.2285	0.2285
$\Delta\alpha_4^{\text{CC3}}$	1.6473	1.6509
$\Delta\alpha_6^{\text{CC3}}$	9.8084	9.1503

is known to capture a majority of the triple-excitation effects. We managed to calculate $\Delta\alpha_n^{\text{CC3}}$ with doubly augmented basis sets daXZ, $X = 2, \dots, 7$, but calculations of $\Delta\alpha_n^{\text{CCSDT}}$ are feasible only for $X = 2, \dots, 5$ at this augmentation level. Based on a set of preliminary calculations, we found that the triply augmented basis sets taXZ give almost the same results as daXZ and, in order to reduce the computational costs, the latter basis sets are adopted. In calculation of both triple-excitation contributions we use the contracted variants of the daXZ basis sets.

In the determination of the $\Delta\alpha_n^{\text{T}}$ contribution we face an additional technical difficulty. The CCSD and CC3 calculations reported here were carried out with the help of the DALTON package, which is able to determine the dispersion coefficients directly. However, the CCSDT (and higher-order) methods are not implemented in this program, and we employ the CFOUR and MRCC packages for these calculations. Unfortunately, with the latter two codes the dispersion coefficients are not computed explicitly. Instead, one has to perform calculations of the frequency-dependent polarizability at a grid of frequencies and determine the coefficients in the expansion (6) by fitting. This procedure is an additional source of potential error that has to be controlled. Fortunately, we are able to perform benchmark calculations at the CC3 level of theory, where the dispersion coefficients can be determined both directly and by fitting, to judge the accuracy of the procedure.

As an example, we provide details of the aforementioned benchmark calculations within the da4Z basis set. The polarizability was calculated at the CC3 level of theory for 31 frequencies uniformly spaced in the interval $\omega \in [0.000, 0.150]$ including the endpoints. The largest frequency corresponds to the wavelength 303.76 nm, and hence the whole experimentally relevant range of frequencies is covered. Independently, the dispersion coefficients were calculated directly at the same level of theory. In this work we are not interested in dispersion coefficients of higher order than sixth. Nonetheless, we found that inclusion of additional coefficients proportional to ω^8 and ω^{10} stabilizes the fitting procedure and improves the accuracy. Therefore, the expansion (6) used in the fitting procedure includes all even powers of ω up to ω^{10} . Incorporation of higher powers of ω does not change the results in a meaningful way, and hence they were eliminated to reduce the risk of overfitting. In Table II we compare the $\Delta\alpha_n^{\text{CC3}}$ coefficients obtained by fitting and from the direct calculation within the da4Z basis set. Overall, the fitting procedure yields reliable values of the required coefficients. For $n = 0$ and $n = 2$ the fitted results are essentially

identical to those calculated directly. Only for $n = 6$ do we observe a substantial deviation, but this is acceptable within the present context. Based on this benchmark calculation we shall assume in the remainder of the paper that the fitting procedure is able to deliver the accuracy of at least four significant digits for the second-order coefficient, at least three significant digits for the fourth-order coefficient, and at least one significant digit for the sixth-order coefficient.

In Table III we report results of the calculations of the $\Delta\alpha_n^{\text{CC3}}$ and $\Delta\alpha_n^{\text{T}}$ contributions. The former contribution was calculated directly, while the fitting procedure was used for the latter. The results obtained with the da2Z basis set are somewhat erratic, but starting with $X = 3$ the convergence pattern towards the CBS limit becomes regular. For the $\Delta\alpha_n^{\text{CC3}}$ and $\Delta\alpha_n^{\text{T}}$ contributions we adopted exactly the same extrapolation scheme and error estimation method as in the preceding CCSD calculations. The final estimates of the $\Delta\alpha_n^{\text{CC3}}$ and $\Delta\alpha_n^{\text{T}}$ contributions and the corresponding error bars are given in Table III. While the results for the $\Delta\alpha_6^{\text{CC3}}$ contribution are not given explicitly, the same procedure as for the lower-order coefficients gives

$$\Delta\alpha_6^{\text{CC3}} = 16.85(30). \quad (12)$$

The contribution $\Delta\alpha_6^{\text{T}}$ is neglected; see the discussion in Sec. III. The same is true for contributions of higher excitations to the sixth-order dispersion coefficient.

Next, we consider the contributions to the polarizability originating from quadruple excitations with respect to the reference determinant. The full CCSDTQ computations scale as N^{10} with the system size and are very costly. To reduce this cost, it is customary to employ noniterative models that account for quadruple excitations, such as CCSDT(Q) [55,56] or CCSDT[Q] [57]. Unfortunately, as the electronic wave function is not well defined in these methods, they cannot be used for determination of dynamic response properties or excitation spectra. Another option is to employ the CC4 model [56], which is free from this drawback and has recently been shown to deliver very accurate excitation energies. However, to the best of our knowledge, calculation of the dynamic polarizabilities at the CC4 level of theory is not implemented in any electronic structure package at present. Therefore, in determination of the quadruple excitations contribution to the polarizability and dispersion coefficients, denoted $\Delta\alpha_n^{\text{Q}}$, the full CCSDTQ method is used in this work.

In Table IV we report the calculations of the $\Delta\alpha_n^{\text{Q}}$ contribution. Due to the aforementioned high cost of these computations, daXZ basis sets only up to $X = 4$ were feasible. Similarly as for other contributions, $\Delta\alpha_n^{\text{Q}}$ was calculated for a finite set of frequencies followed by an analytical fitting procedure. In general, the behavior of the results is similar as in the case of the $\Delta\alpha_n^{\text{T}}$ correction (cf. Table III), but the convergence with respect to the basis set size is noticeably faster. We employ the extrapolation formula (8) from the $X = 3, 4$ pair to eliminate the basis set incompleteness error, as shown in Table IV. In order to estimate the error of these results, we repeat the same procedure for extrapolation of the $\Delta\alpha_n^{\text{T}}$ correction and compare with more reliable results from Table III. The error bars given in Table IV were obtained under the assumption that the relative error in the $\Delta\alpha_n^{\text{Q}}$ contribution

TABLE III. Linear-response frozen-core triple-excitation contribution to the static polarizability and dispersion coefficients, $\Delta\alpha_n^{\text{CC3}}$ and $\Delta\alpha_n^{\text{T}}$, of the argon atom calculated using the doubly augmented daXZ basis sets as discussed in the paper.

X	$\Delta\alpha_0^{\text{CC3}}$	$\Delta\alpha_2^{\text{CC3}}$	$\Delta\alpha_4^{\text{CC3}}$	$\Delta\alpha_0^{\text{T}}$	$\Delta\alpha_2^{\text{T}}$	$\Delta\alpha_4^{\text{T}}$
2	0.0452	0.3335	1.9729	0.0006	0.0333	0.2909
3	-0.0175	0.2244	1.6777	0.0051	0.0609	0.4627
4	-0.0250	0.2285	1.6473	0.0029	0.0551	0.3846
5	-0.0133	0.3445	2.3298	0.0010	0.0413	0.3171
6	-0.0069	0.4022	2.6685	0.0009	0.0373	0.3012
7	-0.0054	0.4186	2.7659	—	—	—
8	-0.0047	0.4261	2.8083	—	—	—
∞	-0.0031(4)	0.4427(68)	2.9018(473)	0.0007(2)	0.0312(62)	0.2764(553)

extrapolated from the $X = 3, 4$ basis set pair is no larger than for the $\Delta\alpha_n^{\text{T}}$ contribution calculated in the same way.

It is worth pointing out an unusual feature of the triple and quadruple excitation contributions to the static polarizability. The total triple excitation contribution (that is, the sum of the CC3 and CCSDT contributions), equal to roughly -0.0024 , is smaller in absolute terms than the quadruple excitation contribution, -0.0045 ; see Tables III and IV. This unexpected phenomenon is a consequence of a peculiar behavior of the $\Delta\alpha_0^{\text{CC3}}$, which accidentally crosses zero in the vicinity of $\omega = 0$. A similar phenomenon does not occur for the quadruple excitations, explaining the unusual ratio of the two corrections. Moreover, this feature is not observed for the dispersion coefficients. In fact, for both the second- and fourth-order coefficients, the quadruple excitation contribution is about 50 times smaller than the triple excitation effects, in line with the expectations based on the conventional wisdom.

Finally, we study the contribution of higher-order excitations to the polarizability and dispersion coefficients. The contributions of pentuple, $\Delta\alpha_n^{\text{P}}$, and hextuple, $\Delta\alpha_n^{\text{H}}$, excitations were calculated within the da2Z basis set. Unfortunately, these calculations are unfeasible with a larger basis set, and hence it is not possible to perform an extrapolation. Therefore, we assign a conservative uncertainty estimate of 50% to the values calculated within the da2Z basis. The following results were obtained using the fitting procedure described in the preceding paragraphs:

$$\begin{aligned}
 \Delta\alpha_0^{\text{P}} &= -0.0007(3), & \Delta\alpha_0^{\text{H}} &= -0.00002(1), \\
 \Delta\alpha_2^{\text{P}} &= -0.0050(24), & \Delta\alpha_2^{\text{H}} &= -0.00009(5), \\
 \Delta\alpha_4^{\text{P}} &= -0.0386(193), & \Delta\alpha_4^{\text{H}} &= 0.0002(1).
 \end{aligned} \quad (13)$$

It is also worth pointing out the rapid convergence of the results with respect to the maximum excitation level included

TABLE IV. Coupled-cluster quadruple excitation contributions to the static polarizability and dispersion coefficients, $\Delta\alpha_n^{\text{Q}}$, of the argon atom calculated using the doubly augmented daXZ basis sets.

X	$\Delta\alpha_0^{\text{Q}}$	$\Delta\alpha_2^{\text{Q}}$	$\Delta\alpha_4^{\text{Q}}$
2	-0.0114	-0.0593	-0.3400
3	-0.0128	-0.0866	-0.5383
4	-0.0085	-0.0477	-0.2858
∞	-0.0045(10)	-0.0122(45)	-0.0549(64)

in the coupled-cluster wave function. Taking the $\Delta\alpha_2$ coefficient as an example, the best estimate of the single and double excitations contribution is $-1.8797(32)$, triple excitations: $0.4739(92)$, quadruple excitations: $-0.0122(45)$, pentuple excitations: $-0.0050(24)$, and finally hextuple excitations: $-0.00009(5)$. In this light, the contributions of higher-order excitations can be neglected, as they are most likely smaller than the combined uncertainty of other terms. Therefore, the contribution of septuple and higher excitations is not considered in this work.

C. Core correlation contribution

In the calculations discussed in the previous subsection, we adopted the frozen-core approximation, neglecting the correlation contribution from the $1s^2 2s^2 2p^6$ core orbitals. The influence of the core correlation is expected to be small, but nonetheless nonnegligible within the present accuracy goals.

To eliminate this source of uncertainty, we carried out additional calculations at the CC3, CCSDT, and CCSDTQ levels of theory with all electrons correlated. The corrections accounting for the core-core and core-valence correlations are defined as the difference between the results obtained with all electrons correlated and with frozen $1s^2 2s^2 2p^6$ orbitals. These corrections are denoted as, for example, $\Delta\alpha_n^{\text{AE-CC3}}$ in the case of the core orbitals correction calculated using the CC3 method.

In Table V we report results of the calculations of the $\Delta\alpha_n^{\text{AE-CC3}}$ correction using the modified daXZ basis sets that include the tight functions with large Gaussian exponents for better description of the core region of the wave function. The results are extrapolated to the complete basis set limit using

TABLE V. Contribution the core-core and core-valence correlations to the static polarizability and dispersion coefficients of argon calculated at the CC3 level of theory, $\Delta\alpha_n^{\text{AE-CC3}}$, using the daXZ basis sets.

X	$\Delta\alpha_0^{\text{AE-CC3}}$	$\Delta\alpha_2^{\text{AE-CC3}}$	$\Delta\alpha_4^{\text{AE-CC3}}$
2	-0.0052	-0.0294	-0.1526
3	-0.0321	-0.1274	-0.5662
4	-0.0353	-0.1383	-0.6027
5	-0.0365	-0.1348	-0.5572
6	-0.0370	-0.1315	-0.5372
∞	-0.0379(9)	-0.1264(50)	-0.5060(312)

the formula (8). The corresponding uncertainty is estimated as the difference between the extrapolated value and the result obtained with the largest basis set available.

It is also necessary to estimate the contribution of higher-order excitations to the core-core and core-valence correlation correction. Unfortunately, all-electron calculations using the CCSDT and CCSDTQ method are extremely costly. This is a result of a larger number of active electrons in comparison with valence-only computations (8 vs 18 active particles). Additionally, the dacXZ basis sets include the aforementioned tight functions, and hence their total size is significantly increased in comparison with their valence counterparts. Because of these obstacles, we managed to perform all-electron CCSDT calculations only within $X = 2, 3$ basis sets, while for the CCSDTQ method we are limited solely to $X = 2$.

Fortunately, the $\Delta\alpha_n^{\text{AE-T}}$ and $\Delta\alpha_n^{\text{AE-Q}}$ corrections are small and do not have to be calculated very accurately. In the former case two basis sets are available, and hence the extrapolation towards the CBS is possible. However, the $X = 2$ is not reliable enough to make such extrapolation beneficial. In fact, considering the CC3 data included in Table V, extrapolation from the $X = 2, 3$ basis set pair overestimates the limit by roughly 50%. On the other hand, the $X = 3$ result has an error smaller than 15%. Therefore, a more accurate result is most likely obtained by simply taking the value of $\Delta\alpha_n^{\text{AE-T}}$ obtained within the $X = 3$ basis and assigning a large uncertainty of 15%. This gives

$$\begin{aligned}\Delta\alpha_0^{\text{AE-T}} &= -0.0051(8), \\ \Delta\alpha_2^{\text{AE-T}} &= -0.0516(78), \\ \Delta\alpha_4^{\text{AE-T}} &= -0.3167(476).\end{aligned}\quad (14)$$

Finally, we consider the $\Delta\alpha_n^{\text{AE-Q}}$ correction, where only one basis set is available. To estimate the CBS limit of this correction we assume that it converges at the same rate as the CC3 contribution. The limit is then obtained by scaling the $\Delta\alpha_n^{\text{AE-Q}}$ correction obtained within the $X = 2$ basis by the ratio of the $\Delta\alpha_n^{\text{AE-CC3}}$ contributions as follows:

$$\Delta\alpha_n^{\text{AE-Q}}(\text{CBS}) = \frac{\Delta\alpha_n^{\text{AE-CC3}}(\text{CBS})}{\Delta\alpha_n^{\text{AE-CC3}}(X=2)} \Delta\alpha_n^{\text{AE-Q}}(X=2). \quad (15)$$

This leads to the following estimates:

$$\begin{aligned}\Delta\alpha_0^{\text{AE-Q}} &= -0.0006(3), \\ \Delta\alpha_2^{\text{AE-Q}} &= 0.0014(7), \\ \Delta\alpha_4^{\text{AE-Q}} &= 0.0554(277),\end{aligned}\quad (16)$$

where we assigned an uncertainty of 50% to the values obtained by scaling. The error of the $\Delta\alpha_n^{\text{AE-Q}}$ contribution obtained in this way is large, but in absolute terms this has little influence on the overall uncertainty of our predictions.

V. RELATIVISTIC CORRECTIONS TO THE POLARIZABILITY

To reach the required accuracy level in theoretical determination of the polarizability of argon, relativistic corrections have to be considered. Indeed, even for the neon atom which is much lighter, the relativistic effects constitute about two parts

per thousand of the total value. Our framework for calculation of the relativistic contributions to the static polarizability and dispersion coefficients is based on two alternative methods. The first one is the standard first-order perturbation theory based on the Breit-Pauli Hamiltonian [58]

$$\hat{H}_{\text{BP}} = \hat{P}_4 + \hat{D}_1 + \hat{D}_2 + \hat{B}, \quad (17)$$

where the operators appearing above are defined as

$$\hat{P}_4 = -\frac{1}{8c^2} \sum_i \nabla_i^4, \quad (18)$$

$$\hat{D}_1 = \frac{\pi}{2c^2} Z \sum_i \delta(\mathbf{r}_{ia}), \quad (19)$$

$$\hat{D}_2 = \frac{\pi}{c^2} \sum_{i>j} \delta(\mathbf{r}_{ij}), \quad (20)$$

$$\hat{B} = \frac{1}{2c^2} \sum_{i>j} \left[\frac{\nabla_i \cdot \nabla_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_j) \nabla_i}{r_{ij}^3} \right], \quad (21)$$

where Z is the nuclear charge and c denotes the speed of light in vacuum. We avoid the use of the fine-structure constant α in this work as it may easily be confused with the polarizability. The corrections to the polarizability and dispersion coefficients resulting from the operators (17) will be denoted by the symbol $\Delta\alpha_n^X$, where X in the superscript denotes the perturbing operator. Following the usual convention, we refer to these corrections as mass-velocity ($X = \text{MV}$), one-electron Darwin ($X = \text{D1}$), two-electron Darwin ($X = \text{D2}$), and Breit ($X = \text{B}$), in the same order as appearing in Eq. (17). The sum of the first two corrections (MV and D1) is referred to as the Cowan-Griffin (CG) correction [59]. Another frequently used name for the $\Delta\alpha_n^{\text{B}}$ term is the orbit-orbit correction, but we refer to this quantity as the Breit correction for consistency with previous works. The expectation values of the operators in Eqs. (18)–(21) are calculated analytically at the CCSD(T) level of theory as described in Ref. [60].

The second approach to determination of the relativistic corrections is based on the Douglas-Kroll-Hess [61–63] theory of the second order (DKH2). In this method the one-electron part of the Hamiltonian is replaced by an effective operator arising from a specific decoupling transformation applied to the Dirac equation for one-electron systems. In the DKH2 variant the decoupling is carried out to the second order in the external potential. The practical advantage of the DKH2 Hamiltonian is the fact that it can easily be used together with any method that is able to calculate polarizabilities. The same is not true for the Breit-Pauli Hamiltonian; to the best of our knowledge, analytic calculation of the full BP correction to the polarizability (and dispersion coefficients) is not implemented in any electronic structure package. On the other hand, the DKH2 completely neglects the two-electron corrections (D2 and B), but in comparison with the Cowan-Griffin approximation it includes terms of orders higher than $1/c^2$. The relativistic correction obtained using the DKH2 method is denoted by the symbol $\Delta\alpha_n^{\text{DKH2}}$.

The Breit-Pauli correction to the static polarizability was calculated using the finite-field approach. The electric field of a small finite strength was added to the Hamiltonian, and the

TABLE VI. Relativistic corrections to the static polarizability of the argon atom calculated using the doubly augmented dacXZ basis sets at the all-electron CC3 level of theory. In the last row we provide results extrapolated to the complete basis set limit according to Eq. (8) and the corresponding error estimate.

X	One-electron corrections				Two-electron corrections	
	$\Delta\alpha_0^{\text{MV}}$	$\Delta\alpha_0^{\text{D1}}$	Total Cowan-Griffin	$\Delta\alpha_0^{\text{DKH2}}$	$\Delta\alpha_0^{\text{D2}}$	$\Delta\alpha_0^{\text{B}}$
2	-0.1380	0.1572	0.0192	0.0198	0.0002	0.0061
3	-0.1474	0.1667	0.0192	0.0198	0.0003	0.0066
4	-0.1452	0.1638	0.0186	0.0191	0.0002	0.0065
5	-0.1446	0.1629	0.0183	0.0188	0.0002	0.0065
∞	-0.1439(7)	0.1618(11)	0.0179(3)	0.0184(4)	0.0001(1)	0.0065(1)

second derivative of the Breit-Pauli corrections was extracted using the simplest finite difference formula. The strength of the electric field within range [0.00,0.01] was considered, and for a wide interval around ca. 0.075 the results were stable to four significant digits. This strength of the field was applied in all calculations reported here. In Table VI we show relativistic corrections to the static polarizability of argon calculated using the Breit-Pauli and DKH2 approaches (all-electron CC3 method within dacXZ basis sets, $X = 2, \dots, 5$). The results were extrapolated to the CBS limit using the formula (8). The error was estimated as a difference between the value extrapolated using the $X = 4, 5$ basis set pair, and the raw results obtained within $X = 5$ basis. Only for the D2 correction is a modification of this procedure required; it is known [64] that this correction converges to the CBS limit as X^{-1} , and hence proper changes to Eq. (8) were introduced similarly as in Refs. [65–70].

First, let us consider the differences between the Cowan-Griffin and DKH2 corrections. The error of both methods is of the order $1/c^4$, and hence we expect them to give a similar answer, provided that the perturbation theory remains valid for argon. One can see from Table VI that both methods agree within their mutual error estimates. Based on that, we conclude that DKH2 is a reliable method for calculation of the one-electron relativistic corrections, and we apply it also in calculations of the dispersion coefficients. The obtained results of the $\Delta\alpha_n^{\text{DKH2}}$ corrections are given in Table VII with the same extrapolation and error estimation method as for the static polarizability.

From Table VI we can also judge the importance of two-electron relativistic effects in the present context. The two-electron Darwin correction is entirely negligible. Its contribution is smaller than the uncertainty of other corrections. We tacitly assume that the same is true for the dispersion

coefficient and hence omit it in further analysis. However, the situation is entirely different in the case of the Breit correction. Indeed, due to significant cancellation between the mass-velocity and one-electron Darwin corrections (which have opposite signs), the Breit correction is only about three times smaller than the total Cowan-Griffin correction. Such phenomena appear to be a common feature in calculations for many-electron systems. Moreover, the contribution of the one-electron relativistic effects increases in magnitude (on a relative basis) for the dispersion coefficients in comparison with the static polarizability (roughly 0.6% and 1.5% for α_2 and α_4 , respectively, while only 0.2% for α_0). We can expect that the same is true for the Breit correction, and hence the omission of this quantity in determination of the dispersion coefficient would significantly increase the overall error of our results. As mentioned above, no implementation of the Breit correction to the dispersion coefficients has been reported yet, and the standard finite-field approach is not applicable to the frequency-dependent quantities.

In order to circumvent this problem, let us first analyze the results from Table VI more closely. A striking feature of the results obtained for the Breit correction is the fast convergence with respect to the basis set size. Indeed, even within the smallest dac2Z basis, the accuracy of the calculated Breit correction would be acceptable (with wider error bars). The apparent insensitivity of the Breit correction to the quality of the basis set suggests that the dynamic correlation effects, which typically require high angular momenta to achieve convergence, may not be important for this quantity. To verify this hypothesis we recomputed the Breit correction to the static polarizability using the Hartee-Fock theory, which includes no dynamic correlation, as well as the MP2 theory, which is the simplest correlated method. In Table VIII the obtained results are compared with the CC3 data reproduced from Table VI for ease of comparison. Results given in Table VIII

TABLE VII. Relativistic corrections $\Delta\alpha_n^{\text{DKH2}}$ obtained at the CC3 level of theory within the dacXZ basis sets (DKH2 effective Hamiltonian).

X	$\Delta\alpha_0^{\text{DKH2}}$	$\Delta\alpha_2^{\text{DKH2}}$	$\Delta\alpha_4^{\text{DKH2}}$
2	0.0198	0.1859	1.3507
3	0.0198	0.1832	1.3331
4	0.0191	0.1736	1.2453
5	0.0188	0.1701	1.2173
∞	0.0184(4)	0.1658(43)	1.1827(346)

TABLE VIII. The relativistic Breit corrections to the static polarizability ($\Delta\alpha_0^{\text{B}}$) obtained at various levels of theory (all electrons correlated where applicable) using the dacXZ basis sets.

X	Hartree-Fock	MP2 method	CC3 method
2	0.0062	0.0061	0.0061
3	0.0066	0.0067	0.0066
4	0.0066	0.0066	0.0065
5	0.0066	0.0066	0.0065

confirm our hypothesis that the correlation contribution to the Breit correction is tiny and the Hartree-Fock method provides entirely satisfactory accuracy.

We assume that the unimportance of the correlation contributions to the Breit correction holds true also for the dispersion coefficients. In the Appendix we develop analytic equations that allow us to calculate this correction to the frequency-dependent polarizability at the Hartree-Fock level of theory. From these calculations we obtain

$$\begin{aligned}\Delta\alpha_2^{\text{B}} &= 0.0530(26), \\ \Delta\alpha_4^{\text{B}} &= 0.2750(138).\end{aligned}\quad (22)$$

The uncertainty estimates are based on a small contribution of the electron correlation to the Breit correction, which amounts to only about 1% for the static polarizability. In the case of $\Delta\alpha_2^{\text{B}}$ and $\Delta\alpha_4^{\text{B}}$ we conservatively assumed that they contribute by no more than 5%. As expected, the Breit correction to the dispersion coefficients is sizable, constituting about a quarter of the total relativistic contribution. Therefore, omission of this term would significantly increase our final error.

Having included all effects of the order of $1/c^2$ we should consider the possible significance of the relativistic effects of the order of $1/c^4$. These effects originate from higher-order terms in the Foldy-Wouthuysen transformation of the Dirac equation and from the second-order contribution from the Breit-Pauli Hamiltonian [71]. The required calculations are very complicated even for the ground state of helium atom and so far have not been performed for the polarizability of helium. To gauge the magnitude of these $1/c^4$ effects in argon we considered the effect of the second-order spin-orbit interaction on the atomic polarizability. This interaction vanishes in the first-order of perturbation theory and hence was not included in the Breit-Pauli Hamiltonian, Eq. (17). Nonetheless, the spin-dependent terms enter in higher orders by coupling triplet electronic excitations to the singlet ground state. While such terms are expected to be small, there is no reason to neglect them *a priori*. Unfortunately, rigorous evaluation of the contribution of the second-order spin-orbit interaction in argon is computationally unfeasible at present. Therefore, to estimate the magnitude of the spin-orbit contributions we performed fully relativistic Hartree-Fock calculations based on the four-component Dirac-Coulomb Hamiltonian as implemented in the DIRAC program [72,73]. In order to extract the spin-dependent contributions to the static polarizability, two sets of calculations were performed. The first set was based on the conventional Dirac-Coulomb Hamiltonian, while in the second the spin-dependent terms were eliminated using the method of Dylla [74]. The spin-dependent contribution to the static polarizability, denoted $\Delta\alpha_0^{\text{SO}}$ here, was obtained as a difference of the corresponding results from two sets. In the calculations we used the uncontracted basis sets from Sec. IV to expand the large component of the spinor. While these basis sets were optimized in the nonrelativistic framework and hence are suboptimal in the four-component calculations, this is acceptable for relatively light systems such as argon atom. The small-component basis was generated automatically using the restricted kinetic balance prescription.

The spin-dependent contributions to the static polarizability converge rapidly with respect to the size of the basis set.

For example, the results obtained with da4z and da5z differ by merely one part per 1000, and the difference between da5z and da6z is by an order of magnitude smaller. Therefore, we adopt the value obtained within the da6z basis as the final result. The major contribution to the uncertainty of this quantity comes from the neglected correlation effects. To account for this, we adopt a conservative 20% error estimate. This gives the final spin-dependent contribution to the static polarizability equal to

$$\Delta\alpha_0^{\text{SO}} = 0.0012(2). \quad (23)$$

This correction is smaller than the combined uncertainty of other contributions. In the case of the dispersion coefficients, these uncertainties are significantly larger on a relative basis, and hence the spin-dependent terms can be neglected.

VI. QUANTUM ELECTRODYNAMICS CORRECTIONS TO THE POLARIZABILITY

The next contributions to the polarizability and dispersion coefficients originate from the quantum electrodynamics (QED) effects, $\Delta\alpha_n^{\text{QED}}$. In this work we apply the following correction [75–77]

$$\Delta\alpha_n^{\text{QED}} = \frac{8}{3\pi c} \left(\frac{19}{30} + 2 \ln c - \ln k_0 \right) \Delta\alpha_n^{\text{D1}}, \quad (24)$$

where $\Delta\alpha_n^{\text{D1}}$ is the relativistic D1 correction calculated in the previous section and $\ln k_0$ is the so-called Bethe logarithm [58,78] (related to the mean-excitation energy of the system). In comparison with the rigorous nonrelativistic quantum electrodynamics (NRQED) theory [75–77], several approximations were adopted to arrive at Eq. (24). First, the two-electron QED corrections were neglected. There are two corrections of this type; the first is essentially the D2 relativistic correction scaled by a small numerical factor. Taking into account that the D2 correction to the polarizability is already negligible, there is little point in including the corresponding QED correction. The second two-electron QED correction is the so-called Araki-Sucher term [79,80]. While this contribution can be calculated within the Gaussian basis set [81–84], it is typically even smaller than the D2 correction and hence is entirely omissible. Another approximation used in Eq. (24) is neglect of the external electric field dependence of the Bethe logarithm. As discussed at length in Ref. [19], $\ln k_0$ is sensitive primarily to the electronic wave function in the region close to the nucleus. This regime is dominated by the strong electric field generated by the nucleus, and hence the influence of the (perturbatively small) external electric field is very small. The excellent agreement between theory and experiment for the polarizability of the neon atom [19,20], where the same approximation was adopted in the calculations, confirms that the field dependence of the Bethe logarithm is indeed tiny. The same conclusion was reached in calculations for the helium atom where the electric-field derivative of the Bethe logarithm was calculated rigorously [14,18].

The Bethe logarithm for argon was calculated at the Hartree-Fock level of theory using the same formalism as in our previous work devoted to the neon atom [19]. Details of these calculations will be reported in a separate publication.

The value of the Bethe logarithm for argon adopted here reads

$$\ln k_0 = 8.7610. \quad (25)$$

Based on comparison with more accurate calculations for few-electron atoms, we estimate that the accuracy of this quantity is 1%–2%, which does not contribute significantly to the overall error.

With all aforementioned approximations taken into account, calculation of the $\Delta\alpha_n^{\text{QED}}$ correction amounts to scaling the appropriate $\Delta\alpha_n^{\text{D1}}$ by a numerical factor of approximately -0.0437 . In the case of the static polarizability we use the $\Delta\alpha_0^{\text{D1}}$ calculated in the previous section. For the dispersion coefficients the $\Delta\alpha_n^{\text{D1}}$ terms were calculated using the theory developed in the Appendix. This leads to the following contributions:

$$\begin{aligned} \Delta\alpha_0^{\text{QED}} &= -0.0071(7), \\ \Delta\alpha_2^{\text{QED}} &= -0.0223(22), \\ \Delta\alpha_4^{\text{QED}} &= -0.1039(104), \end{aligned} \quad (26)$$

where we adopted a conservative 10% error bars to account for all approximations in Eq. (24).

It is also instructive to estimate the magnitude of the higher-order QED effects, $\Delta\alpha_n^{\text{QED+}}$. It is well known that the dominant QED contribution of the order $1/c^4$ is the so-called one-loop term [85]. In the present case it takes the form

$$\Delta\alpha_n^{\text{QED+}} = \frac{2Z}{c^2} \left(\frac{427}{96} - 2 \ln 2 \right) \Delta\alpha_n^{\text{D1}}. \quad (27)$$

With the knowledge of the $\Delta\alpha_n^{\text{D1}}$ calculated previously, the one-loop term can be obtain by scaling with the numerical factor of roughly 0.0059. This gives the following estimates:

$$\begin{aligned} \Delta\alpha_0^{\text{QED+}} &= 0.0010(2), \\ \Delta\alpha_2^{\text{QED+}} &= 0.0030(7) \\ \Delta\alpha_4^{\text{QED+}} &= 0.0140(35). \end{aligned} \quad (28)$$

We adopt a wide error bars of 25% to account for the missing $1/c^4$ QED terms.

VII. FINITE NUCLEAR MASS AND SIZE CORRECTIONS TO THE POLARIZABILITY

In all preceding calculations, the nucleus of the argon atom was effectively treated as a stationary point charge with infinite mass. For completeness, we here consider two corrections that go beyond this simple picture. First, we consider the finite nuclear size (FNS) correction $\Delta\alpha_0^{\text{FNS}}$ which takes into account that the nucleus has a finite dimension. For many-electron atoms this correction to the static polarizability is calculated from the formula [86]

$$\Delta\alpha_0^{\text{FNS}} = \frac{4}{3} \frac{\langle r_c^2 \rangle}{\tilde{\lambda}^2} \Delta\alpha_0^{\text{D1}}, \quad (29)$$

where $\langle r_c^2 \rangle$ is the averaged square of the nuclear charge radius and $\tilde{\lambda} \approx 386.2$ fm is the reduced Compton wavelength of the electron. We employ the value $\langle r_c^2 \rangle = 11.512$ fm² for the ⁴⁰Ar isotope, which was obtained in Ref. [87] using the two-parameter Fermi model of the nuclear charge distribution. The

uncertainty of this quantity reported in Ref. [87] is negligible in the present context. Using the value $\Delta\alpha_0^{\text{D1}}$ from Table VI we find

$$\Delta\alpha_0^{\text{FNS}} = 1.7 \times 10^{-5}. \quad (30)$$

This correction is negligible in comparison with other sources of error. Since there is no reason to believe that the FNS correction is substantially larger for the dispersion coefficients, it has been neglected in our analysis.

Next, we consider the finite nuclear mass (FNM) correction. In the case of the static polarizability, it can be determined from the formula for the diagonal Born-Oppenheimer correction (DBOC) [88]

$$\Delta\alpha_0^{\text{FNM}} = \frac{1}{2M_{\text{nuc}}} \partial_\varepsilon^2 |_{\varepsilon=0} \langle \Psi_0 | \nabla_{\text{nuc}}^2 | \Psi_0 \rangle, \quad (31)$$

where Ψ_0 is the ground-state wave function, M_{nuc} is the nuclear mass, ε denotes the strength of the external electric field, and ∇_{nuc} is the gradient operator with respect to the coordinates of the nucleus. As we expect the contribution of the FNM correction to be relatively small, it is sufficient to calculate $\Delta\alpha_0^{\text{FNM}}$ using the simplest correlated theory which is the MP1 method described in Refs. [89,90]. The derivative with respect to the electric field in Eq. (31) is calculated using the finite-difference approach with the same settings as described in Sec. V. The final value of the $\Delta\alpha_0^{\text{FNM}}$ correction adopted here was obtained by extrapolating the results from the da4Z/da5Z basis set pair according to Eq. (8). It reads

$$\Delta\alpha_0^{\text{FNM}} = 1.9(3) \times 10^{-4}, \quad (32)$$

where the error estimate is equal to the difference between the extrapolated value and the result obtained within the da5Z basis set. This correction is essentially negligible in comparison with other sources of error, and the same conclusion is most likely true for the dispersion coefficients as well. Therefore, we neglect the FNM mass effects in determination of the polarizability dispersion.

VIII. MAGNETIC SUSCEPTIBILITY

As discussed in Sec. III, the magnetic susceptibility does not have to be determined as accurately as the polarizability, and relative accuracy of around 10% is entirely sufficient. Therefore, in our treatment we neglect the frequency dependence of this quantity and concentrate solely on the static magnetic susceptibility, χ_0 . It is worth pointing out that for isolated atoms the frequency dependence of χ_0 comes only from paramagnetic terms (which are minor in absolute terms), and hence it is highly unlikely that the frequency contribution to χ_0 exceeds 1% for argon; see Ref. [19].

Additionally, we neglect relativistic, QED, and finite nuclear mass or size corrections to χ_0 . Note that calculation of these corrections is a significant challenge and has not been attempted thus far (without additional approximations to the theoretical formalism) even for the helium atom. Therefore, such calculations are beyond the scope of the present work, and here we focus solely on the “nonrelativistic” value of χ_0 . Parenthetically, we note that the use of the term “nonrelativistic” may be viewed as a misnomer in this context, because the magnetic susceptibility in itself is of the order $1/c^2$ and

hence vanishes in the nonrelativistic limit, $c \rightarrow \infty$. However, the use of this name appears to be common in the literature, and hence we follow this naming convention.

Neglecting terms of higher order in $1/c$ and assuming that the nucleus has an infinite mass, the atomic magnetic susceptibility is related to the mean-square electron-nucleus distance through the formula [58]

$$\chi_0 = -\frac{1}{6c^2} \left\langle \sum_i r_i^2 \right\rangle, \quad (33)$$

which has roots in the Langevin theory of diamagnetism [91]. In this section we focus on accurate determination of the value of $\langle \sum_i r_i^2 \rangle$ for argon. For brevity, we adopt a shorthand notation $\langle r^2 \rangle \equiv \langle \sum_i r_i^2 \rangle$. As will become apparent, in our calculations we include several corrections which are smaller than our stated accuracy goal and hence could possibly be neglected. Nonetheless, our motivation is to establish how accurately the nonrelativistic value of χ_0 can be determined at present. This provides an outlook as to how accurately the relativistic (and other) corrections must be computed in subsequent papers. In the calculations of $\langle r^2 \rangle$ we adopt a similar strategy as for the nonrelativistic contribution to the polarizability with only minor modifications. In particular, the same basis sets are used, including the augmented and core-valence functions, and the calculations are split into valence-only (frozen $1s^2 2s^2 2p^6$ core orbitals) and all-electron components.

First, we consider the Hartree-Fock contribution, denoted $\langle r^2 \rangle_{\text{HF}}$ further in the text. As the HF equations for atoms can be solved using a grid based approach with extremely high accuracy, there is little point in attempting to reproduce these results within a Gaussian basis. Therefore, we take $\langle r^2 \rangle_{\text{HF}} = 26.0344$ from Ref. [92], which is essentially exact for our purposes to all digits given.

The second major contribution to $\langle r^2 \rangle$ was calculated at the frozen-core CCSD(T) level of theory, $\Delta \langle r^2 \rangle_{\text{SD(T)}}$, using the daXZ basis sets. Similarly as for the polarizability, we found that further augmentation of the basis sets leads to tiny changes in the results, which are not worth a significant increase of the computational time. Note that the CCSD(T) method is used here rather than the CC3 theory employed for the polarizability. This choice is justified by the observation that both CC3 and CCSD(T) have a similar accuracy, yet the latter is usually significantly less expensive due to the noniterative treatment of the triple excitations. Such a shortcut was not available in the case of the (dynamic) polarizability as this quantity is not well defined within the CCSD(T) model. In Table IX we report values of the $\Delta \langle r^2 \rangle_{\text{SD(T)}}$ correction calculated with basis sets $X = 2, \dots, 9$. The CBS limit of this quantity is obtained by extrapolation using the formula (8) with $X = 8, 9$. The uncertainty is estimated as twice the difference between the extrapolated values from $X = 8, 9$ and $X = 7, 8$ basis set pairs, analogously as for the polarizability; see Sec. IV.

Next, we consider corrections to the magnetic susceptibility accounting for higher-order excitations with respect to the reference determinant. They are denoted by the symbols $\Delta \langle r^2 \rangle_{\text{T}}$ [the difference between CCSDT and CCSD(T) results], $\Delta \langle r^2 \rangle_{\text{Q}}$ (the difference between CCSDTQ and

TABLE IX. Valence coupled-cluster calculations of the mean square electron-nucleus distance, $\langle r^2 \rangle$, for argon atom obtained within the daXZ basis set family.

X	$\Delta \langle r^2 \rangle_{\text{SD(T)}}$	$\Delta \langle r^2 \rangle_{\text{T}}$	$\Delta \langle r^2 \rangle_{\text{Q}}$	$\Delta \langle r^2 \rangle_{\text{P}}$
2	0.2298	0.0035	0.0004	-0.0006
3	0.0909	0.0007	0.0007	-0.0010
4	0.0156	-0.0008	0.0020	—
5	-0.0104	-0.0017	—	—
6	-0.0227	-0.0019	—	—
7	-0.0290	—	—	—
8	-0.0326	—	—	—
9	-0.0349	—	—	—
∞	-0.0408(4)	-0.0022(3)	0.0032(12)	-0.0012(2)

CCSDT), and so on. We consider corrections up to pentuple excitations, $\Delta \langle r^2 \rangle_{\text{P}}$, and higher-order corrections are neglected based on their small magnitude. For example, the $\Delta \langle r^2 \rangle_{\text{H}}$ correction calculated within the da2Z basis set amounts to only about -1×10^{-5} . Even if one conservatively assumes that within this small basis the $\Delta \langle r^2 \rangle_{\text{H}}$ correction is underestimated by a factor of 20, the resulting value is still smaller than the uncertainties of other contributions and hence can be safely neglected without increasing the overall error. Noting the rapid convergence of the results with respect to the excitation level, the same is true for contributions of even higher excitations.

The calculated higher-order contributions to the magnetic susceptibility are given in Table IX. The CBS limits are obtained by the standard extrapolation, Eq. (8), using the largest two basis sets available for a given quantity. However, because in calculation of these corrections we are unable to employ basis sets as large as for $\Delta \langle r^2 \rangle_{\text{SD(T)}}$, a more conservative uncertainty estimate is used. Namely, the error of the CBS limit is computed as a difference between the extrapolated value and the result obtained within the largest basis set feasible for a given quantity.

Next, we consider core-valence contribution to $\langle r^2 \rangle$, defined as the difference between results obtained with all occupied orbitals correlated and with frozen $1s^2 2s^2 2p^6$ core orbitals. In determination of this correction we adopt an analogous strategy as in the valence calculations, with the exception that daXZ basis sets supplemented with additional tight functions are used. The core-valence corrections are denoted by the symbols $\Delta \langle r^2 \rangle_{\text{AE-SD(T)}}$, $\Delta \langle r^2 \rangle_{\text{AE-T}}$, and so on. The results of the calculations obtained in the same way as for the valence contribution are given in Table X.

A somewhat surprising phenomenon encountered when comparing results from Tables IX and X is the fact that the valence contribution calculated at the CCSD(T) level of theory is smaller (in absolute terms) than the corresponding core-valence contribution. This feature is observed only in the CCSD(T) calculations and absent in any other CC variant. Moreover, even looking at the Hartree-Fock reference function, the contribution of the $1s^2 2s^2 2p^6$ core orbitals is about two orders of magnitude smaller than of the valence shells. This unusual behavior of the correlation contribution at the CCSD(T) level of theory is somewhat unfortunate as the core

TABLE X. All-electron coupled-cluster calculations of the mean square electron-nucleus distance, $\langle r^2 \rangle$, for argon atom obtained within the dacXZ basis set family.

X	$\Delta \langle r^2 \rangle_{\text{AE-SD(T)}}$	$\Delta \langle r^2 \rangle_{\text{AE-T}}$	$\Delta \langle r^2 \rangle_{\text{AE-Q}}$
2	-0.0092	-0.0003	0.0004
3	-0.0389	-0.0005	0.0001
4	-0.0555	-0.0001	—
5	-0.0640	—	—
6	-0.0681	—	—
∞	-0.0743(62)	0.0002(3)	0.0000(2)

corrections cannot be calculated with basis sets as large as in the valence calculations. As a result, the uncertainty of the $\Delta \langle r^2 \rangle_{\text{AE-SD(T)}}$ component actually dominates our error budget for the magnetic susceptibility. Larger core-valence basis sets need to be optimized in the future if a significant error reduction is desired. It is also worth pointing out that the $\Delta \langle r^2 \rangle_{\text{AE-T}}$ and $\Delta \langle r^2 \rangle_{\text{AE-Q}}$ corrections are essentially negligible at present.

By summing all calculated contributions we obtain the final estimate of the mean-square electron-nucleus distance in argon atom equal to

$$\langle r^2 \rangle = 25.9193(64), \quad (34)$$

where the final error is calculated by adding squares of errors of individual contributions and taking the square root. According to Eq. (33), this translates to the following value of the magnetic susceptibility of argon:

$$\chi_0 = -2.3004(6) \times 10^{-4}. \quad (35)$$

We would like to stress that above result is based on purely “nonrelativistic” formula (33), and the corresponding error estimate takes into account only the uncertainties in $\langle r^2 \rangle$. Other corrections to χ_0 such as relativistic, quantum electrodynamics, etc., are completely neglected and not included in the above error bars. Nonetheless, assuming the magnitude of these corrections is similar as for the static polarizability, one can conclude that the value given above is accurate to at least 1%. As discussed in Sec. III, this level of accuracy is sufficient from the point of view of refractive coefficient measurements. In the subsequent section, the result given above is compared with the available literature data.

IX. FINAL RESULTS AND DISCUSSION

In Table XI we present a summary of the theoretical results obtained in this work for the static polarizability and dispersion coefficients for argon. The final estimates (denoted “total” in Table XI) are obtained by summing all relevant contributions. The total error is obtained by calculating the sum of squares of individual uncertainties and taking the square root. This approach is justified by the standard error propagation formulas under the assumption that all contributions to the final results are independent variables in the statistical sense.

In the case of the sixth-order dispersion coefficient, we used a simplified computational scheme where only the Hartree-Fock, valence CCSD, and valence CC3 contributions are included. By summing these quantities we obtain the final

TABLE XI. The final error budget of the calculations of the static polarizability and dispersion coefficients for the argon atom.

	$n = 0$	$n = 2$	$n = 4$
Nonrelativistic valence ($3s^23p^6$) contributions			
α_n^{HF}	11.4726(1)	25.6162(1)	78.9658(2)
$\Delta\alpha_n^{\text{SD}}$	-0.3642(4)	1.8797(32)	12.3670(99)
$\Delta\alpha_n^{\text{CC3}}$	-0.0031(4)	0.4427(68)	2.9018(473)
$\Delta\alpha_n^{\text{T}}$	0.0007(2)	0.0312(62)	0.2764(553)
$\Delta\alpha_n^{\text{Q}}$	-0.0045(10)	-0.0122(45)	-0.0549(64)
$\Delta\alpha_n^{\text{P}}$	-0.0007(3)	-0.0050(24)	-0.0386(193)
$\Delta\alpha_n^{\text{H}}$	0.0000(1)	0.0000(1)	0.0002(1)
Nonrelativistic core ($1s^22s^22p^6$) correlation contributions			
$\Delta\alpha_n^{\text{CC3}}$	-0.0379(9)	-0.1264(50)	-0.5060(312)
$\Delta\alpha_n^{\text{T}}$	-0.0051(8)	-0.0516(78)	-0.3167(476)
$\Delta\alpha_n^{\text{Q}}$	-0.0006(3)	0.0014(7)	0.0554(277)
Relativistic and QED corrections			
$\Delta\alpha_n^{\text{DKH2}}$	0.0184(4)	0.1658(43)	1.1827(346)
$\Delta\alpha_n^{\text{D2}}$	0.0001(1)	—	—
$\Delta\alpha_n^{\text{B}}$	0.0065(1)	0.0530(26)	0.2750(138)
$\Delta\alpha_n^{\text{SO}}$	0.0012(2)	—	—
$\Delta\alpha_n^{\text{QED}}$	-0.0071(7)	-0.0223(22)	-0.1039(104)
$\Delta\alpha_n^{\text{QED+}}$	0.0010(2)	0.0030(7)	0.0140(35)
Other minor corrections			
$\Delta\alpha_n^{\text{FNS}}$	0.0000(1)	0.0000(1)	0.0000(1)
$\Delta\alpha_n^{\text{FNM}}$	0.0002(1)	—	—
Total	11.0775(19)	27.976(15)	95.02(11)
Rel. accuracy	$1.7 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$

estimate

$$\alpha_6 = 382.5. \quad (36)$$

Because the accuracy of α_6 is not critical, we do not attempt a rigorous error estimation for this quantity. However, by analyzing the impact of analogous approximations on the lower-order dispersion coefficients, it is safe to assume that the value of α_6 given above has the relative error no larger than 10%. According to the discussion from Sec. III, this is entirely sufficient from the point of view of metrology.

In order to verify the accuracy of the theoretical predictions, we first compare the final results obtained for the static polarizability with the experimental data. As expected, our value for α_0 is significantly less accurate than the latest experiment of Gaiser and Fellmuth [21]. Nonetheless, the experimental value is within the error bars estimated by us. In fact, the relative error with respect to the data of Gaiser and Fellmuth [21] is about five times smaller than the uncertainty estimated from theory. This suggests that our error estimation protocol is conservative and leads to overestimation of the uncertainty, but may also be in part due to fortuitous error cancellation. Therefore, we are reluctant to arbitrarily decrease our uncertainty estimates based solely on this comparison.

Concerning the dispersion coefficients, the results provided by us appear to be the most accurate reported thus far, see Table XII. We improve the accuracy by more than an order of magnitude in comparison with the available data. Unfortunately, more accurate theoretical and/or experimental values

TABLE XII. Comparison with other theoretical and experimental literature values of α_n . The error estimation is not present in cases where it has not been provided by the original authors. All values are given in the atomic units.

	α_0	α_2	α_4
Experimental or semiempirical			
Kumar and Thakkar [93]	11.08(11)	27.89(28)	95.62(96)
Orcutt and Cole [94]	11.0753(54)	—	—
Buckley <i>et al.</i> [95]	11.0774(10)	—	—
Gaiser and Fellmuth [21]	11.077183(27)	—	—
Theoretical			
Pawłowski <i>et al.</i> ^a [24]	11.102	27.996	94.846
Lupinetti <i>et al.</i> ^b [23]	11.07	—	—
This work	11.0775(19)	27.976(15)	95.02(11)

^aCC3 level of theory, sextuple-zeta GTO basis.

^bFinite-field CCSD(T) calculations.

for this quantities are not available. However, in the recent work by Egan *et al.* [96] the molar polarizability of argon was determined for a single laser frequency corresponding to the wavelength $\lambda_E = 632.9908(2)$ nm ($\omega_E = 0.071981$ in the atomic units, red He-Ne laser). After converting to the unit system used in the present work their result reads

$$\alpha_{\text{exp.}}(\omega_E) = 11.22431(17). \quad (37)$$

To compare this value with the results obtained in the present work, we use the expansion (6). For the static polarizability we adopt the value of Gaiser and Fellmuth [21], while the dispersion coefficients are taken from Table XI, and the value from Eq. (35) is used for the magnetic susceptibility. Note that the results of Egan *et al.* [96] are based on laser refractometry experiments, and hence the sum of static polarizability and magnetic susceptibility must be used for the frequency-independent component to allow for a meaningful comparison. The contributions of the sixth- and higher-order dispersion coefficients of the polarizability, as well as of the frequency dependence of the magnetic susceptibility, are negligible for the laser frequency under consideration. This leads to the following theoretical estimate:

$$\alpha_{\text{theory}}(\omega_E) = 11.22445(11). \quad (38)$$

As one can see, the theoretical and experimental results are in agreement. While the experimental value lies slightly outside the error bars of $\alpha_{\text{theory}}(\omega_E)$, they are mutually within their combined uncertainty. It is also worth pointing out that the relative uncertainty of the theoretical data, roughly 10 ppm, is of comparable magnitude as of the experiment. This comparison proves that by combining the static polarizability determined by Gaiser and Fellmuth [21] with the dispersion and magnetic susceptibility derived from theory, one obtains the most reliable data for the polarizability at a finite frequency available in the literature. According to our analysis from Sec. III the data reported in this work are accurate enough to apply the same procedure to other experimentally relevant laser wavelengths above roughly 450 nm. Therefore, we believe that the main results of this work, besides establishing a rigorous benchmark

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

	χ_0
Experimental	
Havens [97]	$-2.15(2) \times 10^{-4}$
Mann [98]	$-2.19(2) \times 10^{-4}$
Abonnenc [99]	-2.15×10^{-4}
Barter <i>et al.</i> [100]	$-2.16(2)^a \times 10^{-4}$
	$-2.16(15)^b \times 10^{-4}$
Theoretical	
Yoshizawa and Hada ^c [101]	-2.22×10^{-4}
Ruud <i>et al.</i> ^d [102], Jaszuński <i>et al.</i> ^d [103]	-2.31×10^{-4}
Reinsch and Meyer ^e [104]	-2.32×10^{-4}
Levy and Perdew ^f [105], Desclaux ^f [106]	-2.30×10^{-4}
This work	$-2.30(2) \times 10^{-4}$

^aOriginal error estimate from Ref. [100].

^bRevised error estimate proposed in Ref. [22].

^cMP2-DKH2($V + \mathbf{A}$) method, 23s16p16d16f10g GTO basis.

^dMCSCF calculations with 3s3p3d4s4p active orbitals.

^ePNO-CEPA calculations, 14s11p4d GTO basis.

^fNumerical relativistic Dirac-Fock.

for other theoretical methods, will find use in metrology and related fields.

Regarding the magnetic susceptibility, our final result reads

$$\chi_0 = -2.30(2) \times 10^{-4}, \quad (39)$$

where we have adopted a global 1% uncertainty estimate to account for the missing relativistic, quantum electrodynamics, etc., corrections. In Table XIII we compare this value with the experimental and theoretical data available in the literature. The most frequently cited experimental result is given in the work of Barter *et al.* [100], $-2.16(2) \times 10^{-4}$. However, it has to be pointed out that this result is not an independent measurement, but rather an arithmetic average of three previous experimental values [97–99] used to calibrate the apparatus. It has recently been suggested [22] that an issue with purity of argon gas in these three experiments could have been an additional source of error not accounted for in the uncertainty estimates. This led to the revised error estimate, $-2.16(15) \times 10^{-4}$, which we adopt in this work.

From Table XIII, we see that all theoretical calculations reported in the literature, with the exception of the paper of Yoshizawa and Hada [101], lead to a value $\chi_0 = -2.30 \times 10^{-4}$ or lower. By comparison, the experimental results cluster around $\chi_0 = -2.15 \times 10^{-4}$, a difference of roughly 6%–7% in relative terms. In analogy with the current state of data for helium and neon, we strongly recommend that the current theoretical result (39) is used as an interim reference value. In future works, we plan to calculate the magnetic susceptibility of all noble gases with significantly higher accuracy, including all relevant physical effects beyond Eq. (33). We believe that this will establish a solid reference value for most applications. However, in order to validate and double check the results, new independent measurements of the magnetic

susceptibility of noble gases with modern setups and rigorous error control would be extremely valuable. The same is true for verification of theoretical results by a set of independent calculations, preferably within a different framework.

X. CONCLUSIONS

In this work we have reported first-principles theoretical calculations of the dipole polarizability and magnetic susceptibility of the argon atom. Frequency dependence of the latter is neglected, while for the former it is taken into account by means of power series expansion in terms of the so-called dispersion coefficients (Cauchy coefficients). This approach is sufficient in terms of accuracy for experimentally relevant wavelengths below the first resonant frequency.

In the reported calculations, we include all nonnegligible physical effects including the relativistic, quantum electrodynamics, finite nuclear mass, and finite nuclear size corrections. The dominant nonrelativistic clamped-nuclei contribution is computed using a hierarchy of coupled-cluster methods combined with Gaussian basis sets up to nonuple-zeta quality optimized specifically for this task. Relativistic effects are determined using either the Breit-Pauli Hamiltonian or DKH effective approach, with excellent agreement between these two methods. Other minor corrections are calculated with help of the first-order perturbation theory.

The final results, with inclusion of all relevant physical effects, are $\alpha_0 = 11.0775(19)$ for the static polarizability and $\alpha_2 = 27.976(15)$ and $\alpha_4 = 95.02(11)$ for the second and fourth dispersion coefficients, respectively. We additionally determined the sixth-order dispersion coefficient, $\alpha_6 = 382.5$, but with a significantly larger uncertainty of about 10%. Our result obtained for the static polarizability agrees (within the estimated uncertainty) with the most recent experimental data [21] but is less accurate. The dispersion coefficients determined in this work appear to be the most accurate in the literature, improving by more than an order of magnitude upon previous estimates. By combining the experimentally determined value of the static polarizability with the dispersion coefficients from our calculations, the polarizability of argon can be calculated with accuracy of around 10 ppm for wavelengths above roughly 450 nm.

Additionally, in this work we calculate the static magnetic susceptibility of argon, which relates the refractive index of dilute argon gas with its pressure. While our result for this quantity is less accurate than in the case of the polarizability, it provides a starting point for more rigorous calculations in the future. In subsequent papers, we shall report relativistic calculations of the magnetic susceptibility of noble atoms.

The results reported in this work increase the current knowledge of several fundamental properties of atomic argon. This is important from the point of view of quantum metrology, especially for a new pressure standard based on thermophysical properties of gaseous argon.

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APPENDIX A: TWO-ELECTRON RELATIVISTIC CORRECTIONS TO THE DYNAMIC POLARIZABILITY

In the following, the exact wave function is denoted by the symbol $|\Psi_0\rangle$ and the electronic Hamiltonian of the system by H . The exact ground state energy is denoted by E_0 . The dynamic dipole polarizability at a real frequency ω (away from the resonant frequencies of the system) of the ground state is defined as

$$\alpha(\omega) = -\frac{1}{3}\langle\Psi_0|\mathbf{r}\frac{Q}{H-E_0+\omega}\mathbf{r}|\Psi_0\rangle + \text{g.H.c.}, \quad (\text{A1})$$

where $Q = 1 - |\Psi_0\rangle\langle\Psi_0|$ is the projection operator onto the subspace orthogonal to Ψ_0 and $\mathbf{r} = \sum_i \mathbf{r}_i$ is the electronic dipole operator. Note that Q commutes with the Hamiltonian of the system and any analytic function of H . The symbol ‘‘g.H.c.’’ denotes the generalized Hermitian conjugation, which amounts to exchanging wave functions in bra and ket, and reversing the sign of the frequency, i.e., $\omega \rightarrow -\omega$.

Let us define the first-order response function Ψ_1 by the formula

$$|\Psi_1\rangle = -\frac{Q}{H-E_0+\omega}\mathbf{r}|\Psi_0\rangle. \quad (\text{A2})$$

It can be obtained by solving the following equation:

$$(H-E_0+\omega)|\Psi_1\rangle + \mathbf{r}|\Psi_0\rangle = 0, \quad (\text{A3})$$

With help of the response function the polarizability can be rewritten as

$$\alpha(\omega) = \frac{1}{3}\langle\Psi_0|\mathbf{r}|\Psi_1\rangle + \text{g.H.c.} \quad (\text{A4})$$

Assume that the Hamiltonian is modified by adding a small perturbation, i.e., $H \rightarrow H + \lambda V$, where V is an operator and λ controls the strength of the perturbation. When the perturbation is switched on, all quantities defined above become dependent on λ , but we do not write this explicitly. We are interested in the derivative of the polarizability with respect to λ for $\lambda = 0$, i.e., $\partial_\lambda|_{\lambda=0}\alpha(\omega)$.

The response of the exact wave function to the perturbation, $|\Psi_V\rangle \equiv \partial_\lambda|_{\lambda=0}|\Psi_0\rangle$, is found by solving

$$(H-E_0)|\Psi_V\rangle + (V-\langle V\rangle)|\Psi_0\rangle = 0, \quad (\text{A5})$$

subject to the orthogonality condition $\langle\Psi_0|\Psi_V\rangle = 0$, where for any operator X , the symbol $\langle X\rangle$ stands for the expectation value $\langle\Psi_0|X|\Psi_0\rangle$. The derivative of the polarizability can be formally expressed as

$$\partial_\lambda|_{\lambda=0}\alpha(\omega) = \frac{1}{3}\langle\Psi_0|\mathbf{r}|\partial_\lambda|_{\lambda=0}\Psi_1\rangle + \frac{1}{3}\langle\Psi_V|\mathbf{r}|\Psi_1\rangle + \text{g.H.c.} \quad (\text{A6})$$

The above expression is somewhat overcomplicated as it involves the derivative of the response function with respect to λ . To eliminate this quantity we first note that according to Eq. (A3)

$$\langle \Psi_0 | \mathbf{r} | \partial_\lambda |_{\lambda=0} \Psi_1 \rangle = -\langle \Psi_1 | (H - E_0 + \omega) | \partial_\lambda |_{\lambda=0} \Psi_1 \rangle. \quad (\text{A7})$$

Next, by differentiation of Eq. (A3) with respect to λ one can show that

$$\begin{aligned} & -\langle \Psi_1 | (H - E_0 + \omega) | \partial_\lambda |_{\lambda=0} \Psi_1 \rangle \\ & = \langle \Psi_1 | (V - \langle V \rangle) | \Psi_1 \rangle + \langle \Psi_1 | \mathbf{r} | \Psi_V \rangle. \end{aligned} \quad (\text{A8})$$

We are left with the final formula

$$\partial_\lambda |_{\lambda=0} \alpha(\omega) = \frac{2}{3} \langle \Psi_1 | \mathbf{r} | \Psi_V \rangle + \frac{1}{3} \langle \Psi_1 | (V - \langle V \rangle) | \Psi_1 \rangle + \text{g.H.c.} \quad (\text{A9})$$

In this formulation we have adopted no approximations thus far. However, in actual calculations we use the Hartree-Fock determinant as $|\Psi_0\rangle$. By applying the Slater-Condon rules and noting that \mathbf{r} is a one-electron operator, one can show that the response function $|\Psi_1\rangle$ can be represented as a linear combination of singly excited determinants. In our calculations the operator V is a two-electron quantity [see Eq. (21)], and hence the perturbed wave function $|\Psi_V\rangle$ is expanded in terms of all singly and doubly excited determinants.

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