PHYSICAL REVIEW A **93**, 032515 (2016)

Theoretical determination of the polarizability dispersion and the refractive index of helium

Mariusz Puchalski,[1,2] Konrad Piszczatowski,[2] Jacek Komasa,[1] Bogumił Jeziorski,[3] and Krzysztof Szalewicz[2]
[1]*Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89B, 61-614 Poznań, Poland*
[2]*Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716, USA*
[3]*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

(Received 5 February 2016; published 23 March 2016)

The refractive index n of gaseous helium can be measured by optical interferometry so accurately that it can be used to establish a pressure standard which is expected to be superior to the current standard based on the height of a mercury column. The new standard requires knowledge of the dynamic polarizability of helium atom with accuracy significantly higher than obtainable in the best experiments, but possible to achieve computationally. Calculations of this quantity are presented at relativistic and quantum electrodynamics levels of theory including relativistic nuclear recoil effects. The uncertainties of the results are carefully estimated. Our recommended value of the dynamic polarizability at the He-Ne laser wavelength of 6329.908 Å, equal 1.39181197(14) a.u., has uncertainty at least two orders of magnitude smaller than that of recent measurements and is sufficiently accurate to establish a new pressure standard. Purely *ab initio* values of the refraction coefficient n are computed using our polarizability, literature values of magnetic susceptibility, and dielectric virial coefficients. It is shown that $n - 1$ can be predicted by theory as a function of density and temperature with uncertainty of 1 ppm for pressures up to 3 MPa.

DOI: 10.1103/PhysRevA.93.032515

I. INTRODUCTION

Future metrology standards are expected to be partly based on physical quantities computed from first principles since some observables, such as properties of the helium atom and properties of bulk helium resulting from interactions between helium atoms, can now be theoretically predicted with accuracy rivaling and sometimes exceeding the best experimental determinations. Examples include the ionization and excitation energies [1] as well as the static polarizability of the helium atom [2], or the virial coefficients describing departures of helium from the ideal gas behavior [3]. High accuracy theoretical values can also be used to calibrate experimental apparatuses. An example of a possible metrology standard utilizing theory input is the standard of temperature based on acoustic gas thermometry [4]. One of the metrology standards scheduled to be replaced in the near future is the current standard of pressure which employs a mercury column, i.e., the pressure p is obtained from the measurement of the column height h: $p = \rho g h$, where ρ is the density of mercury and g is the gravitational acceleration. Replacement of this standard is desirable for several reasons: the toxicity of mercury, the possibility of improving the accuracy [although the uncertainty of the current standard is a fairly high 2.6 parts per million (ppm)], and finally one would prefer a more portable equipment than the current 3 m tall instrument containing 250 kg of mercury [5]. It has been recently proposed [5,6] that a pressure standard can be based on optical interferometry measurements of the refractive index n of helium gas. For the ideal gas, $n = 1 + 2\pi(\alpha + \chi)\rho$, where α is the polarizability and χ is the diamagnetic susceptibility (also called magnetizability) of the helium atom, whereas ρ is the particle density (number of particles per unit volume). Combining this expression with the ideal gas equation $p = kT\rho$, where k is the Boltzmann constant and T is temperature, we obtain

$$p = (n - 1)\,\frac{kT}{2\pi(\alpha + \chi)}. \qquad (1)$$

The quantities n, α, and χ depend on the radiation wavelength λ, which is close to 6330 Å for the envisaged apparatus [7]. For a nonideal gas, one has to add small terms to the right-hand side of Eq. (1) containing the second and possibly third power of $n - 1$ and appropriate dielectric and density virial coefficients [8].

The quantity $n - 1$ can be measured directly via optical interferometry. The simplest apparatus consists of a Fabry-Perot cavity of length L. One first performs a measurement when the cavity is empty and the laser is tuned to achieve the resonance condition $2L = m\lambda = mc/f_0$, where m is an integer number and f_0 denotes frequency. Then the measurement is repeated with the cavity filled with helium. The wavelength required for the resonance remains the same, which means that the laser has now been tuned to another frequency $f_p = v/\lambda = c/(n\lambda)$, where c and v are the speeds of light in vacuum and in helium, respectively. Thus, n is determined by the frequency ratio. One can also interpret this experiment as measuring the apparent (optical) length of the cavity $L' = mc/(2f_p)$ equal to nL. This problem is equivalent to the measurement of the displacement $L' - L = (n - 1)L$, which needs to be determined to within at least 1 ppm to achieve a useful standard. Since $n - 1 \approx 3 \times 10^{-5}$ and $L \approx 0.15$ m, the distance $(n - 1)L = 4.5\ \mu$m has to be determined to 4.5 pm uncertainty, which is achievable using Fabry-Perot-based metrology [9]. Actually, the envisaged apparatus will use variable length cavities, one pressurized and three empty, constructed in such a way that the end of each cavity can be displaced by exactly the same amount. Measurements will be performed at the same time for the filled and empty cavities, one for the initial length of the cavities and another one for the extended cavities. This eliminates the problem of the change of length under pressure. Several factors contribute to uncertainties, but can be controlled so that this method does allow one to reach a better than 1 ppm accuracy in the determination of $n - 1$ [6].

The product kT in Eq. (1), also needed to determine pressure, is currently known with an uncertainty of 0.9 ppm near the triple point of water [10] and is the subject of active research in the metrology community which may further improve its accuracy.

The realization of the new standard requires also the knowledge of α and χ. The static value of α can be measured with an accuracy of about 9 ppm [8], clearly insufficient for the projected accuracy of the standard and the only option at the present time is to obtain this quantity from theory. Since χ is five orders of magnitude smaller than α, it does not need to be known very accurately and it can be computed using the nonrelativistic ground-state wave function from the expression $\chi = -e^2\langle r^2\rangle/3m_\mathrm{e}c^2$, where e and m_e are the electron charge and mass and $\langle r^2\rangle$ is the expectation value of the square of the electron-nucleus distance. The virial coefficients needed when Eq. (1) is extended beyond the ideal gas case are known accurately enough from theory [3,11]. The goal of the present work was to compute the dynamic polarizability of helium with an accuracy of 0.2 ppm which is sufficient for the initial implementation of the standard and for its improved future versions. We also analyze the values of the refractive index determined purely from theory as functions of ρ and T. Such values can be used to calibrate gas refractometers or to correct errors in interferometric length measurements [12].

An abridged account of our work has recently been published [13]. In the present paper we provide details of the derivations of the formulas used, discuss convergence of our calculations in basis set size, and demonstrate how the estimates of uncertainties were obtained. We also present results for the ^{3}He isotope to enable corrections of measurements for such impurity. We have computed some new contributions relative to Ref. [13], representing the QED correction to the polarizability dispersion at the order $1/c^3$. These contributions turned out to be larger than we have estimated in Ref. [13] and therefore our new value of $\alpha(\lambda)$ at $\lambda = 6329.908$ Å is slightly outside the uncertainty range given in Ref. [13]. Finally, we discuss in detail the expansion of n in powers of ρ, investigating several terms that are usually not considered but might give nonnegligible contributions at 0.1 ppm level.

Many calculations of the helium atom polarizability have been published, but none of them has achieved the required accuracy of 0.2 ppm. In order to discuss literature results we start with defining the various contributions to this quantity. Since the angular frequency ω of the laser radiation used in the envisaged pressure standard is about 10 times smaller than the first resonance of the helium atom, the frequency dependence of α can be efficiently calculated from the power series expansion:

$$\alpha(\omega) = \alpha_0 + \alpha_2\,\omega^2 + \alpha_4\,\omega^4 + \cdots\,, \tag{2}$$

where α_0 is the static dipole polarizability. We will later see that this series indeed converges so quickly that only a few lowest terms are needed even with our very high accuracy goal in mind. The coefficients α_k, $k > 0$, describing the dispersion of the dynamic polarizability, will be referred to as the polarizability dispersion coefficients, or dispersion coefficients for short. We shall use the atomic unit a_0^3, where a_0 is the Bohr radius $a_0 = \hbar^2/(m_e e^2)$, as the unit of polarizability, and the inverse of the atomic unit of time $t_0 = \hbar^3/(m_e e^4)$, as the unit of frequency. For comparison with experiments, it is convenient to convert the frequency to the wavelength, so that

$$\alpha(\lambda) = A_0 + A_2\,\lambda^{-2} + A_4\,\lambda^{-4} + \cdots\,, \tag{3}$$

where $A_k = (2\pi c)^k\,\alpha_k$, c being the velocity of light. When the wavelength is measured in Å, and time in atomic units t_0, then the conversion factor $2\pi c$ can be conveniently written as f Å$/t_0$, where f is a dimensionless constant which can be expressed in terms of the very accurately known Rydberg constant R_∞ [10], namely $f = 5 \times 10^7\,R_\infty^{-1}\,\mathrm{cm}^{-1}$. In this work we used the value $f = 455.633525275$.

For the light systems like helium, each α_k can be expanded in powers of the fine structure constant $e^2/(\hbar c)$,

$$\alpha_k = \alpha_k^{(0)} + \alpha_k^{(2)} + \alpha_k^{(3)} + \cdots\,, \tag{4}$$

$\alpha_k^{(l)}$ being proportional to the lth power of this constant. Since the fine structure constant is equal to c^{-1} expressed in atomic units, to avoid notational clash with polarizability, we will use c^{-1} to denote the fine structure constant and from now on c will be treated as a dimensionless parameter equal to 137.0359991 [10]. Thus, each $\alpha_k^{(l)}$ is proportional to c^{-l}. We shall refer to $\alpha_k^{(2)}$ as the relativistic corrections. The corrections $\alpha_k^{(3)}$, $\alpha_k^{(4)}$, etc., are due to radiative as well as higher-order relativistic effects predicted by quantum electrodynamics (QED), and will be referred to as the QED effects.

The nuclear mass dependence of the nonrelativistic polarizability $\alpha_k^{(0)}$ can be taken into account exactly, but for the relativistic and QED corrections one has to use an expansion in powers of the ratio of the electron mass m_e to the nuclear mass m_α, i.e., in powers of $1/M = m_\mathrm{e}/m_\alpha$. Apparently no derivation of these effects has been published, so it will be included in the present paper. Since $1/M$ is of the order of 10^{-4}, keeping the linear term is entirely sufficient and the relativistic corrections can be represented in the form

$$\alpha_k^{(l)} = \alpha_k^{(l0)} + \alpha_k^{(l1)}, \quad l \geqslant 2, \tag{5}$$

where $\alpha_k^{(l0)}$ are computed with the infinite nuclear mass and $\alpha_k^{(l1)}$ are corrections of the order of $1/(Mc^l)$, referred to as the recoil corrections. These recoil corrections are expected to be negligible except for the static ones $\alpha_0^{(21)}$ and $\alpha_0^{(31)}$ and, possibly, for the leading relativistic recoil correction $\alpha_2^{(21)}$ to the polarizability dispersion.

The most recent, high-accuracy theoretical determination of the static polarizability of helium has been reported in Ref. [2]. The nonrelativistic value $\alpha_0^{(0)} = 1.383809986\;a_0^3$ obtained in this reference agrees with an earlier result of Pachucki and Sapirstein [14] and is accurate up to nine digits, which is more than sufficient for our 0.2 ppm accuracy goal.

Calculations of the relativistic correction $\alpha_0^{(2)}$ have been reported in Refs. [2,14–17]. The earlier calculations of Refs. [15,16] are now known to be insufficiently accurate, whereas the values from Refs. [2,14,17] are mutually consistent and accurate up to 0.03 μa_0^3 ($\mu a_0^3 \equiv 10^{-6}\,a_0^3$). This uncertainty contributes only 0.02 ppm to the total error budget of α. One should point out, however, that the calculations of Refs. [2,14,17] neglected the recoil correction $\alpha_0^{(21)}$, i.e., the nuclear mass dependence of $\alpha_0^{(2)}$. This recoil effect has been estimated in Ref. [2] to amount to $-0.07(2)\mu a_0^3$ (the last one or two digits in parentheses will always denote the uncertainty estimate of the quoted result).

The QED correction $\alpha_0^{(30)}$ was calculated by Pachucki and Sapirstein [14] neglecting the electric-field dependence of the Bethe logarithm. The neglected effect, relatively small but hard to compute, was considered in Ref. [2] and found to contribute only 0.193(2) μa_0^3 to the static polarizability. This value, resulting from cancellations of much larger terms, represents only about 0.6% of the total QED correction $\alpha_0^{(30)}$. Since the computed effect, i.e., the second electric-field derivative of Bethe logarithm, was unexpectedly small (Pachucki and Sapirstein [14] estimated its contribution to $\alpha_0^{(30)}$ at 10% of $\alpha_0^{(30)}$) we decided to verify the result of Ref. [2] by an independent calculation [18]. The result of this calculation, equal to 0.183(1) μa_0^3, confirms that the considered effect is indeed very small. The change in the total polarizability resulting from using the improved value of the second electric field derivative of Bethe logarithm amounts to -0.010 μa_0^3 (or 0.007 ppm of the total value) and is practically negligible.

An accurate calculation of the next order QED correction $\alpha_0^{(40)}$ would be extremely complicated and was not reported in the literature. In Ref. [2] $\alpha_0^{(40)}$ was approximated by the electric-field derivative of the one-loop contribution to the Lamb shift [2,19]. The error of this approximation was assumed to be at 40% level [2]. Later, Pachucki found [1] that the error of an analogous approximation, applied to excitation energies of helium atom, is only about 5%. Therefore, in the present work we reduced the estimated error of $\alpha_0^{(40)}$ from 40% to 25%, which we believe is still conservative. This results in a contribution to the total uncertainty amounting to 0.14 μa_0^3 or 0.1 ppm, which dominates our uncertainty budget.

The dispersion coefficients α_k ($k = 2,4,6$) were calculated thus far only by Bhatia and Drachman (BD)—first at the nonrelativistic level [20] and then with the inclusion of the leading relativistic correction [16]. These authors did not provide any estimates of the uncertainty of the obtained results. Their relativistic corrections do depend on the nuclear mass but the recoil effect $\alpha_k^{(21)}$ was not correctly taken into account (also for $k = 0$) since the form of the Breit-Pauli Hamiltonian used by Bathia and Drachman did not have the proper (complete through the $1/M$ terms) dependence on the nuclear mass. In Ref. [16], Bhatia and Drachman reported also the values of the A_k coefficients from Eq. (3). These coefficients were, however, incorrectly converted from the reduced Rydberg units used in the calculations. The mass dependent factor $(1 + m_e/m_\alpha)^k$, appearing in the correct conversion formula, was erroneously replaced by its square $(1 + m_e/m_\alpha)^{2k}$.

The plan of this paper is as follows. In Sec. II we review theory of helium dynamic polarizability at the nonrelativistic level. In Sec. III we derive the relativistic corrections to this quantity, in particular their nuclear mass dependence (relativistic nuclear recoil effects). In Sec. IV we define an approximate QED correction to the polarizability dispersion computed in this work. The numerical details such as the functionals used to optimize wave functions and the choice of basis sets are discussed in Sec. V. Section VI A presents our results for the polarizability and in Sec. VI B we compare these results with experiment. Section VI C presents expressions defining the virial expansion for the refractive index, while in Sec. VI D we compare such first-principles expansion to experimental data.

II. NONRELATIVISTIC LEVEL OF THEORY

The frequency-dependent dipole polarizability $\alpha(\omega)$ of an atom in a quantum state ψ is defined by the expression

$$\alpha(\omega) = \langle\psi|z\,\mathcal{R}(\omega)z\psi\rangle + \langle\psi|z\,\mathcal{R}(-\omega)z\psi\rangle, \tag{6}$$

where z is the operator of the dipole coupling with the external electric field oscillating with the frequency ω, $\mathcal{R}(\omega)$ is the frequency dependent reduced resolvent of the Hamiltonian H (possibly relativistic),

$$\mathcal{R}(\omega) = Q\,(QH - E + \omega)^{-1}, \tag{7}$$

$Q = 1 - |\psi\rangle\langle\psi|$, and E is the energy of the state ψ. For the helium atom, $z = z_1 + z_2$, where z_i is the z coordinate of the vector pointing from the nucleus to the ith electron. The frequency-dependent resolvent satisfies the identity

$$\mathcal{R}(\omega) = \mathcal{R} - \omega\,\mathcal{R}\,\mathcal{R}(\omega), \tag{8}$$

where $\mathcal{R} = Q\,(QH - E)^{-1}$ is the static reduced resolvent of H. Iterating Eq. (8), one obtains the power series expansion

$$\mathcal{R}(\omega) = \sum_{k=0}^{\infty}(-\omega)^k\,\mathcal{R}^{k+1}, \tag{9}$$

which converges for ω smaller than the first resonance frequency. When this expansion is inserted into the definition (6), one obtains the following expression for the dispersion coefficients α_k:

$$\alpha_k = 2\,\langle\psi|z\,\mathcal{R}^{k+1}z|\psi\rangle, \quad k = 0, 2, 4, \ldots. \tag{10}$$

At the nonrelativistic level of theory the resolvent $\mathcal{R}$ in Eq. (10) is replaced by the reduced resolvent

$$\mathcal{R}_0 = Q_0\,(Q_0H_0 - E_0)^{-1}, \tag{11}$$

of the nonrelativistic Hamiltonian

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M}(\nabla_1 + \nabla_2)^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \tag{12}$$

and the wave function ψ by the eigenfunction ψ_0 of this Hamiltonian corresponding to the eigenvalue E_0. The projector Q_0 in Eq. (11) is defined as $Q_0 = 1 - |\psi_0\rangle\langle\psi_0|$. The resulting nonrelativistic expression for $\alpha_k^{(0)}$,

$$\alpha_k^{(0)} = 2\,\langle\psi_0|z\,\mathcal{R}_0^{k+1}z|\psi_0\rangle, \tag{13}$$

includes the finite nuclear mass effect exactly, i.e., to infinite order in $1/M$. In Eq. (12) and in all further equations we use atomic units unless otherwise stated.

The basis-set-independent formula (13) corresponds to the matrix definition of Eq. (5) from the paper of Bhatia and Drachman [16], based on pseudospectral expansion and given in the reduced Rydberg units. Atomic structure calculations are often performed in such units obtained by replacing the electron mass m_e with the reduced mass $\mu_\mathrm{e} = m_\mathrm{e}/(1 + m_\mathrm{e}/m_\alpha)$ in the definition of the reduced bohr or reduced hartree. However, when the mass-dependent term $-(\nabla_1 + \nabla_2)^2/(2M)$ in the nonrelativistic Hamiltonian is included, there is no advantage of using the reduced units. Moreover, when relativistic and QED corrections are considered, the use of the reduced units may easily lead to misunderstandings. Therefore, we never use the reduced units in the present work.

III. RELATIVISTIC CORRECTIONS

To account for the leading relativistic corrections of the order of $1/c^2$, we add to the nonrelativistic Hamiltonian of Eq. (12) the perturbation consisting of appropriate terms from the Breit-Pauli Hamiltonian [21,22]. For singlet states, this perturbation can be taken in the form

$$B = B_1 + B_2, \tag{14}$$

where

$$\begin{aligned} B_1 = &-\frac{1}{8c^2}\left(\nabla_1^4 + \nabla_2^4\right) + \frac{\pi}{c^2}[\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)] + \frac{\pi}{c^2}\delta(\boldsymbol{r}_{12}) \\ &+ \frac{1}{2c^2}\left[\nabla_1 r_{12}^{-1}\nabla_2 + (\nabla_1 \boldsymbol{r}_{12}) r_{12}^{-3}(\boldsymbol{r}_{12}\nabla_2)\right] \end{aligned} \tag{15}$$

is the infinite-nuclear-mass Breit-Pauli operator [21], and

$$\begin{aligned} B_2 = \frac{1}{Mc^2}\big[&\nabla_1 r_1^{-1}\nabla_1 + (\nabla_1 \boldsymbol{r}_1) r_1^{-3}(\boldsymbol{r}_1\nabla_1) + \nabla_1 r_1^{-1}\nabla_2 \\ &+ (\nabla_1 \boldsymbol{r}_1) r_1^{-3}(\boldsymbol{r}_1\nabla_2) + \nabla_2 r_2^{-1}\nabla_1 + (\nabla_2 \boldsymbol{r}_2) r_2^{-3}(\boldsymbol{r}_2\nabla_1) \\ &+ \nabla_2 r_2^{-1}\nabla_2 + (\nabla_2 \boldsymbol{r}_2) r_2^{-3}(\boldsymbol{r}_2\nabla_2)\big] \end{aligned} \tag{16}$$

is the electron-nucleus Breit (orbit-orbit) interaction of the order of $1/(Mc^2)$ [22]. Note that we wrote the last term in B_1 and the whole B_2 in a manifestly Hermitian form. Commuting the appropriate operators, one can show that these forms are equivalent to those used in Refs. [21,22]. The complete Breit-Pauli Hamiltonian contains also terms of the order of $1/(M^2c^2)$ and $1/(M^3c^2)$, but these are completely negligible for helium polarizability at the current accuracy goals and need not be considered in this work.

The total atomic Hamiltonian in the Breit-Pauli approximation can now be written as

$$H_{\mathrm{BP}} = H_0 + H_1 + B_1 + B_2, \tag{17}$$

where H_0 is the Hamiltonian of Eq. (12) with $M = \infty$, i.e., it is the infinite nuclear mass Hamiltonian, and

$$H_1 = -(\nabla_1 + \nabla_2)^2/2M. \tag{18}$$

From now on H_0 will always denote the infinite nuclear mass Hamiltonian. The infinite-nuclear-mass relativistic correction $\alpha_k^{(20)}$ is obtained from the Hamiltonian $H_0 + B_1$ by considering the contribution linear in B_1, while the recoil correction $\alpha_k^{(21)}$, of the order of $1/Mc^2$, is obtained from the full Hamiltonian of Eq. (17) by considering the contribution linear in B_2 and the contribution bilinear in H_1 and B_1.

A. Infinite nuclear mass

To obtain expressions for $\alpha_k^{(20)}$, we start from Eq. (10) with $\mathcal{R}$ interpreted as the reduced resolvent of the Hamiltonian $H = H_0 + B_1$ and ψ as an eigenfunction of this Hamiltonian, and subsequently extract terms linear in B_1. Expanding $\mathcal{R}$ and ψ redefined in such a way in powers B_1 (or $1/c^2$) one obtains

$$\psi = \psi_0 - \mathcal{R}_0 B_1 \psi_0 + O(1/c^4) \tag{19}$$

and

$$\mathcal{R} = \mathcal{R}_0 - \mathcal{R}_0 \overline{B}_1 \mathcal{R}_0 + \mathcal{R}_0^2 B_1 P_0 + P_0 B_1 \mathcal{R}_0^2 + O(1/c^4), \tag{20}$$

where ψ_0 is the ground-state wave function of H_0, $\mathcal{R}_0$ is the reduced resolvent of H_0, $\overline{B}_1 = B_1 - \langle\psi_0|B_1\psi_0\rangle$, and $P_0 = |\psi_0\rangle\langle\psi_0|$.

When Eqs. (19) and (20) are inserted into Eq. (10), the last two terms in Eq. (20) do not contribute and after extracting the terms linear in B_1 one obtains

$$\alpha_0^{(20)} = -4\,\langle\psi_0|B_1\mathcal{R}_0 z \mathcal{R}_0 z\psi_0\rangle - 2\,\langle\psi_0|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0 z\psi_0\rangle, \tag{21}$$

$$\begin{aligned} \alpha_2^{(20)} = &-4\big\langle\psi_0\big|B_1\mathcal{R}_0 z\mathcal{R}_0^3 z\psi_0\big\rangle - 4\big\langle\psi_0\big|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0^3 z\psi_0\big\rangle \\ &-2\big\langle\psi_0\big|z\mathcal{R}_0^2\overline{B}_1\mathcal{R}_0^2 z\psi_0\big\rangle, \end{aligned} \tag{22}$$

$$\begin{aligned} \alpha_4^{(20)} = &-4\big\langle\psi_0\big|B_1\mathcal{R}_0 z\mathcal{R}_0^5 z\psi_0\big\rangle - 4\big\langle\psi_0\big|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0^5 z\psi_0\big\rangle \\ &-4\big\langle\psi_0\big|z\mathcal{R}_0^2\overline{B}_1\mathcal{R}_0^4 z\psi_0\big\rangle - 2\big\langle\psi_0\big|z\mathcal{R}_0^3\overline{B}_1\mathcal{R}_0^3 z\psi_0\big\rangle, \end{aligned} \tag{23}$$

$$\begin{aligned} \alpha_6^{(20)} = &-4\big\langle\psi_0\big|B_1\mathcal{R}_0 z\mathcal{R}_0^7 z\psi_0\big\rangle - 4\big\langle\psi_0\big|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0^7 z\psi_0\big\rangle \\ &-4\big\langle\psi_0\big|z\mathcal{R}_0^2\overline{B}_1\mathcal{R}_0^6 z\psi_0\big\rangle - 4\big\langle\psi_0\big|z\mathcal{R}_0^3\overline{B}_1\mathcal{R}_0^5 z\psi_0\big\rangle \\ &-2\big\langle\psi_0\big|z\mathcal{R}_0^4\overline{B}_1\mathcal{R}_0^4 z\psi_0\big\rangle, \end{aligned} \tag{24}$$

where we used the fact that all integrals are real. Relativistic corrections $\alpha_k^{(20)}$, $k \geqslant 8$, give a negligible contribution for the relevant frequencies.

B. Recoil corrections

The relativistic recoil corrections can be calculated directly as the $1/(Mc^2)$ term in the perturbation expansion based on the Hamiltonian partitioning of Eq. (17). Since the perturbation operators H_1, B_1, and B_2 are proportional to $1/M$, $1/c^2$, and $1/(Mc^2)$, respectively, each recoil correction $\alpha_k^{(21)}$ is the sum of the part linear in B_2, denoted by $\alpha_k^{(21)}(B_2)$, and of the bilinear term $\alpha_k^{(21)}(H_1B_1)$,

$$\alpha_k^{(21)} = \alpha_k^{(21)}(B_2) + \alpha_k^{(21)}(H_1B_1). \tag{25}$$

The linear part $\alpha_0^{(21)}(B_2)$ can be derived in the same way as the term $\alpha_0^{(20)}$. We interpret Eq. (10) as based on the Hamiltonian $H = H_0 + B_2$, expand $\mathcal{R}$ and ψ in powers of B_2, and extract terms linear in B_2. In this way we obtain

$$\alpha_0^{(21)}(B_2) = -4\,\langle\psi_0|B_2\mathcal{R}_0 z\mathcal{R}_0 z\psi_0\rangle - 2\,\langle\psi_0|z\mathcal{R}_0\overline{B}_2\mathcal{R}_0 z\psi_0\rangle. \tag{26}$$

To obtain the bilinear part $\alpha_0^{(21)}(H_1B_1)$, we proceed in a similar way. We interpret Eq. (10) as based on the Hamiltonian $H = H_0 + B_1 + H_1$, expand $\mathcal{R}$ and ψ in powers of B_1 and H_1, and extract terms bilinear in B_1 and H_1. It is convenient to do this in two stages. First we expand in powers of B_1 keeping $H_0 + H_1$ together. One obtains then the expression of the form of Eq. (21) with $\mathcal{R}_0$ and ψ_0 interpreted as the resolvent and wave function of the Hamiltonian $H_0 + H_1$. Expanding this formula in powers of H_1 and retaining the linear part in H_1 one obtains the desired expression for $\alpha_0^{(21)}(H_1 B_1)$:

$$\begin{aligned}\alpha_0^{(21)}(H_1B_1) = {}& 4\langle\psi_0|z\mathcal{R}_0 z\mathcal{R}_0\overline{H}_1\mathcal{R}_0 B_1\psi_0\rangle + 4\,\langle\psi_0|z\mathcal{R}_0 z\mathcal{R}_0\overline{B}_1\mathcal{R}_0 H_1\psi_0\rangle + 4\langle\psi_0|z\mathcal{R}_0\overline{H}_1\mathcal{R}_0 z\mathcal{R}_0 B_1\psi_0\rangle\\ &+ 4\,\langle\psi_0|z\mathcal{R}_0\overline{B}_1\mathcal{R}_0 z\mathcal{R}_0 H_1\psi_0\rangle + 4\langle\psi_0|z\mathcal{R}_0\overline{H}_1\mathcal{R}_0\overline{B}_1\mathcal{R}_0 z\psi_0\rangle + 4\,\langle\psi_0|H_1\mathcal{R}_0 z\mathcal{R}_0 z\mathcal{R}_0 B_1\psi_0\rangle\\ &- 4\langle\psi_0|z\mathcal{R}_0 z\psi_0\rangle\big\langle\psi_0\big|H_1\mathcal{R}_0^2 B_1\psi_0\big\rangle - 4\,\big\langle\psi_0\big|z\mathcal{R}_0^2 z\psi_0\big\rangle\langle\psi_0|H_1\mathcal{R}_0 B_1\psi_0\rangle,\end{aligned} \tag{27}$$

where $\overline{H}_1 = H_1 - \langle\psi_0|H_1\psi_0\rangle$.

The sum of Eqs. (26) and (27) represent the rigorous definition of the recoil correction $\alpha_0^{(21)}$. However, since H_1 is small, $\alpha_0^{(21)}(H_1 B_1)$ can be obtained with sufficient accuracy from the finite difference expression

$$\alpha_0^{(21)}(H_1B_1) \approx \alpha_0^{(20)}(H_0 \to H) - \alpha_0^{(20)}, \tag{28}$$

where $\alpha_0^{(20)}(H_0 \to H)$ denotes the expression of Eq. (21) in which the resolvent and wave function are computed with the full nonrelativistic Hamiltonian $H = H_0 + H_1$. The difference between this approximate expression and the exact expression of Eq. (27) is of order of $1/(M^2c^2)$ and is negligible for our purposes. In practice we computed $\alpha_0^{(21)}(H_1B_1)$ from Eq. (28).

We also considered the relativistic recoil correction to the polarizability dispersion $\alpha_2^{(21)}$. Its linear part $\alpha_2^{(21)}(B_2)$ can be obtained from the formula of Eq. (22) with B_1 replaced by B_2. Instead of the exact expression for the bilinear part $\alpha_2^{(21)}(H_1B_1)$, which is quite complicated, it is more convenient to use the finite difference formula similar to Eq. (28),

$$\alpha_2^{(21)}(H_1B_1) \approx \alpha_2^{(20)}(H_0 \to H) - \alpha_2^{(20)}, \tag{29}$$

where now $\alpha_2^{(20)}(H_0 \to H)$ denotes the expression of Eq. (22) in which the resolvent and wave function are computed with the full nonrelativistic Hamiltonian $H = H_0 + H_1$. The right-hand side of Eq. (29) is of infinite order in H_1 and differs from $\alpha_2^{(21)}(H_1B_1)$ by negligible terms of the order of $1/(M^2c^2)$. The correction $\alpha_2^{(21)}$ turned out to be so small that recoil corrections to higher dispersion coefficients can be assumed to be negligible.

IV. QED AND FINITE NUCLEAR SIZE CORRECTIONS

An accurate calculation of the QED contribution $\alpha_2^{(30)}$ to the dispersion coefficient α_2 is very complicated and is beyond the scope of this work. An estimate of the size of this correction can be obtained, however, using the approximation employed by Pachucki and Sapirstein [14] in their calculations of the QED correction to the polarizability. In this approximation, the electric-field dependence of the Bethe logarithm is neglected and the QED correction to the polarizability is calculated in the same way as the leading relativistic correction of the order of $1/c^2$, except that the $1/c^2$ components of the Breit-Pauli operator are replaced by the effective QED operators of the order of $1/c^3$. These operators are [14]

$$C_1 = \frac{1}{c^3}\frac{8}{3}\left(\frac{19}{30} - 2\ln\frac{1}{c} - \ln k_0\right)[\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)], \tag{30}$$

$$C_2 = \frac{1}{c^3}\left(\frac{164}{15} + \frac{14}{3}\ln\frac{1}{c}\right)\delta(\boldsymbol{r}_{12}), \tag{31}$$

$$C_3 = -\frac{1}{c^3}\frac{7}{6\pi}P\big(r_{12}^{-3}\big), \tag{32}$$

where $\ln k_0$ is the atomic (electric-field independent) Bethe logarithm and $P(r_{12}^{-3})$ is the operator distribution defined via its matrix elements as [23,24]

$$\begin{aligned}\langle\phi_1|P\big(r_{12}^{-3}\big)\phi_2\rangle = \lim_{a\to 0}&\langle\phi_1|[\theta(r_{12}-a)r_{12}^{-3} + 4\pi(\gamma + \ln a)\\ &\times \delta(\boldsymbol{r}_{12})]\phi_2\rangle,\end{aligned} \tag{33}$$

with γ denoting the Euler-Mascheroni constant and $\theta(x)$ the Heaviside step function.

When the operator B_1 in Eqs. (21) and (22)–(24) is replaced by the sum of the operators C_1, C_2, and C_3 one obtains the expressions for approximate values of the corrections $\alpha_0^{(30)}$ and $\alpha_k^{(30)}$, $k > 2$. Pachucki and Sapirstein assumed [14] that the error of their approximation applied to $\alpha_0^{(30)}$ is 10%. We now know [2,18] that this error is actually much smaller and amounts to only about 0.6%. We conservatively assume that the error of the Pachucki-Sapirstein approximation applied to $\alpha_k^{(30)}$, $k = 2,4,6$, is also less than 10%. In view of the smallness of this QED effect, this level of accuracy is more than sufficient for the purpose of the present work.

Although the static relativistic recoil correction $\alpha_0^{(21)}$ is already quite small (it enters at the 0.1 ppm level) we also considered the static QED recoil correction $\alpha_0^{(31)}$, since the smallness of the former results from some cancellations of large contributions, see Sec. VI A. This correction can be computed by differentiating the corresponding energy expression [25,26] with respect to the electric field. We performed calculations of approximate value of $\alpha_0^{(31)}$ neglecting the electric field dependence of Bethe logarithm and found it to be about 10 times smaller than the effect of relativistic recoil $\alpha_0^{(21)}$. We have not added this preliminary value of $\alpha_0^{(31)}$ to our recommended value of the static polarizability but included it in the total error budget of our calculation.

We have also computed the correction for finite nuclear size. This is a nonrelativistic effect but it can be easily obtained as a byproduct of the relativistic or QED calculation. This correction is defined as the second electric-field derivative of the following expression for the corresponding energy shift [27]:

$$\delta E_{\text{f.s.}} = \frac{4\pi}{3}\, r_\alpha^2\, \langle\psi|\, \delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)\, |\psi\rangle, \tag{34}$$

where $r_\alpha = 1.676$ fm [28] is the nuclear charge radius of ^{4}He.

V. COMPUTATIONAL DETAILS

To evaluate the expressions for the nonrelativistic polarizabilities $\alpha_k^{(0)}$ and the relativistic corrections $\alpha_k^{(2i)}$, $i = 0,1$, we need an accurate representation of the helium ground-state wave functions ψ_0 and ψ of H_0 and $H_0 + H_1$, respectively. These functions were obtained by minimizing the conventional Rayleigh-Ritz functional for the Hamiltonians H_0 and H, respectively. We also need several auxiliary functions. The functions $\phi_0^{(k)} = \mathcal{R}_0^k z \psi_0$, $k = 1,\ldots,7$, were obtained recursively by minimizing the following Hylleraas functionals:

$$J_0^{(k)}[\widetilde{\phi}] = \langle\widetilde{\phi}|H_0 - E_0|\widetilde{\phi}\rangle - 2\big\langle\widetilde{\phi}\big|\phi_0^{(k-1)}\big\rangle, \tag{35}$$

whereas the functions $\xi_0^{(k)} = \mathcal{R}_0 z \phi_0^{(k)}$, $k = 1,\ldots,7$, were obtained using the functionals

$$K_0^{(k)}[\widetilde{\xi}] = \langle\widetilde{\xi}|H_0 - E_0 + P_0|\widetilde{\xi}\rangle - 2\big\langle\widetilde{\xi}\big|Q_0 z \phi_0^{(k)}\big\rangle. \tag{36}$$

The analogous functions $\phi^{(k)} = \mathcal{R}^k z \psi$ and $\xi^{(k)} = \mathcal{R} z \phi^{(k)}$, $k = 1,\ldots,7$, defined with the full nonrelativistic Hamiltonian $H = H_0 + H_1$, were computed using the functionals obtained from Eqs. (35) and (36), respectively, by dropping the subscripts 0.

The trial functions used in all minimization processes were expanded as linear combinations of the so-called Slater geminals

$$(1 + \mathcal{P}_{12})\, Y(\boldsymbol{r}_1,\boldsymbol{r}_2) \sum_{i=1}^{N} c_i\, \exp(-\alpha_i\, r_1 - \beta_i\, r_2 - \gamma_i\, r_{12}), \tag{37}$$

where $\mathcal{P}_{12}$ is the electron permutation operator while $Y(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is equal to z_1 in the calculations of $\phi_0^{(k)}$ or $\phi^{(k)}$ and to 1 in the calculations of $\xi_0^{(k)}$ or $\xi^{(k)}$. The functions $\xi_0^{(k)}$ contain both S- and D-symmetry components since $\phi_0^{(k)}$ have P symmetry. However, the D-wave component does not contribute to the matrix elements needed to evaluate $\alpha_k^{(l0)}$ or $\alpha_k^{(l1)}$. Therefore, we expanded the trial functions $\widetilde{\xi}$ in a basis of S symmetry only. We included the projector P_0 in the quadratic term of Eq. (36) to make the optimized functions orthogonal to ψ_0. This projector would impose exact orthogonality if $\widetilde{\xi}$ and ψ_0 were expanded in the same basis. In practice, orthogonality violation is so small that there is no need to perform projection after optimization. We have chosen the basis of Slater geminals as it leads to higher accuracy and shorter expansions, when compared to the Gaussian-geminal basis [29], and simpler integral expressions [30–32] when compared to the Hylleraas basis set.

The linear coefficients c_i were obtained using standard linear algebra algorithms, while to determine the nonlinear parameters we employed two strategies: the full optimization (FO), when all nonlinear parameters defining the basis set are fully optimized, and the stochastic optimization (SO), when the nonlinear parameters for basis function are chosen in a quasistochastic way.

In each step of the FO procedure, parameters of one basis function were optimized using the Powell method [33], while other functions were kept fixed. After all functions were optimized in this way, the process was repeated and many passes over all functions were done until the convergence was reached. Using this procedure we obtained a 600-term basis set of S symmetry resulting in the ground-state energy $E_0 = -2.903724377034119574$ for the infinite nuclear mass Hamiltonian, differing only by 2.4×10^{-17} from the most accurate literature value [34]. The wave function ψ_0 corresponding to this energy, and the nuclear mass dependent function ψ expanded in the same basis set, were used in full optimizations of all auxiliary functions and in calculations of the relativistic corrections. The basis sets for auxiliary functions optimized with infinite nuclear mass were used without further reoptimizations in calculations with finite nuclear masses, except as noted later.

The SO approach [35–38] generates nonlinear parameters pseudorandomly from intervals whose positions and sizes are optimized. In the simplest implementation, the parameters α_i, β_i, γ_i of each basis function are pseudorandomly generated with a uniform distribution from a three-dimensional box $[A_1,A_2] \times [B_1,B_2] \times [C_1,C_2]$. The parameters were constrained by $\alpha_i + \beta_i > \epsilon$, $\beta_i + \gamma_i > \epsilon$, $\gamma_i + \alpha_i > \epsilon$, with $\varepsilon = \sqrt{2\,I}$, where I is the ionization potential of helium. This ensures that the wave function for $r_1,r_2 \to \infty$ falls off sufficiently rapidly to represent a bound state. If a randomly generated geminal fails to fulfill these requirements, it is rejected and another one is generated until the conditions are met. One can achieve a considerably higher accuracy by using two boxes with 50% of parameters in each box. While the 12 parameters characterizing these boxes, i.e., A_i^j, B_i^j, C_i^j, $i,j = 1,2$, were optimized without any restrictions (negative values of A_1^j, B_1^j, C_1^j were allowed), the two boxes optimized to ranges modeling the short-range and medium-range asymptotics of the helium wave functions. Unlike the case of calculations involving the FO procedure, the ground-state functions used in the SO optimizations and in the calculations of polarizability components were expanded in basis sets of varying size, with the basis sets, used for auxiliary functions, always 50% larger than the basis sets used for the ground-state functions. The best ψ_0 function obtained by the stochastic approach with 800 basis functions gives the energy $E_0 = -2.90372437703411927$ differing from that of Ref. [34] by about 3×10^{-16}.

While the optimizations of the basis sets for the auxiliary functions in the FO method were performed separately for each such function, in the SO approach we optimized the nonlinear parameters using the functionals of Eqs. (35) and (36) only for $\phi_0^{(1)} = \mathcal{R}_0 z \psi_0$ and $\xi_0^{(1)} = \mathcal{R}_0 z \phi_0^{(1)}$. The same nonlinear parameters were then used in the evaluation of all functions with $k > 1$. After $\phi_0^{(1)}$ was optimized, the Hamiltonian H_0 was diagonalized in the basis set obtained in this optimization. The resulting eigenvectors $\widetilde{\psi}_i$ (pseudostates) and energies $\widetilde{E}_i$ were used to construct powers of the resolvent

$$\widetilde{\mathcal{R}}_0^k \equiv \sum_{i\neq 0} \frac{|\widetilde{\psi}_i\rangle\langle\widetilde{\psi}_i|}{(\widetilde{E}_i - E_0)^k}, \tag{38}$$

where E_0 is still the eigenvalue of ψ_0 obtained from Rayleigh-Ritz minimization. The functions $\phi_0^{(k)}$ for $k > 1$ were obtained directly from $\phi_0^{(k)} = \widetilde{\mathcal{R}}_0^{k-1}\,\phi_0^{(1)}$ and the resolvent power of Eq. (38), rather than from Eq. (35). We proceeded similarly in the case of functions $\xi_0^{(k)}$, i.e., the basis expanding $\xi_0^{(1)}$ was nonlinearly optimized using Eq. (36) and then $\xi_0^{(k)}$ were obtained directly from $\xi_0^{(k)} = \widetilde{\mathcal{R}}_0\, z\, \widetilde{\mathcal{R}}_0^{k-1}\phi_0^{(1)}$.

The full optimization allowed us to use smaller basis sets than the stochastic one, however it was more time consuming. All nonlinear optimizations were performed with infinite nuclear mass, except for the FO calculations with 600 basis functions, when the finite mass was used. To eliminate possibilities of numerical errors, the FO and SO programs were written completely independently by different authors of this work. Also the integral and linear algebra subroutines adopted in the SO and FO programs were different.

For the ratio of alpha particle and electron masses, we assumed the recent CODATA value [10]: $M = m_\alpha/m_e = 7294.2995361$.

VI. NUMERICAL RESULTS AND DISCUSSION

A. Polarizability

Table I shows the basis set convergence of the nonrelativistic polarizability coefficients $\alpha_k^{(0)}$ for $k = 0,2,4,6$, using basis sets up to $N = 600$ (1200) for the FO (SO) approach. As expected, the full optimization gives a faster convergence. This happens despite the fact that the auxiliary basis sets were 50% larger for the stochastic optimizations. Note also that the two approaches used a different strategy concerning the ground-state functions used in the optimization: always of size 600 in FO, but variable and equal to 2/3 of the size of the auxiliary basis in SO. In the iterative process, the size of all auxiliary basis sets was the same for all functions $\phi_0^{(k)}$ and $\xi_0^{(k)}$, $k = 1,2,\ldots,7$. The largest basis sets in both approaches give about the same number of convergent digits, ranging from 13 for $k = 0$ to about 10–11 for $k = 6$. The recommended values of $\alpha_k^{(0)}$ are listed in Table II together with their uncertainties taken as half of the difference between the results in the two largest SO basis sets (we will use the same method for all other uncertainties resulting from basis set incompleteness in the remainder of this paper). The comparison with the FO results shows that these estimates are very conservative and the true uncertainties are likely an order of magnitude smaller.

TABLE I. Basis set convergence of the nonrelativistic polarizability dispersion coefficients $\alpha_k^{(0)}$ for ^{4}He (in atomic units $a_0^3 t_0^k$). The basis sets were optimized with infinite nuclear mass, except as noted.

	N[a,b]	FO	SO
$\alpha_0^{(0)}$	200	1.383809986297	1.383809985180
	400	1.383809986406	1.383809986360
	600	1.383809986408	1.383809986406
	800		1.383809986408
$\alpha_2^{(0)}$	200	1.543210818712	1.543210804681
	400	1.543210818742	1.543210818331
	600	1.543210818814	1.543210818782
	800		1.543210818816
$\alpha_4^{(0)}$	200	2.042655014893	2.042654953070
	400	2.042655014971	2.042655012581
	600	2.042655014972	2.042655014745
	800		2.042655014989
$\alpha_6^{(0)}$	200	2.930406844 35	2.930406814988
	400	2.930406997915	2.930406988863
	600	2.930406997989[c]	2.930406996551
	800		2.930406997993

[a] In the FO calculations N-term basis set was used for auxiliary functions. For ψ_0 a 600-term basis was always used.

[b] In the SO calculations N-term basis was used for ψ_0. For auxiliary functions $3N/2$ terms were used.

[c] The nonlinear optimization with the ^{4}He nuclear mass.The optimization with the infinite nuclear mass gives 2.930406997918.

TABLE II. Comparison of the recommended values of the nonrelativistic polarizability dispersion coefficients $\alpha_k^{(0)}$ for ^{4}He (in $a_0^3 t_0^k$) with the results of Bhatia and Drachman [20,39] converted from the reduced Rydberg to atomic units. The numbers in parentheses denote uncertainties at the last digit estimated as described in the text.

	BD	Present
$\alpha_0^{(0)}$	1.383809991[a]	1.383809986408(1)
$\alpha_2^{(0)}$	1.543210859[a]	1.54321081882(1)
$\alpha_4^{(0)}$	2.04257748[b]	2.0426550150(1)
$\alpha_6^{(0)}$	2.9304058[b]	2.9304069980(7)

[a] Reference [39].

[b] Reference [20].

In Table II our recommended values of the nonrelativistic polarizability dispersion coefficients $\alpha_k^{(0)}$ are compared with the data obtained by Bhatia and Drachman [20,39] with Hylleraas bases of up to 525 functions [39]. These authors did not provide any estimations of uncertainties of their results. Our values, being significantly more accurate, confirm generally good, seven to nine significant digits accuracy of the calculations of Bhatia and Drachman. An exception is their value of $\alpha_4^{(0)}$, which is accurate only to about four digits. Using the SO procedure, we also calculated the next four coefficients: $\alpha_8^{(0)} = 4.39500532(1)$, $\alpha_{10}^{(0)} = 6.7725956(1)$, $\alpha_{12}^{(0)} = 10.622083(1)$, and $\alpha_{14}^{(0)} = 16.86118(1)$ a.u., where the numbers in parentheses are estimated uncertainties at the last digit. These coefficients will not be needed for the experiments that motivated the present work, but may be of interest for other applications.

Table III presents the basis set convergence of the relativistic corrections $\alpha_k^{(20)}$ for $k = 0,2,4,6$. As can be seen, the convergence is much slower than in the case of the nonrelativistic calculations. This is due to the fact that the relativistic corrections contain the operator B_1 and the functionals used by us to optimize wave functions do not. Therefore, the functionals are not sensitive to wave function values in some areas of the configuration space relevant for $\alpha_k^{(20)}$. Since the relativistic operators are highly singular, we cannot use them to optimize auxiliary functions. Table III shows that the SO procedure leads now to a faster convergence than FO. This can be explained by the fact that the randomly chosen exponents cover space more uniformly and are less

TABLE III. Basis set convergence of the relativistic corrections $\alpha_k^{(20)}$ to the polarizability of helium in units of $10^{-6} \times a_0^3 t_0^k$. All results correspond to infinite nuclear mass.

	N[a]	FO	SO
$\alpha_0^{(20)}$	200	−80.36522	−80.36069
	400	−80.35895	−80.35988
	600	−80.35992	−80.35990
	800		−80.35991
$\alpha_2^{(20)}$	200	−33.05372	−33.06922
	400	−33.06159	−33.06601
	600	−33.06535	−33.06572
	800		−33.06576
$\alpha_4^{(20)}$	200	5.16633	5.04608
	400	5.02018	5.04504
	600	5.05884	5.05114
	800		5.05105
$\alpha_6^{(20)}$	200	63.04596	62.85627
	400	62.86418	62.79715
	600	62.82590	62.85095
	800		62.85003

[a] See Table I for details on sizes of basis sets.

biased towards an accurate representation of the nonrelativistic auxiliary functions than the FO exponents. Consequently, SO bases can also be effective in describing those parts of the wave function that are important for the evaluation of the expectation values of relativistic operators. One should, however, also take into account that in each row of Table III the SO auxiliary bases were 50% larger than the FO ones. Thus, we used the SO results to propose the recommended values of the relativistic corrections and to estimate the corresponding uncertainties. Nevertheless, the agreement between FO and SO results is still very good, to about six, five, three, and three digits for $k = 0,2,4,6$, respectively, more than sufficient for the accuracy goals of the present work. Also, for $k = 0$ the FO result is within the estimated uncertainty of the SO result.

In Table IV our recommended values of the terms $\alpha_k^{(20)}$ are compared with substantially less accurate results of Bhatia and Drachman [16] published without error bars. The BD values agree with ours to two, two, and one digit for $k = 0,2,4$, respectively. Several accurate calculations of the relativistic corrections to the static polarizability have been recently reported in the literature [2,14,17]. The results of these calculations, amounting to $-80.34(2)$ [17], $-80.358(27)$ [14], and $-80.35(2)$ [2], are consistent with our more accurate value $-80.35991(1)$. Units of $10^{-6} \times a_0^3 t_0^k$ (or $\mu a_0^3 t_0^k$) are used here and in subsequent discussions when we refer to relativistic corrections.

TABLE IV. Comparison of our recommended values of the relativistic corrections $\alpha_k^{(2i)}$ to the polarizability of ^{4}He with the results of Bhatia and Drachman [16] converted from the reduced Rydberg to the atomic units. All values in units of $10^{-6} \times a_0^3 t_0^k$.

	BD	Present
$\alpha_0^{(20)}$	−80.062	−80.35991(1)
$\alpha_0^{(21)}$		−0.0935(1)[a]
$\alpha_2^{(20)}$	−32.629	−33.06576(2)
$\alpha_2^{(21)}$		−0.144(1)[a]
$\alpha_4^{(20)}$	4.814	5.05105(5)
$\alpha_6^{(20)}$		62.8500(5)

[a] Uncertainties are due to approximations made in Eqs. (28) and (29).

Table IV also presents the relativistic recoil corrections $\alpha_0^{(21)}$ and $\alpha_2^{(21)}$. The recommended value of the static correction $\alpha_0^{(21)} = -0.0935\ \mu a_0^3$ results from some cancellation of its components $\alpha_0^{(21)}(H_1 B_1)$ and $\alpha_0^{(21)}(B_2)$, equal to 0.1559 and -0.2494, respectively. The recoil correction $\alpha_2^{(21)}$ to the leading dispersion coefficient is equal to $-0.144\ \mu a_0^3 t_0^2$. Also in this case, we observe a cancellation of the components $\alpha_2^{(21)}(B_2) = -0.463$ and $\alpha_2^{(21)}(H_1 B_1) = 0.319$. Since for the frequency of interest the correction $\alpha_2^{(21)}$ is multiplied by $\omega^2 \approx 0.005\ t_0^{-2}$, its contribution to $\alpha(\omega)$ is negligible at the current accuracy goal.

It should be pointed out that the relativistic corrections computed by Bhatia and Drachman [16] depend on the nuclear mass and, strictly speaking, should not be compared with our, nuclear-mass-independent values of $\alpha_k^{(20)}$, $k = 0,2,4$. This mass dependence results from the fact that BD incorrectly assumed that the individual terms in the Breit-Pauli Hamiltonian are proportional to (inverse) powers of the reduced electron mass rather than the real mass. Therefore, although the nuclear-mass-dependent component of their relativistic corrections is of the order of $1/(Mc^2)$, it differs from the $\alpha_k^{(21)}(H_1 B_1)$ term of the true recoil correction. Additionally, Bhatia and Drachman completely neglected the contributions of the B_2 operator $\alpha_k^{(21)}(B_2)$, which were shown by us to be as important as the $\alpha_k^{(21)}(H_1 B_1)$ contributions. Thus, their relativistic corrections cannot be viewed as approximations to $\alpha_k^{(20)} + \alpha_k^{(21)}$. However, since the effects of the order of $1/(Mc^2)$ are very small, the differences between our relativistic corrections and those of BD are mainly due to the differences in the basis sets used in the calculations rather than to the treatment of the nuclear mass dependence.

Table V presents the nonrelativistic coefficients $\alpha_k^{(0)}$ computed for ^{3}He. The relativistic corrections $\alpha_k^{(20)}$ for ^{3}He are the same as for ^{4}He, while the recoil corrections $\alpha_k^{(21)}$ are obtained from $\alpha_k^{(20)}$ by scaling with the mass ratio $m(^4\mathrm{He})/m(^3\mathrm{He})$. These results are needed for the pressure standard to account for possible ^{3}He impurities.

In Table VI we compare our nonrelativistic and relativistic A_k coefficients with the results of Bhatia and Drachman [16]. The uncertainties of our results are the same as in Tables II and IV, i.e., were estimated from the convergence in basis set size. The uncertainties of sums of corrections were obtained as square roots of the sums of squares of the individual uncertainties. Since, for $k \geqslant 2$, the A_k coefficients given in Eq. (15) of Ref. [16] contain a unit conversion error, in Table VI we compare our results with the coefficients obtained from Eqs. (12) and (13) of Ref. [16] correctly converted to atomic units. One can see that for the static polarizability the nonrelativistic part of the BD result is much more accurate than

TABLE V. Basis set convergence of the nonrelativistic polarizabilities for ^{3}He (in atomic units $a_0^3 t_0^k$). The mass of 5495.8852754(50) m_e was assumed for the ^{3}He nucleus [10].

	N[a]	SO
$\alpha_0^{(0)}$	200	1.384012178892
	400	1.384012180127
	600	1.384012180174
	800	1.384012180176
$\alpha_2^{(0)}$	200	1.543561452717
	400	1.543561466826
	600	1.543561467291
	800	1.543561467326
$\alpha_4^{(0)}$	200	2.043306592379
	400	2.043306653740
	600	2.043306655983
	800	2.043306656229
$\alpha_6^{(0)}$	200	2.931624071865
	400	2.931624250938
	600	2.931624258920
	800	2.931624260374

[a] N is the basis set size used for ψ_0, whereas for auxiliary functions $3N/2$ functions were used.

TABLE VI. Coefficients A_k (in $a_0^3\,\text{Å}^k$) in the expansion of the polarizability of ^{4}He in inverse powers of wavelength λ compared to the values of Bhatia and Drachman [16]. The values listed in the BD column were obtained from Eqs. (12) and (13) of Ref. [16] by correctly converting to atomic units.

		BD	Present
A_0	nonrelativistic	1.383809991	1.383809986408(1)
	relativistic	-0.000080062	$-0.0000804534(1)$[a]
	total	1.383729929	1.3837295330(1)
A_2	nonrelativistic	3.2037352×10^5	$3.20373512523(2)\times10^5$
	relativistic	-0.0000677×10^5	$-0.0000689439(3)\times10^5$ [b]
	total	3.2036675×10^5 [c]	$3.2036661813(3)\times10^5$
A_4	nonrelativistic	8.8032133×10^{10}	$8.8035474950(6)\times10^{10}$
	relativistic	0.0000207×10^{10}	$0.000021769(2)\times10^{10}$
	total	8.8032341×10^{10} [d]	$8.803569264(2)\times10^{10}$
A_6	nonrelativistic	2.621934×10^{16}	$2.6219353156(6)\times10^{16}$
	relativistic		$0.0000562340(4)\times10^{16}$
	total	2.621934×10^{16} [e]	$2.6219915496(7)\times10^{16}$

[a] Includes the recoil correction $\alpha_0^{(21)}$ of the order of $1/(Mc^2)$, equal to $-0.0000000935(1)\, a_0^3$.

[b] Includes the recoil correction $\alpha_2^{(21)}$ of the order of $1/(Mc^2)$, equal to $-0.0299(2)\, a_0^3\, \text{Å}^2$.

[c] The coefficient at λ^{-2} given in Eq. (15) of Ref. [16] as equal to 3.204546×10^5 was incorrectly converted from the reduced Rydberg to atomic units.

[d] The coefficient at λ^{-4} given in Eq. (15) of Ref. [16] contains a typographic error.

[e] The coefficient at λ^{-6} given in Eq. (15) of Ref. [16] as equal to 2.624092×10^{16} was incorrectly converted from the reduced Rydberg to atomic units.

TABLE VII. Dynamic polarizability of ^{4}He (in a_0^3) at $\lambda = 6329.908$ Å. The reported uncertainties are estimated based on the convergence in basis sets, except as marked. When no error bar is given the last digit is certain. In such case the full calculated value with an error bar estimate can be obtained from the data given in Tables II–IV and VI.

Static	nonrelativistic	1.3838099864
	$1/c^2$	-0.0000803599
	$1/(Mc^2)$	$-0.0000000935(1)$[a]
	$1/c^3 - \partial_\mathcal{E}^2 \ln k_0$ term	0.0000304738(1)
	$\partial_\mathcal{E}^2 \ln k_0$ term[b]	0.000000183(1)
	$1/c^4$	0.00000056(14)[a]
	finite nuclear size	0.0000000217(1)
	total	1.38376077(14)
λ^{-2}	nonrelativistic	0.007995798
	$1/c^2$	-0.000000171
	$1/(Mc^2)$	-0.000000001
	$1/c^3$	0.00000032(3)[a]
	total	0.00799595(3)
λ^{-4}	nonrelativistic	0.000054836
	$1/c^2$	0.0000000001
	$1/c^3$	0.0000000031(3)[a]
	total	0.000054840
λ^{-6}	nonrelativistic	0.000000408
λ^{-8}	nonrelativistic	0.0000000032
$\alpha(\lambda) - \alpha_0$	present[c]	0.00805120(3)
	BD[d]	0.008050871
Total	present	1.39181197(14)
	Ref. [13]	1.39181164(14)[e]
	BD[f]	1.391780800

[a] The uncertainty accounts for the neglected terms or a contamination with terms higher order in $1/M$, see text.

[b] Contribution of the second electric-field derivative of Bethe logarithm $\partial_\mathcal{E}^2 \ln k_0$ from Ref. [18].

[c] The contribution of the λ^{-10} term, amounting to 2.5×10^{-11}, is negligible.

[d] Calculated using correctly converted A_k constants. Equation (15) of Ref. [16] gives 0.008052951, i.e., 0.03% error resulting in 1.7 ppm error in the total value of $\alpha(6329.908\ \text{Å})$.

[e] Table I of Ref. [13]. Note that the value of $\alpha(6329.908\ \text{Å})$ given in the abstract contains a typographical error.

[f] Using the static value of BD equal to 1.383729929.

the relativistic one: it agrees with our result to nine significant digits, while the relativistic part agrees only to two significant digits. However, as we will discuss below, the main source of error in the static polarizability of Bhatia and Drachman are the $1/c^3$ and $1/c^4$ QED corrections neglected by these authors.

The total BD's dynamic polarizability coefficients, A_2, A_4, and A_6, agree to six, four, and five significant digits, respectively, with our values computed through the $1/c^2$ terms. However, our results have about five more accurate digits than BD's results for each k. The relativistic contributions to A_2 and A_4 computed by BD are significantly less accurate than the nonrelativistic ones: the agreement with our values is only to two significant digits. Since these contributions are small, this low accuracy does not appreciably affect the reasonably good agreement of total BD coefficients with ours. As in the

TABLE VIII. Individual contributions to $\alpha_k^{(n0)}$ in units of $\mu a_0^3 t_0^k$. The value of atomic Bethe logarithm $\ln k_0$, equal to 4.37016022306(2), was taken from Ref. [40].

	$\alpha_0^{(20)}$	$\alpha_2^{(20)}$	$\alpha_4^{(20)}$	$\alpha_6^{(20)}$
$-\frac{1}{8}(\nabla_1^4 + \nabla_2^4)$	$-$987.87668	$-$1924.5778	$-$3595.712	$-$6632.50
$\pi\,[\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)]$	864.68014	1773.3634	3367.181	6259.44
$\pi\,\delta(\boldsymbol{r}_{12})$	66.07068	150.5050	298.872	569.09
$\frac{1}{2}[\nabla_1 r_{12}^{-1}\nabla_2 + (\nabla_1 \boldsymbol{r}_{12}) r_{12}^{-3}(\boldsymbol{r}_{12}\nabla_2)]$	$-$23.23406	$-$32.3564	$-$65.290	$-$133.18
Total	$-$80.35991	$-$33.0657	5.051	62.85
	$\alpha_0^{(30)}$	$\alpha_2^{(30)}$	$\alpha_4^{(30)}$	$\alpha_6^{(30)}$
$\frac{8}{3}(\frac{19}{30} - 2\ln\frac{1}{c} - \ln k_0)[\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)]$	32.69114	67.0459	127.3034	236.65
$(\frac{164}{15} + \frac{14}{3}\ln\frac{1}{c})\delta(\boldsymbol{r}_{12})$	$-$1.84591	$-$4.2049	$-$8.351	$-$15.90
$-\frac{7}{6\pi} P(r_{12}^{-3})$	$-$0.37142	$-$0.9396	$-$1.966	$-$3.86
Total	30.47381	61.9014	116.988	216.89
	$\alpha_0^{(40)}$	$\alpha_2^{(40)}$	$\alpha_4^{(40)}$	$\alpha_6^{(40)}$
$4\pi(\frac{427}{96} - 2\ln 2)\,[\delta(\boldsymbol{r}_1) + \delta(\boldsymbol{r}_2)]$	0.563 89	1.156 5	2.196	4.08

case of A_0, the main source of error in BD's A_k coefficients are the QED corrections $\alpha_k^{(30)}$, $k = 2,4,6$, neglected by BD.

Table VII gives the components of the dynamic polarizability of ^{4}He computed at the wavelength of 6329.908 Å (close to the one used in the proposed apparatus). Our final value differs by 0.33 μa_0^3 from the value published in Ref. [13], i.e., about twice the uncertainty estimated in that work. The main reason for this difference is the $\alpha_2^{(30)}$ correction, equal to 0.32 μa_0^3, neglected in Ref. [13] and included now. In Ref. [13] we incorrectly assumed that this $1/c^3$ correction should be at least a few times smaller than the relativistic $1/c^2$ correction $\alpha_2^{(20)}$. We did not realize that the value of $\alpha_2^{(20)}$ was accidentally very small due to strong cancellations among its components, see Table VIII. Such cancellations do not occur at the $1/c^3$ level, so the $\alpha_2^{(30)}$ correction is actually greater than $\alpha_2^{(20)}$ and the $\alpha_2^{(30)}\omega^2$ contribution becomes significant. The individual contributions to $\alpha_k^{(20)}$ and $\alpha_k^{(30)}$ are presented in Table VIII for $k = 0,2,4,6$. It can be seen that the cancellations depend significantly on k and at $k = 4$ the total $1/c^2$ relativistic correction becomes three orders of magnitude smaller than its largest component and more than one order of magnitude smaller than the $1/c^3$ QED correction. It is gratifying to observe that the $1/c^4$ QED correction is always significantly smaller than the total $1/c^3$ effect. It should be noted that due to the neglect of the electric-field derivative of Bethe logarithm the uncertainties of $\alpha_k^{(30)}$, $k = 2,4,6$ are assumed to be 10%. These uncertainties are much larger than those resulting from the basis set convergence. The term $\alpha_0^{(30)}$ is free from this error. In Table VII we used its recent value [18] which is somewhat more accurate than that of Ref. [2].

Most of the uncertainties in Table VII result from estimates of basis set convergence. All uncertainties of this type are completely negligible compared to the uncertainties resulting from neglected terms. The largest one is from the neglected $1/c^4$ terms and is estimated at 0.14 μa_0^3, as discussed earlier. The next in size is the uncertainty of $\alpha_2^{(30)}\omega^2$ amounting to 0.03 μa_0^3. The remaining uncertainties are expected to be smaller. Since we add uncertainties in squares, the overall uncertainty amounts also to 0.14 μa_0^3 or 0.1 ppm, i.e., it is the same as in Ref. [13].

Let us discuss other neglected terms that can possibly change our result. Since $\alpha_0^{(40)}$ is so small, 0.56 μa_0^3, it is unlikely that higher order terms in powers of $1/c$ could be relevant. The QED recoil correction $\alpha_0^{(31)}$ of the order of $1/(Mc^3)$ is most likely negligible based on the size of $\alpha_0^{(21)} = 0.093\ \mu a_0^3$, and on the observation that $\alpha_0^{(21)}$ is not anomalously small due to strong internal cancellations. We performed preliminary calculations of $\alpha_0^{(31)}$ (neglecting the electric field dependence of Bethe logarithm), which show that this correction is indeed about 10 times smaller than $\alpha_0^{(21)}$. Analogous dispersion contribution $\alpha_2^{(31)}$ can therefore be assumed negligible. In order to reduce the present uncertainty estimate one should first of all compute the other than one-loop contributions to the correction $\alpha_0^{(40)}$. However, since the accuracy level achieved so far is sufficient for the purpose of the new pressure standard, such computation is not necessary at the present time.

Table VII compares also our final results to those of Bhatia and Drachman [16] (after conversion errors are corrected). The dispersion parts $\alpha(\lambda) - \alpha_0$ agree to four significant digits which means that BD's error from this term would amount to 0.2 ppm of the final result. The total polarizabilities $\alpha(6329.908\ \text{Å})$ obtained by us and by BD differ much more significantly, by 22 ppm, and this discrepancy originates almost completely from the static polarizability, mainly due to the QED effects neglected by these authors. The second source of the discrepancy is our significantly improved value of the static relativistic correction.

B. Comparison with experiment

Table IX compares our results with experimental data from Refs. [8,41–43]. The comparisons are made in terms of the molar polarizability $A_\varepsilon = 4\pi N_A \alpha/3$, where N_A is the Avogadro constant. The decreased uncertainty of our value of $A_\varepsilon(0)$ compared to Ref. [2] results mainly from the decrease

TABLE IX. Comparison of theoretical and experimental molar polarizabilities (in $\mathrm{cm}^3/\mathrm{mol}$, wavelength in Å).

$A_\varepsilon(0)$	present	0.51725413(6)[a]
	Ref. [2]	0.517 254 19(10)
	expt. [8]	0.5172535(47)
$A_\varepsilon(6329.908)$	present	0.52026369(6)
	expt. [41,42]	0.5213(1)[b]
	expt. [43]	0.5220(3)[c]

[a] The uncertainties from α, N_A, and a_0 equal to 0.05, 0.02, and $0.0004\ \mathrm{cm}^3/\mathrm{mol} \times 10^{-6}$ are added in squares. The Avogadro constant of $6.02214129(27) \times 10^{23}\ \mathrm{mol}^{-1}$ [10] was used.

[b] The value listed in Refs. [41,42] is $A_\varepsilon(6329.9\ \text{Å}) + A_\mu(6329.9\ \text{Å})$ at $T = 323$ K. Since $A_\mu(0) = -0.0000079224\ \mathrm{cm}^3/\mathrm{mol}$, see text, the quoted value is independent of this correction.

[c] We took the polarizability listed in Table 1 of Ref. [43] (at the wavelength of 6329.9 Å) and assumed it has the same relative uncertainty as the refractivity in Table 2 of that reference.

of the uncertainty of N_A, see footnote a of Table IX. The agreement of our value with the experimental result of Schmidt *et al.* [8], obtained using a microwave cavity resonator [44], is very good, with the discrepancy of $0.6 \times 10^{-6}\ \mathrm{cm}^3/\mathrm{mol}$, eight times smaller than the experimental uncertainty and ten times larger than the theoretical one. Thus, the current theory is two orders of magnitude more accurate than the best experiment in the static case.

We have not listed in the table older experimental results determined from dielectric constant measurements since these values are of low accuracy. In particular, the value obtained by Kirouac and Bose [45], equal to $0.5210(2)\ \mathrm{cm}^3/\mathrm{mol}$, and the one obtained by Huot and Bose [46], equal to 0.5196(2) $\mathrm{cm}^3/\mathrm{mol}$, agree to only two significant digits both with our value and with the value of Ref. [8] and are incompatible with either result. This comparison shows the scale of progress in experimental determinations of polarizabilities.

In Table IX we also compare results of our calculations to experimental dynamic polarizabilities. Whereas the theoretical value is as accurate as for the static case, all the experiments are now two orders of magnitude less accurate than the best experiment for the static case. Thus, for the dynamic polarizabilities, theory is about four orders of magnitude more accurate than experiments. The experiments of Refs. [41,42] measured the sum of the molar polarizability and the magnetizability $A_\mu = 4\pi N_A \chi/3$. Since we compare to our values of A_ε only, we have subtracted A_μ from the experimental results. The static nonrelativistic value of A_μ is $-0.000007922\,4(4)\ \mathrm{cm}^3/\mathrm{mol}$, converted from $\chi = -0.000021194(1)\, a_0^3$ computed by Bruch and Weinhold [47] with an account of the nuclear motion. We assigned the uncertainty assuming that the relativistic corrections enter at the fifth significant digit. As one can see, the experimental results for dynamic polarizabilities are not accurate enough to be sensitive to A_μ. The agreement with the values of Achtermann *et al.* [41,42] is only to three significant digits and the discrepancy between our and their result is ten times larger than their uncertainty. The agreement with the result of Birch [43] is even worse, but due to the larger uncertainty assigned in this work, our result is now only five times outside this uncertainty. These facts show how critical theoretical results are for the new standard of pressure since it requires the knowledge of the dynamic rather than static polarizabilities.

C. Refractive index

In the low density limit, the dependence of p on n, α, χ, and kT is given by Eq. (1) derived for an ideal gas. To derive an equation accounting for the nonideality effects, we can start from the density expansions for the relative dielectric permittivity ε_r and relative magnetic permeability μ_r:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{4\pi}{3}\alpha[\rho + b_\varepsilon(T)\rho^2 + c_\varepsilon(T)\rho^3 + \cdots], \tag{39}$$

$$\frac{\mu_r - 1}{\mu_r + 2} = \frac{4\pi}{3}\chi[\rho + b_\mu(T)\rho^2 + c_\mu(T)\rho^3 + \cdots], \tag{40}$$

where ρ is the particle density, expressed here in atomic units a_0^{-3}. Equation (39) truncated at the term linear in ρ is the well-known Clausius-Mossotti relation that is discussed in most textbooks on electricity and magnetism. Its magnetic analog, Eq. (40), is much less known, but can be found in Ref. [48] and has been used in recent experimental work [8,49]. Equations (39) and (40) provide the definitions of the electric $(b_\varepsilon, c_\varepsilon, \ldots)$ and magnetic $(b_\mu, c_\mu, \ldots)$ virial coefficients. Since $n^2 = \varepsilon_r \mu_r$ by definition, these virial coefficients determine also the virial expansion of n,

$$n = 1 + a_n\,\rho + b_n\,\rho^2 + c_n\,\rho^3 + \cdots. \tag{41}$$

To find the relation between the refractivity virial coefficients b_n, c_n, ... and the dielectric b_ε, c_ε, ... and magnetic virial coefficients one first solves Eqs. (39) and (40) for ε_r and μ_r by expansion in powers of density

$$\varepsilon_r = 1 + 4\pi\alpha(\rho + b_\varepsilon\rho^2 + c_\varepsilon\rho^3) + \frac{(4\pi)^2}{3}\alpha^2(\rho^2 + 2b_\varepsilon\rho^3) + \frac{(4\pi)^3}{9}\alpha^3\rho^3 + O(\rho^4), \tag{42}$$

$$\mu_r = 1 + 4\pi\chi(\rho + b_\mu\rho^2 + c_\mu\rho^3) + \frac{(4\pi)^2}{3}\chi^2(\rho^2 + 2b_\mu\rho^3) + \frac{(4\pi)^3}{9}\chi^3\rho^3 + O(\rho^4), \tag{43}$$

and then expands the square root of the product of the obtained expansions. The result is

$$a_n = 2\pi(\alpha + \chi), \tag{44}$$

$$b_n = 2\pi\left(\alpha b_\varepsilon + \tfrac{1}{3}\pi\alpha^2 + \chi b_\mu + \tfrac{1}{3}\pi\chi^2 + 2\pi\alpha\chi\right), \tag{45}$$

$$c_n = 2\pi\left(\alpha c_\varepsilon + \tfrac{2}{3}\pi\alpha^2 b_\varepsilon + \tfrac{10}{9}\pi^2\alpha^3\right), \tag{46}$$

where we neglected all contributions to c_n containing magnetic quantities. This is a very reasonable approximation for helium since χ is about five orders of magnitude smaller than α and the magnetic permeability virial coefficients b_μ and c_μ (unknown) can be expected to be also much smaller than the dielectric ones b_ε and c_ε. Equation (41) can be used with the polarizability, susceptibility, and virial coefficients computed from first principles to predict the dependence of n on ρ which can then be confronted with experiments.

If Eq. (41) is squared, one obtains Eq. (4) of Schmidt *et al.* [8] except for small terms neglected by these authors and for a missing numerical factor in one of their terms. To see this equivalence, one needs to note some differences between the symbols used: our ρ denotes particle density, whereas that of Ref. [8] molar density and Ref. [8] uses molar dielectric virial coefficients $b = N_A b_\varepsilon$ and $c = N_A^2 c_\varepsilon$. Our derivation shows that a factor of 2 is missing in front of the $A_\varepsilon^2\, b\, \rho^2$ term on the right-hand side of Eq. (4) of Ref. [8].

To generalize Eq. (1), we first solve Eq. (41) for ρ by expanding it in powers of $n-1$,

$$\rho = \frac{1}{a_n}(n-1) - \frac{b_n}{a_n^3}(n-1)^2 + \left(\frac{2b_n^2}{a_n^5} - \frac{c_n}{a_n^4}\right)(n-1)^3 + \cdots . \tag{47}$$

When $n-1$ is measured and the remaining quantities entering Eq. (47) are known from theory or experiment, the value of ρ can be computed from this equation and then substituted into the virial equation of state

$$p = kT[\rho + B(T)\rho^2 + C(T)\rho^3 + \cdots], \tag{48}$$

again assuming that the virial coefficients $B(T)$ and $C(T)$ are known, allowing the determination of pressure. Thus, Eqs. (47) and (48) provide the required generalization of Eq. (1).

D. Comparison of refractivity virial coefficients with experiment

The refractivity virial coefficients are compared with experiments in Table X. In the case of the coefficient a_n, experimental results are usually presented in terms of $a_r \equiv \frac{2}{3}a_n$. If density is expressed in mol/cm^3 and a_n in cm^3/mol, then $a_r = A_\varepsilon + A_\mu$. We will use the conversion factor 1 cm^3/mol $= 11.20587208\ a_0^3$.

Our recommended value of static A_ε is 0.51725413(6) cm^3/mol, cf. Table IX. If we add to it $A_\mu = -0.0000079224(4)$ cm^3/mol from Ref. [47], we get a_r listed in Table X. Note that a_r was actually the quantity measured by Schmidt *et al.* [8]. These authors obtained then the value of A_ε that we compared with earlier by subtracting a theoretical magnetic contribution of -0.0000080 cm^3/mol (we added back this term for the present comparisons). As can be expected from the comparison presented in Table IX, Schmidt's *et al.* value of a_r listed in Table X is in excellent agreement with our result, as it differs from it by only 1.4 ± 9.1 ppm. One may add that to achieve such agreement, Schmidt *et al.* had to measure the refractive index n with an uncertainty of a few parts per billion [8].

TABLE X. Comparison of the theoretical virial expansion of the refractive index with experimental results. The quantities $a_r = \frac{2}{3}a_n$, b_n, and c_n are in units of cm^3/mol, cm^6/mol^2, and cm^9/mol^3, respectively, whereas λ is in Å.

$a_r(0)$	present	0.51724620(6)
	expt. [8]	0.5172455(47)
$a_r(6329.908)$	present[a]	0.52025577(6)
	expt. [41,42]	0.5213(1)
	expt. [43]	0.5220(3)
$b_n(0)$	present, 273.16 K	0.0244(3)
$b_n(6329.908)$	present,[a] 273.16 K	0.0238(3)
	present,[a] 303 K	0.0184(3)
	present,[a] 323 K	0.0150(3)
	expt. [42]	0.000(15)
$c_n(0)$	present, 273.16 K	−0.96(25)

[a] We neglected the frequency dependence of χ, a negligible effect for the helium atom [47].

Similarly as in the case of static a_r, we expect the comparisons of frequency-dependent a_r's with experiments to follow those made for A_ε. To compute our $a_r(6329.908\ \text{Å})$, we neglected the frequency dependence of A_μ, which is negligible for the helium atom [47]. Our value, listed in Table X, can be compared with the experimental determinations of Achtermann *et al.* [41,42] and Birch [43]. The values from these papers, listed in Table X, are identical to those listed in Table IX since A_μ, as noted earlier, does not affect the significant digits. One may note that the poor agreement of these measurements with older *ab initio* calculations was discussed already by Bhatia and Drachman [16] and by Stone and Stejskal [12]. In Ref. [13] we also compared values published by Leonard [50], mistakenly taking from this paper a theoretical value cited by this author.

In order to compute b_n and c_n from Eqs. (45) and (46), we need in addition to the values of α and χ, the values of the dielectric virial coefficients b_ε and c_ε. We will neglect the term χb_μ in Eq. (45) since χ is very small and b_μ is expected to be smaller than b_ε. Note that b_n and c_n are dependent on temperature, in contrast to a_n.

The dielectric virial coefficients $b_\varepsilon(T)$ have been reported in several papers [11,51–53], including their frequency dependence [11,53]. To compute $b_\varepsilon(T)$, one needs the values of the interaction induced polarizability of the helium dimer. The most accurate values of this quantity have been computed by Cencek *et al.* in Ref. [54]. These authors also used the best available helium dimer potential. However, they used only the classical statistical mechanics expression for $b_\varepsilon(T)$. The estimated uncertainties of $b_\varepsilon(T)$ relative to the exact classical value are 0.3% at $T = 298.15$ K. An earlier paper by Rizzo *et al.* [11] used a quantum statistical mechanics approach [51] for $b_\varepsilon(T)$. Although the quantum corrections to the classical result are almost negligible for $T > 77$ K, we used the values of b_ε from Ref. [11] since their classical limits agree very well with the results of Ref. [54]. We assumed an uncertainty of 0.4% in b_ε in view of this agreement and the smallness of quantum corrections. Note that the dielectric virial coefficients used in Ref. [11] are defined as $B_\varepsilon = A_\varepsilon b_\varepsilon$. Interpolating between the values at $T = 261$ and 274 K, we get $B_\varepsilon(273.16\ \text{K}) = -0.0506$ cm^6/mol^2, which leads to $b_\varepsilon = -0.0978(4)$ cm^3/mol and then to the value of $b_n = 0.0244(3)$ cm^6/mol^2, listed in Table X. The uncertainty of the latter value comes entirely for the uncertainty of b_ε. The third and fourth term in Eq. (45) make negligible contribution and there is a substantial cancellation between the first two terms. At the wavelength $\lambda = 6329.908$ Å, the value of b_n is reduced to 0.0238(3) cm^6/mol^2 (we used here the value of $b_\varepsilon = -0.0996(4)$ cm^3/mol, obtained from the dispersion data published in Ref. [11]).

Our values of b_n can be compared with the values inferred from the measurements of Achtermann *et al.* [42], performed at $T = 303$ and 323 K using the wavelength $\lambda = 6329.9$ Å.

These authors determined the coefficient b_r defined as

$$b_r = \tfrac{2}{3}\, b_n - \tfrac{1}{4}\, a_r^2. \tag{49}$$

Using their values of $a_r = 0.5213(1)$ cm^3/mol and $b_r = -0.068(10)$ cm^6/mol^2, one finds that $b_n = 0.000(15)$ cm^6/mol^2 for both temperatures considered (Achtermann *et al.* noted that "the term $2b_n/3$ is zero"). We list in Table X our values of b_n for the two temperatures considered in Ref. [42]. We used the values of $b_\varepsilon(303) = -0.1065(4)$ cm^3/mol and $b_\varepsilon(323) = -0.1108(4)$ cm^3/mol from the dispersion data published in Ref. [11]. It is seen that our values of b_n are only very slightly outside the error bars of the zero result from the experiment. The values of b_n do decrease with temperature, but our calculations indicate that they will cross zero only around 415 K.

Using the value $c_\varepsilon = -1.38$ cm^6/mol^2 computed by Heller and Gelbart [55], we evaluated also the coefficient c_n. We assumed that this value has the uncertainty equal to the difference between the theoretical value and the experimental result of $-1.7(9)$ cm^6/mol^2 (interpolated from the data of Ref. [46]).

Although the values of b_n and c_n are not very accurate, the contributions involving these coefficients are rather small around $T = 273.16$ K. Thus, the current accuracy of our first-principles virial expansion is sufficient to predict $n - 1$ with a 1 ppm uncertainty for pressures up to 3 MPa, i.e., for the helium densities up to about 0.0015 mol/cm^3. To extend this range of pressure, more accurate values of the dielectric viral coefficients as well as some information about the magnetic coefficient b_μ will be required.

VII. CONCLUSIONS

The frequency dependent polarizability of the helium atom has been computed as the expansion in powers of angular frequency ω. We conservatively estimate that the static polarizability and the dispersion coefficients have uncertainties better than 1 ppm. Results are given both for ^{4}He and ^{3}He isotopes. For the wavelength of 6329.908 Å considered by us the ω^8 and higher terms give negligible contribution (below 0.01 ppm). The relativistic and QED effect were included up to terms proportional to $1/c^4$. For the static polarizabilities this inclusion was complete for the $1/c^2$ and $1/c^3$ terms, whereas $1/c^4$ terms were represented by the dominating component. The effect of finite nuclear mass was taken into account exactly at the nonrelativistic level, whereas at the relativistic level the terms proportional to $1/(Mc^2)$ were computed for the static and leading dispersion terms.

Our final result is $\alpha(6329.908\ \text{Å}) = 1.39181197(14)\ a_0^3$. It is different by 0.33 μa_0^3 from our value published recently in Ref. [13]. The difference is due to QED contribution to the polarizability dispersion, which was neglected in Ref. [13]. The main source of uncertainty of our recommended value of polarizability is coming from the neglected $1/c^4$ terms in the static polarizability. We estimated that other terms neglected by us contribute below the 0.1 ppm level.

For the static case, the uncertainty of our polarizability is two orders of magnitude smaller than the uncertainty of the experiment [8]. For the dynamic case, relevant for the pressure standard, the uncertainty of our polarizability is the same as in the static case, but experiments are four orders of magnitude less accurate than the theoretical value [41–43].

Combining our values with literature calculations, we constructed a first-principles virial expansion for the refraction coefficient. We estimate that it can predict $n - 1$, to 1 ppm accuracy up to the pressure of 3 MPa. To increase this limit, more accurate *ab initio* values of the density and dielectric virial coefficients will be needed.

ACKNOWLEDGMENTS

The authors thank Dr. Jay Hendricks and Dr. Jack Stone for valuable discussions. This work was supported by the National Institute of Standards and Technology Grant No. 60NANB13D209, by National Science Foundation Grant CHE-1152899 and by the NCN Grant No. 2012/07/B/ST4/01347.

---

[1] K. Pachucki, Phys. Rev. A **74**, 022512 (2006).
[2] G. Łach, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. **92**, 233001 (2004).
[3] W. Cencek, M. Przybytek, J. Komasa, J. B. Mehl, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **136**, 224303 (2012).
[4] M. R. Moldover, R. M. Gavioso, J. B. Mehl, L. Pitre, M. de Podesta, and J. T. Zhang, Metrologia **51**, R1 (2014).
[5] J. Hendricks, J. Ricker, P. Egan, and G. Strouse, Phys. World **67**, 13 (2014).
[6] J. Stone, P. Egan, D. Gerty, J. Hendricks, D. Olson, J. Ricker, G. Scace, and G. Strouse, NCSL Int. Measure **8**, 67 (2013).
[7] J. H. Hendricks (private communication, 2015).
[8] J. W. Schmidt, R. M. Gavioso, E. F. May, and M. R. Moldover, Phys. Rev. Lett. **98**, 254504 (2007).
[9] J. R. Lawall, J. Opt. Soc. Am. **22**, 2786 (2005).
[10] P. J. Mohr, B. N. Taylor, and D. B. Newell, Rev. Mod. Phys. **84**, 1527 (2012).
[11] A. Rizzo, C. Hättig, B. Fernandez, and H. Koch, J. Chem. Phys. **117**, 2609 (2002).
[12] J. A. Stone and A. Stejskal, Metrologia **41**, 189 (2004).
[13] K. Piszczatowski, M. Puchalski, J. Komasa, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. **114**, 173004 (2015).
[14] K. Pachucki and J. Sapirstein, Phys. Rev. A **63**, 012504 (2000).
[15] W. R. Johnson and K. T. Cheng, Phys. Rev. A **53**, 1375 (1996).
[16] A. K. Bhatia and R. J. Drachman, Phys. Rev. A **58**, 4470 (1998).
[17] W. Cencek, K. Szalewicz, and B. Jeziorski, Phys. Rev. Lett. **86**, 5675 (2001).
[18] M. Puchalski, J. Komasa, B. Jeziorski, and K. Szalewicz (unpublished).
[19] K. Pachucki, Phys. Rev. Lett. **84**, 4561 (2000).
[20] A. K. Bhatia and R. J. Drachman, Can. J. Phys. **75**, 11 (1997).
[21] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Springer, Berlin, 1957).

[22] G. W. F. Drake, in *Long-Range Casimir Forces*, edited by F. S. Levin and D. A. Micha (Plenum, New York, 1993), p. 107.

[23] H. Araki, Prog. Theor. Phys. **17**, 619 (1957).

[24] J. Sucher, Phys. Rev. **109**, 1010 (1958).

[25] K. Pachucki and J. Sapirstein, J. Phys. B **33**, 455 (2000).

[26] K. Pachucki, J. Phys. B **31**, 5123 (1998).

[27] P. J. Mohr, J. Griffith, and J. Sapirstein, Phys. Rev. A **87**, 052511 (2013).

[28] I. Angeli, At. Data Nucl. Data Tables **87**, 185 (2004).

[29] J. Mitroy, S. Bubin, K. Varga, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, and D. Blume, Rev. Mod. Phys. **85**, 693 (2013).

[30] V. I. Korobov, J. Phys. B **35**, 1959 (2002).

[31] F. Harris, A. M. Frolov, and V. H. Smith, J. Chem. Phys. **121**, 6323 (2004).

[32] F. Harris, Int. J. Quantum Chem. **105**, 857 (2005).

[33] M. J. D. Powell, Comp. J. **7**, 155 (1964).

[34] H. Nakashima and H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007).

[35] V. I. Kukulin and V. M. Krasnopol'skii, J. Phys. G **3**, 795 (1977).

[36] S. A. Alexander, H. J. Monkhorst, and K. Szalewicz, J. Chem. Phys. **85**, 5821 (1986).

[37] V. I. Korobov, Phys. Rev. A **61**, 064503 (2000).

[38] M. Puchalski, U. D. Jentschura, and P. J. Mohr, Phys. Rev. A **83**, 042508 (2011).

[39] A. K. Bhatia and R. J. Drachman, J. Phys. B **27**, 1299 (1994).

[40] V. I. Korobov, Phys. Rev. A **85**, 042514 (2012).

[41] H. J. Achtermann, G. Magnus, and T. K. Bose, J. Chem. Phys. **94**, 5669 (1991).

[42] H. J. Achtermann, J. G. Hong, G. Magnus, R. A. Aziz, and M. J. Slaman, J. Chem. Phys. **98**, 2308 (1993).

[43] K. P. Birch, J. Opt. Soc. Am. A **8**, 647 (1991).

[44] J. B. Mehl, M. R. Moldover, and L. Pitre, Metrologia **41**, 295 (2004).

[45] S. Kirouac and T. K. Bose, J. Chem. Phys. **64**, 1580 (1976).

[46] J. Huot and T. K. Bose, J. Chem. Phys. **95**, 2683 (1991).

[47] L. W. Bruch and F. Weinhold, J. Chem. Phys. **117**, 3243 (2002); Erratum **119**, 638 (2003).

[48] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

[49] E. F. May, M. R. Moldover, and J. W. Schmidt, Phys. Rev. A **78**, 032522 (2008).

[50] P. J. Leonard, At. Data Nucl. Data Tables **14**, 21 (1974).

[51] R. Moszynski, T. G. A. Heijmen, and A. van der Avoird, Chem. Phys. Lett. **247**, 440 (1995).

[52] R. Moszynski, T. G. A. Heijmen, P. Wormer, and A. van der Avoird, J. Chem. Phys. **104**, 6997 (1996).

[53] H. Koch, C. Hättig, H. Larsen, J. Olsen, P. Jorgensen, B. Fernandez, and A. Rizzo, J. Chem. Phys. **111**, 10108 (1999).

[54] W. Cencek, J. Komasa, and K. Szalewicz, J. Chem. Phys. **135**, 014301 (2011).

[55] D. F. Heller and W. M. Gelbart, Chem. Phys. Lett. **27**, 359 (1974).