Frequency-dependent polarizability of helium including relativistic effects with nuclear recoil terms

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Future metrology standards will be partly based on physical quantities computed from first principles rather than measured. In particular, a new pressure standard can be established if the dynamic polarizability of helium can be determined from theory with an uncertainty smaller than 0.2 ppm.

We also obtained an accurate expansion of the helium refractive index in powers of density.

Some physical quantities, for example, properties of the helium atom and interaction energies of helium atoms, can now be computed from first principles with precision rivaling and sometimes exceeding the best experimental determinations [1–3]. Therefore, quantities of this type can be used in establishing metrology standards. One example is a possible standard of temperature based on acoustic gas thermometry [4]. Another example is a pressure standard based on optical interferometry [5]. The current pressure standard dating back more than 300 years is realized by mercury manometers and can not be further improved. Also, the reference manometers are far from portable: 3 m high and containing 250 kg of mercury, a substance banned due to its toxicity. Since pressure is one of the most widely containing 250 kg of mercury, a substance banned due to its toxicity. Since pressure is one of the most widely

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1/7294.2995361. Since $1/M$ is of the order of $10^{-4}$, keeping the linear term is entirely sufficient and such contributions can be represented in the form $\alpha_k^{(l)} = \alpha_k^{(0 l)} + \alpha_k^{(1 l)}$, $l \geq 2$, where $\alpha_k^{(0 l)}$ are computed with the infinite nuclear mass and $\alpha_k^{(1 l)}$ are corrections of the order of $1/(M c^2)$, referred to as the recoil corrections. These recoil corrections are expected to be negligible except for the static ones $\alpha_0^{(21)}$ and $\alpha_{\infty}^{(21)}$ and, possibly, for $\alpha_2^{(21)}$.

For comparisons with experiments, it is convenient to convert frequency to wave length $\lambda = 2\pi c \omega / h \epsilon$.

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

(2)

When $\alpha(\lambda)$ remains in atomic units and $\lambda$ is measured in nm, the relation is $A_k = f^k \alpha_k$, $f = 2\pi c a_0 / \text{nm} = 45.56335253$ (with $a_0 = 0.05291772109$ nm).

For $\alpha_0$ contributions, our more accurate values are consistent with Ref. 1 to all digits published except for the term describing the electric-field dependence of Bethe’s logarithm and for $\alpha_0^{(40)}$. We computed the former term using a new method since Ref. 1 was the only source for this quantity. The contributions of this component from the two calculations differ only marginally, by 0.011 $\mu a_0^3$. The term $\alpha_0^{(40)}$ was estimated in Ref. 1 by the contribution from the simple one-loop expression [11] and the uncertainty of this term was assumed to be 40%. Later, it was shown in Ref. 12 that the error of one-loop approximation applied to the excitation energies of helium is only about 5%. Therefore, we reduced our estimate from 40% to 25% or 0.14 $\mu a_0^3$, which we believe is still conservative.

The dispersion coefficients $\alpha_k$ ($k = 2, 4, 6$) were calculated thus far only by Bhatia and Drachman (BD) [13, 14]. However, these authors did not provide any estimates of the uncertainties. Their relativistic contributions do depend on the nuclear mass but the recoil effect, $\alpha_2^{(21)}$, was not correctly taken into account. Furthermore, the $A_k$ coefficients were incorrectly converted from the reduced Rydberg units: the factor $(1 + m_e / m_0)^k$, appearing in the correct conversion formula, was erroneously replaced by its square $(1 + m_e / m_0)^{2k}$.

At the nonrelativistic level of theory, $\alpha(\omega)$ of an atom in a quantum state $\psi$ is defined by the standard polarization propagator expression

$$\alpha(\omega) = \langle \psi | z R(\omega) | \psi \rangle + \langle \psi | z R(-\omega) | \psi \rangle,$$  

(3)

where $z = z_1 + z_2$, with $z_i$ denoting electron coordinates, and $R(\omega) = Q (QH - E + \omega)^{-1}$ is the resolvent of the atomic Hamiltonian $H$, with $Q = 1 - P = 1 - |\psi\rangle \langle \psi|$ and $E$ being the energy of state $\psi$. For the helium atom

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{2M} (\nabla_1 + \nabla_2)^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_1 r_2}.$$  

(4)

$R(\omega)$ satisfies the identity $\mathcal{R}(\omega) = \mathcal{R} - \omega \mathcal{R}^2 \mathcal{R}(\omega)$, where $\mathcal{R} = Q (QH - E)^{-1}$ is the static (reduced) resolvent of $H$. Iterating this expression and inserting it into Eq. (3), one obtains

$$\alpha_k^{(0)} = 2 \langle \psi | z \mathcal{R}^{k+1} z | \psi \rangle .$$  

(5)

To account for the leading relativistic contributions of the order of $1/c^2$ assuming infinite nuclear mass, we add to the Hamiltonian of Eq. (4) the perturbation from the Breit-Pauli Hamiltonian [15] obtaining

$$\alpha_0^{(20)} = -4 \langle \psi | B_1 R_0 z R_0 z | \psi \rangle - 2 \langle \psi | z R_0 \overline{B}_1 R_0 z | \psi \rangle,$$  

$$\alpha_2^{(20)} = -4 \langle \psi | B_1 R_0 z R_0^3 z | \psi \rangle = 4 \langle \psi | z R_0 \overline{B}_1 R_0^3 z | \psi \rangle - 2 \langle \psi | z R_0 \overline{B}_1 R_0^3 z | \psi \rangle,$$  

$$\alpha_4^{(20)} = -4 \langle \psi | B_1 R_0 z R_0^5 z | \psi \rangle - 4 \langle \psi | z R_0 \overline{B}_1 R_0^5 z | \psi \rangle - 2 \langle \psi | z R_0 \overline{B}_1 R_0^5 z | \psi \rangle,$$  

$$\alpha_6^{(20)} = -4 \langle \psi | B_1 R_0 z R_0^7 z | \psi \rangle - 4 \langle \psi | z R_0 \overline{B}_1 R_0^7 z | \psi \rangle - 4 \langle \psi | z R_0 \overline{B}_1 R_0^7 z | \psi \rangle - 2 \langle \psi | z R_0 \overline{B}_1 R_0^7 z | \psi \rangle,$$

where

$$B_1 = -\frac{1}{8c^4} (\nabla_1^4 + \nabla_2^4) + \frac{\pi}{c^2} [\delta(r_1) + \delta(r_2)] + \frac{\pi}{c^2} \delta(r_{12}) + \frac{1}{2c^2} \{ \nabla_1 r_{12}^{-1} \nabla_2 + (\nabla_1 r_{12}^{-1} \nabla_1 r_{12}^{-3} (r_1 r_2) - \nabla_1 r_{12}^{-2} \nabla_2 + \nabla_2 r_{12}^{-1} \nabla_1 + \nabla_2 r_{12}^{-2} \nabla_2) r_{12}^{-3} (r_1 r_2) \} .$$  

(6)

The two components are given by

$$\alpha_0^{(21)}(B_2) = -4 \langle \psi | B_2 R_0 z R_0 z | \psi \rangle - 2 \langle \psi | z R_0 \overline{B}_2 R_0 z | \psi \rangle ,$$  

(8)

and

$$\alpha_0^{(21)}(H_1 B_1) = 4 \langle \psi | z R_0 z R_0 \overline{H}_1 R_0 B_1 | \psi \rangle + \langle \psi | z R_0 z R_0 \overline{B}_1 R_0 H_1 | \psi \rangle + \langle \psi | z R_0 \overline{H}_1 R_0 z R_0 B_1 | \psi \rangle + \langle \psi | z R_0 \overline{B}_1 R_0 z R_0 H_1 | \psi \rangle + \langle \psi | z R_0 \overline{H}_1 R_0 z R_0 B_1 | \psi \rangle + \langle \psi | z R_0 \overline{B}_1 R_0 z R_0 H_1 | \psi \rangle - \langle \psi | z R_0 z | \psi \rangle \langle \psi | H_1 \overline{R}_0 B_1 | \psi \rangle - \langle \psi | R_0 \overline{R}_0 z | \psi \rangle \langle \psi | H_1 \overline{R}_0 B_1 | \psi \rangle ,$$  

(9)
The correction $\alpha_2^{(21)}$ is very small and can be computed using a finite difference expression

$$\alpha_2^{(21)} \approx \alpha_2^{(20)}(B_1 \rightarrow B_2) + \alpha_2^{(20)}(H_0 \rightarrow H) - \alpha_2^{(20)}, \quad (10)$$

valid to the order of $1/(Mc^2)^2$, where $B_1 \rightarrow B_2$ means that operator $B_1$ in the expression for $\alpha_2^{(20)}$ should be replaced by $B_2$ and similarly $H_0 \rightarrow H$ means that quantities computed with the Hamiltonian $H_0$ should be replaced by those computed with $H$.

To evaluate $\alpha_0^{(1)}$, accurate representations of the helium ground-state wave functions $\psi_0$ and $\psi$ were obtained by minimizing the conventional Rayleigh-Ritz functional for the Hamiltonians $H_0$ and $H$, respectively. The auxiliary functions were obtained recursively from Hylleraas-type functionals

$$J_0^{(n)}(\phi) = \langle \tilde{\phi}|H_0 - E_0 + P_0|\phi\rangle - 2\langle \tilde{\phi}|\phi_0^{(n-1)} \rangle \quad (11)$$

for $\phi_0^{(n)} = R_0 z\psi_0$ and

$$K_0^{(n)}(\psi) = \langle \tilde{\psi}|H_0 - E_0 + P_0|\psi\rangle - 2\langle \tilde{\psi}|(1 - P_0)z\phi_0^{(n)} \rangle \quad (12)$$

for $\psi_0^{(n)} = R_0 z\phi_0^{(n)}$, and analogous functionals obtained by dropping all the subscripts 0 for $\phi^{(n)} = R^n z\tilde{\phi}$ and $\psi^{(n)} = R^n z\tilde{\psi}$. The trial functions used in all minimization processes were expanded in bases of Slater single-particle functions

$$\tilde{\phi} = (1 + P_{12}) Y(r_1, r_2) \sum_{i=1}^N C_i e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_1 r_2}, \quad (13)$$

where $P_{12}$ is the transposition operator whereas $Y(r_1, r_2) = z_1$ in calculations of $\phi^{(n)}_0$ and $\phi^{(n)}$ and $Y(r_1, r_2) = 1$ otherwise. One may note that the functions $\psi^{(n)}_0$ and $\psi^{(n)}$ contain also a $D$ component, but it does not contribute to matrix elements that are needed. The linear coefficients were obtained by solving the appropriate set of linear equations, while to determine the nonlinear parameters we employed two strategies: the full optimization (FO) and the stochastic optimization (SO). In the latter case, the parameters $\alpha_i, \beta_i, \gamma_i$ are pseudo-randomly generated from a box with optimized dimensions. We used two boxes to model the short-range and medium-range asymptotics of the wave functions. To eliminate possibilities of numerical errors, the FO and SO based codes (including the integral and linear algebra routines) were programmed entirely independently by different members of our team.

The contributions $\alpha_k^{(0)}$ for $k = 0, 2, 4, 6$ were computed for several values of $N$, up to 600 (800) in the FO (SO) approach, both optimizations giving at least 11 convergent digits, with FO converging faster. Our results agree to 9, 8, 4, and 7 digits, respectively, with the values obtained by BD [13]. Using the SO procedure, we also calculated: $\alpha_8^{(0)} = 4.395060532(1), \alpha_{10}^{(0)} = 6.7725956(1), \alpha_{12}^{(0)} = 10.622083(1), \text{and } \alpha_{14}^{(0)} = 16.861181(1)$ $\mu a_0^3$.

For the relativistic contributions $\alpha_k^{(20)}, k = 0, 2, 4, 6$, the convergence is much slower than in the nonrelativistic case. This is due to the fact that we use nonrelativistic functionals which are sensitive to wave function values in different regions of the configuration space than the relativistic operators (these operators are too singular to be used in optimizations). The SO procedure leads now to a faster convergence than FO since randomly chosen exponents cover the space more uniformly than FO exponents. Thus, we used the SO results as our recommended values and in estimates of uncertainty. Nevertheless, the agreement to 6, 5, 3, and 3 digits, respectively, between the two sets of results is more than sufficient for the present purposes. Our values are substantially more accurate than those of BD [14], with agreement to only 2, 2, and 1 digit, respectively (BD did not compute $\alpha_k^{(20)}$). For $\alpha_0^{(20)}$, our results are consistent with, but significantly more accurate than calculations of Refs. [1, 16, 17]. The relativistic recoil contribution $\alpha_0^{(21)} = -0.0935(1) \mu a_0^3$. Its smallness 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 $-0.2494 \mu a_0^3$, respectively. The contribution $\alpha_2^{(21)}$ is equal to $-0.144(1) \mu a_0^3$, so it is virtually negligible.

It should be pointed out that the relativistic contributions computed by BD [14] depend on the nuclear mass and, strictly speaking, should not be compared with our, nuclear-mass-independent contributions $\alpha_k^{(20)}$. This is because these authors 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 part of their relativistic contributions is of the order of $1/(Mc^2)$, it differs from the $\alpha_k^{(21)}(B_1 H_1)$ part of the true recoil correction. Additionally, BD completely neglected the contribution $\alpha_k^{(21)}(B_2)$. Thus, their relativistic contributions cannot be viewed as approximations to $\alpha_k^{(20)} + \alpha_k^{(21)}$. Since the effects of the order of $1/(Mc^2)$ are very small, the differences between our relativistic contributions and those of BD are mainly due to the differences in basis sets used in the calculations rather than to the treatments of the nuclear mass dependence.

After correcting the units conversion error in Ref. 14 as discussed earlier, the $A_k$ coefficients computed by BD agree with our values to 5, 6, 4, and 5 digits for $k = 0, 2, 4, 6$, respectively. For $k = 0$, the discrepancy is mainly due to the $1/c^4$ terms not considered by BD. The reasons for the relatively low accuracy of $A_k$ are unclear. Due to the smallness of the relativistic contributions to $A_k$, the overall agreement is good despite the fact that the relativistic contributions from BD work are significantly less accurate than ours.

In Table I, we present the dynamic polarizability of $^4$He. In addition to the contributions discussed earlier,
TABLE I. Dynamic polarizability of $^4$He [$a_o$] at $\lambda = 632.9908$ nm.

| $\lambda^{-2}$ | nonrelativistic | $1/c^2$ | $-0.000 000 00075(1)$ |
|----------------|----------------|---------|----------------------|
| $\lambda^{-4}$ | nonrelativistic | $1/c^4$ | $0.000 000 00014(1)$ |
| $\lambda^{-8}$ | nonrelativistic | $1/c^8$ | $0.000 000 00032(1)$ |

$\alpha(\lambda) - \alpha(0)$ present | $0.008 050 871(1)$ |

$\alpha(0)$ present | $1.391 811 64(14)$ |

$\alpha(0)$ BD | $1.391 780 800$ |

$^a$ Includes the recoil contribution of the order of $1/(Mc^2)$ equal to $-0.000 000 000935(1)$. $^b$ From Ref. 1 except for the contribution from the electric field derivative of the Bethe logarithm equal to $0.000 000 182(1)$ [18]. $^c$ Computed adding the correction term $(4/3)\pi r_n^2 \delta(\delta r_1 + \delta r_2)$ to $H$, where $r_n = 1.676$ fm is the nuclear radius. $^d$ Including the recoil correction of the order of $1/c^2$ equal to $-0.000 000 00075(1)$. $^e$ The contribution of the $\lambda^{-10}$ term, amounting to $2.5 \times 10^{-11}$, is negligible. $^f$ Calculated using correctly converted $A_k$ constants. Equation (15) of Ref. 14 gives $0.008 052 951$, i.e., $0.03\%$ error resulting in 1.7 ppm error in the total value of $\alpha(632.9908)$. $^g$ Using the static value of BD equal to 1.383 729 929.

we included the effect of finite nuclear size which is almost negligible. The dispersion part of $\alpha(632.9908)$, i.e., the contribution explicitly dependent on wavelength, agrees to 6 significant digits with the result of BD (after conversion errors are corrected) due to the high, eight-digit accuracy of BD’s $\alpha_0(0)$ contribution. However, the total polarizability obtained by us differs significantly, agreement to 5 digits and discrepancy of about 22 ppm, from BD’s result. As already discussed, this difference is mainly due to the QED effects neglected by these authors. The second source of the difference is our significantly improved value of the static relativistic component. The uncertainty of our recommended value of $\alpha(632.9908)$ amounts 0.14 $\mu a_o^3$, i.e., about 0.1 ppm. This accuracy is sufficient for the purpose of the new pressure standard but one should ask if any neglected effects could contribute above the uncertainty estimate. The potential candidates are the QED recoil correction $\alpha_{00}^{(31)}$ of the order of $1/(Mc^3)$, the QED contribution to the polarizability dispersion $\alpha_{02}^{(30)}$ of the order of $1/c^3$ and, finally, and probably most importantly, the remaining, other than one-loop contributions to $\alpha_{02}^{(40)}$ of the order of $1/c^4$. We believe that such neglected contributions should not contribute more than 0.1 ppm but are investigating such terms.

TABLE II. Virial expansion of refractive index. $a_c = \frac{3}{2} a_o$, $b_n$, and $c_n$ are in units of cm$^3$/mol, cm$^2$/mol$^2$, and cm$^4$/mol$^3$, respectively, and $\lambda$ is in nm. 1 cm$^3$/mol = 11.205 8721 $a_o$.

| $a_c$ | present | $0.517 246 21(6)$ |
| $b_n$ | 273.16 K | $0.0245(2)$ |
| $c_n$ | present | $0.0978(2)$ |

$^a_a = 8.694 292 29(9) a_o^3$ or 0.775 869 31(8) (4) cm$^3$/mol, where the second uncertainty originates from the Avogadro constant $6.022 141 29(27) \times 10^{23}$. $^b$ Computed using $\chi = -0.000 021 194(1) a_o^3 [23]$, the uncertainty reflects the estimated size of relativistic contributions. $^c a_o = 8.744 8758(9) a_o^3 = 0.780 383 35(8) (4) cm^3/mol$. $^d$ We neglected the frequency dependence of $\chi$, a relativistic effect expected to be very small. $^e$ Inferred from measured value of $n = 383.809 98641(1)$, i.e., 0.03% error resulting in 1.7 ppm error in the total value of $\alpha(632.9908)$. $^f$ Using the static value of BD equal to 1.383 729 929.

the virial expansion for the refractive index can be written as

$$n = 1 + a_n \rho + b_n \rho^2 + c_n \rho^3 + \cdots, \quad (14)$$

$$a_n = 2 \pi (\alpha + \chi), \quad (15)$$

$$b_n = 2 \pi (\alpha b_n + \frac{3}{2} \pi \alpha^2 c + \chi b_n + \frac{1}{2} \pi \chi^2 + 2 \pi \alpha \chi), \quad (16)$$

$$c_n = 2 \pi (\alpha c + \frac{3}{2} \pi \alpha^2 b + \frac{19}{2} \pi \alpha^2 \alpha), \quad (17)$$

where $\rho$ is density, $b_n$ and $c_n$ are the dielectric virial coefficients and $b_n$ is the magnetic permeability virial coefficient. We have written down the term $\chi b_n$ in Eq. (16), but we will neglect it in numerical calculations since $\chi$ is about five orders of magnitude smaller than $a$ and $b_n$ (unknown) is expected to be at the most of the same order as $b_n$. We completely ignored the magnetic part of $c_n$ in Eq. (17). After Eq. (14) is squared, it becomes consistent with Eq. (4) of Ref. 6 within the terms included in Eq. (17).
density, or, when combined with the virial equation of state, also for a determination of pressure.

The virial coefficients are presented in Table II. The agreement with the measurement of Schmidt et al. [6] is excellent, to within 1.4±9.1 ppm. Note that the authors of Ref. 6 reported the value of \( a_r \) with a subtracted magnetic contribution \( 4\pi \chi/3 = -0.0000080 \text{ cm}^3/\text{mol} \), which was added back in Table II. The agreement with measurements at 632.9908 nm [19–21] is, however, poor, as noticed earlier comparing with older theoretical results by BD [14] and by Stone and Stejskal [9]. The disagreement with the measurement of Leonard [22] is smaller, only about twice the experimental uncertainty. The apparent better agreement of theory with this experiment (within 1 \( \sigma \)) found in Ref. 14 was due to the neglect [14] of the nonlinear dependence of density on pressure. The values of \( b_n \) and \( c_n \) presented in Table II have uncertainties due entirely to uncertainties of \( b_\varepsilon \) and \( c_\varepsilon \). The third and fourth term in Eq. (16) make negligible contributions and there is substantial cancellation between the first two terms. The experimental \( b_n \) determined from the values measured in Ref. [20] is consistent with zero, which is almost within the combined uncertainties. From our data and from the \( b_\varepsilon(T) \) data of Ref. 24 we predict that \( b_n \) will vanish only around 415 K. Since \( b_n \) is small at \( T=273.16 \text{ K} \) and higher temperatures, its accuracy is sufficient to predict \( n-1 \) with a 1 ppm uncertainty for pressures up to 10 MPa.

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