QED calculation of the dipole polarizability of helium atom
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Abstract

The QED contribution to the dipole polarizability of the \(^4\)He atom was computed, including the effect of finite nuclear mass. The computationally most challenging contribution of the second electric-field derivative of Bethe logarithm was obtained using two different methods: the integral representation method of Schwartz and the sum-over-states approach of Goldman and Drake. The results of both calculations are consistent, although the former method turned out to be much more accurate. The obtained value of the electric-field derivative of Bethe logarithm, equal to 0.0485572(14) in atomic units, confirms the small magnitude of this quantity found in the only previous calculation [Phys. Rev. Lett. \textbf{92}, 233001 (2004)], but differs from it by about 5%. The origin of this difference is explained. The total QED correction of the order of \(\alpha^3\) in the fine-structure constant \(\alpha\), amounts to 30.6671(1)\(\cdot\)10\(^{-6}\), including the 0.1822\(\cdot\)10\(^{-6}\) contribution from the electric field derivative of Bethe logarithm and the 0.01112(1)\(\cdot\)10\(^{-6}\) correction for the finite nuclear mass, all values in atomic units. The resulting theoretical value of the molar polarizability of helium-4 is 0.517 254 08(5) cm\(^3\)/mol with the error estimate dominated by the uncertainty of the QED corrections of order \(\alpha^4\) and higher. Our value is in agreement but is an order of magnitude more accurate than the result 0.517 254 4(10) cm\(^3\)/mol of the most recent experimental determination [Phys. Rev. Lett. \textbf{120}, 123203 (2018)].
I. INTRODUCTION

Accurate knowledge of the electric dipole polarizability $\alpha_d$ of helium is critical for the development of new primary standards of temperature [1–3] (which is of importance due to the new definition of kelvin [4, 5]), and for novel realizations of pressure employing electrical [6, 7], microwave [8], or optical methods [9, 10]. This significance of the polarizability is a consequence of the direct linear relation $(\varepsilon_r - 1)k_B T = 4\pi\alpha_d p$ connecting at low density the relative electric permittivity $\varepsilon_r$ (and consequently the refractive index $n$) with the gas pressure $p$ and the thermodynamic temperature $T$. The Boltzmann constant $k_B$, appearing here, is now fixed at $1.380649 \cdot 10^{-23}$ J/K. Corrections to this linear relation, depending the second and higher powers of density $\rho$, are small for helium [9, 11] and can be determined with much lower relative accuracy than the targeted accuracy of $p$ or $T$. An information about an accurate value of $\alpha_d$ is also essential in experimental determinations of density and dielectric virial coefficients of rare gases using dielectric-constant gas thermometry [12, 13]. One may note that the knowledge of accurate value of the dipole polarizability of helium was employed the experimental determinations of the value of the Boltzmann constant [14, 15], before this constant was fixed by the new SI definition of kelvin [16, 17].

For microwave [8] and optical [9, 10] methods, the dependence of $\alpha_d$ on frequency $\omega$ is relevant, but for helium the frequency dependent part of $\alpha_d(\omega)$ is small [18] for experimentally useful frequencies [19], and does not have to be known with high relative accuracy. One may also note that the index of refraction depends not only on $\alpha_d(\omega)$ but also on the static magnetic susceptibility $\chi$ and, at the $10^{-7}$ level, on other frequency dependent magnetic and quadrupole contributions [20]. In this work we consider only the static dipole polarizability $\alpha_d$.

Since the helium atom is a very small system bound by electromagnetic forces, its properties, including the polarizability, can be computed with very high accuracy using the quantum electrodynamics (QED) theory. The strong nuclear forces can be accounted for by the empirical values of the nuclear mass and nuclear charge radius. The nuclear polarizability and effects of the weak interactions give a completely negligible contribution to the atomic polarizability. The current status of the QED theory in the description of helium atom has been recently examined in Ref. 21. No relative discrepancies higher than $10^{-8}$
have been found [21] between the best theoretical calculations of transition energies and their most reliable experimental determinations. In some cases the agreement between theory and experiment reaches even the $10^{-9}$ level [22]. Since in thermal metrology the required relative accuracy is at most at the $10^{-7}$ level, one can be confident that the theory tested in Ref. 21 is sufficient for a metrology-useful prediction of the static polarizability of helium.

The nonrelativistic polarizability of helium $\alpha_d^{(0)}$, defined by the standard Schrödinger-Coulomb equation, can be computed with accuracy limited only by the accuracy of the experimental value of the electron-to-nucleus mass ratio. The most accurate value of $\alpha_d^{(0)}$ for $^4$He reported in the literature, $1.383\,809\,986\,408(1)\,a_0^3$, where $a_0 = \hbar^2/(m_e e^2)$ is the atomic unit of length, has a relative error $10^{-12}$, see Table I in Ref. 23. The leading relativistic correction to $\alpha_d^{(0)}$, being of the second order in the fine-structure constant $\alpha$ and denoted by $\alpha_d^{(2)}$, can be computed using the Breit-Pauli Hamiltonian [24] and is also known with more than sufficient accuracy. Its value for $^4$He is $-80.4534(1)\cdot10^{-6}\,a_0^3$ [18], the reported uncertainty of $10^{-10}\,a_0^3$ accounts for neglected terms of the order of $\alpha^2(m_e/m_\alpha)^2$, where $m_\alpha$ is the nuclear mass.

Calculation of the next correction, $\alpha_d^{(3)}$, of the order of $\alpha^3$, requires a field-theoretic, QED treatment of the electron-electron and electron-nucleus interaction that takes into account the effects of the electron self-energy and the vacuum polarization. The first calculation of $\alpha_d^{(3)}$ was reported by Pachucki and Sapirstein [25] in 2001. These authors assumed the infinite nuclear mass, i.e., considered the nuclear-mass-independent part $\alpha_d^{(3,0)}$ of $\alpha_d^{(3)}$, and neglected the computationally demanding second electric-field derivative $\partial_2^2 E \ln k_0$ of the so-called Bethe logarithm $\ln k_0$. To estimate the uncertainty of their calculation they assumed that $\partial_2^2 \ln k_0$ represents at most 10% of the known field-independent value of $\ln k_0$, which translated into about 10% error in $\alpha_d^{(3,0)}$. The complete calculation of $\alpha_d^{(3,0)}$, including the effect of $\partial_2^2 \ln k_0$, was reported in Ref. 26. The obtained value of $\partial_2^2 \ln k_0$, equal 0.0512(4), turned out to be about an order of magnitude smaller than the estimate made by Pachucki and Sapirstein [25] and about two orders of magnitude smaller than the atomic value of $\ln k_0$. The $\partial_2^2 \ln k_0$ independent part of $\alpha_d^{(3,0)}$ obtained by Lach et al. [26] agreed well with the calculations of Pachucki and Sapirstein [25].

The calculation of $\partial_2^2 \ln k_0$ is computationally complex and error-prone since it involves numerical treatment of divergent integrals, and since the final, unexpectedly small value of
\( \partial^2 \ln k_0 \) results from cancellations of terms much larger than \( \partial^2 \ln k_0 \). Therefore, it is clear that an independent confirmation of the results of Ref. 26 is needed. The main purpose of the present work was to perform a new, substantially more accurate calculations of \( \partial^2 \ln k_0 \) to verify the accuracy of the value obtained in Ref. 26 and to obtain an improved value of \( \alpha^{(3,0)} \). To achieve this goal we employed two different methods to compute Bethe logarithms: the modification of the integral representation method of Schwartz [27] proposed recently by Pachucki and Komasa [28] and the sum-over-states method of Goldman and Drake [29–31] modified by us to compute the second derivative of \( \ln k_0 \). Another objective of this work was to include the nuclear-mass dependent part \( \alpha^{(3,1)} \) of \( \alpha^{(3)} \), referred to as the QED recoil correction, which has not been computed before. By adding the computed values of \( \alpha^{(3,0)} \) and \( \alpha^{(3,1)} \), a definitive value of the \( \alpha^3 \) QED correction to the polarizability of helium will become available for metrological and other applications.

The plan of this paper is as follows. In Secs II and III we present calculations of \( \partial^2 \ln k_0 \) performed using the integral representation and the sum-over-states methods, respectively. Sec. IV contains the description of the calculation of the QED recoil correction to the polarizability of helium. Finally, in Sec. V a summary of the obtained results is presented and the conclusion of this work are formulated. Appendix contains a derivation of a constant defining the the asymptotic behavior of the integrand used in Sec. II to compute \( \partial^2 \ln k_0 \).

Unless otherwise stated, the atomic units are used throughout this papers. We assume that \( \alpha=1/137.0359991 \), \( a_0 = 0.052917721 \) nm and that the mass of the \( ^4\text{He} \) nucleus equals 7294.2999536 \( m_e \). For the Avogadro number, we take the new SI value of \( 6.02214076 \times 10^{23} \).

II. INTEGRAL REPRESENTATION APPROACH TO THE ELECTRIC-FIELD DERIVATIVE OF BETHE LOGARITHM

The formula for \( \alpha^{(3,0)} \) can be obtained by the electric-field differentiation of the general expression for the \( \alpha^3 \) QED correction \( E^{(3,0)} \) to the energy of two electrons in a nondegenerate singlet state, derived by Araki and Sucher [32, 33] in the 1950s. In the compact, present-day notation this formula can be written in the form, see e.g., Ref. 21,

\[
E^{(3,0)} = \alpha^3 \left[ 8 \left( \frac{19}{30} - 2 \ln \alpha - \ln k_0 \right) D_1 + \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) D_2 - \frac{7}{6\pi} A_2 \right],
\]

(1)
where

\[
D_1 = \langle \psi | \delta^3(\mathbf{r}_1) + \delta^3(\mathbf{r}_2) | \psi \rangle,
\]

(2)

\[
D_2 = \langle \psi | \delta^3(\mathbf{r}_{12}) | \psi \rangle,
\]

(3)

\[
A_2 = \langle \psi | P(r_{12}^3) | \psi \rangle \equiv \lim_{a \to 0} \langle \psi | \theta(r_{12} - a) r_{12}^{-3} + 4\pi (\gamma + \ln a) \delta^3(\mathbf{r}_{12}) | \psi \rangle,
\]

(4)

with \( \delta^3(\mathbf{r}) \) being the three-dimensional Dirac distribution, \( \gamma \) the Euler-Mascheroni constant, \( \theta(x) \) the Heaviside step function, and \( \psi \) the ground-state eigenfunction of the nonrelativistic electronic Hamiltonian \( H \) of the considered system. The quantity \( \ln k_0 \), appearing also in Eq. (1), is the Bethe logarithm defined as the quotient

\[
\ln k_0 = \frac{\langle \psi | \mathbf{p} (H - E) \ln [2(H - E)] | \mathbf{p} | \psi \rangle}{\langle \psi | \mathbf{p} (H - E) | \mathbf{p} | \psi \rangle},
\]

(5)

where \( E \) is the ground-state eigenvalue of \( H \), i.e., \( (H - E)\psi = 0 \), and \( \mathbf{p} = \mathbf{p}_1 + \mathbf{p}_2 \) is the total momentum operator for the electrons. The numerator and the denominator in Eq. (5) will be denoted by \( N \) and \( D \), respectively. One can show that \( D = 4\pi D_1 \). In our case, \( H = H_0 + \mathcal{E}(z_1 + z_2) \), where \( H_0 \) is the nonrelativistic electronic Hamiltonian for the helium atom and \( \mathcal{E}(z_1 + z_2) \) is the perturbation due to a uniform static electric field \( \mathcal{E} \) directed along the \( z \) axis. Thus, all quantities in Eqs. (1)-(5) depend on the electric field strength \( \mathcal{E} \). In this and in the next section, we assume that the nuclear mass is infinite and that \( H_0 \) contains only electronic kinetic energy.

Differentiating Eq. (1) twice with respect to \( \mathcal{E} \) and reversing the sign, one obtains [25, 26]

\[
\alpha^{(3,0)}_d = \alpha^3 \left[ -\frac{8}{3} \left( \frac{19}{30} - 2 \ln \alpha - \ln k_0 \right) \partial^2_{\mathcal{E}} D_1 + \frac{8}{3} D_1 \partial^2_{\mathcal{E}} \ln k_0 
\right.
\]

\[
- \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) \partial^2_{\mathcal{E}} D_2 + \frac{7}{6\pi} \partial^2_{\mathcal{E}} A_2 \right],
\]

(6)

where all electric-field derivatives and the quantities \( \ln k_0 \) and \( D_1 \) which are not differentiated are taken at \( \mathcal{E} = 0 \).

The evaluation of the derivatives \( \partial^2_{\mathcal{E}} D_1 \), \( \partial^2_{\mathcal{E}} D_2 \), and \( \partial^2_{\mathcal{E}} A_2 \) is relatively easy and can be done using the double-perturbation theory formula,

\[
\partial^2_{\mathcal{E}} X = 4 \langle \psi_0 | z R_0 z R_0 \hat{X} | \psi_0 \rangle + 2 \langle \psi_0 | z R_0 (\hat{X} - \langle \psi_0 | \hat{X} | \psi_0 \rangle) R_0 z \psi_0 \rangle,
\]

(7)

where \( X = D_1 \), \( D_2 \), or \( A_2 \), \( \hat{X} \) stands for the operators appearing in Eqs. (2)-(4), \( z = z_1 + z_2 \), \( \psi_0 \) is the ground-state eigenfunction of \( H_0 \), i.e., \( H_0 \psi_0 = E_0 \psi_0 \), and \( R_0 = (1 - P_0)(H_0 - E_0 + P_0)^{-1} \) is the reduced resolvent of \( H_0 \), with \( P_0 \) being the projection on \( \psi_0 \).
To evaluate $\partial_2^2 E_1$, $\partial_2^2 D_2$, and $\partial_2^2 A_2$ via Eq. (7), we need two auxiliary functions: the first-order function $R_0 z\psi_0$ of natural $P$ symmetry and the $S$-wave part of the second-order function $R_0 z R_0 z\psi_0$. These auxiliary functions were represented using the basis set of exponentially correlated Slater functions of the form

$$\tilde{\psi}(r_1, r_2) = (1 + P_{12}) \sum_{i=1}^{K} c_i Y(r_1, r_2) e^{-\xi_i r_1 - \eta_i r_2 - \nu_i r_{12}},$$

where $P_{12}$ exchanges vectors $r_1$ and $r_2$ and $Y(r_1, r_2)$ is the angular factor equal to $z_1$ or 1 in the present case. The linear and nonlinear parameters in Eq. (8) were obtained by minimizing the static form ($\omega = 0$) of the Hylleraas functional

$$\mathcal{F}[\tilde{\psi}] = \langle \tilde{\psi}| H_0 - E_0 + \omega|\tilde{\psi} \rangle + 2\langle \tilde{\psi}| h \rangle$$

where the function $h$ is equal to $z\psi_0$ or $z R_0 z\psi_0$. The ground-state wave function $\psi_0$ was also represented by Eq. (8). All nonlinear parameters $\xi_i$, $\eta_i$, and $\nu_i$ were fully optimized for bases with $K$ equal 128, 256, and 512. The results are shown in Table I.

**TABLE I.** Mean values and their second electric-field derivatives obtained with the basis sets optimized in this work. The values of $\sigma$ are conservative error estimates of the values computed for $K = 512$. They were obtained by observing the pattern of convergence with increasing $K$ and by performing additional calculations with other basis sets.

| $K$  | $D_1$     | $\partial_2^2 D_1$ | $D_2$     | $\partial_2^2 D_2$ | $A_2$     | $\partial_2^2 A_2$ |
|------|-----------|---------------------|-----------|---------------------|-----------|---------------------|
| 128  | 3.620 860 71 | -5.168 613 9 | 0.106 345 341 | -0.394 937 6 | 0.989 274 6 | -2.573 745 |
| 256  | 3.620 858 67 | -5.168 624 4 | 0.106 345 364 | -0.394 937 4 | 0.989 273 9 | -2.573 764 |
| 512  | 3.620 858 63 | -5.168 624 1 | 0.106 345 370 | -0.394 937 4 | 0.989 273 6 | -2.573 766 |
| $\sigma$ | 0.000 000 01 | 0.000 000 01 | 0.000 000 001 | 0.000 000 1 | 0.000 000 2 | 0.000 002 |

Inspecting the values collected in Table I, we see that our calculations of $D$, $\partial_2^2 D$, $\partial_2^2 D_2$, and $\partial_2^2 A_2$ are accurate to better than 1 ppm level. Using the values obtained with the largest basis set and the best literature value [34] of the atomic Bethe logarithm $\ln k_0 = 4.370 160 223 070 3(3)$, we find that the neglect of $\partial_2^2 \ln k_0$, i.e., the approximation used by
Pachucki and Sapirstein [25], leads to the value of $30.4738(1) \cdot 10^{-6}$ as an approximation to $\alpha_d^{(3,0)}$. This value agrees very well with the result of $30.474(1) \cdot 10^{-6}$ published in Ref. 25.

The computation of the electric-field derivative of $\ln k_0$ is substantially more complicated than the computation of expectation values $D_1$, $D_2$, and $A_2$ and their electric field derivatives. In this section we present the calculation of $\ln k_0$ using the integral representation method of Schwartz [27] in a computationally convenient formulation proposed by Pachucki and Komasa [28]. In this formulation, the electric-field dependent Bethe logarithm $\ln k_0$ is computed as the integral

$$\ln k_0 = \int_0^1 \frac{f(t) - f_0 - f_2 t^2}{D t^3} dt,$$

(10)

where $f_0 = \langle \psi|p^2\psi \rangle$, $f_2 = -2D$, and the function $f(t)$ is defined by

$$f(t) = \omega J(\omega) = \omega \langle \psi | p (H - E + \omega)^{-1} p \psi \rangle$$

(11)

with $\omega = (1 - t^2)/(2t^2)$. The denominator $D$ as well as the expectation values in the definitions of $J(\omega)$, $f_0$ and $f_2$ are assumed here to be obtained with the electric-field-dependent ground-state eigenfunction $\psi$ of $H$. Schwartz [27] and Forrey and Hill [35] developed the asymptotic, large-$\omega$ expansion of $J(\omega)$ that can be transformed into the expansion of $f(t)$ at small $t$ which, up to the $t^4$ term, takes the form [28]

$$f(t) \sim f_{\exp}(t) = f_0 + f_2 t^2 + f_3 t^3 + f_4 t^4 \ln t + f_4 t^4,$$

(12)

where $f_3 = 16D$, $f_4 = 64D$ and $f_4 = 2D (8C_3 + 16 \ln 2 - 1)$. The constant $C_3$ determines the $\omega^{-3}$ term (equal to $4DC_3 \omega^{-3}$) in the asymptotic expansion of $J(\omega)$. The computation of $C_3$ and its electric-field derivative $\partial^2_c C_3$ is discussed in Appendix.

Performing the electric-field differentiation of Eq. (10) and setting $E = 0$, one obtains

$$\partial^2_c \ln k_0 = \int_0^1 \frac{\partial^2_c f(t) - \partial^2_c f_0 - \partial^2_c f_2 t^2}{D t^3} dt - \frac{\partial^2_c D}{D} \ln k_0,$$

(13)

where $\partial^2_c f_0 = \partial^2_c \langle \psi_0|p^2\psi_0 \rangle$, $\partial^2_c f_2 = -2\partial^2_c D$, whereas $D$ and $\ln k_0$ on the right-hand side represent the atomic, field-independent values of these quantities. Equation (12) shows that the integrand in Eq. (13) is finite at $t = 0$ so the integral is convergent. However, at small values of the argument $t$, the function $\partial^2_c f(t)$ is very difficult to compute accurately using finite basis set expansions. Actually, when $\partial^2_c f(t)$, $\partial^2_c f_0$, and $\partial^2_c f_2$ are computed using a finite basis of the form of Eq. (8), the singularity of the integrand at $t = 0$ is not canceled.
and the integral diverges. To circumvent this difficulty, the integral over $t$ was separated into two parts: part 1 from 0 to $\epsilon \ll 1$ and part 2 from $\epsilon$ to 1, with only part 2 computed using numerical values of $\partial_\xi^2 f(t)$. Part 1 was obtained by approximating $\partial_\xi^2 f(t)$ using Eq. (12) and its generalization involving higher powers of $t$. To reduce the contribution from part 1, it is convenient to subtract $\partial_\xi^2 f_3 t^3 + \partial_\xi^2 f_4 l t^4 \ln t + \partial_\xi^2 f_4 t^4$ from the numerator in the integrand of Eq. (13) and integrate the counterterms analytically. The resulting expression for $\partial_\xi^2 \ln k_0$ takes then the form

$$
\partial_\xi^2 \ln k_0 = \int_0^1 \frac{\partial_\xi^2 f(t) - \partial_\xi^2 f_{\exp}(t)}{D t^3} \, dt + \frac{\partial_\xi^2 f_4}{2D} - \frac{\partial_\xi^2 D}{D} \ln k_0,
$$

(14)

where

$$
\partial_\xi^2 f_4 = 16 D \partial_\xi^2 C_3 + 2 \partial_\xi^2 D (8C_3 + 16 \ln 2 - 1).
$$

(15)

To derive Eq. (14), the use has been made of the fact that the integral over $f_3 + f_4 \ln t$ accidentally vanishes for helium. The integrand $I(t)$ in Eq. (14) behaves at small $t$ as $f_5 l t^2 \ln t + f_5 t^2$ and for small $\epsilon$ gives a very small contribution to $\partial_\xi^2 \ln k_0$. Accurate computation of $f_5 l$ and $f_5$ would be very difficult and was not attempted. Approximate values of these parameters were obtained, as discussed in more detail below, by interpolating $I(t)$ for $0 < t < \epsilon$ using a few $t \geq \epsilon$ values of $I(t)$.

From Eq. (14) we see that to obtain $\partial_\xi^2 \ln k_0$ we need (in addition to $D$ and $\partial_\xi^2 D$) accurate values of $\partial_\xi^2 \langle \psi_0 | p^2 | \psi_0 \rangle$, $C_3$, $\partial_\xi^2 C_3$, and $\partial_\xi^2 f(t)$ for $t \geq \epsilon$. The computation of $\partial_\xi^2 \langle \psi_0 | p^2 | \psi_0 \rangle$ and $\partial_\xi^2 C_3$ was performed using Eq. (7) and the basis set of Eq. (8). The computation of $\partial_\xi^2 C_3$ and $C_3$ is somewhat intricate since matrix elements that have to be evaluated are more complex than the matrix elements of $p$ or $\delta^3(r)$, see Appendix for details. The results of these computations are displayed in Table II.

In view of the very strong cancellation between $\partial_\xi^2 f(t)$ and $\partial_\xi^2 \langle \psi_0 | p^2 | \psi_0 \rangle$ at small $t$, it is important that the accuracy of $\partial_\xi^2 \langle \psi_0 | p^2 | \psi_0 \rangle$ is very high. As shown in Table II this quantity was computed with a relative error of less than $10^{-12}$.

The calculation $\partial_\xi^2 f(t)$ was done via the computation of $\omega \partial_\xi^2 J(\omega)$ for $\omega = (1 - t^2)/(2t^2)$. The appropriate expression for $\partial_\xi^2 J(\omega)$ is obtained by double electric-field differentiation of
TABLE II. Parameters defining the behavior of $f(t)$ at small $t$. See caption to Table I for the definition of $\sigma$.

| $K$  | $\langle \psi_0 | p^2 \psi_0 \rangle$ | $\frac{\partial^2}{\partial \omega^2} \langle \psi_0 | p^2 \psi_0 \rangle$ | $C_3$   | $\frac{\partial^2}{\partial \omega^2} C_3$ |
|------|--------------------------------------|---------------------------------|---------|----------------------------------|
| 128  | 6.12558770381709                     | $-9.01208233363$               | 5.000826| $-0.04928$                       |
| 256  | 6.12558770423964                     | $-9.01208233972$               | 5.000634| $-0.05249$                       |
| 512  | 6.12558770423993                     | $-9.01208233974$               | 5.000624| $-0.05230$                       |
| $\sigma$ | 0.00000000000002                    | 0.000000000001                 | 0.000002| 0.00002                          |

a In Eq. (29) of Ref. 36, Korobov uses the value 5.000 624 87 without giving an uncertainty estimate.

Eq. (11). The result of this differentiation can be written in the form [26]

$$\frac{\partial^2}{\partial \omega^2} J(\omega) = 4 \langle \psi_0 | z R_0 z R_0 p R(\omega) p \psi_0 \rangle + 4 \langle \psi_0 | z R_0 p R(\omega) z R(\omega) p \psi_0 \rangle$$

$$+ 2 \langle \psi_0 | z R_0 p R(\omega) p R_0 z \psi_0 \rangle + 2 \langle \psi_0 | p R(\omega) z R(\omega) p \psi_0 \rangle$$

$$- 2 \langle \psi_0 | z R_0^2 z \psi_0 \rangle \langle \psi_0 | p R(\omega) p \psi_0 \rangle - 2 \langle \psi_0 | z R_0 z \psi_0 \rangle \langle \psi_0 | p R^2(\omega) p \psi_0 \rangle,$$

(16)

where $R(\omega) = (H_0 - E_0 + \omega)^{-1}$ is the frequency dependent resolvent of the field-free Hamiltonian $H_0$. Some terms in Eq. (16) are singular at $\omega = 0$, but these singularities as well as the $\omega$ independent parts cancel so that $\frac{\partial^2}{\partial \omega^2} J(0) = 0$ and, as a consequence, both $\frac{\partial^2}{\partial \omega^2} f(t)$ and the derivative of $\frac{\partial^2}{\partial \omega^2} f(t)$ with respect to $t$ vanish at $t = 1$.

To evaluate $\frac{\partial^2}{\partial \omega^2} f(t)$ via Eq. (16), we can employ the functions $R_0 z \psi_0$ and $R_0 z R_0 z \psi_0$ used to obtain $\frac{\partial^2}{\partial \omega^2} D$ but we also have to compute, for each value of $\omega$, several auxiliary functions: the first-order function $R(\omega) p \psi_0$ as well as the scalar, pseudovector, and tensor components of the second-order functions $R(\omega) p R_0 z \psi_0$ and $R(\omega) z R(\omega) p \psi_0$. All these functions were computed variationally for each required value of $\omega$ using appropriate versions of the functional (9). The trial functions $\tilde{\psi}$ were expanded using the basis set of Eq. (8) with the angular factors corresponding to the symmetry of considered auxiliary function. For the vector and pseudovector functions we set $Y(r_1, r_2) = x_1$ or $z_1$ and $x_1 z_2 - z_1 x_2$, respectively. For the functions of $D$ symmetry the basis consists of two parts each containing $K$ terms: the first part with the angular factor $x_1 z_1$ or $r_1^2 - 3 z_1^2$ and the second part with the factors $x_1 z_2 + z_1 x_2$ or $r_1 r_2 - 3 z_1 z_2$. For each value of $t$ on a grid of 100 points between 0.01 and
1.0 (and a few additional points below 0.01), full optimizations of all nonlinear parameters were performed for three successively increasing basis sets labeled by the integers $K = 128$, 256, and 512 which specify also the size of the basis used to expand $\psi_0$.

In Table III we show the basis set convergence of the integrand $I(t)$ in Eq. (14) for small values of $t$. It is seen that the convergence, very good at $t > 0.005$, deteriorates dramatically for small values of $t$. At $t = 0.002$, the value of $I(t)$ is not accurate enough to be used in numerical integration. This is shown in Table IV where we list the values of the integral of $I(t)$ from $\epsilon$ to 1 computed with our two largest basis sets. The integral from 0.005 to 1 turns out to be sufficiently accurate and we have chosen $\epsilon = 0.005$ to separate the integration range in Eq. (14) into the “small $t$” and “large $t$” parts. Using $\epsilon$ larger than 0.005 gives more accurate values of the “large $t$” integral, cf. Table IV, but is not advantageous since, as shown in Table V, the error of the whole calculation is determined by the interpolation error in the range $t < \epsilon$ (performing the integration using every second point we verified that the error of our numerical integration procedure is smaller than $10^{-8}$ and therefore negligible compared to other error sources).

**TABLE III.** Basis set convergence of the integrand $I(t)$ in Eq. (14) for small values of $t$. $K$ denotes the basis set size used to represent $\psi_0$ and the auxiliary functions. Extrapolated results were obtained assuming exponential decay of error. The uncertainty $\sigma$ is defined as the difference of the two preceding rows.

| $K$   | $I(0.002)$         | $I(0.005)$         | $I(0.01)$          | $I(0.02)$          | $I(0.03)$          |
|-------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 128   | -21.91782900      | 0.14613471         | 2.22617850         | 9.34234812         | 20.52412502        |
| 256   | -2.78361795       | 0.49908734         | 2.30166902         | 9.34931045         | 20.52630907        |
| 512   | 0.03568909        | 0.50676476         | 2.30195231         | 9.34932498         | 20.52631193        |
| extrp.| 0.52288119        | 0.50693547         | 2.30195337         | 9.34932501         | 20.52631194        |
| $\sigma$ | $4.9 \cdot 10^{-1}$ | $1.7 \cdot 10^{-4}$ | $1.1 \cdot 10^{-6}$ | $3.0 \cdot 10^{-8}$ | $3.8 \cdot 10^{-9}$ |
TABLE IV. Integral of I(t) from ε to 1 computed with our two largest basis sets. The uncertainty σ is defined as the difference of the two preceding rows.

| K  | ε = 0.002 | ε = 0.005 | ε = 0.01 | ε = 0.015 | ε = 0.02 |
|----|-----------|-----------|----------|-----------|----------|
| 256| 65.32851048 | 65.32854759 | 65.32840496 | 65.32799881 | 65.32720487 |
| 512| 65.32856319 | 65.32854787 | 65.32840479 | 65.32799878 | 65.32720488 |
| σ | 5.3 · 10^{-5} | 2.8 · 10^{-7} | 1.7 · 10^{-7} | 3.4 · 10^{-8} | 2.3 · 10^{-9} |

The integral from 0 to ε was obtained analytically by interpolating I(t) with the function

\[ \tilde{I}(t) = \sum_{k=2}^{n} (a_k t^k \ln t + b_k t^k) \]  (17)

using our best (extrapolated) values of I(t) for t = ε and for 2n – 3 next higher values of t. The results of this integration are shown in Table V as a function of n together with the corresponding values of \( \partial^2 \ln k_0 \) obtained from Eq. (14) using our best values of D and \( \partial^2 D \) (from Table I), of \( C_3 \) and \( \partial^2 C_3 \) (from Table II), and of the “large t” integral (from Table IV). One should note that the obtained values of \( \partial^2 \ln k_0 \) are more than three orders of magnitude smaller than the individual terms in Eq. (14).

TABLE V. Dependence of the integral of I(t) from 0 to ε = 0.005 and of the value of \( \partial^2 \ln k_0 \) on the length n of the fit function of Eq. (17). For the t ≥ ε integral we took 65.32854787, cf. Table IV.

| n  | \( \int_0^\epsilon I(t)dt \) | \( \partial^2 \ln k_0 \) |
|----|----------------|----------------|
| 2  | 0.00001736 | 0.04855859 |
| 3  | 0.00001636 | 0.04855759 |
| 4  | 0.00001608 | 0.04855731 |
| 5  | 0.00001599 | 0.04855722 |

Table V shows that the integral from 0 to ε is very small but its relative accuracy is not high. From the observed convergence pattern we can infer that the value this integral
amounts to 0.0000160(14) with the uncertainty conservatively estimated by the total spread of values shown in Table V. Taking into account the error estimations for both integration regions, we find that the value of $\partial^2 \ln k_0$ obtained using the integral representation method is 0.0485572(14). This value differs by about 5% from the value 0.0512(4) reported in Ref. 26. The origin of this difference is discussed in Sec. III.

### III. SUM-OVER-STATES APPROACH TO THE ELECTRIC-FIELD DERIVATIVE OF BETHE LOGARITHM

To resolve the discrepancy between the values of $\partial^2 \ln k_0$ obtained in Sec. II and in Ref. 26, we performed computations using the sum-over-state approach [29–31]. In this approach, the numerator $N$ in Eq. (5) is represented by the spectral expansion in terms of the eigenfunctions $\psi_n$ of the excited states of the Hamiltonian $H$,

$$N = \sum_n \omega_n \ln(2\omega_n) |\langle \psi_0 | p \psi_n \rangle|^2,$$

(18)

where $\omega_n$ are the excitation energies. In practice, an expansion in terms of pseudostates diagonalizing $H$ in an appropriately chosen basis set is used [29]. Although the pseudostate expansion is converging extremely slowly (it is on the verge of divergence [37]), it has been successfully applied [38–41], also in the acceleration gauge [42, 43], to accurately compute electric-field-free values of $\ln k_0$. In this section we present the application of this method to compute $\partial^2 \ln k_0$ for the ground state of the helium atom in a static electric field $\mathcal{E}$.

To cope with the extremely slow convergence of the pseudostate expansion, we use a parameter $L > 0$ which attenuates the importance of highly excited states and enables us to control the convergence rate. Using the integral representation of $\ln \omega_n$

$$\ln \omega_n = \ln(1 + L) - \ln \left(1 + \frac{L}{\omega_n}\right) + (\omega_n - 1) \int_L^\infty \frac{d\omega}{(\omega + \omega_n)(\omega + 1)},$$

(19)

one can show that $N$ can be written in the form

$$N = N_L + D \ln(2L + 2) + \int_L^\infty g(\omega)d\omega,$$

(20)

where

$$N_L = -\sum_n \omega_n \ln \left(1 + \frac{L}{\omega_n}\right) |\langle \psi_0 | p \psi_n \rangle|^2$$

(21)
and
\[ g(\omega) = \omega J(\omega) - \langle \psi_0 | p^2 | \psi_0 \rangle + \frac{D}{\omega + 1}. \] (22)

One may note that the modification of the original approach of Goldman-Drake, as defined by Eqs. (20)-(22), bears close resemblance to the approach used by Korobov [34, 36], see also Ref. 44.

When the energies \( \omega_n \) of the excited states are large (much larger than \( L \)) the successive contributions in the summation in Eq. (21) decrease with \( n \) as \( L |\langle \psi_0 | p | \psi_n \rangle|^2 \). This should be compared with the \( \omega_n \ln \omega_n |\langle \psi_0 | p | \psi_n \rangle|^2 \) decrease of terms in Eq. (18). One can thus expect that the convergence of the summation in the expression for \( N_L \) will be faster than the convergence of the series in Eq. (18). When \( L \) is sufficiently large, the last term in Eq. (20) is small and can be easily computed using the large-\( \omega \) asymptotic expansion of \( g(\omega) \)

\[ g(\omega) = g_3 \omega^{-3/2} + g_4 \omega^{-2} \ln \omega + g_4 \omega^{-2} + g_5 \omega^{-5/2} + \cdots, \] (23)

where the coefficients \( g_3 = 4 \sqrt{2} D \), \( g_4 = -8 D \), and \( g_5 = (4C_3 - 1) D \) can be obtained by changing the variable in the expansion of Eq. (12), or directly from the work of Schwartz [27]. Forrey and Hill [35] derived an expression for \( g_5 \) but this expression is too complex to evaluate in practice.

Carrying out the \( \omega \) integration in Eq. (20) using the first three terms in the asymptotic expansion of \( g(\omega) \) and adding the result to the first two terms in this equation, one obtains the following expression for \( \ln k_0 \):

\[ \ln k_0 = \ln k_0(L) + R_L, \] (24)

where

\[ \ln k_0(L) = \frac{N_L}{D} + \ln(2L + 2) + 8\sqrt{2}L^{-1/2} - 8L^{-1} \ln L + (4C_3 - 9)L^{-1} \] (25)

and \( R_L \) is the error resulting from truncating the asymptotic series of Eq. (23). We know from the work of Forrey and Hill [35] that \( R_L \) vanishes with increasing \( L \) as

\[ R_L = C_4 L^{-3/2} + C_5 L^{-2} \ln L + C_6 L^{-2} + O(L^{-5/2}). \] (26)

Knowing this error formula, one can perform the extrapolation of \( \ln k_0(L) \) and obtain an improved value of \( \ln k_0 \) by solving a small system of linear equations.
In view of Eq. (25), the second electric-field derivative of \( \ln k_0(L) \) is given by the expression

\[
\frac{\partial^2}{\partial \mathcal{E}^2} \ln k_0(L) = \frac{1}{D} \left[ \frac{\partial^2}{\partial \mathcal{E}^2} N_L - \frac{N_L}{D} \frac{\partial^2}{\partial \mathcal{E}^2} D \right] + \frac{4}{L} \frac{\partial^2}{\partial \mathcal{E}^2} C_3. \tag{27}
\]

The derivative of the error \( \frac{\partial^2}{\partial \mathcal{E}^2} \mathcal{R}_L \) has the same large-\( L \) behavior as \( \mathcal{R}_L \) so that \( \frac{\partial^2}{\partial \mathcal{E}^2} \ln k_0(L) \) can be extrapolated in the same way as \( \ln k_0(L) \) using Eq. (26).

Since the intermediate wave functions \( \psi_n \) of the pseudostates and the excitation energies \( \omega_n \) in Eq. (21) depend on the electric field \( \mathcal{E} \), the differentiation of \( N_L \) with respect to \( \mathcal{E} \) is much more difficult than the differentiation of \( D \) or \( \langle \psi | \mathbf{p}^2 \psi \rangle \). A suitable sum-over-states expression for \( \frac{\partial^2}{\partial \mathcal{E}^2} N_L \) can be obtained from the formula

\[
\frac{\partial^2}{\partial \mathcal{E}^2} N_L = \int_0^L \omega \frac{\partial^2}{\partial \mathcal{E}^2} J(\omega) d\omega - L \frac{\partial^2}{\partial \mathcal{E}^2} \langle \psi_0 | \mathbf{p}^2 \psi_0 \rangle \tag{28}
\]

resulting from Eqs. (20) and (22). Using Eq. (16) and noting that terms diverging linearly with \( L \) are eliminated with the help of Eq. (7), one finds that \( \frac{\partial^2}{\partial \mathcal{E}^2} N_L \) can be written as the sum of six contributions

\[
\frac{\partial^2}{\partial \mathcal{E}^2} N_L = I_A + I_B + I_C + I_D + I_E + I_F, \tag{29}
\]

defined by

\[
I_A = -4 \sum_n \lambda(\omega_n) \langle \psi_0 | z R_0 z \mathbf{p} \psi_n \rangle \langle \psi_n | \mathbf{p} \psi_0 \rangle, \tag{30}
\]

\[
I_B = -2 \sum_n \lambda(\omega_n) \langle \psi_0 | z R_0 \mathbf{p} \psi_n \rangle \langle \psi_n | \mathbf{p} R_0 z \psi_0 \rangle, \tag{31}
\]

\[
I_C = 2 \langle \psi_0 | z R_0^2 z \psi_0 \rangle \sum_n \lambda(\omega_n) \langle \psi_0 | \mathbf{p} \psi_n \rangle^2, \tag{32}
\]

\[
I_D = -2 \langle \psi_0 | z R_0 z \psi_0 \rangle \sum_n \kappa(\omega_n) \langle \psi_0 | \mathbf{p} \psi_n \rangle^2, \tag{33}
\]

\[
I_E = 4 \sum_k \sum_n \gamma(\omega_k, \omega_n) \langle \psi_0 | z R_0 \mathbf{p} \psi_k \rangle \langle \psi_k | z \psi_n \rangle \langle \psi_n | \mathbf{p} \psi_0 \rangle, \tag{34}
\]

\[
I_F = 2 \sum_l \sum_k \sum_n \phi(\omega_l, \omega_k, \omega_n) \langle \psi_0 | \mathbf{p} \psi_l \rangle \langle \psi_l | z \psi_k \rangle \langle \psi_k | z \psi_n \rangle \langle \psi_n | \mathbf{p} \psi_0 \rangle, \tag{35}
\]
where

\[ \lambda(t) = t \ln \left( 1 + \frac{L}{t} \right), \]  
(36)

\[ \kappa(t) = \ln \left( 1 + \frac{L}{t} \right) - \frac{L}{L + t}, \]  
(37)

\[ \gamma(s, t) = \frac{\lambda(s) - \lambda(t)}{s - t}, \]  
(38)

\[ \phi(r, s, t) = -\frac{\lambda(r)}{(r - s)(r - t)} - \frac{\lambda(s)}{(s - t)(s - r)} - \frac{\lambda(t)}{(t - r)(t - s)}. \]  
(39)

Equations (38) and (39) are valid when all arguments \( r, s, \) and \( t \) are different. If \( t = s \) then \( \gamma(s, s) = \kappa(s) \). This case is very unlikely however since the states \( \psi_k \) and \( \psi_n \) in Eq. (34) are of different parity. The function \( \phi(r, s, t) \) is symmetric in its arguments. This may be used to simplify somewhat the summations in Eq. (35). When only two arguments are equal, for instance \( r \) and \( t \) (\( \psi_l \) and \( \psi_n \) are of the same parity), one obtains

\[ \phi(r, s, r) = \frac{r}{(r - s)^2} \left[ \ln \left( 1 + \frac{L}{r} \right) - \ln \left( 1 + \frac{L}{s} \right) \right] + \frac{L}{(L + r)(r - s)}. \]  
(40)

In an unlikely case when all arguments are equal (\( \psi_k \) must be of different parity than that of \( \psi_l \) and \( \psi_n \)), one finds

\[ \phi(r, r, r) = \frac{L^2}{2r(L + r)^2}. \]  
(41)

To obtain the final formula for the analytic second derivative of the Drake and Goldman expression for \( \ln k_0 \), we have to eliminate the logarithmic divergencies in the square bracket of Eq. (27) by taking the limit \( L \to \infty \). This is not entirely straightforward since the logarithmic divergencies in the individual components of \( \partial^2 E_N \), given by Eqs. (30)-(35), must be isolated and shown to cancel against appropriate counterterms resulting from \((N_L/D) \partial^2 E_D\).

To identify these counterterms, we replace \( N_L \) in Eq. (27) by the large-\( L \) estimate

\[ N_L = N - D \ln(2L) + O(L^{-1/2}), \]  
(42)
resulting from Eqs. (20) and (23), and write the difference in the square brackets in Eq. (27) as

\[ \partial^2 E_N - \frac{N_L}{D} \partial^2 E_D = \partial^2 E_N + \partial^2 E_D \ln L - (\ln k_0 - \ln 2) \partial^2 E_D + O(L^{-1/2}). \]  
(43)

The derivative \( \partial^2 E_D \) is calculated in practice using the relation \( D = 4\pi D_1 \) with \( D_1 \) given by the right-hand side of Eq. (2), but to obtain the counterterms needed to cancel the
logarithmic divergence of the individual contributions to $\partial^2 E_N$, cf. Eqs. (30)-(35), we differentiate the expression $\langle \psi_0 | p(H - E_0) p\psi_0 \rangle$ also defining $D$. The second derivative of this expression at $E=0$ is

$$
\partial^2 E D = 2\langle \partial^2 E \psi_0 | p(H - E_0) p\psi_0 \rangle - \langle \psi_0 | p^2 \psi_0 \rangle \partial^2 E_0
$$

where $\partial E \psi_0 = -R_0 z \psi_0$, $\partial^2 E \psi_0 = 2R_0 z R_0 z \psi_0 - \langle \psi_0 | z R_0^2 z \psi_0 \rangle \psi_0$, and $\partial^2 E_0 = -2\langle \psi_0 | z R_0 z \psi_0 \rangle$, are the appropriate derivatives of the wave function and the energy. Inserting these derivatives into Eq. (44), one finds that $\partial^2 E D$ can be written as a sum of the following five terms

$$
\partial^2 E D = D_A + D_B + D_C + D_D + D_E,
$$

where

$$
D_A = 4 \sum_n \omega_n \langle \psi_0 | z R_0 z R_0 p \psi_n \rangle \langle \psi_n | p \psi_0 \rangle,
$$

$$
D_B = 2 \sum_n \omega_n \langle \psi_0 | z R_0 p \psi_n \rangle \langle \psi_n | p R_0 z \psi_0 \rangle,
$$

$$
D_C = -2\langle \psi_0 | z R_0^2 z \psi_0 \rangle \sum_n \omega_n |\langle \psi_0 | p \psi_n \rangle|^2,
$$

$$
D_D = 2\langle \psi_0 | z R_0 z \psi_0 \rangle \langle \psi_0 | p^2 \psi_0 \rangle,
$$

$$
D_E = -4\langle \psi_0 | z R_0 p z p \psi_0 \rangle.
$$

Let us now consider the logarithmically divergent terms in Eqs. (30)-(34). To isolate them we need the following large-$L$ estimates

$$
\lambda(t) = t \ln L - t \ln t + O(L^{-1})
$$

$$
\kappa(t) = \ln L - \ln t - 1 + O(L^{-1}).
$$

Inserting Eqs. (51) and (52) into Eqs. (30)-(34), it is easy to see that all terms proportional to $\ln L$ cancel exactly against the second term on the right-hand side of Eq. (43). More specifically, the $\ln L$ component of $I_X$ cancels against $D_X \ln L$, $X=A,B,C,D,E$, cf. Eqs. (46)-(49). What remains after these cancellations is the sum of contributions given by Eqs. (30)-(34) in which the factors $\lambda(t)$ and $\kappa(t)$ are replaced by $-t \ln t$ and $-\ln t - 1$, respectively, and the $\gamma(s,t)$ factor by

$$
\gamma_{\infty}(s,t) = -s \ln s - t \ln t
$$

$$
\frac{s \ln s - t \ln t}{s - t}
$$

16
for \( s \neq t \) and by \( \gamma_\infty(t, t) = -\ln t - 1 \), when \( s=t \).

To finish the discussion of the \( L \to \infty \) limit, we still have to consider the contribution from the \( I_F \) term of Eq. (35), which is finite at large \( L \). One can easily show that the \( L \to \infty \) limit of the factor \( \phi(r, s, t) \), denoted by \( \phi_\infty(r, s, t) \), is given by

\[
\phi_\infty(r, s, t) = \frac{r \ln r}{(r-s)(r-t)} + \frac{s \ln s}{(s-t)(s-r)} + \frac{t \ln t}{(t-r)(t-s)},
\]

(54)

when all arguments \( r, s, \) and \( t \) are different, and

\[
\phi_\infty(r, r, t) = \frac{t (\ln t - \ln r)}{(r-t)^2} + \frac{1}{r-t},
\]

(55)

\[
\phi_\infty(r, r, r) = \frac{1}{2r}.
\]

(56)

when two of them or all three are equal.

Summarizing, the final formula for the second derivative of the Goldman-Drake expression for the Bethe logarithm is

\[
\partial_\xi^2 \ln k_0 = \frac{1}{D} (G_A + G_B + G_C + G_D + G_E + G_f) - (\ln k_0 - \ln 2) \frac{\partial_\xi^2 D}{D},
\]

(57)

where

\[
G_A = 4 \sum_n \omega_n \ln \omega_n \langle \psi_0 | zR_0 zR_0 p\psi_n \rangle \langle \psi_n | p\psi_0 \rangle,
\]

(58)

\[
G_B = 2 \sum_n \omega_n \ln \omega_n \langle \psi_0 | zR_0 p\psi_n \rangle \langle \psi_n | pR_0 z\psi_0 \rangle,
\]

(59)

\[
G_C = -2 \langle \psi_0 | zR_0^2 z\psi_0 \rangle \sum_n \omega_n \ln(\omega_n) |\langle \psi_0 | p\psi_n \rangle|^2,
\]

(60)

\[
G_D = 2 \langle \psi_0 | zR_0 z\psi_0 \rangle \sum_n (1 + \ln \omega_n) |\langle \psi_0 | p\psi_n \rangle|^2,
\]

(61)

\[
G_E = 4 \sum_k \sum_n \gamma_\infty(\omega_k, \omega_n) \langle \psi_0 | zR_0 p\psi_k \rangle \langle \psi_k | z\psi_n \rangle \langle \psi_n | p\psi_0 \rangle,
\]

(62)

\[
G_F = 2 \sum_l \sum_k \sum_n \phi_\infty(\omega_l, \omega_k, \omega_n) \langle \psi_0 | p\psi_l \rangle \langle \psi_l | z\psi_k \rangle \langle \psi_k | z\psi_n \rangle \langle \psi_n | p\psi_0 \rangle.
\]

(63)

All components in the expression for \( \partial_\xi^2 \ln k_0 \) are finite, but substantial cancellations of individual terms can occur and the final value of \( \partial_\xi^2 \ln k_0 \) is expected to be at least two orders of magnitude smaller than the individual contributions in Eq. (57).

Since \( N_L = 0 \) when \( L = 0 \), one can think of deriving Eq. (57) by differentiation of Eq. (20) setting \( L = 0 \). The individual integrals resulting then from the application of Eq. (16) are
divergent at infinity and require regularization that in practice is the same as the one used by us to derive Eqs. (57)-(63). Thus, $L$ can be viewed as a regularization parameter needed to derive the second derivative of the Goldman-Drake expression for the Bethe logarithm.

The problem of finding a basis to represent pseudostates needed to accurately compute the quantities defined by Eqs. (58)-(63) presents a serious challenge. Unless $L$ is very small, the same problem appears in calculating the quantities defined by Eqs. (30)-(35). The difficulty stems from the fact that pseudostates with extremely high energies are required to converge the logarithmic sums of the form of Eq. (18) or Eq. (21) and, also, from the additional flexibility needed to describe the polarization by the external electric field. To obtain a suitable basis, we followed the procedure employed by Korobov [42, 45] in his highly accurate calculations of Bethe logarithms for the helium atom. In his method, the parameters $\xi_i, \eta_i$ and $\nu_i$ defining the basis functions of Eq. (8) are distributed stochastically within one or several three-dimensional boxes while the positions and sizes of these boxes are determined by minimizing the Hylleraas functional of Eq. (9) setting $\omega = 0$ and replacing the inhomogeneity function $h$ by $h_1 = (z_1 r_i^{-3} + z_2 r_i^{-3})\psi_0$. The singular behavior of $h_1$ at $r_i \rightarrow 0$ increases the flexibility of the basis at small $r_i$ which is needed to represent pseudostates with very high energies. The inhomogeneity function $h_1$ was used by us to optimize bases of natural $P$ symmetry. To optimize bases of $S$ and $D$ symmetry, we used the same Hylleraas functional but with the inhomogeneity $h$ replaced by the $S$ and $D$ part, respectively, of the function $h_2 = (z_1 r_i^{-3} + z_2 r_i^{-3})R_0 z\psi_0$. To optimize bases of $P^e$ symmetry, the inhomogeneity $h_3 = (x_1 r_i^{-3} - z_2 r_i^{-3})R_0 x\psi_0$ was used.

The basis set for pseudostates of natural $P$ symmetry needed to evaluate $N_L$ via Eq. (21) was constructed as follows. We start with the primary box $[A_1, A_2] \times [B_1, B_2] \times [C_1, C_2]$ with a uniform stochastic distribution of $K_0$ triples of real exponents $\xi_i, \eta_i, \nu_i$. This box defines $K_0$ basis functions. Then, following the ideas presented in Refs. 42 and 45, we build a set of secondary boxes $[\tau^k A_1', \tau^k A_2'] \times [B_1', B_2'] \times [C_1', C_2']$, $k = 0, \ldots, 14$, where $\tau = A_2/A_1$ and where $A_1', A_2', B_1', B_2', C_1', C_2'$ are parameters subject to nonlinear optimization together with the primary box parameters $A_1, A_2, B_1, B_2, C_1, C_2$. In each secondary box, we distribute stochastically $n_k K_0/25$ basis functions, where $n_k = 10, 8, 6, 5, 4, 3, 2, 2, 2, 1, 1, 1, 1, 1$ for $k = 0, \ldots, 14$, respectively. The parameters $\xi_i, \eta_i, \nu_i$ were always constrained by the conditions $\xi_i + \eta_i > \sqrt{2I}$, $\eta_i + \nu_i > \sqrt{2I}$, $\nu_i + \xi_i > \sqrt{2I}$, where $I$ is the ionization potential.
of helium. This ensures that the basis functions fall off sufficiently rapidly when \( r_1, r_2 \to \infty \) to represent a bound state. If a randomly generated basis function fails to fulfill these conditions, it is rejected and another one is generated.

To represent pseudostates of \( P \) symmetry, we used \( 3K_0 \) basis functions defined by 12 nonlinear parameters. The bases with \( K_0 = 100, 200, \) and 400 were optimized. To represent \( \psi_0 \), we used a single box with \( K_0 \) basis functions and box parameters determined by minimizing the ground-state energy. The helium atom energies obtained using bases with \( K_0 = 100, 200, \) and 400 terms were only \( 9 \times 10^{-10}, 11 \times 10^{-12}, \) and \( 5 \times 10^{-14} \) above the accurate ground-state energy of the helium atom [46–48].

Using the pseudostates obtained with the basis sets optimized as described above, we evaluated \( N_L \) via Eq. (21) for \( L = 100, 200, 500, 1000 \). The resulting values of \( \ln k_0(L) \), cf. Eq. (25), are shown in Table VI. It is seen that the convergence with increasing \( L \) is very slow, as expected from the error estimate of Eq. (26), and that the basis set convergence is also slow, deteriorating appreciably with the increase of \( L \). The extrapolation to \( L = \infty \) based on the error estimate of Eq. (26) is, however, quite effective reducing the error of \( \ln k_0 \) by three orders of magnitude compared to the \( L = 1000 \) value given in Table VI. Specifically, applying Eq. (26) for \( L = 100, 200, 500, 1000 \), neglecting the \( \mathcal{O}(L^{-5/2}) \) terms, and solving for the unknown variables \( \ln k_0, C_4, C_5 \) and \( C_6 \) we obtain \( \ln k_0 = 4.370 \, 162 \, 1 \) when \( K_0 = 400 \). This value has the relative error of \( 5 \cdot 10^{-7} \) comparing to the best available value [34] and is significantly more accurate than the results of the first two applications of the Schwartz method [27, 49].

| \( K_0 \) \( \backslash \) \( L \) | 100 | 200 | 500 | 1000 |
|---|---|---|---|---|
| 100 | 4.410 654 707 | 4.385 346 797 | 4.374 273 575 | 4.371 701 275 |
| 200 | 4.410 629 878 | 4.385 315 192 | 4.374 232 108 | 4.371 652 027 |
| 400 | 4.410 629 718 | 4.385 314 986 | 4.374 231 829 | 4.371 651 683 |

To calculate the second electric-field derivative of Bethe logarithm, we need also bases of scalar \( S \), pseudovector \( P^e \), and natural \( D \)-symmetry. The specific composition of these
bases was as follows. For the $S$ symmetry, we used seven boxes. The first box, containing $K_0/2$ functions, was the same as optimized earlier in the calculations of the ground-state wave function $\psi_0$. The second box was optimized using the modified Hylleraas functional and also contains $K_0/2$ functions. The remaining five boxes had exponentially growing sides $[\tau^n A'_1, \tau^n A'_2]$, $k = 0, \ldots, 4$ with $\tau = A_2/A_1$ defined by the parameters $A_1$ and $A_2$ optimized for the second box. These boxes contain $n_k K_0/25$ basis functions, where $n_k = 7, 6, 5, 4, 3$ for $k = 0, \ldots, 4$. In this way, by optimizing 12 nonlinear parameters, we have generated the total of $2K_0$ scalar functions.

For pseudostates of $P^e$ and $D$ symmetry, we used six boxes. The primary boxes contained $K_0$, and $3/2K_0$ basis functions in the case of the $P^e$ and $D$ symmetry, respectively. The remaining five boxes had exponentially increasing sides as for the $S$ symmetry. These five boxes contained $K_0$, and $5/2K_0$ basis functions for the $P^e$ and $D$ symmetry, respectively, distributed proportionally in the same way as in the case of the last five, exponentially growing boxes of $S$ symmetry. In total, we stochastically generated $2K_0$ basis functions of $P^e$ symmetry and $4K_0$ functions of $D$ symmetry. In each case 12 nonlinear parameters were optimized. Bases for the first-order functions $R_0 z \psi_0$ and $R_0 p_z \psi_0$ and for the second-order function $R_0 z R_0 z \psi_0$ ($S$ symmetry only) contained $K_0$ elements and were obtained from a single box, optimized using appropriate Hylleraas functionals.

Using the bases optimized for $K_0 = 100, 200, \text{and} 400$, we evaluated the $L$ dependence of $\partial^2_{L} \ln k_0(L)$, see Eq. (27), for $L = 50, 100, 200, 500$. The results are shown in Table VII. It is seen that the convergence both in $K_0$ and in $L$ is much slower than in the case of $\ln k_0(L)$. This is due to the loss of at least two digits in the subtraction in Eq. (28) and to the much

| $K_0 \backslash L$ | 50   | 100  | 200  | 500  |
|-------------------|------|------|------|------|
| 100               | 0.041523 | 0.044121 | 0.049995 | 0.050930 |
| 200               | 0.044327 | 0.046739 | 0.048492 | 0.049303 |
| 400               | 0.044476 | 0.046882 | 0.048075 | 0.048617 |

TABLE VII. $L$ dependence of $\partial^2_{L} \log k_0(L)$, see Eq. (27). For $\partial^2_{L} C_3$ we assumed the value $-0.05230$, see Table II and Appendix.
increased basis set sensitivity of the components of Eq. (29) compared to the already hard to converge summation in Eq. (21). The slowest convergence occurs in computing the $I_B$ contribution of Eq. (31), which determines the final accuracy of $\partial_\xi^2 \ln k_0(L)$. In fact, the results for $L=1000$ were not accurate enough to perform a reliable extrapolation and are not shown in Table VII. Also the values of the limit $L=\infty$ obtained from Eq. (57) were very inaccurate and are not reported.

Employing the values of $\partial_\xi^2 \ln k_0(L)$ obtained with $L = 50, 100, 200, 500$, and the error formula of Eq. (26), we find that the extrapolated values of $\partial_\xi^2 \ln k_0$ are 0.04924 and 0.04875 when bases with $K_0=200$ and $K_0=400$, respectively, are used. From these values one can infer that the accurate value of $\partial_\xi^2 \ln k_0$ is smaller than 0.00487, in disagreement with the result of Ref. 26. Based on the convergence pattern observed by us, it is very difficult to assign a reliable uncertainty to the value of $\partial_\xi^2 \ln k_0$ resulting from our sum-over-states calculation. We estimate that this uncertainty is no worse than about 0.005 (i.e. about 1%) and that our sum-over-states value of $\partial_\xi^2 \ln k_0$ amounts to 0.0487(5). This value differs by 5% from the value published in Ref. 26, but is in perfect agreement with the value obtained by us in Sec. II using the Schwartz method. It is clear that in the case of polarizability calculation the Schwartz method is much more accurate (since the nonlinear optimizations are performed for each value of the frequency $\omega$) but the Goldman-Drake approach can be used as an independent check of the result obtained using the Schwartz method.

We made some effort to explain the difference (of about 5%) between the results of our calculations (obtained using two different methods) and the result of Ref. 26 obtained by an application of the original version of the Schwartz method. We found that the observed disagreement has three sources: (i) the omission of the singular, $\psi_0$ contribution to the resolvent $R(\omega)$ in Eq. (16) for $\partial_\xi^2 J(\omega)$ used in Ref. 26 [the singularity $\omega^{-1}$, and the $\omega$ independent terms cancel out in the final expression for $\partial_\xi^2 J(\omega)$, so this contribution is small], (ii) the insufficiently accurate value of $\partial_\xi^2 \langle \psi_0 | p^2 \psi_0 \rangle$ used in Ref. 26 to evaluate the integral defining $\partial_\xi^2 \ln k_0$, and (iii) the value of $\partial^2 E_{C^3}$ employed in Ref. 26 was incorrect since it was computed from an incomplete formula, missing the explicit electric-field contribution $\partial^2 E_{C^3(2)}$ derived in Appendix of the present work.
IV. QED RECOIL CORRECTION

Theory of nuclear mass dependence of the $\alpha^3$ QED correction for two-electron systems has been given by Pachucki in Ref. 50. The expressions derived in this reference have been applied for the first time in Ref. 51 for the lowest $S$ states of the helium atom and subsequently for other excited states of helium [21] and helium like ions [52], as well as for the low-lying states of lithium [53], beryllium [54], and boron [55] atoms. The leading correction $E^{(3,1)}$, of the order of $1/M \equiv m_e/m_\alpha$, can be written as sum of three contributions $E^{(3,1)}_{R1}$, $E^{(3,1)}_{R2}$, and $E^{(3,1)}_{R3}$. The first two represent the change linear in $1/M$ of the ingredients in Eq. (1) that results from adding to $H$ the nuclear kinetic energy operator $P^2/(2m_\alpha)$ corresponding to the recoil momentum $P = -(p_1 + p_2)$. The first contribution, $E^{(3,1)}_{R1}$, accounts for the effect of $p_1^2/(2m_\alpha) + p_2^2/(2m_\alpha)$. It can be obtained by scaling Eq. (1) with the reduced mass $\mu/m_e \approx 1 - 1/M$, resulting in

$$E^{(3,1)}_{R1} = \frac{1}{M} \left( -3E^{(3,0)} + 2E \frac{\partial}{\partial E} E^{(3,0)} + \alpha^3 \frac{8}{3} D_1 - \alpha^3 \frac{14}{3} D_2 \right), \quad (64)$$

where the second term in the parentheses is a consequence of the electric-field dependence of the scaled wave function $\mu^0 \psi(\mu r_1, \mu r_2, \mu^2 E)$, while the last two terms originate from the $\ln \mu$ dependence of the Bethe logarithm $\ln k_0$ [51] and from the $\mu^3 \ln \mu^{-1}$ scaling of the Araki-Sucher term $A_2$ [52]. The second contribution, $E^{(3,1)}_{R2}$, is due to the mass polarization term $H_{MP} = p_1 p_2/m_\alpha$ and requires new calculations. It has the form

$$E^{(3,1)}_{R2} = \alpha^3 \frac{1}{M} \left[ \frac{8}{3} \left( \frac{19}{30} - 2 \ln \alpha - \ln k_0 \right) \partial_M D_1 - \frac{8}{3} D_1 \partial_M \ln k_0 \right. \\
+ \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) \partial_M D_2 - \frac{7}{6\pi} \partial_M A_2 \right], \quad (65)$$

where $\partial_M$ denotes the derivative with respect to $1/m_\alpha$ when only the mass polarization term $H_{MP}$ is added to $H$. The third contribution is a generalization of the Salpeter correction known for the hydrogen atom [56]. It has the form [50]

$$E^{(3,1)}_{R3} = \alpha^3 \frac{4}{M} \left[ \left( -2 \ln \alpha + \frac{62}{9} - \frac{8}{3} \ln k_0 \right) D_1 - \frac{7}{6\pi} A_1 \right], \quad (66)$$

where

$$A_1 = \langle \psi | P(r_{1}^{-3}) + P(r_{2}^{-3}) | \psi \rangle \quad (67)$$

with the distribution $P(r^{-3})$ defined by Eq. (4).
When \( \mathcal{E} = 0 \), the evaluation of \( E^{(3,1)}_{R1} \) and \( E^{(3,1)}_{R3} \) is no more difficult than the evaluation of \( E^{(3,0)} \). To evaluate of \( E^{(3,1)}_{R2} \), we need also the derivatives \( \partial_M D_1 \), \( \partial_M D_2 \), \( \partial_M A_2 \), and \( \partial_M \ln k_0 \). The first three of them can be easily obtained from the double perturbation theory expression

\[
\partial_M X = -2 \langle \psi | \hat{X} R_0 H_{MP} \psi \rangle,
\]

where \( \hat{X} \) stands for the operators appearing in Eqs. (2)-(4). Since \( 1/M \) is very small, these derivatives can also be obtained with sufficient accuracy using the finite difference method. Analytic evaluation of the derivative \( \partial_M \ln k_0 \) is nontrivial. It has been performed for the first time by Pachucki and Sapirstein [51]. Currently the most accurate value of \( \partial_M \ln k_0 = 0.0943894(1) \) has been reported by Yerokhin and Pachucki [52]. Somewhat less accurate value of \( \partial_M \ln k_0 = 0.09438(1) \) has been obtained by Drake and Goldman [39] using the finite difference method. Using the result from the former reference and the finite difference calculation of the remaining derivatives, we found that \( E^{(3,1)} = -5.12993 \cdot 10^{-9} \), in agreement with the value \( -5.129925 \cdot 10^{-9} \) reported in Ref. 52.

Performing electric field differentiation of Eqs. (64)-(66), setting \( \mathcal{E} = 0 \), and reversing the sign, we find

\[
\alpha_{d}^{(3,1)} = \alpha_{R1}^{(3,1)} + \alpha_{R2}^{(3,1)} + \alpha_{R3}^{(3,1)},
\]

(68)

where

\[
\alpha_{R1}^{(3,1)} = \frac{1}{M} \left( \alpha_{d}^{(3,0)} - \alpha^3 \frac{8}{3} \partial_D^2 D_1 + \alpha^3 \frac{14}{3} \partial^2 D_2 \right),
\]

(69)

\[
\alpha_{R2}^{(3,1)} = \frac{1}{M} \left[ - \frac{8}{3} \left( \frac{19}{30} - 2 \ln \alpha - \ln k_0 \right) \partial_M \partial_D^2 D_1 - \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) \partial_M \partial_D^2 D_2 
\]

\[
+ \frac{7}{6\pi} \partial_M \partial^2 A_2 + \frac{8}{3} \partial_D^2 D_1 \partial_M \ln k_0 + \frac{8}{3} \partial_M D_1 \partial_D^2 \ln k_0 + \frac{8}{3} D_1 \partial_M \partial_D^2 \ln k_0 \right],
\]

(70)

\[
\alpha_{R3}^{(3,1)} = \frac{4}{M} \left[ \left( \frac{2}{3} \ln \alpha - \frac{62}{9} \right) \partial_D^2 D_1 + \frac{8}{3} D_1 \partial_D^2 \ln k_0 + \frac{7}{6\pi} \partial_D^2 A_1 \right].
\]

(71)

Equation (69) can also be obtained by performing the reduced mass scaling of Eq. (64) and observing that \( \partial_D^2 \ln k_0 \) scales as \( \mu^{-4} \) with the reduced mass \( \mu \). The first four terms in the square brackets of Eq. (70) can be obtained by performing the \( \partial_M \) differentiation of the approximate expression for \( \alpha_{d}^{(3,0)} \) used by Pachucki and Sapirstein [25]. Since, as found in Ref. 26 and confirmed in the present work, the derivative \( \partial_D^2 \ln k_0 \) neglected by Pachucki and Sapirstein is very small, we employed the same approximation and neglected
the last two terms in the square brackets in Eq. (70). Actually, we know the contribution of the penultimate term, containing the product $\partial M D_1 \partial^2 \ln k_0$. This contribution equals to $-1.3 \cdot 10^{-12}$ and is completely negligible. The contribution of the last term can be estimated assuming that the $\partial M$ derivative of $\partial^2 \ln k_0$ is of the same order of magnitude as $\partial^2 \ln k_0$ (the $\partial M$ derivatives appear to be always smaller than or of the same order of magnitude as the differentiated quantities, see Table 1 of Ref. 51; the same holds for the $\partial M$ derivatives of $\partial^2 E_1$, $\partial^2 E_2$, and $\partial^2 E A_2$). Making this assumption, we find that the neglected contribution of $\partial M \partial^2 \ln k_0$ is of the order of $10^{-11}$ and is negligible compared to other contributions to the recoil correction. This justifies the Pachucki-Sapirstein approximation in evaluating $\alpha_d^{(3,1)}$.

To compute the $\partial M$ derivatives of the expectation values, we used the finite difference method and our largest basis set, $N = 512$, developed to obtain the derivatives shown in Table I. We have found that $\alpha R_1^{(3,1)} = 0.00484$, $\alpha R_2^{(3,1)} = 0.00087$, $\alpha R_3^{(3,1)} = 0.00541$, and that the whole QED recoil correction $\alpha d^{(3,1)}$ is equal to 0.01112(1), with all values in the units of $10^{-6} a_0^3$.

The assumed uncertainty results from a conservative estimate of the neglected electric-field derivatives of $\ln k_0$

V. SUMMARY OF THE RESULTS AND CONCLUSIONS

We performed calculations of the main, $\alpha^3$ QED contribution to the static polarizability of helium including the hard-to-compute electric-field dependence of Bethe logarithm and the finite nuclear mass (recoil) effects. This work complements earlier studies of the leading relativistic correction [51, 57], relativistic recoil effects [18], and the QED correction in the infinite nuclear mass approximation [26, 51]. Our calculations of the second electric-field derivative of the Bethe logarithm $\partial^2 \ln k_0$, performed using the integral representation method of Schwartz [27], see Sec. II, confirm the very small value of this quantity found in Ref. 26. However, the value of $\partial^2 \ln k_0$ obtained by us, equal to 0.0485572(14), is smaller than the value of Ref. 26, equal to 0.0512(4), by about 6 times the error estimate given in Ref. 26. To resolve this discrepancy, we performed, see Sec. III, calculations of $\partial^2 \ln k_0$ using a different method based on the direct summation of the spectral representation of $\partial^2 \ln k_0$ in terms of pseudostates, along the lines suggested by Goldman and Drake [29] and Korobov [36]. The result of this second calculation, equal to 0.00487(5), is consistent with the result the
calculation using the integral representation method of Schwartz but is inconsistent with the result of Ref. 26.

TABLE VIII. Static polarizability of helium 4 (in $a_0^3$ unless otherwise noted) including relativistic and QED corrections. 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.

| Calculation                                      | Value               |
|--------------------------------------------------|---------------------|
| nonrelativistic                                   | 1.383 809 986 4$^a$ |
| $\alpha^2$ relativistic                          | $-0.000 080 359 9^a$|
| $\alpha^2/M$ relativistic recoil                 | $-0.000 000 093 5(1)^b$ |
| $\alpha^3$ QED $- \partial_\kappa^2 \ln k_0$ term | 0.000 030 473 8     |
| $\partial_\kappa^2 \ln k_0$ term                | 0.000 000 182 2     |
| $\alpha^2/M$ QED recoil                          | 0.000 000 011 12(1)$^c$ |
| $\alpha^4$ QED                                   | 0.000 000 56(14)$^d$ |
| finite nuclear size                               | 0.000 000 021 7(1)$^e$ |
| total                                            | 1.383 760 78(14)    |
| molar polarizability $\frac{4\pi}{3} \alpha d N_A$ | 0.517 254 08(5)$^f,g$ |
| experiment, Ref. 58                              | 0.517 254 4(10)$^f$ |

$^a$ Ref. 23.

$^b$ The uncertainty accounts for the included of terms of the order of $1/M^2$ and of higher order [18].

$^c$ The uncertainty due to the neglect of the mixed derivative $\partial_\kappa \partial_\mu^2 \ln k_0$ in Eq. (70).

$^d$ The uncertainty accounts for an incomplete calculation of the $\alpha^4$ QED correction to polarizability, see Ref. 18.

$^e$ Ref. 18.

$^f$ In cm$^3$/mole.

$^g$ Using the nonrelativistic polarizability of the $^3$He atom, equal to 1.38401218(1) [23] and scaling the recoil corrections with the mass ratio of 1.32711 one finds that the molar polarizability of helium-3 is 0.517 329 65(5) cm$^3$/mole.

After including the contribution of $\partial_\kappa^2 \ln k_0$, the total value of the $\alpha^3$ QED correction
to the polarizability of helium in the infinite nuclear mass approximation amounts to 30.6560(1) \cdot 10^{-6} a_0^3. We derived a formula for the correction to this value due to the finite nuclear mass (the QED recoil correction). In evaluating this formula we neglected $\partial_2^2 \ln k_0$ and the mass-polarization effect on $\partial_2^2 \ln k_0$, given by the mixed derivative $\partial_M \partial_2^2 \ln k_0$. This approximation is well justified, see Sec. IV, in view the smallness of $\partial_2^2 \ln k_0$, compared to other ingredients of Eqs. (69)-(71). The value of the $\alpha^3$ QED recoil correction $\alpha_d^{(3,1)}$ obtained by us equals to 0.01112(1) \cdot 10^{-6} a_0^3 and is only about 9 times smaller than the $\alpha^2$ relativistic recoil correction $\alpha_d^{(2,1)}$. It may be of interest to note that the significance of the finite mass contributions to the nonrelativistic, $\alpha_d^{(0)}$, relativistic, $\alpha_d^{(2)}$, and QED, $\alpha_d^{(3)}$, components of the static polarizability of helium 4 are quite different. Specifically, we found that $\alpha_d^{(0,1)}/\alpha_d^{(0)} \approx 3.2/M$, $\alpha_d^{(2,1)}/\alpha_d^{(2)} \approx 8.5/M$, $\alpha_d^{(3,1)}/\alpha_d^{(3,0)} \approx 2.7/M$.

In Table VIII, the results of our calculations are added to the data obtained in earlier work [18, 23] and compared with the most recent experimental determination [58] of $\alpha_d$, given in terms of the molar polarizability $A_\epsilon = 4 \pi \alpha_d N_A / 3$. The agreement between theory and experiment is very good, although the uncertainty of the experimental value is an order of magnitude larger than that of the theoretical determination. This high theoretical accuracy appears to be presently sufficient for metrological purposes [9–11]. As shown in Table VIII, this accuracy is currently limited by the incomplete calculation of the $\alpha^4$ QED correction. Complete calculations of this correction for the energy levels of helium have been very challenging [52, 59, 60] and have not been attempted when the effect of the interaction with external electric field is included in the Hamiltonian. The recent successful calculation of the $\alpha^4$ QED correction for the hydrogen molecule [61] shows that a similar calculation for the helium atom in the uniform electric field, a system of the same symmetry as H2, may be possible if accuracy higher than achieved in the present work is required for metrological or other applications.

**APPENDIX**

In this Appendix we present derivation of the second electric-field derivative of the $C_3$ coefficient that determines the $\omega^{-3}$ term (equal to $4DC_3 \omega^{-3}$) in the large-$\omega$ asymptotic expansion of $J(\omega)$. To obtain this expansion, we consider an auxiliary function $\varphi$ defined
by
\[
(H - E + \omega) \varphi = p \psi.
\] (72)
where \(\psi\) is the real ground-state eigenfunction of the Hamiltonian \(H = H_0 + \mathcal{E}z\). For the sake of brevity, in Eq. (72) and in further in the text we suppress the dependence of \(\varphi\) on \(\mathcal{E}\) and on \(\omega\). Obviously \(J(\omega) = \langle p \psi | \varphi \rangle\), but it is advantageous to compute \(J(\omega)\) from the expression
\[
J(\omega) = \langle \varphi | p \psi \rangle + \langle \psi | p \varphi \rangle - \langle \varphi | H - E + \omega | \varphi \rangle,
\] (73)
which for an approximate \(\varphi\) gives \(J(\omega)\) with an error quadratic in the error of \(\varphi\) [and provides a lower bound to \(J(\omega)\)]. Following Schwartz [27], we write \(\varphi\) in the form
\[
\varphi = \frac{1}{\omega} p \psi + i U,
\] (74)
where the real function \(U\) collects terms that vanish faster than \(\omega^{-1}\). Inserting Eq. (74) into Eqs (72) we find that \(U\) obeys the relation
\[
(H - E + \omega) U = -\frac{2}{\omega} a \psi - \frac{2}{\omega} \mathcal{E} k \psi.
\] (75)
and that \(J(\omega)\) can be represented in the form
\[
J(\omega) = \frac{1}{\omega} \langle \psi | p^2 \psi \rangle - D \frac{4}{\omega^2} - \frac{4}{\omega} \langle a \psi | U \rangle - \frac{4}{\omega} \mathcal{E} \langle \psi | U \rangle k - \langle U | H - E_0 + \omega | U \rangle,
\] (76)
where \(k\) is the unit vector on the \(z\) axis and \(a = r_1 r_1^{-3} + r_2 r_2^{-3}\), so that \([H, p] = 2i(a - \mathcal{E} k)\).

It is obvious that the solution of Eq. (75) can be written as \(U = U_1 + U_2\), where
\[
U_2 = -\frac{2}{\omega^2} \mathcal{E} k \psi
\] (77)
and \(U_1\) is the solution of Eq. (75) with the last term neglected. Schwartz [27] has found an approximate solution for \(U_1\) which, when inserted in Eq. (76), correctly recovers the \(\omega^{-5/2}\), \(\omega^{-3}\ln \omega\), and \(\omega^{-3}\) terms in the large-\(\omega\) asymptotic expansion of \(J(\omega)\). His result is [27]
\[
U_1 = -\frac{2}{\omega^2} \sum_i \frac{r_i}{r_i^3} \left[1 - e^{-\mu r_i}(1 + \mu r_i)\right] \psi,
\] (78)
where \(\mu = (2\omega)^{1/2}\). In deriving Eq. (78), Schwartz neglected the potential energy terms in the Hamiltonian on the l.h.s. of Eq. (75), see Ref. 62 for an alternative derivation based on
this assumption. Thus, Eq. (78) is valid also for an atom in the electric field that enters \( U_1 \) only through the field dependence of \( \psi \).

Combining Eqs. (76)-(78), we find after some cancellations that

\[
J(\omega) = \frac{1}{\omega} \langle \psi | p^2 \psi \rangle - \frac{D}{\omega^2} J_1(\omega) + J_2(\omega) + \mathcal{O}(\omega^{-7/2}),
\]

(79)

where

\[
J_1(\omega) = -\frac{4}{\omega} \langle a \psi | U_1 \rangle - \langle U_1 | H - E_0 + \omega | U_1 \rangle
\]

and

\[
J_2(\omega) = -\frac{4}{\omega} \langle a \psi | U_2 \rangle - \frac{4}{\omega} \mathcal{E} \langle \psi | U_2 \rangle k - \langle U_2 | H - E_0 + \omega | U_2 \rangle = \frac{4}{\omega^3} \epsilon^2 + \frac{8}{\omega^3} \langle \psi | a_z \psi \rangle \mathcal{E},
\]

(81)

with \( a_z = a k \). Derivation of the large-\( \omega \) expansion of \( J_1(\omega) \) is complicated. It has been performed through the \( \omega^{-3} \) term by Schwartz [27]. His result, confirmed by Forrey and Hill [35], is

\[
J_1(\omega) = \frac{4\sqrt{2}D}{\omega^9/2} - \frac{8D}{\omega^3} \ln \omega + \frac{4D}{\omega^3} C_3^{(1)} + \mathcal{O}(\omega^{-7/2}).
\]

(82)

where the coefficient \( C_3^{(1)} \), depending on \( \mathcal{E} \) via \( \psi \), is given by the expression [27, 35]

\[
C_3^{(1)} = 4 \left( \frac{1}{2} \ln 2 - \frac{1}{2} - \gamma \right) - \frac{1}{D} \int_0^\infty \ln r \frac{d^2 \bar{\rho}(r)}{dr^2} dr + \frac{2}{D} \langle \psi | r_1 r_2 r_1^{-3} r_2^{-3} \psi \rangle,
\]

(83)

with \( \bar{\rho}(r) \) denoting the angular average of the electron density \( \rho(r) = \langle \psi | \delta(r-r_1) + \delta(r-r_2) | \psi \rangle \).

From Eqs. (79), (81), and (82), it is clear that \( C_3 = C_3^{(1)} + C_3^{(2)} \), where \( C_3^{(2)} \) is the contributions from \( J_2(\omega) \) given by

\[
C_3^{(2)} = \frac{1}{D} \epsilon^2 + \frac{2}{D} \langle \psi | a_z \psi \rangle \mathcal{E}.
\]

(84)

Calculating the second electric-field derivative at \( \mathcal{E} = 0 \) we arrive at

\[
\partial_\mathcal{E}^2 C_3^{(2)} = \frac{2}{D} - \frac{8}{D} \langle \psi_0 | z R_0 a_z \psi_0 \rangle.
\]

(85)

Since \( \langle \psi_0 | z R_0 a_z \psi_0 \rangle = 1/2 \), we finally obtain, cf. Table I,

\[
\partial_\mathcal{E}^2 C_3^{(2)} = -\frac{2}{D} = -0.04395503(1).
\]

(86)

The numerical evaluation of \( \partial_\mathcal{E} C_3^{(1)} \) is much more difficult. Performing electric-field differentiation of Eq. (83), one finds

\[
\partial_\mathcal{E} C_3^{(1)} = -\frac{1}{D} \left( \partial_\mathcal{E}^2 I_1 - \frac{I_1}{D} \partial_\mathcal{E}^2 D \right) + \frac{2}{D} \left( \partial_\mathcal{E}^2 I_2 - \frac{I_2}{D} \partial_\mathcal{E}^2 D \right),
\]

(87)
where $I_1$ and $I_2$ are the integrals

$$I_1 = \int_0^\infty \ln r \frac{d^2 \tilde{\rho}(r)}{dr^2} \, dr$$

(88)

and

$$I_2 = \langle \psi | r_1 r_2 r_1^{-3} r_2^{-3} | \psi \rangle.$$

(89)

The electric field derivatives $\partial_Z^2 I_2$ and $\partial_Z^2 \rho(r)$, needed for the evaluation of $\partial_Z^2 C_3^{(1)}$ via Eqs. (87) and (88), were computed using Eq. (7) and basis sets with $K_0 = 128$, 256, and 512 optimized as described in Sec. II. The convergence of calculations was rather slow and we found that $\partial_Z^2 C_3^{(1)} = -0.00834(2)$. The same value was obtained using an alternative formula for $C_3^{(1)}$ in which the last two terms in Eq. (83) are replaced by the finite part of $(\psi | a^2 \psi) / D$, cf. Eq. (19) in Ref. 27. One may note that the contribution $\partial_Z^2 C_3^{(2)}$, derived in the present work, is about five times larger in absolute value than the second electric-field derivative of the formula for $C_3$ given in Ref. 27.

Adding up $\partial_Z^2 C_3^{(1)}$ and $\partial_Z^2 C_3^{(2)}$, we finally find that $\partial_Z^2 C_3 = -0.05230(2)$. This value compares reasonably well with the value $-0.053(1)$ obtained from fitting the derivative of $t^{-3} \partial_Z^2 f(t)$ at $t = 0$, cf. Eqs. (12) and (15).

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