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Ulrich D. Jentschura

Missouri University of Science and Technology, ulj@mst.edu

Mariusz Puchalski

Peter J. Mohr

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Thermal correction to the molar polarizability of a Boltzmann gas

U. D. Jentschura,¹ M. Puchalski,^{1,2} and P. J. Mohr³

¹*Department of Physics, Missouri University of Science and Technology, Rolla, Missouri 65409-0640, USA*

²*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, PL-60-780 Poznań, Poland*

³*National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8420, USA*

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Metrology in atomic physics has been crucial for a number of advanced determinations of fundamental constants. In addition to very precise frequency measurements, the molar polarizability of an atomic gas has recently also been measured very accurately. Part of the motivation for the measurements is due to ongoing efforts to redefine the International System of Units (SI), for which an accurate value of the Boltzmann constant is needed. Here we calculate the dominant shift of the molar polarizability in an atomic gas due to thermal effects. It is given by the relativistic correction to the dipole interaction, which emerges when the probing electric field is Lorentz transformed into the rest frame of the atoms that undergo thermal motion. While this effect is small when compared to currently available experimental accuracy, the relativistic correction to the dipole interaction is much larger than the thermal shift of the polarizability induced by blackbody radiation.

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I. INTRODUCTION

Spectacular progress in frequency metrology of simple atoms such as hydrogen [1–3] and helium [4] has led to advances in our understanding of fundamental constants [5] and of their conceivable variation with time [6]. However, transition frequencies are not the only quantities that can be measured accurately using currently available experimental methods. The (static) molar polarizability A_ϵ of the helium-4 atom has been determined in Ref. [7] as

$$A_\epsilon = \frac{\alpha_d N_A}{3\epsilon_0} = 0.5172535(47) \frac{\text{cm}^3}{\text{mol}}, \quad (1)$$

where N_A is the Avogadro constant, ϵ_0 is the vacuum permittivity, and α_d is the static electric dipole polarizability of helium.

Recently, the topic of gas thermometry has received considerable attention through efforts to accurately measure the Boltzmann constant as the basis for a possible redefinition of the kelvin in the International System of Units (SI) [8–16]. The kelvin can be defined by assigning an exact specified value to the Boltzmann constant, and in order to move forward with the redefinition, it is necessary to know the current measured value as accurately as possible so the specified value is well chosen [17].

The molar polarizability of helium-4 is also known from theory, so an experiment that measures polarizability can instead be interpreted as a measurement of pressure or a determination of the Boltzmann constant k_B . The principle of the measurement of k_B in [7] is as follows. The refractive index ϵ_r of the helium gas is deduced by measuring microwave resonance frequencies of a helium-filled quasispherical cavity as a function of pressure and temperature. The index of refraction is related to the molar density ρ of the helium and its molar polarizability by the Clausius–Mossotti equation

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \approx A_\epsilon \rho. \quad (2)$$

In the evaluation of the measurement, a theoretical correction is applied to this formula, which is mainly due to the diamagnetic

susceptibility of the helium [see Eq. (1) of Ref. [7]]. The refractive index ϵ_r thus determines the product

$$A_\epsilon \rho = \frac{\alpha_d}{3\epsilon_0} N_A \rho. \quad (3)$$

Knowing A_ϵ from Eq. (1), one can solve for ρ . The Boltzmann constant k_B follows from the real-gas equation [“virial equation of state of helium gas”; see Eq. (2) of Ref. [7]]. This equation is approximated by the ideal-gas equation $p \approx R T \rho$, where $R = k_B N_A$ is the molar gas constant. A crucial point of the measurement [7] is that the resonator is maintained within a few millikelvins of the triple point of water, which is defined to be 273.16 K in the SI. Measuring the pressure, stabilizing T , and having determined ρ , one can finally solve for R and k_B , determining the Boltzmann constant.

As outlined, an accurate value of the atomic polarizability is a prerequisite for the measurement of k_B . In a thermal bath, the atom is subjected not only to the probing low-frequency microwave radiation but also to thermal blackbody radiation. By definition, the atomic polarizability describes a second-order process where one of the two probing photons is absorbed, while the other photon is emitted by the atom. Additional interactions involve the absorption and emission of blackbody photons and require fourth-order perturbation theory. At room temperature ($T = 300$ K), the blackbody radiation correction amounts to a relative shift [18] of the molar polarizability of helium by 4.0×10^{-18} . This relative shift is numerically small, and it would be somewhat surprising if the dominant thermal shift of the molar polarizability in an atomic gas at room temperature were as small as this.

We thus analyze a further shift of the polarizability here, which is due to the relativistic correction to the dipole interaction due to the thermal motion of the atoms. In this Brief Report, we use units with $\hbar = c = \epsilon_0 = 1$. Calculations are reported in Sec. II, and conclusions are drawn in Sec. III.

II. CALCULATION

It has been known for some time that the interaction of a compound system with an external electromagnetic field

receives a correction (“Röntgen term”) when the atom moves with respect to the electromagnetic field. The thermal motion of atoms in a typical atomic gas at room temperature follows Boltzmann statistics because the scale of the interatomic interactions (van der Waals and Casimir-Polder) is long compared to the de Broglie wavelength of the moving atoms. The well-known Röntgen term follows from the relativistic analysis of the electromagnetic interaction of a compound system with an external electromagnetic field \vec{E} .

The interaction of a compound system with the field is described by the interaction Hamiltonian

$$H_I = -\vec{D} \cdot \vec{E}, \quad D^i = \sum_{a=0}^N e_a x_a^i, \quad (4)$$

where the summation index a is over all constituent particles of the system, with the value $a = 0$ being reserved for the atomic nucleus. The charge of the a th particle is denoted as e_a . By x_a^i we denote the i th Cartesian component of the distance of the a th electron from the mass center. The total number of particles in the compound system is N . The dipole polarizability of an atom can be written as [Eq. (4) of Ref. [19]]

$$\alpha_d(\omega) = \frac{e^2}{3} \sum_{i=1}^3 \sum_{\pm} \langle \Psi_0 | \left(\sum_{n=1}^N x_n^i \right) \times \frac{1}{H - E_0 \pm \omega} \left(\sum_{n=1}^N x_n^i \right) | \Psi_0 \rangle, \quad (5)$$

where $|\Psi_0\rangle$ is the atomic ground state. Here the sum over $n = 1, \dots, N$ is over all the atomic electrons (the atomic nucleus is at the origin of the coordinate system). Evidently, the dipole polarizability is essentially the second-order dipole interaction. For a spherically symmetric ground state, all Cartesian components $i = 1, 2, 3$ contribute equally to the dynamic polarizability, and the factor of $1/3$ results from integration over angles in each component of the dipole matrix element. For small frequencies $\omega \rightarrow 0$, the symmetric limit $\pm \omega \rightarrow 0$ leads to the replacement

$$\sum_{\pm} \frac{1}{H - E_0 \pm \omega} \rightarrow 2 \left(\frac{1}{H - E_0} \right)' \quad (6)$$

and

$$\alpha_d(\omega) \rightarrow \alpha_d(0) \rightarrow \alpha_d, \quad (7)$$

where we denote the reduced Green’s function that enters the static polarizability by a prime [20].

For an atom in motion, as described in Ref. [21], the Lorentz boost modifies the dipole interaction to be

$$H'_I = -\vec{D} \cdot \left[\vec{E} + \frac{1}{M} (\vec{\Pi} \times \vec{B}) - \frac{\vec{\Pi}}{2M} \left(\frac{\vec{\Pi}}{M} \cdot \vec{E} \right) \right]. \quad (8)$$

Here $M = \sum_a m_a$ is the total mass of the compound system (atom), \vec{E} and \vec{B} are the external electric and magnetic fields, respectively, and $\vec{\Pi} = \sum_a \vec{p}_a$ is the total momentum of the compound system. The term proportional to the magnetic field vanishes after angular averaging over the directions of motion of the atoms. For the term quadratic in $\vec{\Pi}$, the angular averaging

leads to a factor $1/3$ in the effective dipole interaction, leading to the correction

$$H'_I = -\vec{D} \cdot \left[\vec{E} - \frac{\vec{\Pi}}{2M} \left(\frac{\vec{\Pi}}{M} \cdot \vec{E} \right) \right] \rightarrow -\vec{D} \cdot \vec{E} \left(1 - \frac{v^2}{6c^2} \right), \quad (9)$$

where the factor of c is restored in the denominator.

The magnitude of the dipole interaction correction has a simple physical interpretation. The dipole interaction of an atom is essentially the energy shift due to an applied electric field. In its rest frame, the moving atom sees a boosted electric field, which, after averaging over directions of the velocity, yields a correction factor of $(1 + v^2/3c^2)$ to the dipole energy. Transformation of the dipole energy in the rest frame of the atom to the laboratory frame yields an additional correction factor of $(1 - v^2/2c^2)$ for a net correction of $(1 - v^2/6c^2)$ for the effective dipole interaction as given in Eq. (9). Evidently, the dipole correction has not been examined in detail beyond the linear interaction, so we apply the same argument to the effective dipole polarizability. In this case, the interaction is quadratic in the electric field, so the correction factor is $(1 + 2v^2/3c^2)$ for the boosted field strength. The transformation to the laboratory frame is the same, so the net correction is $(1 + v^2/6c^2)$. With this factor, the effective dipole polarizability of the moving atom is

$$\alpha'_d = \alpha_d \left(1 + \frac{v^2}{6c^2} \right). \quad (10)$$

We are now in a position to average over the thermal ensemble. With $\beta = 1/(k_B T)$, where k_B is the Boltzmann constant and T is the thermodynamic temperature, the Boltzmann velocity distribution is

$$f(\vec{v}) = \left(\frac{\beta M}{2\pi} \right)^{3/2} \exp \left(-\frac{\beta M \vec{v}^2}{2} \right), \quad (11)$$

so that

$$\int d^3 v f(\vec{v}) = 1. \quad (12)$$

In accordance with the equipartition theorem, we find

$$\langle \vec{v}^2 \rangle = \frac{3}{\beta M} = \frac{3 k_B T}{M}, \quad (13)$$

so that the correction to the polarizability is

$$\alpha'_d \rightarrow \alpha_d \left(1 + \frac{k_B T}{2M c^2} \right) \equiv \alpha_d (1 + \delta), \quad (14)$$

where the last expression serves as a definition of δ . For room temperature $T = 300$ K and helium atoms, using physical constants from Ref. [5], we have a relative shift of

$$\delta = \frac{k_B T}{2M c^2} = 3.47 \times 10^{-12}. \quad (15)$$

This effect is still small when compared to the experimental accuracy reported in Ref. [7]. However, it turns out to be much larger than the shift of the polarizability due to blackbody radiation, which was previously calculated in Ref. [18].

III. CONCLUSIONS

High-precision measurements of the molar polarizability of atoms in gaseous environments have become important for the determination of fundamental constants (e.g., the Boltzmann constant) and for pressure and temperature metrology. The thermal corrections to the molar polarizability are of importance because they represent effects that cannot be easily brought under experimental control and would require difficult adjustments of the experiments unless they can be shown to be negligible.

For an atom *at rest*, immersed in a thermal bath, the blackbody radiation correction to the polarizability [18] is due to a fourth-order interaction with the electromagnetic field (two blackbody photons and two photons of the probing field) and is numerically small. However, the measurement of the

polarizability usually proceeds in a Boltzmann gas, where atoms are in thermal motion. In this Brief Report, we find that the dominant thermal shift of the molar polarizability in the latter case is due to the Röntgen term, i.e., due to the necessity of transforming the probing electric field into the rest frame of the moving atom by a Lorentz transformation and transforming the energy shift back into the laboratory frame. The corresponding shift is given in Eq. (15) and amounts to $\delta = 3.47 \times 10^{-12}$ for helium at room temperature.

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