

Optical properties of helium including relativistic corrections

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We have obtained very accurately calculated nonrelativistic values of the index of refraction and the Verdet constant of helium gas. We have used the Breit-Pauli operator to obtain corrections of order α^2 to the same optical quantities. This required us to analyze the scattering of light by helium atoms correct up to third order: second order in the electromagnetic field and first order in the Breit-Pauli operator. We compare these results with experimental values and find some significant discrepancies. [S1050-2947(98)06212-X]

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I. INTRODUCTION

Many years ago, Dalgarno and Kingston [1] calculated the refractive indices and Verdet constants of the inert gases using a semiempirical method. Recently, Pendrill [2] has re-examined the problem of relating the macroscopic and microscopic polarizabilities of helium gas, with the ultimate goal of deriving an independent value of the Boltzmann constant. He has used some of the best experimental results and our variationally obtained polarizabilities [3] and has clearly discussed the relation between the two. He has found that there is a small but significant discrepancy between theory and experiment, even when some relativistic corrections have been included [4].

The purpose of the present paper is to derive and calculate the first few coefficients in an expansion of both the index of refraction and the Verdet constant in inverse powers of the optical wavelength. The effect of relativity up to order α^2 will be included by the use of the Breit-Pauli operator. We will then compare the improved theory with experiment.

II. THE NONRELATIVISTIC CALCULATION

The helium atom, with two electrons of mass m_e and a nucleus of charge 2 and mass M , is described by the following nonrelativistic Hamiltonian (in reduced Rydberg units, with lengths in reduced Bohrs):

$$H = -\nabla_1^2 - \nabla_2^2 - K\nabla_1 \cdot \nabla_2 - \frac{4}{r_1} - \frac{4}{r_2} + \frac{2}{r_{12}}, \quad (1)$$

where $K = 2m_e/(M + m_e) = 2.741\,493 \times 10^{-4}$ for ${}^4\text{He}$. We wish to perturb the ground state of the helium atom with the dipole operator

$$Z = 2(z_1 + z_2) \quad (2)$$

and the usual dipole polarizability is obtained by second-order perturbation theory:

$$\alpha_1 = \sum_p \frac{\langle 0|Z|p\rangle\langle p|Z|0\rangle}{E_p - E_0}, \quad (3)$$

where α_1 is the static dipole polarizability. If the static field is replaced by an oscillating field (an electromagnetic wave),

it is possible to define a frequency-dependent polarizability $\alpha(\omega)$ from which the index of refraction can be obtained. Two terms replace the single perturbation sum of Eq. (3), as indicated schematically in Fig. 1. One represents uncrossed photon lines, and the other represents crossed lines. The expression for the polarizability in this case is the following:

$$\begin{aligned} \alpha(\omega) &= \frac{1}{2} \sum_p \langle 0|Z|p\rangle\langle p|Z|0\rangle \\ &\times \left\{ \frac{1}{E_p - (E_0 + \omega)} + \frac{1}{(E_p + 2\omega) - (E_0 + \omega)} \right\} \\ &= \sum_p \frac{\langle 0|Z|p\rangle\langle p|Z|0\rangle(E_p - E_0)}{(E_p - E_0)^2 - \omega^2}. \end{aligned} \quad (4)$$

In both terms the initial state includes the incident photon of energy ω , but the intermediate states contain either no photons or two; the denominators in the first expression show this clearly. Since the index of refraction involves coherent scattering, all the photons are in the forward direction, and their momentum is not relevant.

Let us define a set of ‘‘generalized dipole polarizabilities’’ as follows:

$$\{\beta_1, \gamma_1, \delta_1, \epsilon_1, \zeta_1, \eta_1\} = \sum_p \frac{\langle 0|Z|p\rangle\langle p|Z|0\rangle}{(E_p - E_0)^{\{2,3,4,5,6,7\}}}. \quad (5)$$

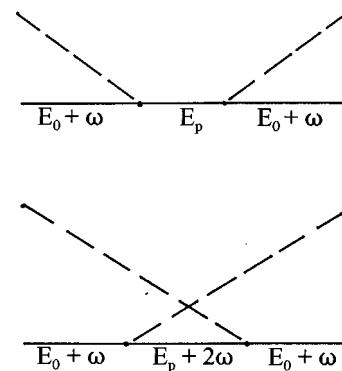


FIG. 1. Diagrams symbolizing the nonrelativistic calculation of $\alpha(\omega)$, with energies of each state indicated.

It is then convenient to expand the denominator in Eq. (4) in powers of $\omega/(E_p - E_0) \leq 0.2$ for wavelengths of visible light:

$$\alpha(\omega) = \alpha_1 + \gamma_1 \omega^2 + \epsilon_1 \omega^4 + \eta_1 \omega^6 + \dots \quad (6)$$

(Only four of these generalized polarizabilities are needed here, but the rest will appear later.)

In principle, the intermediate states $|p\rangle$ should be the complete set of eigenstates of the unperturbed Hamiltonian H , of the appropriate symmetry and angular momentum $L=1$, but in practice we use a finite set of pseudostates in their place. These are obtained by diagonalizing the Hamiltonian in a large, but finite, Hylleraas basis set, and the ground state $|0\rangle$ is obtained in the same way. (The description of these $L=1$ and 0 functions is given in detail in Ref. [5].) Using this method five of these quantities (α_1 to ϵ_1) have been calculated recently with high accuracy [6]; the values obtained for ${}^4\text{He}$ are $\alpha_1 = 1.383\,241\,01$, $\beta_1 = 0.707\,521\,493$, $\gamma_1 = 0.385\,538\,368$, $\delta_1 = 0.218\,735\,026$, and $\epsilon_1 = 0.127\,538\,649$, in reduced atomic units. The last two quantities were not computed in [6], but their values are $\zeta_1 = 0.075\,827\,657$ and $\eta_1 = 0.045\,731\,135$.

III. RELATIVISTIC CORRECTIONS

The next step is to calculate the effect of the Breit-Pauli relativistic Hamiltonian on the frequency-dependent polarizability. The Breit-Pauli operator B has the following form:

$$B = \alpha^2 \left\{ -\frac{1}{4} [\nabla_1^4 + \nabla_2^4] + 2\pi [\delta(\vec{r}_1) + \delta(\vec{r}_2)] + 2\pi \delta(\vec{r}_{12}) + \frac{1}{r_{12}} [\vec{\nabla}_1 \cdot \vec{\nabla}_2 + \hat{r}_{12} \cdot (\hat{r}_{12} \cdot \vec{\nabla}_1) \vec{\nabla}_2] \right\}. \quad (7)$$

We have previously [7] calculated the effect of the operator B on the static polarizability of two-electron systems (applied specifically to the lithium ion). That calculation required third-order perturbation theory, with B retained to first order and Z to second order. The expression that was evaluated is

$$\Delta \alpha_1 = B_{00} \sum_n \frac{Z_{0n} Z_{n0}}{\Delta_n^2} - \sum_{nm} \left[\frac{2Z_{0n} Z_{nm} B_{m0} + Z_{0n} B_{nm} Z_{m0}}{\Delta_n \Delta_m} \right], \quad (8)$$

where $O_{ab} \equiv \langle a|O|b\rangle$ and $\Delta_n \equiv E_n - E_0$. Here we have taken account of the facts that the ground state has angular momentum $L=0$, the excited states n, m have $L=0$ or 1 , and B is rotationally invariant.

To proceed from Eq. (8) to the corresponding relativistic correction to the frequency-dependent polarizability, we imagine inserting the operator B in all possible places in Fig. 1. B does not change the number of photons, so it is only necessary to add $\pm\omega$ to each denominator that corresponds to a dipole vertex Z . That is,

$$\Delta \alpha(\omega) = \frac{1}{2} \left[\frac{Z_{0n} Z_{n0}}{(\Delta_n \pm \omega)^2} B_{00} - 2 \frac{Z_{0n} Z_{nm} B_{m0}}{(\Delta_n \pm \omega) \Delta_m} - \frac{Z_{0n} B_{nm} Z_{m0}}{(\Delta_n \pm \omega)(\Delta_m \pm \omega)} \right], \quad (9)$$

where summation over upper and lower signs is now understood. This expression is symmetric in ω and its expansion involves even powers only. Up to ω^4 the expansion corresponding to Eq. (6) is the following:

$$\Delta \alpha(\omega) = \sum_{p=0}^2 C_p \omega^{2p},$$

where

$$C_p = (2p+1) q_p B_{00} - \sum_{nm} \left[\frac{Q_{nm}}{\Delta_n^{2p}} + P_{nm} S_{2p}(n, m) \right]. \quad (10)$$

In Eq. (10) we have used the following definitions:

$$q_0 = \beta_1, \quad q_1 = \delta_1, \quad q_2 = \zeta_1, \\ Q_{nm} = \frac{2Z_{0n} Z_{nm} B_{m0}}{\Delta_n \Delta_m}, \quad P_{nm} = \frac{Z_{0n} B_{nm} Z_{m0}}{\Delta_n \Delta_m}, \quad (11) \\ S_k(n, m) = \sum_{j=0}^k \frac{1}{\Delta_n^j \Delta_m^{k-j}}.$$

IV. RESULTS AND COMPARISON WITH EXPERIMENT

We have evaluated the expansion coefficients C_p for $p=0, 1, 2$, using the same pseudostates that were used to evaluate the ordinary second-order sums α_1 to η_1 , but in this case double summations must be carried out, increasing the computation time significantly. We have previously evaluated the leading term, C_0 , which is involved in the static polarizability [7], and the result for all three coefficients is

$$\Delta \alpha(\omega) = -8.0029 \times 10^{-5} - 8.1516 \times 10^{-6} \omega^2 + 3.006 \times 10^{-7} \omega^4, \quad (12)$$

and the relativistic expression for the frequency-dependent polarizability of helium becomes

$$\alpha_{\text{rel}}(\omega) = 1.383\,160\,981 + 0.385\,530\,216 \omega^2 + 0.127\,538\,95 \omega^4 + 0.045\,731\,14 \omega^6. \quad (13)$$

We have kept quite a few digits in each of these coefficients, but it is not clear that they are all accurate; since ω is small for all the cases of interest here, the higher coefficients need not be too exact. The last term in Eq. (13) has not been modified from its nonrelativistic value, since the effect of relativity here would be absolutely negligible.

To make comparison with experiment, we must first convert ω (which is in reduced Rydberg units) to wavelength in more conventional units:

$$\omega = \frac{4\pi a_0}{\alpha(1-K/2)\lambda} = \frac{911.391\,98}{\lambda(\text{\AA})}. \quad (14)$$

Next, the polarizability, which has been calculated in reduced units, must be rewritten in terms of the standard unit, a_0^3 . The result of these two changes is the following:

$$\alpha(\lambda) = 1.383\,729\,930 + \frac{3.204\,546 \times 10^5}{\lambda^2} + \frac{8.822\,907 \times 10^{10}}{\lambda^4} + \frac{2.624\,092 \times 10^{16}}{\lambda^6} a_0^3, \quad (15)$$

where the wavelength is measured in Å units. Optical measurements usually return values for $n-1$, where the index of refraction n is very close to 1 for helium at standard conditions. But there are higher-order corrections in the relation between the polarizability (a single atom property) and the index of refraction, due to the effect of the medium. This is accounted for by the Lorenz-Lorentz equation:

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} N_L a_0^3 \alpha(\lambda) = 16.677\,18 \times 10^{-6} \alpha(\lambda) \equiv z, \quad (16)$$

where N_L is Loschmidt's number. Solving for n to second order in z , we find [8]

$$n-1 \approx \frac{3}{2}z + \frac{3z^2}{8} = 34.615\,27 \times 10^{-6} + \frac{8.016\,511}{\lambda^2} + \frac{2.207\,154 \times 10^6}{\lambda^4} + \frac{6.564\,503 \times 10^{11}}{\lambda^6}. \quad (17)$$

From this expression we can obtain a formula for the Verdet constant, measuring the rotation of the plane of polarization in the Faraday effect:

$$V = -\frac{e}{2mc^2} \lambda \frac{dn}{d\lambda} = \frac{1.616\,813 \times 10^7}{\lambda^2} \left[1 + \frac{5.506\,521 \times 10^5}{\lambda^2} + \frac{2.456\,618 \times 10^{11}}{\lambda^4} \right] \mu \text{ min/oer cm}. \quad (18)$$

In Ref. [2] a careful comparison of experiment and theory was made, at a time when the only relativistic correction known [4] was for the constant term in Eq. (17). Although the wavelength dependence (the dispersion) of $n-1$ was good, the absolute value was displaced by a significant amount. (From the extensive literature it appears that the absolute value is quite difficult to measure accurately.) Nevertheless, one absolute value of $n-1$ has been recommended by Leonard [9] at the common calibration wavelength $\lambda = 5462.258 \text{ Å}$: $(n-1) \times 10^6 = 34.895 \pm 0.01$. This may be compared with the value from Eq. (17) of $34.886\,46 \pm 0.000\,02$, where the error shown is the value of the last term included. These two values differ by only 0.009, just less than Leonard's estimated error. On the other hand, the single carefully analyzed point given by Achtermann *et al.* [10] at $\lambda = 6329.9 \text{ Å}$ gives the value $(n-1) \times 10^6 = 34.887 \pm 0.007$, to be compared with the present value of $34.816\,73 \pm 0.000\,01$. These two values differ by 10 times the standard deviation of the experimental value. Also in Ref. [9] there is a table of values of the Verdet constant. At $\lambda = 5000 \text{ Å}$, Eq. (18) gives $V = 0.661\,22 \pm 0.000\,25$ versus the experimental value of 0.637, while at $\lambda = 8000 \text{ Å}$ we get $V = 0.254\,816 \pm 0.000\,015$ compared with the experimental value of 0.246 (all in units of $\mu \text{ min/oer cm}$). There is a significant discrepancy here that is larger than the relativistic effects that have concerned us in this work.

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