On the empirical dipole polarizability of He from spectroscopy of HeH⁺

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Using a long-range polarization potential for HeH⁺, we can obtain an empirical value for the Boltzmann constant \( k_B \) with an order of magnitude greater precision than the previous best experimental value based on the dipole polarizability of \(^4\)He. We find that relativistic and QED effects of order \( \alpha^2 \) in the fine structure constant are crucial in the quadrupole polarizability in order to fit the dipole polarizability with this precision using the polarization potential. By calculating finite-mass corrections for \(^3\)He, we also present theoretical values for the dipole and quadrupole polarizabilities of \(^3\)He with 9 and 7 digits of precision respectively.

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In November 2014, the SI system of scientific units is expected to undergo the biggest change in its 64 year history. Currently, temperature is defined based on the triple point of water, which is rather arbitrary, and due to the precision at which this property is known, the current definition of temperature is unsatisfactory for temperatures below 20 K and above 1300 K.

In the new system, the Boltzmann constant \( k_B \) will be defined to be exact, and the triple point of water is derived from \( k_B \), rather than the other way around. Paramount to this new SI system, is the need for a precise and reliable value of \( k_B \). Currently the relative uncertainty in \( k_B \) is \( 9.1 \times 10^{-7} \) which is more than an order of magnitude larger than other fundamental constants (for example, it is \( 4.4 \times 10^{-8} \) for the Avogadro constant \( N_A \), and \( 2.2 \times 10^{-8} \) for the elementary charge \( e \)). A much more reliable value of \( k_B \) can be determined from a high-precision measurement of the static dipole polarizability \( \alpha_1 \) of a substance:

\[
k_B = \alpha_1 \frac{N_A^2 (\epsilon_r + 2)}{3p\epsilon_0 (\epsilon_r - 1)},
\]

where the vacuum permittivity \( \epsilon_0 \) is defined exactly, the pressure \( p \) at which the experiment is conducted can be reliably held fixed, and the refractive index of the substance can be measured extremely accurately. Gaseous helium has received enormous attention as a candidate substance for the experiment which re-defines \( k_B \), because \( \alpha_1 \) is known theoretically to at least 8 digits [1] and experimentally to at least 6 [2].

In 2009 the resonance dipole-dipole interaction \( C_3 \) of Li was empirically determined with a higher precision than any previously determined oscillator strength for any system, by an order of magnitude [3][4]. This was made possible by a fit of 17 477 high-precision spectroscopic measurements to a potential with a correct theoretical model for the long-range potential built into it: the longest-range term of the model was \(-C_3/r^3\), so the fitted value of \( C_3 \) was based on these 17 477 high-precision measurements. The case for He is similar, except instead of \( C_3 \) we are interested in \( \alpha_1 \) which is related to the longest-range term \(-\frac{1}{2}\alpha_1/r^4\) of the polarization potential of HeH⁺. The more accurate the model for the polarization potential, the better the determination of \( \alpha_1 \) by the fit.

The theory for the polarization potential between a neutral atom and a far away charge is related to the theory for an ionic core interacting with a far away electron in a Rydberg atom, and has a rich history dating back to at least 1933 [5]. At that time the adiabatic potential from the electric multipoles for systems with a zero angular momentum core was derived up to \( 1/r^6 \). Non-adiabatic corrections up to \( 1/r^6 \) were derived in 1968 independently by Kleinman et al. and Dalgaro et al. [6], and the full electric multipole potential including both adiabatic and non-adiabatic contributions up to \( 1/r^8 \), for systems where the core has no angular momentum, was first derived in 1982 by Drachman [7].

In 2012 Woods and Lundeen [8] have derived corrections to this potential for systems where the core has non-zero angular momentum. Drachman’s potential is only the result of the first order in the tensor expansion of Woods and Lundeen, but the latter derived adiabatic and non-adiabatic terms up to \( 1/r^8 \), and up to 5th order in the tensor expansion. Woods and Lundeen also presented energy corrections due to relativity and due to various magnetic interactions. It turns out that all of these post-Drachman terms are zero for all known isotopes of He\(^1\)S with a half-life of \( > 1 \) ms, due to the nuclear spin always being \( < \frac{3}{2} \), the lack of additional angular momentum, and the lack of an electric charge.

The rotationless \((J = 0)\) polarization potential for any isotopologue of HeH⁺ including adiabatic and non-adiabatic terms up to \( 1/r^8 \), due to the electric multipoles...
Figure 1. Empirical internuclear potential for the ground electronic state of $^4\text{HeH}^+$ and the theoretical long-range polarization potential using varying numbers of terms in Eq. 3. All long-range coefficients are calculated from Eq. 3 using the most precise current values of the polarizabilities, presented in Table II.

The reduced mass $\tilde{M} \equiv \frac{M_{\text{He}}M_{\text{H}^+}}{M_{\text{He}}+M_{\text{H}^+}}$, which was first introduced for the $\beta_1$ term in [6], significantly reduces the effect of the non-adiabatic terms (represented by $\beta_i$ and $\gamma_i$). All other symbols are described in the caption to Table I and formulas to calculate them are presented in [10].

For large $r$, the potentials for the isotopologues of HeH$^+$ are dominated by the above polarization function. Therefore spectroscopic measurements involving the long-range energy levels of HeH$^+$ can be fit to the eigenenergies of the Hamiltonian containing the above energy functions with $\alpha_1$ treated as a free parameter.

No matter how precisely these spectroscopic measurements are made, the $\alpha_1$ will be determined incorrectly if the models for the polarization functions are not correct. Since there are so many terms appearing in the polarization functions, it is difficult to intuit which effects are necessary to include in each term in order to determine $\alpha_1$ with a greater degree of confidence than the current best empirical value, which was determined by a different technique in 2007 [2].

Determining precisely which effects are necessary to include in the polarization functions for this purpose is needed for two reasons:

1. It will provide an indication of which effects need to be included in the calculation of a polarization model when undertaking similar fitting endeavors for other systems.

2. Fitting model potentials to spectroscopic data becomes more difficult as more terms are included in the long-range potential [3, 11], therefore it is al-
Most of the constants appearing in the above polarization function are not known with very high accuracy, especially for $^4$He. We therefore first calculate these constants with unprecedented precision, including relativistic ($\alpha_{FS}^2$) and third-order QED ($\alpha_{P}^3$) effects for $\alpha_1$, where $\alpha_{FS}$ is the fine structure constant. We then calculate $^4$He and $^3$He finite-mass effects, for $\alpha_2$, $\alpha_{112}$, $\alpha_{1111}$, and $\beta_1$. The value of $\alpha_1$ has been calculated previously in [1], including fourth-order QED ($\alpha_{FS}^4$) effects, but finite-mass corrections were only presented for $^4$He. We therefore use this value for $^3$He, and calculate the finite-mass correction for $^4$He, and combining these with our calculated values of the other constants, Eq. 3 very accurately represents the long-range behavior of the isotopologues of HeH$^+$. 

We then determine how precisely $\alpha_1$ can be determined from a fit to Eq. 3 when varying numbers of terms are included, and with or without the inclusion of relativistic and/or QED effects in the adiabatic quadrupole polarizability $\alpha_2$. We find that when relativistic ($\alpha_{FS}^2$) and/or $\alpha_{P}^3$ QED effects are neglected, $\alpha_1$ can only be predicted correctly to at best 6 digits. When these effects are included in the model, $\alpha_1$ can be determined with 8 digits of precision, which is one order of magnitude more precise than the experimental value determined in [2].

The various polarizabilities calculated in this work were determined following the ideas of numerical calculations presented in [14]. The numerical calculation involves a non-relativistic wavefunction determined variationally. Our wavefunction, consists of explicitly correlated exponential functions [14, 15]. We then calculate the adiabatic and non-adiabatic polarizabilities as introduced in the optical-potential analysis for Rydberg atoms, e.g. [17, 16]. It is noted that Drachman’s definitions in [7] are introduced with Rydberg atomic units, and here we always use Hartree atomic units.

Since we are using very high-precision and fast calculations with explicitly correlated exponential functions for the helium atom, the finite mass corrections are determined here as a difference between the non-relativistic values obtained in the infinite mass limit, and those using the relevant nuclear mass. Uncertainties presented for the leading order non-relativistic contributions as well as for the non-relativistic finite mass corrections are estimated based on numerical convergence. The non-relativistic finite mass effects for the $1/r^k$ coefficients $\alpha_3$, $\beta_2$, $\gamma_1$ and $\alpha_{1111}$, and the relativistic finite mass effects for all terms, are expected to be negligible in our application of the long-range potential. An attempt at the finite mass corrections for $\beta_2$ and $\gamma_1$ was presented in [10]. However, there are additional contributions that are expected to be important, e.g. from the finite mass kinetic energy correction [17], which shows the limitations of a simple generalization from the Rydberg states theory, and possible problems that need to be addressed in a more detailed theory.

Since we consider the internuclear potential in the long-range limit, coefficients of $1/r^n$ with lower values of $n$ have to be evaluated much more accurately, including subtle effects. After $\alpha_1$, the most important contribution to the internuclear potential comes from the quadruple polarizability $\alpha_2$. The non-relativistic value of $\alpha_2$ at leading order has been calculated before [10, 12]. Here, we calculate the non-relativistic value with greater precision, and additionally we calculated finite-mass and relativistic corrections with an analogous approach to the one used for the dipole polarizability $\alpha_1$ in paper [18]. It is based on perturbation theory using the Breit-Pauli operator [19]. Finally we also included the leading QED effects as was done for $\alpha_1$ in [18]. The only estimation comes from assuming the Bethe logarithm $\ln k_0$ as a known constant in the QED Hamiltonian. The neglected effects are very demanding in numerical calculations. We estimated them using 10% uncertainty in the $\ln k_0$ value. This estimate is embodied in the uncertainty of the QED correction value in Table I.

We have included these calculated values in our compiled listing of the current most precise values for various polarizabilities (neglecting finite mass effects) of He in Table II. Finite mass effects are then added to the quantities in Table II in order to obtain the corresponding values for $^3$He and $^4$He. Table I shows the size of these mass polarization corrections for $^4$He and $^3$He, and the final polarizabilities for each isotope. Using the values from Table I and Eq. 3 we calculate high-precision theoretical long-range potentials for the ground electronic states of $^3$HeH$^+$ and $^4$HeH$^+$.

In Fig. 1 we compare the recent empirical potential for $^4$HeH$^+$ from [20], to the long-range potentials corresponding to various approximations constructed by truncating the number of terms used from Eq. 3. It is clear in this figure that the highest bound vibrational levels are in a region where the molecular potential is indeed the long-range polarization potential of Eq. 3. Therefore, fitting the polarization potential (specifically,
Table I. Theoretical polarizabilities from the 0th ($\alpha_i$) and 1st ($\beta_i$) orders of the adiabatic expansion, various orders ($\gamma_i$) of the multipole expansion, and up to fourth order perturbation theory. $\alpha_{112}$ and $\alpha_{1111}$ come from third and fourth order perturbation theory respectively. All polarizabilities are in Hartree atomic units. We used the NIST nuclear masses $M(^4\text{He}) = 4.001506179125(62)$ a.u., $M(^3\text{He}) = 3.0149322468(25)$ a.u.

| Model            | $\alpha_{i}^{3\text{He}}$ | $\alpha_{i}^{4\text{He}}$ |
|------------------|---------------------------|---------------------------|
| $\alpha_{1}$     | 1.38314230(23)            | 1.38376079(23)            |
| $\alpha_{2}$     | 2.444983(6)               | 2.446858(6)               |
| $\alpha_{112}$   | 7.3267069796(16)          | 7.3267069796(16)          |
| $\alpha_{1111}$  | 4.5706414(7)              | 4.5706414(7)              |

Table II. The effect of finite mass corrections yields final polarizabilities for $^3\text{He}$ and $^4\text{He}$. The $^4\text{He}$ dipole polarizability is from [1]. All polarizabilities are in Hartree atomic units.

| Infinite mass | $^3\text{He}$ | $^4\text{He}$ |
|---------------|---------------|---------------|
| $\alpha_1$    | 1.38314230(23) | 1.38376079(23) |
| $\alpha_2$    | 2.444983(6)     | 2.446858(6)    |
| $\alpha_{112}$ | 7.3267069796(16) | 7.3267069796(16) |
| $\beta_1$     | 0.707510144012(5) | 0.708040277158(5) |

Table III. Comparison of fitted values of $\alpha_1$ when fitting to various models. In these models, $\alpha_1$ is treated as a free parameter for the fit, and the rest of the polarizabilities come from Table I $\alpha_2^{\text{FS}}$ (QED) is $\alpha_2$ with the QED term proportional to $\alpha_2^{\text{FS}}$ ignored. Numbers in parentheses represent uncertainties in the last digit(s) of the quantity shown. The uncertainties in the fits are based only on the convergence of the fit. All polarizabilities are in Hartree atomic units.

| Theory                  | $^3\text{He}$      | $^4\text{He}$      |
|-------------------------|--------------------|--------------------|
| Experiment              | 1.38396299(23)     | 1.38376079(23)     |
| $\alpha_1^{\text{FS}}$ | -                  | -                  |
| $\alpha_2^{\text{FS}}$ | 1.384(1)           | 1.384(1)           |
| $\alpha_2^{\text{(no QED)}}$ | 1.3840(1)     | 1.3838(1)          |
| $\alpha_2^{\text{(no rel)}}$ | 1.38397(1)     | 1.38376(1)         |
| $\alpha_2^{\text{(no QED)}}$ | 1.3839630(1)   | 1.3837608(1)       |
| $\alpha_2^{\text{(no QED)}}$ | 1.3839631(1)   | 1.383761(1)        |
| $\alpha_2^{\text{(no QED)}}$ | 1.38396299(1)  | 1.3837608(1)       |
the parameter representing the dipole polarizability $\alpha_1$ to high-precision spectroscopic measurements involving the highest vibrational levels will indeed give us an accurate empirical value for $\alpha_1$. Since in this region all of the long-range potentials look the same, it may appear as if the number of terms used in the polarization model is irrelevant. However, since we are interested in using $\alpha_1$ for a newer, more precise definition of the Boltzmann constant $k_B$, the precision with which $\alpha_1$ is empirically determined is extremely important, and Fig. 2 presents the various approximations to the long-range potential in Le Roy space to emphasize that the potentials are in fact significantly different until at least 5 Å.

In Table III we show that for both $^3\text{HeH}^+$ and $^4\text{HeH}^+$ the dipole polarizability can be determined in agreement with the high-precision (9-digit) theoretical values by a fit to the full polarization function. This is at least one order of magnitude more precise than the best experimental value determined in [2] (see Table III). The table also shows that in order for this, relativistic and QED effects must not be neglected in the calculation of the quadrupole polarizability $\alpha_2$, as otherwise the accuracy of the fitted $\alpha_1$ becomes significantly worse. This result is useful for the study of other atoms beyond He, since it provides an idea of the size of the effects necessary to include in the long-range potential in order to fit $\alpha_1$ with a certain level of desired precision. Finally, the conclusion that, with the right level of accuracy in the long-range potential model, $\alpha_1$ can be obtained empirically with 9 digits of precision, provides testament to the case for using the $\alpha_1$ of He for the new SI definition of temperature.

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