Radiative correction to the helium dimer interaction energy

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Abstract

The leading-order radiative correction to the helium-helium interaction energy at the equilibrium internuclear distance has been calculated for the first time. The result is $-1.27(2)$ mK. The calculations were performed using a new technique of evaluating expectation values of singular operators in connection with the most accurate wave functions of He_2 available today—the exponentially correlated Gaussian functions.

I. INTRODUCTION

The helium dimer ceaselessly attracts attention of both theoreticians and experimentalists. Since the beautiful experiment by Schölkopf and Toennies [1] proving the existence of the bound He_2 system, the theoreticians increased their pains to model the interaction of the two helium atoms. In the last decade, the accuracy of the *ab initio* potentials of the interaction surpassed that offered by an experiment and new standards of thermodynamic parameters have been based on the theoretical data [2]. A need for the He-He interaction potential to the millikelvin accuracy has become pressing. One of the most important contributions in this direction was the determination of the depth of the Born-Oppenheimer (BO) interaction potential well with a near-millikelvin accuracy, $\Delta E_{\rm BO} = -11.009 \pm 0.008$ K [3], which corresponds to the relative precision of 4 ppb in the total energy. For molecules, thus far, such a high accuracy was achievable only in calculations on 2- or 3-electron systems [4].

For its exceptionally shallow interaction potential well (6 ppm of the total energy at the equilibrium distance) the demands imposed on the accuracy of the interaction energy are particularly high. Even small fluctuations in the potential may result in dramatic changes in parameters characterizing the whole system. For instance, the shallow potential accommodates only one vibrational state which lies right below the dissociation level (ca. 1 mK) and an insufficiently accurate description of the long range part of the potential may cause the system to become unbound within the assumed model. Another interesting but cumbersome feature of the helium dimer is its huge spatial extent. The large equilibrium distance, $R_{\rm e}$=5.6 bohr, and in particular, very large average internuclear distance, $\langle R\rangle \approx 100$ bohr, require incorporation of the retardation effects [5–8] and make He_2 an interesting subject from the point of view of the quantum electrodynamics [9, 10].

For the above reasons, inclusion of the non-BO effects is needful. The adiabatic correction, as a function of R, was computed several years ago [11]. Later on, a more accurate value was obtained at the equilibrium distance [12]. Very recently, the relativistic correction at $R_{\rm e}$ was determined by Cencek *et al.* [13]. The only remaining correction which may contribute at the millikelvin level is the radiative one. Computation of this contribution at the equilibrium distance is the subject of the work reported in this paper.

II. METHOD

The clamped nuclei electronic energy E of a molecule is a function of the fine-structure constant α. The quantum electrodynamics predicts that, for R of the order of several bohrs, the expansion of the energy in α takes the form (in atomic units)

$$E = E^{(0)} + E^{(2)} + E^{(3)} + \ldots, \tag{1}$$

where $E^{(n)}$ is of order α^n and may contain some powers of $\ln\alpha$. Each term $E^{(n)}$ can in general be expressed as an expectation value of some effective Hamiltonian on a state Ψ, which is a solution of the nonrelativistic Schrödinger equation. $E^{(0)}$ is the nonrelativistic energy, $E^{(2)}$ represents the relativistic correction expressed by the expectation value of the Breit-Pauli Hamiltonian [14], and $E^{(3)} \equiv E_{\rm QED}$ is the leading-order radiative correction—the topic of this work. The latter correction can be written down as a combination of expectation values of some operators and the Bethe logarithm, $\ln k_0$ [15–17]. For the particular case of the singlet states this correction reads

$$\begin{aligned} E_{\rm QED} \; &= \; \alpha^3 \sum_{i>j} \Bigg\{ \left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right] \langle\Psi\,|\delta(\boldsymbol{r}_{ij})|\,\Psi\rangle \\ &\qquad\qquad -\frac{7}{6\pi}\,\langle\Psi\,|P\left(r_{ij}^{-3}\right)|\,\Psi\rangle \Bigg\} \\ &\quad +\alpha^3 \sum_I \sum_i \left[\frac{19}{30} - 2\ln\alpha - \ln k_0\right] \frac{4Z_I}{3}\,\langle\Psi\,|\delta(\boldsymbol{r}_{iI})|\,\Psi\rangle\,. \end{aligned} \tag{2}$$

For non-singlet states an additional term resulting from the anomalous magnetic moment appears. In the above formula, Z_I is the atomic number of a nucleus I, m is the electron mass and $\delta(\boldsymbol{r})$ stands for the Dirac delta function. The matrix element containing the distribution $P(r_{ij}^{-3})$ is defined as the limit

$$\begin{aligned} &\langle\phi\,|P\left(r^{-3}\right)|\,\psi\rangle \equiv \\ &\lim_{\epsilon\to 0}\int d\boldsymbol{r}\,\phi^*(\boldsymbol{r})\,\psi(\boldsymbol{r})\left[r^{-3}\,\Theta(r-\epsilon) + 4\,\pi\,\delta(\boldsymbol{r})\,(\gamma + \ln\epsilon)\right], \end{aligned} \tag{3}$$

with Θ and γ being the step function and the Euler constant, respectively.

Our ansatz for the nonrelativistic wave function has the form of a K-term linear expansion in an n-electron basis

$$\Psi(\mathbf{r},\boldsymbol{\sigma}) = \hat{\mathcal{A}}\left(\Xi_{n,S,M_S}(\boldsymbol{\sigma})\,\hat{\mathcal{S}}\sum_{k=1}^{K} c_k\psi_k(\mathbf{r})\right), \tag{4}$$

where $\hat{\mathcal{A}}$ and $\hat{\mathcal{S}}$ are permutation and spatial symmetry projectors, respectively, and $\Xi_{n,S,M_S}(\boldsymbol{\sigma})$ is an n-electron spin eigenfunction with the spin quantum numbers S and M_S. As the n-electron spatial basis functions ψ_k we employed exponentially correlated Gaussian (ECG) functions of Singer[18]

$$\psi_k(\mathbf{r}) = \exp\left[-\left(\mathbf{r}-\mathbf{s}_k\right)^T \mathbf{A}_k \left(\mathbf{r}-\mathbf{s}_k\right)\right], \tag{5}$$

where the superscript T denotes a vector transpose. The linear parameters, c_k, were determined by means of the inverse iteration method of solving the standard general symmetric eigenvalue problem. The nonlinear parameters, contained in the vectors $\boldsymbol{s}_k$ and the positive definite matrices $\boldsymbol{A}_k$, were found in an extensive variational optimization process. Detailed description of the ECG method including the optimization strategy employed may be found e.g. in Refs. [4, 19, 20].

III. RESULTS AND DISCUSSION

For the helium dimer, the ECG wave functions are capable of yielding the total energy to an accuracy of 10^{-7} hartree [13]. Such wave functions were employed to compute the expectation values appearing in Eq. (2). Evaluating the QED interaction energy ($\Delta E_{\mathrm{QED}} \sim 10^{-3}$ K) within the supermolecular approach, we subtract two numbers of the order of 10 K and we lose immediately four significant figures of the precision. Thus, in order to get any significant figure of the final result we must compute the QED energy of the dimer to an accuracy of at least 5 significant figures. In the Gaussian-type basis, however, the convergence of the highly singular expectation values evaluated conventionally is too slow to reach a desired accuracy. Fortunately, the rate of convergence can be substantially increased by employing a special technique based on an integral transform [21]. Within this technique, the singularity is moved to a new integral for which an asymptotic formula, guided by the Kato cusp condition, is used. For instance, the expectation value of the Dirac delta operator can be expressed in the following integral form

$$\langle \Psi \left|\delta(\boldsymbol{r})\right| \Psi\rangle = \frac{1}{2\pi^{3/2}} \int_0^\infty \left\langle \Psi \left| 2t^2 \left(3-2t^2r^2\right) e^{-t^2r^2} \right| \Psi \right\rangle dt\,. \tag{6}$$

For t not too large (say $t < t_\Lambda$) the matrix element of $r^2 e^{-t^2 r^2}$ can be computed to a high accuracy. For $t > t_\Lambda$ the integral is evaluated using an analytically derived asymptotic form of the expectation value. Denoting the integrand in Eq. (6) by $f(t)$ we have

$$f(t) = \frac{4Z}{\sqrt{\pi}\, t^2} \langle \Psi | \delta(\boldsymbol{r}) | \Psi \rangle \left(1 + \frac{A_1}{t} + \frac{A_2}{t^2} + \frac{A_3}{t^3} + \cdots \right), \tag{7}$$

where A_i depend on the state under consideration, Ψ, and are obtained by fitting to a large grid of points of $f(t)$. For the electron-nucleus Dirac delta, Z is the nuclear charge whereas for the interelectron delta, $Z = -\frac{1}{2}$. As the leading coefficient in Eq. (7) contains the quantity we are going to compute, the $\langle \Psi | \delta(\boldsymbol{r}) | \Psi \rangle$ in Eq. (6) is computed iteratively with a starting value taken from the conventional expectation value. The convergence is reached in 3-4 iterations.

A similar approach can be applied to the calculation of the Araki-Sucher term, which is defined in Eq. (3). This time we have

$$\left\langle \Psi \left| P\left(r_{ij}^{-3} \right) \right| \Psi \right\rangle = \int_0^\infty (2 \ln t - \gamma)\, f(t)\, dt\,, \tag{8}$$

where

$$f(t) = \left\langle \Psi \left| 2t \left(t^2 r_{ij} - r_{ij}^{-1} \right) e^{-t^2 r_{ij}^2} \right| \Psi \right\rangle . \tag{9}$$

As in the case of the Dirac delta function, the integral with $t < t_\Lambda$ is calculated directly with $f(t)$, while for $t > t_\Lambda$ one applies the asymptotic expansion

$$f(t) = \frac{\pi^{3/2}}{2\, t^2} \langle \Psi | \delta(\boldsymbol{r}_{ij}) | \Psi \rangle \left(1 + \frac{A_1}{t} + \frac{A_2}{t^2} + \frac{A_3}{t^3} + \cdots \right) \tag{10}$$

and calculates A_i by fitting to a large grid of $f(t)$. Alternatively, the A_i coefficients can be obtained from atomic calculations. Watching the convergence of the integrands with the growing size of the basis set, we have chosen $t_\Lambda \approx 100$ as the optimal threshold parameter.

The Bethe logarithm, $\ln k_0$, of a helium dimer is unknown yet. For not too small internuclear distance, however, it can be well approximated by the atomic value [22, 23]

$$\ln k_0 = 4.370\,160\,222\,0(1). \tag{11}$$

This assertion is supported by the presumption that the contribution from the Bethe logarithm to the interaction energy is twice the contribution from the $\ln k_0$ to the polarizability of the helium atom. The numerical value of the latter is known from the work of Łach et al. [24] and amounts to ca. 0.14 ppm of the total polarizability, which justifies well our approximation.

To control the accuracy, the calculations were performed for several basis sets of a successively doubled size, K. The convergence of particular expectation values and the QED interaction energy, $\Delta E_{\rm QED} = E_{\rm QED}({\rm He}_2) - 2E_{\rm QED}({\rm He})$, is shown in Table I. The 'exact' atomic expectation values were taken from literature:

$$\langle\delta(\boldsymbol{r}_i)\rangle = 3.620\,858\,637\,7(3)\ [25], \tag{12a}$$

$$\langle\delta(\boldsymbol{r}_{ij})\rangle = 0.106\,345\,370\,636(2)\ [26], \tag{12b}$$

$$\left\langle P\left(r_{ij}^{-3}\right)\right\rangle = 0.989\,272\,4(13)\ [27]. \tag{12c}$$

The total QED energy correction of the helium atom is

$$E_{\rm QED}({\rm He}) = 57.288\,165\,3(5)\,\alpha^3\ {\rm a.u.} \tag{13}$$

As can be inferred from the last column of Tab. I, the $\Delta E_{\rm QED}$ goes as K^{-3} and for the largest expansions at least 3 significant figures become stable. However, an accidental cancellation between the terms containing $\delta(\boldsymbol{r}_i)$ and $P\left(r_{ij}^{-3}\right)$ has been observed. Therefore, we conservatively assume 0.014 mK as the convergence uncertainty and we estimate also that the missing contribution of the dimer Bethe logarithm term adds another 0.003 mK to the uncertainty. Our recommended, extrapolated value is

$$\Delta E_{\rm QED} = -1.27(2)\,{\rm mK}. \tag{14}$$

To assess the influence of the higher order terms onto the uncertainty in the interaction energy we use the following estimation $\Delta E^{(4)} \approx \alpha\,\Delta E_{\rm QED} R$, which leads to

$$\Delta E^{(4)} \approx \pm 0.05\,{\rm mK}. \tag{15}$$

Eq. (2) has three distinct components: the first two terms depend on the interelectron operators while the third term—on the electron-nucleus operators. At the equilibrium internuclear distance the term containing interelectron Dirac delta operator contributes to $\Delta E_{\rm QED}$ (with the opposite sign) at the microkelvin level and, to a good approximation, might be just neglected. The latter, 'one-electron' term gives ca. 17% of the total correction. The remaining large part of $\Delta E_{\rm QED}$ comes from the term in Eq. (2) containing $P(r_{ij}^{-3})$ and amounts to -1.053 mK. Its accurate determination is indispensable for reliable estimation of the QED correction to the interaction energy. Using an asymptotic expansion, Łach and Jeziorski [28] estimated this term as equal to -1.135 mK which differs from our value by less than 8%.

IV. CONCLUSIONS

This work supplies the last component contributing at the millikelvin level to the interaction energy of He_2 at the equilibrium internuclear distance. All the components are collected in Table II. The value of ΔE_{BO} and its estimated error is based on the convergence of the ECG calculations performed by Cencek *et al.* [13] and agrees well with -11.004 obtained recently by the authors of Ref. [3] in their refined computations. The BO contribution remains the main source of the uncertainty. The adiabatic correction, $\Delta E_{\mathrm{AD}} = -0.013$ K reported in Ref. [11] was later on refined using a more accurate ECG wave function [12] and the latter result is displayed in the table. The leading relativistic contribution comes from very recent ECG computations by Cencek *et al.* [13], based on two different approaches. The first approach makes use of the same integral transform technique which was used in the present paper. In the second approach, a contracted function obtained from atomic calculations has been employed as a core of the optimized molecular wave function. Both methods agree very well in their final results.

Further diminishing of the uncertainty in the interaction energy requires the BO contribution error to be narrowed. Precise evaluation of the Bethe logarithm would also be desired. Nevertheless, the present state of art methods enable modeling of the He-He interaction potential to the accuracy of a few millikelvins.

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TABLE I: Convergence of the expectation values (in atomic units) of He_2 entering the QED energy expression, Eq. (2), and the QED interaction energy, ΔE_{QED}, with the basis set size, K. For comparison, the last line contains twice the values of the atomic helium. The conversion factor from atomic to kelvin units was 315 774.65 and the fine-structure constant $\alpha = 1/137.035\,999\,11(46)$.

K	$\left\langle \sum_{i,I} \delta(\boldsymbol{r}_{iI}) \right\rangle$	$\left\langle \sum_{i>j} \delta(\boldsymbol{r}_{ij}) \right\rangle$	$\left\langle \sum_{i>j} P(r_{ij}^{-3}) \right\rangle$	$\Delta E_{\mathrm{QED}}/\mathrm{mK}$
300	7.240 756	0.212 938 5	1.990 612	−2.835
600	7.241 464	0.212 737 8	1.999 371	−1.524
1200	7.241 585	0.212 698 7	2.001 100	−1.304
2400	7.241 603	0.212 689 3	2.001 526	−1.273
4800	7.241 606	0.212 687 7	2.001 659	−1.271
2 He	7.241 717	0.212 690 7	1.978 544	

TABLE II: Components of the interaction energy of $^4He_2$ at R=5.6 bohr.

Component	Value	Uncertainty	Reference
ΔE_{BO}	−11.001	0.003	Extrap. from [13]
ΔE_{AD}	−0.008 9	0.000 4	[12]
ΔE_{REL}	+0.015 4	0.000 6	[13]
ΔE_{QED}	−0.001 27	0.000 02	This work
$\Delta E^{(4)}$	0.000 00	0.000 05	
ΔE	−10.996	0.004	