Relativistic and Quantum Electrodynamics Effects in the Helium Pair Potential

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(Received 9 February 2010; published 7 May 2010)

The helium pair potential was computed including relativistic and quantum electrodynamics contributions as well as improved accuracy adiabatic ones. Accurate asymptotic expansions were used for large distances R. Error estimates show that the present potential is more accurate than any published to date. The computed dissociation energy and the average R for the $^4\mathrm{He}_2$ bound state are 1.62 ± 0.03 mK and 47.1 ± 0.5 Å. These values can be compared with the measured ones: $1.1^{+0.3}_{-0.2}$ mK and 52 ± 4 Å [R. E. Grisenti *et al.*, Phys. Rev. Lett. **85**, 2284 (2000)].

DOI: 10.1103/PhysRevLett.104.183003 PACS numbers: 31.30.J−, 34.20.Cf

The pair potential for helium represents the simplest, prototypical interaction potential for dispersion bound systems. Its knowledge is of importance in several branches of science, e.g., in low-temperature condensed matter physics [1], spectroscopy [2,3], and metrology [4–6]. In the latter case, purely theoretical first-principle predictions of properties of helium are replacing experimental data and allow creation of more accurate measurement standards for quantities such as temperature or pressure. One more reason for interest in the helium potential is the existence of an unusually large and very weakly bound state of the helium dimer [7]. The size of this dimer was found to be significantly affected [8,9] by the Casimir-Polder (CP) retardation effect [10]. All of this poses challenging accuracy demands for theory.

The determination of the nonrelativistic Born-Oppenheimer (BO) potential for helium, V_{BO}, has been the subject of extensive activity reviewed in Refs. [9,11]. At the equilibrium distance R_e, V_{BO} is known [12] with an estimated uncertainty of 0.2 mK or 2 parts per 10^5, but for some interatomic distances R the relative uncertainties are an order of magnitude larger [9]. Whereas such uncertainties are small enough for current metrology purposes, the expected magnitudes of the post-V_{BO} contributions are too large to be *a priori* neglected for such purposes [4–6].

The main post-V_{BO} physical effects are the leading order coupling of the electronic and nuclear motion, i.e., the adiabatic correction, relativity, and quantum electrodynamics (QED). The adiabatic correction, $V_{\mathrm{ad}}(R)$, has been computed in Ref. [13] using 4-electron explicitly correlated Gaussian (ECG) wave functions and recomputed in Ref. [11] using an orbital approach, with results different by as much as 42% at R_e. The relativistic correction of the order α^2, where $\alpha = 1/137.036$ is the fine structure constant, has been computed accurately in Ref. [14] but only for R_e. It has been computed for a range of R in Ref. [11], but only in the so-called Cowan-Griffin approximation which for R_e is very inaccurate [14]. A part of the QED correction of the order α^3 is accounted for using CP theory, but other α^3 QED terms have been calculated thus far only for R_e [15]. Clearly, the knowledge of the post-V_{BO} terms is far from satisfactory.

In this Letter, we present accurate calculations of the complete α^2 and α^3 contributions [denoted by $V_{\mathrm{rel}}(R)$ and $V_{\mathrm{QED}}(R)$, respectively], as well as recalculations of $V_{\mathrm{ad}}(R)$, for 17 R's from 1 to 12 bohr. Our main goal was to obtain the potential

$$V(R) = V_{\mathrm{BO}}(R) + V_{\mathrm{ad}}(R) + V_{\mathrm{rel}}(R) + V_{\mathrm{QED}}(R) \qquad (1)$$

to within a few parts per 10^4. To ensure high accuracy for $R > 12$ bohr, we evaluated the constants determining the asymptotic behavior of all terms in Eq. (1). The CP terms not included in Eq. (1), denoted later as $V_{\mathrm{ret}}(R)$, are very small but can optionally be added to $V(R)$.

All components of $V(R)$ were obtained using the supermolecular approach, i.e., by computing the difference

$$\Delta Y = \Delta\langle\hat{Y}\rangle = \langle\psi \mid \hat{Y}\psi\rangle - 2\langle\psi_0 \mid \hat{Y}_0\psi_0\rangle, \qquad (2)$$

where $\hat{Y}$ is the operator corresponding to a particular correction, $\hat{Y}_0$ is the atomic part of $\hat{Y}$, ψ and ψ_0 are electronic wave functions for He_2 and He, respectively, both computed in the clamped-nuclei approximation. By replacing $\hat{Y}$ by appropriate operators, one gets the consecutive post-V_{BO} terms in Eq. (1): V_{ad} when $\hat{Y}$ is the operator of the kinetic energy of nuclei, V_{rel} when $\hat{Y}$ is the Breit-Pauli Hamiltonian, and V_{QED} when $\hat{Y}$ is the operator given in Eq. (2) from Ref. [15]. V_{rel} is a sum of components given by the one- and two-electron Darwin operators $\hat{D}_1$ and $\hat{D}_2$, the mass-velocity operator $\hat{H}_1$, and the Breit operator $\hat{H}_2$ (using the notation of Ref. [16]; see also Ref. [14]). We will denote the latter two components as $V_{\mathrm{mv}}(R)$ and $V_{\mathrm{Breit}}(R)$, respectively. V_{QED} can be expressed [15] as an appropriate linear combination of $\Delta\langle\hat{D}_1\rangle$, $\Delta\langle\hat{D}_2\rangle$, and of the so-called Araki-Sucher (AS) contribution [17] obtained when $\hat{Y}$ is replaced by

$$\hat{H}_{\mathrm{AS}} = -\frac{7\alpha^3}{6\pi}\sum_{i<j}^{4} P(r_{ij}^{-3}), \tag{3}$$

where $P(r_{ij}^{-3})$ is the distribution defined, e.g., in Ref. [15] and atomic units are used here and in formulas given below. This procedure is an approximation since the R dependence of the Bethe logarithm, $\ln k_0$, is neglected and the atomic value, equal to 4.370 160 222 0(1) [18], is used. The accuracy of this approximation was recently tested [19] for H_2, where it is more severe, but changes the one-electron part of the QED contribution to the equilibrium depth by less than 2%. For He_2, this one-electron part gives only about 0.25 mK contribution [15] to V_{QED} at R_e. Thus, for He_2 the use of R-dependent $\ln k_0$ would make a negligible, μK level contribution.

We have performed calculations with ECG and orbital basis sets for all R. The latter basis can give more accurate results for large R since it allows for the removal of basis set superposition errors. The ECG and the full configuration-interaction (FCI) orbital results are mutually consistent for *all* R in the sense that their error bars overlap. Thus, for our recommended potential displayed in Table I (see [20] for results at other distances), we have chosen the ECG results at small R and the orbital ones for large R, using the smaller error bars criterion. Only the AS term was computed using ECG bases for all R.

In the ECG approach, we used nearly *exact* values of $\langle \psi_0 | \hat{Y}_0 \psi_0 \rangle$ taken from literature [21]. The ECG values of V_{ad} were obtained following the method of Ref. [13], i.e., by numerically performing the differentiation with respect to nuclear coordinates, but we used larger and better optimized basis sets. The expectation value of $\hat{H}_2$ converges fast to its limit and therefore it was evaluated directly. The remaining three operators in the Breit-Pauli Hamiltonian as well as $\hat{H}_{\mathrm{AS}}$ are highly singular and their expectation values converge very slowly. These values were therefore evaluated employing the integral-transform techniques of Refs. [14,15,22]. To enable basis set extrapolation and estimation of uncertainties, the ECG calculations were performed using bases containing 300, 600, 1200, and 2400 ECG functions. The uncertainties were determined mainly by the difference between the results of calculations with two largest basis sets.

In the calculations employing the orbital basis, we used a two-step procedure: $\Delta Y = \Delta Y^{\mathrm{CCSD(T)}} + \delta Y^{\mathrm{FCI}}$, where $\Delta Y^{\mathrm{CCSD(T)}}$ is the contribution computed using the coupled-cluster method with single, double, and noniterative triple excitations [CCSD(T)] and $\delta Y^{\mathrm{FCI}} = \Delta Y^{\mathrm{FCI}} - \Delta Y^{\mathrm{CCSD(T)}}$. The FCI term was calculated with basis sets significantly smaller that those used for the CCSD(T) term. The CCSD(T) expectation values were obtained using linear response theory. We used doubly augmented Gaussian basis sets (denoted by dXZ) of the triple- to septuple-zeta quality, $X = 3, \ldots, 7$, with exponents optimized in Ref. [23] on the FCI energy of helium atom and on the van der Waals constants through C_{16}. In relativistic calculations, the basis sets were completely uncontracted. The final CCSD(T) results were obtained using the d6Z and d7Z basis sets and the complete basis set extrapolation with the two-point formula $\Delta Y(X) = \Delta Y(\infty) + AX^{-n}$, where $\Delta Y(X)$ is the value obtained for the cardinal number X and A is a constant. Following Ref. [24] and based on comparisons with ECG calculations for small R, we used $n = 1$ for all relativistic terms except for V_{Breit} where we assumed that $n = 1.5$. The absolute difference between the complete basis set extrapolated and the d7Z results was taken as the uncertainty of $\Delta Y(\infty)$. The values of δY^{FCI} were computed with the d4Z and d5Z basis sets. These values were not extrapolated, because the basis set convergence pattern was not well established in this case. Instead, the $X = 5$ result was assumed as the final one and the absolute difference between the $X = 5$ and $X = 4$ results as its uncertainty.

The adiabatic correction was determined slightly differently, using the FCI level of theory only, $V_{\mathrm{ad}} = \Delta Y^{\mathrm{FCI}}$, and numerical differentiation with respect to nuclear coordinates, as in Ref. [25]. This procedure is computationally demanding, so only d3Z and d4Z basis sets could be used in this case. The results were extrapolated using the two-point formula with the exponent $n = 3$. The absolute difference between the extrapolated and d4Z results was assumed as the uncertainty of V_{ad}. The relative errors of the adiabatic, relativistic, and QED corrections are smaller

TABLE I. Components of the ^{4}He-^{4}He potential (in kelvin = 1/315 774.65 hartree, R in bohr = a_0 = 0.529 177 Å). The total squared uncertainty of V was computed by summing squares of the partial uncertainties (in parentheses). V_{BO} is from Ref. [12] (R = 5.6) and [9] (other R's).

R	V_{BO}	V_{ad}	V_{rel}	V_{QED}	V	V_{ret}	Ref. [11]
3.0	3767.681(71)	1.387(7)	−0.2197(23)	0.0942(2)	3768.94(7)	0.000 45	3768.146
4.0	292.570(15)	0.1080(32)	0.0324(14)	0.0089(2)	292.719(15)	0.000 25	292.6337
5.0	−0.4754(65)	−0.0075(13)	0.0240(2)	−0.001 06(4)	−0.460(7)	0.000 15	−0.4774
5.6	−11.0006(2)	−0.0090(5)	0.015 40(4)	−0.001 35(2)	−10.9955(5)	0.000 12	−11.0085
6.0	−9.6819(23)	−0.0072(3)	0.011 43(5)	−0.001 20(4)	−9.6788(23)	0.000 10	−9.6869
7.0	−4.6225(6)	−0.003 33(7)	0.005 77(3)	−0.000 74(3)	−4.6208(6)	0.000 07	−4.6257
12.0	−0.165 92(2)	−0.000 125(1)	0.000 575(2)	−0.000 13(3)	−0.165 60(3)	0.000 02	

than 1%, except obviously near R where a given correction vanishes, and for the adiabatic correction at large R, where relative errors are of the order of 1%. The CCSD(T) and FCI calculations were carried out using the DALTON [26] and LUCIA [27] programs.

To ensure the correct asymptotic behavior of the potential, we evaluated the constants C_n determining the leading terms in the $1/R^n$ expansion of the post-$V_{\rm BO}$ contributions. For $V_{\rm ad}$, $V_{\rm mv}$, $\Delta\langle\hat{D}_1\rangle$, and $\Delta\langle\hat{D}_2\rangle$, we considered $n = 6$, 8, and 10. The determination of C_n for $V_{\rm ad}$ was described in Ref. [28]. The evaluation of C_n for the remaining terms is straightforward [29], and was done with basis d8Z. For $\Delta\langle\hat{D}_1\rangle$ and $V_{\rm mv}$, our values of C_n are consistent with the literature ones [30]. For $V_{\rm Breit}$, we computed only the first two constants C_4 and C_6, obtaining -3.5322×10^{-5} a.u. and -1.894×10^{-4} a.u., respectively. Our value of C_4 agrees within 0.06% with the literature value [31]. The contribution to C_6 from the interatomic part of $\hat{H}_2$ amounts to $-1.387 \cdot 10^{-4}$ a.u. and was computed using an appropriate generalization of the method employed for H_2 in Ref. [19]. The AS term behaves asymptotically as $-C_3/R^3 - C_5/R^5$ where $C_3 = 14\alpha^3/(3\pi)$ and $C_5 = 28\alpha^3\langle r^2\rangle/(3\pi)$, with $\langle r^2\rangle$ denoting the average square of the electron-nucleus distance in helium atom. The values of C_n are given in [20].

The computed values of $V(R)$ were fitted to an analytic function

$$e^{-aR}\sum_{i=0}^{2} P_i R^i + e^{-bR}\sum_{i=0}^{1} Q_i R^i - \sum_{n=3}^{16} f_n(\eta R)\frac{C_n}{R^n}, \tag{4}$$

where $f_n(x) = 1 - e^{-x}(1 + x + x^2/2! + \cdots + x^n/n!)$ is the Tang-Toennies [32] damping function, C_n are fixed, and a, b, η, P_i, and Q_i are adjustable parameters. The constants C_7 and C_9 were neglected. We used the inverse squares of the uncertainties σ as the weighting factors. The parameters are listed in [20]. The maximum and average errors of the fit are 1.07σ and 0.33σ, respectively.

To account for the long-range retardation damping, we computed the CP potential

$$V_{\rm CP}(R) = -\frac{1}{\pi R^6}\int_0^\infty \alpha_d(i\omega)^2 e^{-2\alpha R\omega} P(\alpha R\omega)d\omega, \tag{5}$$

where $P(x) = x^4 + 2x^3 + 5x^2 + 6x + 3$ and $\alpha_d(i\omega)$ is the dipole polarizability of helium at imaginary frequency $i\omega$. We fitted $V_{\rm CP}(R)$ with the rational function $-C_6^{\rm BO}R^{-6}g(\alpha R)$, where $C_6^{\rm BO}$ is the van der Waals constant C_6 computed at the (nonrelativistic) BO level of theory and

$$g(x) = \left(1 + \sum_{n=1}^{5} A_n x^n\right)\bigg/\left(1 + \sum_{n=1}^{6} B_n x^n\right). \tag{6}$$

Only the B_n parameters were free in the least-square optimization. The A_n coefficients were fixed by requiring the correct small and large x behavior of $g(x)$: $A_1 = B_1$, $A_2 = B_2 + C_4/(\alpha^2 C_6^{\rm BO})$, $A_3 = B_3 + B_1 C_4/(\alpha^2 C_6^{\rm BO}) + C_3/(\alpha^3 C_6^{\rm BO})$, $A_4 = \alpha B_5 K_7/C_6^{\rm BO}$, and $A_5 = \alpha B_6 K_7/C_6^{\rm BO}$, where $K_7 = 23\alpha_d^2(0)/(4\pi\alpha)$. The first three of these conditions guarantee that [33]

$$V_{\rm CP}(R) = -C_6^{\rm BO}R^{-6} - C_4R^{-4} - C_3R^{-3} + O(\alpha^4) \tag{7}$$

at $R \ll a_0/\alpha$ and the last two that $V_{\rm CP}(R) = -K_7R^{-7} + O(R^{-9})$ at large R [10]. Equation (7) shows that at short range $V_{\rm CP}(R)$ includes α^0, α^2, and α^3 terms which are already present in our potential, as well as α^4 and higher terms, which we have neglected so far. Therefore the (additive) retardation correction appropriate for our potential is

$$V_{\rm ret}(R) = V_{\rm CP}(R) + C_6^{\rm BO}R^{-6} + C_4R^{-4} + C_3R^{-3}, \tag{8}$$

where the last three terms, with the constants *exactly* the same as those in Eq. (4), eliminate the double counting. This correction, listed in Table I, removes the unphysical R^{-3} and R^{-4} long-range contributions from the potential. Being of the fourth order in α at short range, $V_{\rm ret}(R)$ is virtually negligible for all distances shown in Table I.

It should be pointed out that the addition of $V_{\rm ret}(R)$ does not eliminate all unphysical long-range terms from our potential. The R^{-5} QED term and the R^{-6} relativistic term can be eliminated using the relativistic generalization of the CP theory proposed recently by Pachucki [34]. However, we are not aware of any rigorous procedure allowing the elimination of the R^{-6} QED term and the R^{-6} adiabatic term. We applied an *ad hoc* procedure of damping the R^{-5} and R^{-6} terms by multiplying them with $g^2(\alpha R)$ and $g(\alpha R)$, respectively, where $g(x)$ is given by Eq. (6). This damping had a negligible effect on the observables discussed below.

In Table I, we compare our potential with the theoretical determination from Ref. [11] which also included several post-$V_{\rm BO}$ contributions. The quoted values are not corrected for retardation effects and should be compared with our $V(R)$. In the region of the well and for larger R, the discrepancies are a few times larger than the uncertainties of our potential, and only at $R = 1$ bohr are within our error bars. These discrepancies are consistent with the expected effects from basis set improvements in our calculations as well as from the complete inclusion of the α^2 and α^3 terms in our potential.

The computed properties of the helium dimer are shown in Table II. The retardation corrections included are, of course, different at different levels of theory. The atomic masses were used in solving the radial Schrödinger equation. The use of nuclear masses would decrease the dissociation energy D_0 by 0.030 mK and increase $\langle R\rangle$ by 0.42 Å. However, in view of the results of Ref. [35], the use of nuclear masses is unjustified for systems as large as the helium dimer. Our D_0 and $\langle R\rangle$ differ from the experimental values [7] by 1.7 and 1.2 times the experimental uncertainties, respectively. A measurement with tighter error bars would provide an important check of theory. The possible

TABLE II. Dissociation energy D_0 (in mK) and the average separation $\langle R\rangle$ (in Å) for ^{4}He-^{4}He obtained with atomic masses. "r.c." denotes the retardation correction appropriate for a given level of theory. The S-wave scattering length at the highest level is 90.4 ± 0.9 Å; see [20] for other values.

Potential	D_0	$\langle R\rangle$
$V_{\rm BO}$	1.718	45.77
$V_{\rm BO}$ + r.c.	1.555	47.92
$V_{\rm BO} + V_{\rm ad}$	1.816	44.62
$V_{\rm BO} + V_{\rm ad}$ + r.c.	1.648	46.65
$V_{\rm BO} + V_{\rm ad} + V_{\rm rel}$	1.590	47.43
$V_{\rm BO} + V_{\rm ad} + V_{\rm rel}$ + r.c.	1.610	47.15
$V_{\rm BO} + V_{\rm ad} + V_{\rm rel} + V_{\rm QED}$	1.620	47.02
$V_{\rm BO} + V_{\rm ad} + V_{\rm rel} + V_{\rm QED}$ + r.c.	1.615(34)	47.09(46)
Experiment, Ref. [7]	$1.1(^{+0.3}_{-0.2})$	52(4)

improvements on theoretical side are inclusions of higher order QED and nonadiabatic effects (the further improvements in accuracy of included terms are already accounted for by our error bars). The main α^4 QED contribution is the so-called one-loop correction, considered, e.g., in Ref. [36]. It can be expressed via $\Delta\langle\hat{D}_1\rangle$, and we checked that its effect on dimer properties is negligible. So is the effect of finite size of the helium nucleus, also expressible through $\Delta\langle\hat{D}_1\rangle$. The value of missing nonadiabatic correction is difficult to estimate reliably. In view of the results obtained for H_2 (see Fig. 2 in Ref. [35]), we expect that it is at least several times smaller than the effect of using the atomic mass, which we already included. Thus, our current error bars likely incorporate also the uncertainties resulting from the theory truncation. The accuracy achieved should be sufficient for metrology needs [4,5] in the foreseeable future.

This work was partially supported by a NIST Precision Measurement grant and by the NSF Grant No. CHE-0848589.

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