

Pair Potential with Submillikelvin Uncertainties and Nonadiabatic Treatment of the Halo State of the Helium Dimer

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The pair potential for helium is computed with accuracy improved by an order of magnitude relative to the best previous determination. For the well region, its uncertainties are now below 1 millikelvin. The main improvement is due to the use of explicitly correlated wave functions at the nonrelativistic Born-Oppenheimer (BO) level of theory. The diagonal BO and the relativistic corrections are obtained from large full configuration interaction calculations. Nonadiabatic perturbation theory is used to predict the properties of the halo state of the helium dimer. Its binding energy and the average value of the interatomic distance are found to be 138.9(5) neV and 47.13(8) Å. The binding energy agrees with its first experimental determination of 151.9(13.3) neV [Zeller *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **113**, 14651 (2016)].

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Helium is expected to become an important medium in determining thermodynamic metrology standards and the future International System of Units (SI) [1,2]. Several elements of such standards will be established by *ab initio* quantum mechanical calculations [3–7]. An important theory input is the helium pair potential. Its knowledge is required to account for the imperfection of helium gas and the necessary extrapolations to zero pressure [2]. The more accurate this potential is, the smaller will be the uncertainties of the resulting standards.

There are other reasons of interest in the helium pair potential. The dimer composed of ⁴He atoms, ⁴He₂, has a single very weakly bound vibrational state—an example of a quantum halo state—where atoms move mainly in the classically forbidden tunneling region of the configuration space [8]. This state was the subject of several experimental investigations [9–14]. We present here the development of a new potential with uncertainties reduced by an order of magnitude compared to the previous most accurate determination [15]. This potential and the nonadiabatic perturbation theory [16], accounting for the coupling of the electronic and nuclear motion, are used to obtain an accurate theoretical prediction of the properties of the halo state.

The potential of Ref. [15] contained the Born-Oppenheimer (BO) component from Ref. [17]. Its uncertainty, amounting to several millikelvin (mK) in the well region, was due to the slow convergence of a part of the wave function expanded in terms of orbital products. Since it is impossible to converge the orbital expansion sufficiently well [18], we now follow Refs. [19,20] and expand the BO wave function using the four-electron explicitly correlated Gaussian (ECG) basis. Several improvements to the approach of Refs. [19,20] that have been made recently [21–23] enabled us to perform highly accurate ECG calculations for 46 values of the interatomic distance R .

In Ref. [15], the BO potential of Ref. [17] was combined with the adiabatic (diagonal BO), relativistic, and quantum electrodynamics (QED) contributions, as well as with an appropriate retardation correction [24]. Its uncertainties were almost entirely determined by the uncertainties of the BO component. With the much improved BO potential computed in the present work, the accuracy of the adiabatic and relativistic components from Ref. [15] became insufficient. Therefore, we decided to recompute these components using different methodologies, providing higher accuracy and better error control.

Recently, the wave function of ⁴He₂ has been measured via the Coulomb explosion technique [14], which enabled the first experimental determination of its very small binding energy (151.9 ± 13.3 neV). The most precise calculation for this state was performed [15] in the adiabatic approximation giving the binding energy $D_0 = 136.6 \pm 2.9$ neV when nuclear masses are used to solve the vibrational problem (as required by the mathematical derivation of the adiabatic approximation) or 139.2 ± 2.9 neV when the atomic masses are used (as suggested by physical intuition). The average interatomic separations $\langle R \rangle$ obtained with these masses were 47.50 ± 0.46 Å and 47.09 ± 0.46 Å, respectively, in a minor disagreement with the experimental value of 52 ± 4 Å [13]. To resolve this ambiguity, in the present work we have used the nonadiabatic perturbation theory [16] to account for the coupling of the electronic and nuclear motion. This requires the calculation of an effective R -dependent vibrational mass and of a nonadiabatic correction to the potential [16]. We have developed methods to compute these quantities for many-electron diatomics and report the results in this Letter. To our knowledge, such nonadiabatic calculations have not been performed earlier for systems with more than two electrons.

TABLE I. Components of the ^4He dimer potential in kelvin (1 hartree = 315775.13 K) with R in bohr (1 bohr = 0.529177 Å) and their sum $V = V_{\text{BO}} + V_{\text{ad}} + V_{\text{rel}} + V_{\text{QED}}$. Results for other values of R and the components of V_{rel} are listed in the Supplemental Material [27].

| R | V_{BO} | V_{BO} , Ref. [5] | V_{ad} | V_{rel} | V_{QED} | V | V , Ref. [5] | V_{ret} |
|------|-----------------|----------------------------|-----------------|------------------|------------------|--------------------------|----------------|------------------|
| 3.0 | 3767.7341(38) | 3767.681(71) | 1.3847(15) | -0.2125(17) | 0.09376(22) | 3769.000(4) | 3768.94(7) | 0.00045 |
| 4.0 | 292.58201(86) | 292.570(15) | 0.10585(17) | 0.03322(21) | 0.00891(5) | 292.7300(9) | 292.719(15) | 0.00025 |
| 5.0 | -0.47114(36) | -0.4754(65) | -0.006992(10) | 0.024012(25) | -0.00106(3) | -0.4552(4) | -0.460(7) | 0.00015 |
| 5.6 | -11.00072(20) | -11.0006(2) | -0.008905(10) | 0.015403(15) | -0.001351(23) | -10.99557(20) | -10.9955(5) | 0.00012 |
| 6.0 | -9.68079(16) | -9.6819(23) | -0.007170(4) | 0.011438(11) | -0.00120(4) | -9.67772(16) | -9.6788(23) | 0.00010 |
| 7.0 | -4.62260(10) | -4.6225(6) | -0.0033168(24) | 0.005768(4) | -0.00074(3) | -4.62089(11) | -4.6208(6) | 0.00007 |
| 9.0 | -0.98971(6) | -0.98984(15) | -0.0007328(8) | 0.0019306(6) | -0.000316(29) | -0.98883(7) | -0.9890(2) | 0.00004 |
| 12.0 | | -0.16592(2) | -0.0001261(1) | 0.0005768(1) | -0.000133(26) | -0.16560(3) ^a | -0.16560(3) | 0.00002 |

^aComputed with the same value of V_{BO} as in Ref. [5] (given in the third column).

The ECG wave function employed by us has the form

$$\Psi = \mathcal{A}\Xi(1 + \hat{i}) \left(c_0\phi_0 + \sum_{k=1}^K c_k\phi_k(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \right), \quad (1)$$

where \mathcal{A} is the antisymmetrizer, Ξ is the product of two-electron singlet spin functions, \hat{i} is the inversion through the center of He_2 , and ϕ_k , $k > 0$, are the ECG basis functions:

$$\phi_k(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \prod_{i=1}^4 e^{-\alpha_{ki}|\mathbf{r}_i - \mathbf{X}_{ki}|^2} \prod_{i>j=1}^4 e^{-\beta_{kij}|\mathbf{r}_i - \mathbf{r}_j|^2}. \quad (2)$$

The linear parameters c_k and the nonlinear ones α_{ki} , β_{kij} , and $\mathbf{X}_{ki} = (0, 0, X_{ki})$ are optimized by minimizing the expectation value of the electronic Hamiltonian \hat{H}_{el} . The term $c_0\phi_0$ is included to approximate the product of spinless helium atom wave functions. When performing the nonlinear optimization of Ψ , we used the following fixed form of ϕ_0 :

$$\phi_0 = \mathcal{S} \sum_{l=1}^L b_l \phi_{\alpha_l\beta_l\gamma_l}^A(\mathbf{r}_1, \mathbf{r}_2) \phi_{\alpha'_l\beta'_l\gamma'_l}^B(\mathbf{r}_3, \mathbf{r}_4), \quad (3)$$

where $\mathcal{S} = (1 + \hat{i}P_{13}P_{24})(1 + P_{12})(1 + P_{34})$ with P_{ij} permuting the coordinates of the i th and j th electron, and

$$\phi_{\alpha\beta\gamma}^X(\mathbf{r}_1, \mathbf{r}_2) = e^{-\alpha|\mathbf{r}_1 - \mathbf{X}|^2} e^{-\beta|\mathbf{r}_2 - \mathbf{X}|^2} e^{-\gamma|\mathbf{r}_1 - \mathbf{r}_2|^2} \quad (4)$$

with $\mathbf{X} = (0, 0, 0)$ for $X = A$ and $\mathbf{X} = (0, 0, R)$ for $X = B$. The parameters of ϕ_0 were optimized by minimizing the expectation value of the sum $\hat{H}_A + \hat{H}_B$ of the atomic Hamiltonians [23]. We have set $L = 6788$, obtaining the energy of two noninteracting helium atoms within 0.16 mK of the exact value of Ref. [25]. After all nonlinear parameters in ϕ_k , $k > 0$, were optimized, the final energy was computed with ϕ_0 represented by the product of helium wave functions expanded in terms of 337 symmetrized ECGs of the form of Eq. (4). The energy of two helium atoms computed with this form of ϕ_0 differs from the exact one by 0.02 mK.

The calculations were first performed for the same 16 internuclear distances as in Ref. [17], ranging from 1 to

9 bohr. For each distance, $K = 2400, 3394, 4800$, and 6788 term expansions of the form of Eq. (1) were optimized. Attempts to fit analytic functions to the computed interaction energies have shown that the assumed grid density is insufficient to obtain a fit to within the new, decreased uncertainty. Therefore, we performed calculations at additional 30 values of R located at 0.33 and 0.67 of the distances between the existing 16 points (with R rounded to 0.01 bohr). The nonlinear parameters for the additional values of R were obtained from the wave function of the nearest R from the original set, employing the scaling procedure proposed in Ref. [26].

The interaction energy $E(K)$ was obtained by subtracting the exact atomic energies [25] from the calculated dimer energy, so $E(K)$ is a rigorous variational upper bound. To extrapolate to the complete basis set (CBS) limit, we employed the empirical observation that the ratio $\eta_K = \Delta_{K/\sqrt{2}}/\Delta_K$ with $\Delta_K = E(K) - E(K/\sqrt{2})$ is approximately independent of K . Disregarding a few outliers, we found that the values of η_K are between 1.32 and 3. We have chosen $\eta = 1.32$, to determine the extrapolated interaction energy $E_{\text{extrp}} = E(6788) + \Delta_{6788}/(\eta - 1)$. This choice, resulting in the largest magnitude of the CBS correction, compensates for the incompleteness of the minimization for $K = 6788$. The difference of energies extrapolated with $\eta = 3$ and $\eta = 1.32$ was taken as the uncertainty of E_{extrp} .

The CBS-extrapolated values of the BO interaction energies and their uncertainties are listed in Table I for a subset of distances. The data for other distances are given in the Supplemental Material [27]. The BO energies reported in Ref. [5] are presented for comparison. At all 16 distances where energies from both sets are available, the uncertainties overlap, so both sets of results are consistent. However, the present uncertainties are tighter by about an order of magnitude (from 8 to 23 times for $R < 7$ bohr and from 2.5 to 6 times for other distances), except at 5.6 bohr.

In Ref. [5], the adiabatic correction $E_{\text{ad}}(R)$ was computed via numerical differentiation of the electronic wave function with respect to nuclear positions. In our work, we employed the method proposed by Pachucki and Komasa

[16]. In a space-fixed reference frame, $E_{\text{ad}}(R)$ is expressed as [16]

$$E_{\text{ad}}(R) = \frac{\hbar^2}{m_n} \langle \nabla_R \Psi | \nabla_R \Psi \rangle + \frac{1}{4m_n} \langle \Psi | \mathbf{P}^2 | \Psi \rangle, \quad (5)$$

where \mathbf{R} is the vector joining the nuclei, m_n is the nuclear mass, and \mathbf{P} is the total electronic momentum operator. To avoid the cumbersome differentiation of Ψ with respect to \mathbf{R} , we obtained $\nabla_R \Psi$ by solving the equation [16]

$$(\hat{H}_{\text{el}} - E_{\text{BO}}) \nabla_R \Psi = -(\nabla_R \hat{H}_{\text{el}}) \Psi. \quad (6)$$

The adiabatic correction to the potential is defined as $V_{\text{ad}}(R) = E_{\text{ad}}(R) - 2E_{\text{ad}}^A$, where E_{ad}^A is the atomic adiabatic correction [28]. When $E_{\text{ad}}(R)$ and E_{ad}^A are computed with the same basis, $V_{\text{ad}}(R)$ vanishes at large R in accord with its known asymptotic expansion [29].

The solution $\nabla_R \Psi$ of Eq. (6) was obtained by representing $\nabla_R \Psi$ and Ψ as full configuration interaction (FCI) expansions and solving linear equations for the CI coefficients. By comparing with accurate ECG results, available at small R [5], we found that the orbital basis sets dXZ from Ref. [5] lead to fast convergence provided that they are augmented by one set of p functions obtained by taking the nuclear gradient of the contracted, 19-term s orbital already present in all dXZ bases of Ref. [5]. The dXZ bases augmented in this way will be referred to as the dXZcp bases.

$V_{\text{ad}}(R)$ was calculated using the dXZcp bases up to $X = 6$ for 55 values of R , the same 46 values as in the case of the BO potential and, additionally, for 9 larger distances. The largest FCI calculations employed the wave functions with $\sim 4 \times 10^8$ determinants (at D_{2h} symmetry). All necessary integrals and Hartree-Fock orbitals were computed using the DALTON 2.0 package [30], while the adiabatic corrections were obtained using a FCI code written for the purpose of this work. The values of $V_{\text{ad}}(R)$ were extrapolated to the CBS limit assuming the X^{-3} decay of the error. As our recommended values of $V_{\text{ad}}(R)$, we took the CBS limit based on the d5Zcp and d6Zcp results with uncertainties estimated as the absolute values of the difference between the extrapolated and the d6Zcp result. Combining the new numerical approach and the increased size of basis sets (in Ref. [5], bases up to $X = 4$ were used), we reduced the uncertainty of the adiabatic corrections by an order of magnitude.

The relativistic component $V_{\text{rel}}(R)$ of the potential $V(R)$ was computed for 55 values of R using the same method as in Ref. [5], except that we employed basis sets with larger cardinal numbers X and added p functions to improve the wave function in the vicinity of nuclei. Specifically, we started with the modified dXZ basis sets of Ref. [5] (containing 21 uncontracted s functions) and augmented them by $n \leq 5$ “tight” p functions with exponents larger than those already present in the original dXZ basis. The bases obtained in this way will be denoted as dXZ + np . The exponents of these tight p functions are given in the Supplemental Material [27].

To calculate expectation values of the relativistic operators, we used a composite approach. The main contribution (over 90%) was calculated at the coupled cluster CCSD(T) level of theory [31] using large basis sets (up to d8Z + 5p), whereas the remaining contribution was included applying an additive FCI correction computed with smaller bases (up to d6Z + 5p). The CCSD(T) calculations were performed using the DALTON 2013 package [32], whereas at the FCI level we used a program written for this work. For each internuclear distance, the relativistic potentials were obtained as the difference between the dimer and atomic expectation values, the latter calculated with the dimer basis to remove the basis-set superposition error.

To perform CBS extrapolations, we employed the convergence laws established in Ref. [5], i.e., we assumed that upon increasing the cardinal number X , the error of the Breit correction decays as $X^{-3/2}$ and the errors of the remaining corrections as X^{-1} . The fixed- n extrapolation from bases d($X - 1$)Z + np and dXZ + np will be denoted as d($X - 1, X$)Z + np . We found that the effect of the increased flexibility of the new dXZ + np bases on the relativistic corrections is small, especially for $n > 3$, although it improves somewhat the convergence of the extrapolations. As our recommended CCSD(T) component of the relativistic corrections we took the d(7, 8)Z + 5p extrapolation with uncertainties estimated as the absolute value of the difference between the d(7, 8)Z + 5p and d(6, 7)Z + 5p extrapolations. Similarly, at the FCI level, we used the d(5, 6)Z + 5p extrapolation with uncertainties estimated as the absolute value of the difference between the d(5, 6)Z + 5p and d(4, 5)Z + 5p extrapolations. To check the basis set convergence of the FCI correction, we also carried out FCI calculations for three distances, $R = 2, 5.6,$ and 12 bohr, using the d7Z + 2p basis set, which consists of 512 functions (and generates $\sim 2 \times 10^9$ D_{2h} -adapted determinants). The results of the FCI extrapolations d(6, 7)Z + 2p for $R = 5.6$ and 12 bohr (where the FCI corrections are most relevant) are contained within the proposed error bars, which shows that our uncertainty estimates are reliable.

The calculated one- and two-electron Darwin terms together with the ECG results for the Araki-Sucher term $V_{\text{AS}}(R)$ from Ref. [5] were employed to compute the leading (third-order in the fine structure constant α) QED correction $V_{\text{QED}}(R)$ using the formulas from Ref. [5]. Using Eq. (19) from Ref. [5], we also estimated the α^4 QED correction and found that it is at least 5 times smaller than the uncertainties of $V(R)$. Therefore, this correction was neglected.

The uncertainties of the components of $V_{\text{rel}}(R)$ and of $V_{\text{QED}}(R)$, as well as uncertainties of all components of $V(R)$, were added in squares. Compared to the results from Ref. [5], the uncertainties of $V_{\text{rel}}(R)$ were reduced by a factor of 1.4–17 depending on R . The uncertainties of $V_{\text{QED}}(R)$ remain unchanged as they are dominated by the uncertainty of the Araki-Sucher component. Also the retardation correction, appropriate for the potential including the leading

QED term [24], is the same as in Ref. [5]. As seen in Table I, the uncertainties assigned to all calculated post-BO corrections to the interaction potential are comparable or smaller than the uncertainties of the BO potential.

The computed values of $V_{\text{BO}}(R)$, $V_{\text{ad}}(R)$, $V_{\text{rel}}(R)$, and $V_{\text{QED}}(R)$ were fitted to the analytic functions of the form

$$\sum_{k=1}^M e^{-a_k R} \sum_{i=I_0}^{I_1} P_{ik} R^i - \sum_{n=N_0}^{N_1} f_n(\zeta R) \frac{C_n}{R^n}, \quad (7)$$

where $f_n(x) = 1 - e^{-x}(1 + x + \dots + x^n/n!)$ is the Tang-Toennies [33] damping function, a_k , P_{ik} , and ζ are adjustable parameters, and the summation limits $[M, I_0, I_1, N_0, N_1]$ are $[3, -1, 2, 6, 16]$ for $V_{\text{BO}}(R)$, $[3, 0, 2, 6, 10]$ for $V_{\text{ad}}(R)$, $[3, 0, 2, 4, 8]$ for $V_{\text{rel}}(R)$, and $[2, 0, 2, 3, 6]$ for $V_{\text{QED}}(R)$. The asymptotic constants C_8 for $V_{\text{rel}}(R)$ and C_6 for $V_{\text{QED}}(R)$ are not known and were also adjusted. The remaining constants C_n were fixed and set equal to the known literature values [5, 29, 34, 35]. To impose the correct behavior of $V_{\text{BO}}(R)$ at $R = 0$, we used the theoretical value of the beryllium atom energy $E_{\text{Be}} = -14.667356498$ hartree [36]. We used the inverse squares of uncertainties $\sigma(R)$ as the weighting factors in the least-squares fitting. The maximum and average absolute errors of the fit are 0.92σ and 0.16σ , respectively, for the BO component. Similarly accurate fits were obtained for the remaining components of $V(R)$.

In order to estimate the uncertainties of physical quantities calculated with our potential, we developed functions $\sigma_X(R)$ representing the uncertainties of the calculated components such that their exact values can be assumed to be contained between functions $V_X(R) \pm \sigma_X(R)$, where $V_X(R)$ is the analytic fit of a component X . We found that the functions $\sigma_X(R)$ can be represented as $\sigma_X(R) = s_0 e^{-a_0 R} + \sum_{i=1}^n s_i e^{-a_i R^2}$, where $n = 3$, except for $V_{\text{rel}}(R)$ when $n = 4$. The parameters and the Fortran codes for all fits can be found in the Supplemental Material [27].

To compute the properties of the bound state of ${}^4\text{He}_2$, we used the nonadiabatic perturbation theory [16] applied successfully to the H_2 molecule and its isotopologues [37–41]. In this theory, the energies E and radial wave functions $\chi(R)$ are obtained by solving the radial equation of the form

$$\left(-\frac{\hbar^2}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{J(J+1)\hbar^2}{2\mu_{\perp}(R)R^2} + \mathcal{V}(R) - E \right) \chi(R) = 0, \quad (8)$$

where $\mu_{\parallel}(R)$ and $\mu_{\perp}(R)$ are the R -dependent vibrational and rotational reduced masses

$$\frac{1}{2\mu_{\parallel}(R)} = \frac{1}{m_n} + \mathcal{W}_{\parallel}(R), \quad \frac{1}{2\mu_{\perp}(R)} = \frac{1}{m_n} + \mathcal{W}_{\perp}(R), \quad (9)$$

and $\mathcal{V}(R)$ is the sum of $V(R)$, $V_{\text{ret}}(R)$, and a nonadiabatic correction $V_{\text{na}}(R)$. The expressions for the functions $\mathcal{W}_{\parallel}(R)$, $\mathcal{W}_{\perp}(R)$, and $V_{\text{na}}(R)$ are given in Ref. [37]. One can show that $2\mu_{\parallel}(\infty) = 2\mu_{\perp}(\infty) = m_n + 2m_e + 4m_e^2/m_n + \mathcal{O}(m_e^3/m_n^2)$, where m_e is the electron mass. We employed the known $R \rightarrow \infty$ limits and computed directly the R -dependent parts $\mathcal{W}_{\parallel}^{\text{int}}(R) \equiv \mathcal{W}_{\parallel}(R) - \mathcal{W}_{\parallel}(\infty)$ and $\mathcal{W}_{\perp}^{\text{int}}(R) \equiv \mathcal{W}_{\perp}(R) - \mathcal{W}_{\perp}(\infty)$ of $\mathcal{W}_{\parallel}(R)$ and $\mathcal{W}_{\perp}(R)$.

The values of the functions $\mathcal{W}_{\parallel}^{\text{int}}(R)$, $\mathcal{W}_{\perp}^{\text{int}}(R)$, and $V_{\text{na}}^{\text{int}}(R) \equiv V_{\text{na}}(R) - V_{\text{na}}(\infty)$ were calculated at 52 points in the range $1 \leq R \leq 18$ bohr using a dedicated FCI code and the same dXZcp orbital basis sets as used to calculate the adiabatic correction, see Ref. [28] for the description of the computational algorithm. We employed basis sets with cardinal numbers up to $X = 6$ for $\mathcal{W}_{\parallel}^{\text{int}}(R)$ and $\mathcal{W}_{\perp}^{\text{int}}(R)$ and up to $X = 5$ for $V_{\text{na}}^{\text{int}}(R)$. The recommended values of $\mathcal{W}_{\parallel}^{\text{int}}(R)$, $\mathcal{W}_{\perp}^{\text{int}}(R)$, and $V_{\text{na}}^{\text{int}}(R)$ were obtained by extrapolations from the results computed with two largest basis sets assuming the X^{-3} convergence. The analytic representations of these functions were obtained by fitting the recommended values with functions of the form of Eq. (7) with summation limits $[M, I_0, I_1, N_0, N_1]$ equal to $[2, 0, 3, 8, 8]$ for $\mathcal{W}_{\parallel}^{\text{int}}(R)$, $[2, 0, 2, 8, 8]$ for $\mathcal{W}_{\perp}^{\text{int}}(R)$, and $[3, 0, 2, 6, 8]$ for $V_{\text{na}}^{\text{int}}(R)$. We estimate that in the well region the obtained fits represent the exact values with errors smaller than 5%. Equation (8) was solved numerically using the *Mathematica* software [42].

The computed dissociation energy D_0 and the size $\langle R \rangle$ of the ($J = 0$) bound state are presented in Table II, while the plots of the excess masses $\Delta m_{\parallel}(R) = 2\mu_{\parallel}(R) - m_n$, $\Delta m_{\perp}(R) = 2\mu_{\perp}(R) - m_n$, and of $V_{\text{na}}^{\text{int}}(R)$ are shown in Fig. 1. Our results confirm earlier observation [15] that the adiabatic and relativistic corrections to D_0 and $\langle R \rangle$ are significant, but the effect of retardation is very small when the leading relativistic and QED contributions are included in $V(R)$. The nonadiabatic effect increases D_0 by 2.6 neV and decreases $\langle R \rangle$ by 0.42 Å, i.e., by the same amount as

TABLE II. Dissociation energy D_0 (in neV) and the average separation $\langle R \rangle$ (in Å) for ${}^4\text{He}_2$. $V = V_{\text{BO}} + V_{\text{ad}} + V_{\text{rel}} + V_{\text{QED}}$.

| Potential | D_0 | | $\langle R \rangle$ | |
|--|-----------------------------|-----------|-----------------------|-----------|
| | Nuclear | Atomic | Nuclear | Atomic |
| V_{BO} | 145.2(5) | 147.8(5) | 46.20(7) | 45.80(7) |
| $V_{\text{BO}} + V_{\text{ad}}$ | 153.5(5) | 156.3(5) | 45.03(7) | 44.65(7) |
| $V_{\text{BO}} + V_{\text{ad}} + V_{\text{rel}}$ | 134.1(5) | 136.7(5) | 47.90(8) | 47.48(8) |
| V | 136.7(5) | 139.3(5) | 47.48(8) | 47.07(8) |
| $V + V_{\text{ret}}$ | 136.3(5) | 138.9(5) | 47.55(8) | 47.13(8) |
| $V + V_{\text{ret}} + \text{nonad}$ | 138.9(5) | | 47.13(8) | |
| $V + V_{\text{ret}}, \text{Ref. [15]}$ | | 139.2(29) | | 47.09(46) |
| Expt. | $151.9 \pm 13.3^{\text{a}}$ | | $52 \pm 4^{\text{b}}$ | |

^aRef. [14].

^bRef. [13].

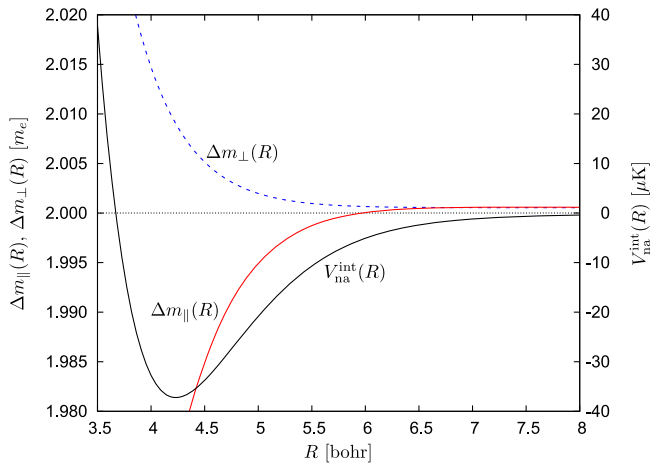


FIG. 1. The R dependence of the excess masses and the nonadiabatic correction to the potential.

does the QED correction. It is interesting to observe that these changes are recovered with excellent accuracy by the adiabatic calculations with atomic masses. We found that the difference between the nonadiabatic values of D_0 and $\langle R \rangle$ and the adiabatic ones computed with atomic masses are only -0.0007 neV and 0.00011 Å, respectively. These differences are negligible due to the small values $\Delta m_{||}(R) - 2m_e$ in the well region ($R > 5$ bohr), as shown in Fig. 1, but can be expected to be larger for helium properties sensitive to the potential at smaller values of R . Our results resolve the long-standing controversy [43–45] about which masses should be used in calculations for weakly bound dimers.

The recommended values of $D_0 = 138.9(5)$ neV and $\langle R \rangle = 47.13(8)$ Å agree with the former best theoretical determinations [15], but have 6 times smaller uncertainties. The small disagreement with the best measured value of $\langle R \rangle$ [13] remains essentially unchanged, but our uncertainty becomes now two orders, rather than one order, smaller than the experimental one. Our value of D_0 differs by 1.8σ and 1.2σ , respectively, from the values $1.1_{-0.2}^{+0.3}$ mK $\approx 95_{-15}^{+25}$ neV [13] and 112_{-16}^{+22} neV [5,46] derived from a nanosieve transmission experiment [13]. The value $D_0 = 151.9 \pm 13.3$ neV, obtained very recently [14] using the Coulomb explosion technique, agrees with our theoretical prediction within 0.98σ .

The interaction energies presented in this Letter establish a new accuracy benchmark for the helium dimer. This improvement was achieved using the ECG approach to solve the four-electron Schrödinger equation in the BO approximation and by computing the post-BO corrections using an improved methodology and significantly larger basis sets. We also computed, for the first time, the effective R -dependent vibrational and rotational masses and the resulting nonadiabatic corrections to the properties of the $^4\text{He}_2$ bound state. These calculations demonstrated that atomic masses should be used in adiabatic calculations for

weakly bound systems. The predicted dissociation energy is in agreement with the experimental determination via the Coulomb explosion method, confirming the reliability of this technique. In a separate publication, we will report applications of the computed potential and effective masses to calculate properties of bulk helium of relevance to metrology.

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