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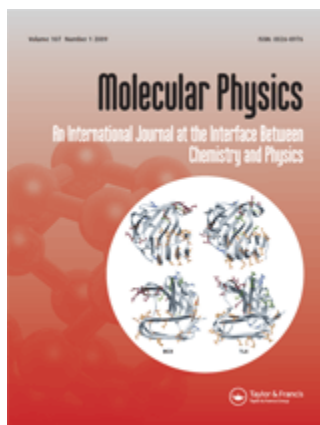
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***Ab initio* potential energy curve for the helium atom pair and
thermophysical properties of the dilute helium gas.**

I. Helium-helium interatomic potential

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A helium-helium interatomic potential energy curve was determined from quantum-mechanical *ab initio* calculations. Very large atom-centred basis sets including a newly developed d-aug-cc-pV8Z basis set supplemented with bond functions and *ab initio* methods up to Full CI were applied. The aug-cc-pV7Z basis set of Gdanitz (*J. Chem. Phys.*, **113**, 5145 (2000)) was modified to be more consistent with the aug-cc-pV5Z and aug-cc-pV6Z basis sets. The diagonal Born-Oppenheimer corrections as well as corrections for relativistic effects were also calculated. A new analytical representation of the interatomic potential energy was fitted to the *ab initio* calculated values. In a following paper this potential model will be used in the framework of the quantum-statistical mechanics and of the corresponding kinetic theory to calculate the most important thermophysical properties of helium governed by two-body and three-body interactions.

Keywords: Helium pair potential; DBOC; Casimir-Polder retardation; cc-pV7Z and cc-pV8Z basis sets

1 Introduction

Hurly and Moldover [1] as well as Hurly and Mehl [2] reported that the most accurate values of the thermophysical properties of helium at low densities can be obtained in two steps. First, the *ab initio* potential energy $V(R)$ for the helium-helium interaction at discrete values of the interatomic separation R including limiting forms of $V(R)$ at large R has to be calculated. The resulting values of $V(R)$ have then to be fitted to a model potential for the interaction of helium atoms. In a second step, the thermophysical properties at low density can be derived from $V(R)$ using the kinetic theory of gases together with standard formulae from quantum-statistical mechanics.

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In 2000 Hurly and Moldover argued on the basis of their analysis that the uncertainties of the calculated values for the thermophysical properties in the temperature range 1 K to 10^4 K were dominated by those of the potential. Hence in 2007 Hurly and Mehl improved the interatomic potential model using more recent *ab initio* $V(R)$ values of a multitude of research groups preferably calculated at $R = 4.0 a_0$ and $R = 5.6 a_0$ ($1 a_0 = 1 \text{ bohr} = 0.052917721 \text{ nm}$). They concluded that it would be desirable to compute $V(R)$ values with comparably low uncertainties for further interatomic distances. In addition, Hurly, Moldover, and Mehl stated that the uncertainties of the calculated thermophysical property values are smaller than the corresponding uncertainties of the experimental data, even for temperatures at which high-precision measurements can comparably easily be performed. They recommended the calculated values to be used as standards in different applications in metrology and to calibrate instruments in order to measure the density, dielectric virial coefficients, viscosity, thermal conductivity, speed of sound, and further properties.

In this contribution new helium-helium interatomic potential energy values are derived from quantum-mechanical *ab initio* calculations using larger basis sets than ever before and including the diagonal Born-Oppenheimer correction and corrections for relativistic effects. The calculations were not only performed for $R = 4.0 a_0$ and $R = 5.6 a_0$, but also for a number of further interatomic separations according to the request by Hurly and Mehl. Furthermore, a new potential model for helium is constructed on the basis of these new values and some from the literature. The *ab initio* values for the potential should be accurate enough to determine viscosity and thermal conductivity coefficients of helium up to an accuracy of 4 to 5 digits. A further aim of the investigation is to extend such calculations to neon in order to generate values of the thermophysical properties to be used for the calibration of measuring instruments.

2 Towards an accurate helium-helium interaction potential curve

The pair-potential energy between two helium atoms represents the best known interatomic potential to date. Being only a four-electron system it is possible to apply *ab initio* methods up to Full-CI with large basis sets. Different theoretical approaches have established that the well depth of the potential is around 11.0 K at a distance of about $5.6 a_0$. A short résumé of the development of the last ten years with regard to a highly accurate potential energy curve for the helium-helium interaction is given here in order to rank our efforts described in this report.

In 2000 Hurly and Moldover [1] summarized and evaluated the results of different *ab initio* calculations for the helium-helium interaction potential from the literature. To determine the parameters of their analytical representation of $V(R)$ they

used for the region of small R ($1 a_0 < R < 2.5 a_0$) the rigorous upper bounds of variational computations of Komasa [3], for intermediate distances ($3 a_0 < R < 7 a_0$) results obtained by Korona et al. [4] with the symmetry-adapted perturbation theory (SAPT), and in the region of large R the asymptotic dispersion coefficients of Bishop and Pipin [5].

The well-depth of (11.06 ± 0.03) K at $R = 5.6 a_0$ which resulted from the SAPT calculations of Korona et al. in 1997 was greater than most *ab initio* values from the literature. Similarly, their potential energies at other interatomic distances were too less repulsive, for example $V(R) = (291.64 \pm 0.9)$ K at $R = 4.0 a_0$. These results were incompatible with more recent high-level *ab initio* calculations. In 1999 van de Bovenkamp and van Duijneveldt [6] performed multireference configuration interaction (MRCI) calculations, employing an atom-centred basis set and a set of midbond functions, and extrapolated to the complete basis set (CBS) limit, yielding a well depth of only (10.99 ± 0.02) K and a value of $V(R) = (292.72 \pm 0.2)$ K at $R = 4.0 a_0$. In the same year, van Mourik and Dunning [7] employed double augmented correlation-consistent (d-aug-cc-pVXZ) basis sets and used the coupled cluster theory with single, double and full triple excitations (CCSDT) and the full configuration interaction method (Full CI) in combination with CCSD(T)-R12 results of Noga et al. [8]. They found 10.990 K for the well-depth and $V(R) = 292.578$ K at $R = 4.0 a_0$. Anderson [9] obtained $V(R) = -(10.98 \pm 0.02)$ K using "exact" quantum Monte Carlo (EQMC) calculations in 2001 and improved this in 2004 [10] to $-(10.998 \pm 0.005)$ K, whereas he found $V(R) = (292.60 \pm 0.20)$ K at $R = 4.0 a_0$. Using the averaged coupled-pair functional (r_{12} -MR-ACPF) method, which is close to FCI calculations, as well as a large atom-centred basis set including k functions and employing an extrapolation to the basis set limit, Gdanitz [11] found $V(R) = -(10.980 \pm 0.004)$ K at $R = 5.6 a_0$ and $V(R) = (292.75 \pm 0.01)$ K at $R = 4.0 a_0$. Klopper [12] also discussed the extrapolated estimates of the helium-helium interaction energies and recommended $V(R) = -(10.99 \pm 0.02)$ K at $R = 5.6 a_0$ and $V(R) = (292.6 \pm 0.3)$ K at $R = 4.0 a_0$ based on the CCSD(T) method using d-aug-cc-pV6Z and d-aug-cc-pV7Z basis sets for extrapolation to the CBS limit. Cencek et al. [13] performed very high-level *ab initio* calculations. First, they employed the Gaussian geminal implementation of the coupled cluster singles and doubles model. Then effects of triple and higher excitations were included using the conventional orbital approach CCSD(T) as well as FCI methods and applying very large correlation-consistent basis sets up to doubly augmented septuple-zeta supplemented with large sets of bond functions. Finally, extrapolation procedures to get the CBS limit led to potential values $V(R) = -(11.009 \pm 0.008)$ K at $R = 5.6 a_0$ and $V(R) = (292.54 \pm 0.04)$ K at $R = 4.0 a_0$. Shortly after Cencek et al. [14] recommended a new rigorous upper bound of -10.9985 K for the nonrelativistic Born Oppenheimer interaction energy at $5.6 a_0$. Very recently, Patkowski et al.

[15] calculated highly accurate interaction energies in the nonrelativistic Born-Oppenheimer approximation for 12 internuclear separations between $3.0 a_0$ and $9.0 a_0$ in a similar way as Cencek et al. [13]. They used the Gaussian geminal CCSD results from Cencek et al. for $R = 4.0 a_0$, $R = 5.6 a_0$, and $R = 7.0 a_0$ and performed Gaussian geminal CCD calculations for the other 9 distances, whereas the singles contribution and the post-CCSD terms were obtained from conventional orbital calculations with still larger basis sets than used by Cencek et al. [13]. Patkowski et al. [15] obtained $V(R) = (-11.0037 \pm 0.031) \text{ K}$ at $R = 5.6 a_0$ and $V(R) = (292.570 \pm 0.015) \text{ K}$ at $R = 4.0 a_0$. A new upper bound value of $V(R) = -11.0003 \text{ K}$ at $R = 5.6 a_0$ was also given (see Ref. 83 of [15]) and additionally a new SAPT value of $V(R) = (-11.000 \pm 0.011) \text{ K}$ at $R = 5.6 a_0$ (see Ref. 53 of [15]).

In principle at this level of accuracy, some further effects have to be taken into account. The diagonal adiabatic correction was calculated from explicitly correlated Gaussian functions by Komasa et al. [16] to be -13.2 mK at $R = 5.6 a_0$ for ^4He , whereas a newer computation concerning only the minimum resulted in -9 mK (see Ref. 7 of Cencek et al. [14]). Cencek et al. [14] computed the lowest-order relativistic correction to the helium-helium interaction energy, again only at the minimum, and obtained $(+15.4 \pm 0.6) \text{ mK}$. The main contribution of this correction comes from the Casimir-Polder retardation [17, 18] which changes for asymptotic separations the C_6/R^6 behavior of the potential into C_7/R^7 . This effect which is also of importance for the only vibrational state of the ^4He dimer [19, 20] will be included into the representation of the helium-helium interaction potential used for the calculation of the thermophysical properties under discussion. Finally, Pachucki and Komasa [21] calculated only at the minimum the leading-order radiative correction according to the quantum electrodynamics to be -1.27 mK . Since this effect is very small, we did not further consider the radiative correction for the complete interaction potential.

3 Basis sets

The cc-pV7Z basis set of Gdanitz [22] consists of a contracted 14s set (ref. 52 of [22]) of which the six most diffuse Gaussian functions are also present as primitives and of even-tempered shells of polarization functions which were generated following the guidelines of Dunning [23]. To be more consistent with the cc-pV5Z basis set (8s set with the four most diffuse functions also as primitives) and the cc-pV6Z basis set (10s set with the five most diffuse functions also as primitives) we have replaced the 14s set used by Gdanitz in his cc-pV7Z basis set with a 12s set which we obtained from the Karlsruhe basis set library [24]. Furthermore, the polarization functions were re-optimized for the 12s set.

To get the aug-cc-pV7Z basis set, diffuse functions should be added, in principle,

following Woon and Dunning [25] by scaling the exponent of the most diffuse function of each angular momentum in the cc-pV7Z basis set for helium using the ratio of the exponents of the two most diffuse functions of the same angular momentum of the aug-cc-pV7Z basis set for hydrogen. However, neither a regular aug-cc-pV7Z nor a cc-pV7Z basis set for hydrogen has become available until now. In order to avoid the construction of a full aug-cc-pV7Z basis set for hydrogen we adopted a different approach. We started by taking a 12s set for hydrogen from the Karlsruhe basis set library [26] and optimized a single diffuse s function by minimizing the ground state SCF energy of H^- resulting in the s part of an aug-cc-pV7Z basis set for hydrogen. This corresponds to the first step in the procedure suggested by Woon and Dunning. Subsequently in a second step, all the diffuse polarization functions should be optimized at the CISD level for the ground state of H^- , a route we did not follow, because this requires the construction of the polarization functions of the cc-pV7Z basis set. Instead of this we used the finding that in the aug-cc-pV6Z basis set the ratio of the two most diffuse polarization function exponents of each angular momentum is very close to the ratio of the two most diffuse s function exponents except for the highest angular momentum where the spacing between the exponents increases. Consequently, we adopted the ratio of the two most diffuse s functions which we optimized in the first step to generate the diffuse p, d, f, g and h functions of the aug-cc-pV7Z basis set for helium. The diffuse i function exponent was extrapolated as the square of the diffuse h function exponent in aug-cc-pV6Z divided by the diffuse g function exponent in aug-cc-pV5Z. Finally, the d-aug-cc-pV7Z basis set was constructed as proposed by Woon and Dunning [25] by expanding the exponents of the two most diffuse functions of each angular momentum in the aug-cc-pV7Z basis set in an even tempered manner.

To develop a d-aug-cc-pV8Z basis set we started by constructing a new contracted 14s set by minimizing the ground state SCF energy of the helium atom. The seven most diffuse functions are also present as primitives. Shells of even tempered polarization functions of up to k symmetry were generated following the guidelines of Dunning [23]. Diffuse functions were added in the same way as for aug-cc-pV7Z. In the first step a 14s set for hydrogen from the Karlsruhe basis set library [27] was used to optimize a single diffuse s function. In the second step the ratio of the exponent of this function and of the exponent of the most diffuse function in the 14s set was applied to generate the diffuse functions up to i symmetry. The diffuse k function exponent was then extrapolated as for aug-cc-pV7Z from the highest angular momentum diffuse functions of aug-cc-pV6Z and aug-cc-pV7Z. Table A1 shows the new d-aug-cc-pV7Z and d-aug-cc-pV8Z basis sets.

In most of our calculations of the helium interaction energy a (4s4p3d3f2g) set of bond functions centred between the two interacting helium atoms was applied. The bond function exponents are: *sp*: 0.06, 0.18, 0.54, 1.62; *df*: 0.15, 0.45, 1.35; *g*:

0.3, 0.9. This set is abbreviated as (44332) throughout this paper. Furthermore, the standard abbreviations aVXZ for aug-cc-pVXZ and daVXZ for d-aug-cc-pVXZ are used.

4 *Ab initio* Calculations

The interaction energies were calculated for 21 different He-He distances between $2.25 a_0$ and $8.0 a_0$. All calculations were performed using the supermolecular approach including a full counterpoise correction [28] as follows:

$$V(R) = \Delta E_{\text{He-He}}(R) = E_{\text{He-He}}(R) - 2 E_{\text{He-Q}}(R), \quad (1)$$

where $E_{\text{He-Q}}(R)$ corresponds to the energy of a helium atom with a ghost basis set at the distance R . Cencek et al. [13] obtained highly accurate results of the CCSD interaction energies within the Gaussian geminal approach [29, 30] for $R = 4.0 a_0$, $R = 5.6 a_0$, and $R = 7.0 a_0$. Therefore, we first calculated the CCSD interaction energies with the daVXZ+(44332) basis sets with $X = 7, 8$ using the conventional CCSD method. Then we extrapolated the correlation part of the CCSD interaction energies $V(\text{CCSD}_{\text{corr}})$ obtained with these two basis sets to the complete basis set (CBS) limit with the formula

$$V_{\text{CCSD}_{\text{corr}}}^{\text{daVXZ}} = V_{\text{CCSD}_{\text{corr}}}^{\text{CBS}} + \alpha(X - 1)^{-\beta}. \quad (2)$$

where the value of β was fixed to 2.13 (see below). The SCF interaction energies were not extrapolated and taken from the daV8Z+(44332) calculations. This is justified by the fact that the SCF part of the interaction energies always converges much faster than the correlation part. With this extrapolation scheme the value for β was chosen to agree precisely with the result of Cencek *et al.* for $V(\text{CCSD})$ at $R = 4.0 a_0$ (304.935 K). We notice that the values at $R = 5.6 a_0$ (−9.1520 K compared to −9.1509 K by Cencek *et al.*) and at $R = 7.0 a_0$ (−4.1799 K vs. −4.1796 K) are also in close agreement.

The next step was to calculate the differences between CCSDT and CCSD for all distances. This contribution accounts for almost all the correlation energy not considered in CCSD. One way to compute this contribution is to split it into two parts. The CCSD(T) [31] and the CCSDT interaction energies are each calculated for the highest possible basis set. Then the differences between CCSD(T) and CCSD as well as the differences between CCSDT and CCSD(T) are extrapolated separately to the CBS limit. The second approach is to extrapolate directly the differences between CCSDT and CCSD to the CBS limit. The first approach seems to be more sensible, because CCSD(T) calculations can be performed with larger basis sets compared to CCSDT. Furthermore, the differences between CCSDT and

CCSD(T) are much smaller and can therefore often be evaluated with sufficient accuracy using smaller basis sets. However, we chose the second approach due to the fact that the differences between CCSDT and CCSD converge very fast to the CBS limit, whereas the two contributions in the first approach converge slower and in opposite directions. Figure 1 illustrates this for $R = 5.6 a_0$. We used daVXZ+(44332) basis sets with $X = 4, 5, 6$ and applied Eq.(2) for the extrapolation of the energy differences in which α and β are fitting parameters.

The remaining differences between Full CI (equivalent to CCSDTQ and CISDTQ for a pair of helium atoms) and CCSDT energies are very small. They were calculated with the daV5Z basis set without bond functions and not extrapolated to the CBS limit.

Results for the CCSD correlation energies for $X = 4$ to $X = 8$ are summarized in Table 1. The differences between CCSDT and CCSD for $X = 4, 5, 6$ as well as the differences between Full CI and CCSDT for $X = 4, 5$ are given in Table 2. The SCF interaction energies and the extrapolated correlation contributions are listed in Table 3 together with the final potential in the nonrelativistic Born-Oppenheimer approximation. The resulting interaction energy at $R = 5.6 a_0$ of -11.001 K agrees very well with the result of Anderson [10] (-10.998 ± 0.005) K and with the result of Patkowski et al. [15] (-11.0037 ± 0.0031) K. Still better agreement is found with the upper bound value -11.0003 K and with the SAPT value of (-11.000 ± 0.011) K both given in [15]. We estimate the uncertainties of our potential energy values to be ± 30 mK at $R = 4.0 a_0$, ± 3 mK at $R = 5.6 a_0$, and ± 2 mK at $R = 7.0 a_0$ in the nonrelativistic Born-Oppenheimer approximation. These estimates are based on the observed convergence behavior of the individual contributions (of the differences between CCSDT and CCSD as well as between Full CI and CCSDT) and are supported by the deviations of our extrapolated CCSD results from the Gaussian geminal CCSD results of Cencek et al. [13]

The lowest-order relativistic correction to the interaction energy was calculated by Cencek et al. [14] at $R = 5.6 a_0$ using the Breit-Pauli approximation [32]. It consists of four terms for a pair of Helium atoms: the mass-velocity term, the orbit-orbit term, and the 1- and 2-electron Darwin terms. Cencek et al. found that the orbit-orbit term, which is implicitly included in the Casimir-Polder retardation [17, 18], is the dominating effect, whereas the 2-electron Darwin term is negligible. Since we account for the retardation effect subsequently in the final potential function (see next section), we limited our computations for the relativistic corrections to the mass-velocity and 1-electron Darwin terms which together form the so-called Cowan-Griffin approximation [33]. The calculations were carried out at the CCSD(T)/daV6Z level. The results are given along with CCSD(T)/daV5Z values in Table 4.

The calculation of the diagonal Born-Oppenheimer correction (DBOC) to the

interaction energies is quite difficult, because calculations are only possible for SCF and CI wavefunctions with the currently publicly available programs. The SCF level is not accurate enough to compute this correction and the CI methods are not size consistent apart from Full CI. However, Full CI is not applicable with the large basis sets required to get a converged result for the DBOC. We therefore evaluated the DBOC at the CISD/daV5Z level. In addition, the BSSE correction was not possible. To correct for the missing size consistency, we modified Eq. (1) and subtracted the energy of the atom pair at a very large separation ($R \geq 20 a_0$) instead of the energy of the two separate atoms. To account for missing electron correlation in CISD we calculated the DBOC differences between CISDT and CISD with the daVQZ basis set and added them to the CISD/daV5Z values. **The calculations were performed for the ^4He isotope.** The results are also given in Table 4.

Our values are in excellent agreement with the calculations of the DBOC from explicitly correlated Gaussian functions by Komasa et al. [16] at short ranges, but differ at intermediate and long ranges. As an example, our value of -9.3 mK at $R = 5.6 a_0$ is inconsistent with the corresponding value by Komasa et al. of -13.2 mK . However, a more recent computation resulted in -9 mK at $R = 5.6 a_0$ (see Ref. 7 of Cencek et al. [14]) which is in very close agreement with our value. This justifies using the DBOC values of the present paper for our new potential function.

The Mainz-Austin-Budapest version of ACES II [34] was utilized for all CCSDT calculations and for the determination of the relativistic corrections. For the Full CI and DBOC computations we used PSI3 [35]. All other calculations were carried out with both program packages.

5 Analytical potential function

Table 5 shows the *ab initio* data including the relativistic corrections (apart from retardation) and the DBOCs chosen for the fit of the potential function. For the short range part of the potential from $1.0 a_0$ to $2.0 a_0$ we used the rigorous upper bound values of Komasa [3] which are still the best values for very small distances, whereas for the range between $2.25 a_0$ and $8.0 a_0$ our new *ab initio* values were taken.

A modification of the potential function given by Tang and Toennies [36] was fitted to the calculated interaction energies:

$$V(R) = A \exp(a_1 R + a_2 R^2 + a_{-1} R^{-1} + a_{-2} R^{-2} + d_1 \sin(d_2 R + d_3)) - \sum_{n=3}^8 f_{2n}(R) \frac{C_{2n}}{R^{2n}} \left[1 - \exp(-bR) \sum_{k=0}^{2n} \frac{(bR)^k}{k!} \right]. \quad (3)$$

The coefficients A , a_1 , a_2 , a_{-1} , a_{-2} , b , d_1 , d_2 , d_3 were fitted to the values in Table 5 with $f_{2n}(R) = 1$ for all n , while the dispersion coefficients C_6 to C_{10} were taken from Zhang et al. [37] and the higher ones were extrapolated using formulae of Thakkar [38]). We slightly modified the C_6 value of Zhang et al. by adding the relativistic correction δC_6 calculated by Moszynski et al. [39] with their bas281 basis set within the Cowan-Griffin approximation. For consistency the higher dispersion coefficients were extrapolated with the nonrelativistic value of C_6 . The potential parameters are listed in Table 6.

Hurly and Mehl [2] applied the same model potential apart from the sin function in the exponential term. It is to note that Hurly and Mehl did not consider relativistic corrections apart from retardation so that they utilized the unmodified C_6 value of Zhang et al. The *ab initio* calculated values for $V(R)$ used in the fit by Hurly and Mehl are also listed in Table 5. In addition, this table gives the unretarded values resulting from the fit of our *ab initio* data to Eq. (3) as well as the corresponding values obtained by Hurly and Mehl with the somewhat simpler equation without the sin function. The table makes evident that a different weighting was applied by Hurly and Mehl compared with the present paper. Their *ab initio* values below $R = 3.0 a_0$ are better represented by the fit, but this region of the potential is not of large importance for the calculation of the thermophysical properties at low density. On the contrary, the values above $R = 3.0 a_0$ which are of higher significance for the thermophysical properties are distinctly better described by our modified potential model.

The functions $f_{2n}(R)$ account for the relativistic retardation of the dipole-dipole term as well as of the next higher dispersion terms for all R if $n = 3 - 5$ [40–42]. For $n > 5$ the approximation $f_{2n}(R) = 1$ was used. The $f_{2n}(R)$ values given in [42] were interpolated using Lagrange's polynomial for 5 points and applied to the potential after the fit. The retardation correction (i.e. the difference between the retarded and the unretarded potentials) which is practically the same for both potential functions is also shown in Table 5.

6 Summary and Conclusions

A new interaction potential for the helium atom pair has been obtained from highly accurate *ab initio* calculations at a large number of helium-helium separations. For this purpose new basis sets were constructed and the series of correlation consistent basis sets for helium was extended up to cc-pV8Z. Thereby diffuse functions for the cc-pV7Z and cc-pV8Z were generated using a simplification of the approach proposed by Woon and Dunning. The results of CCSD calculations with the d-aug-cc-pV7Z and d-aug-cc-pV8Z basis sets supplemented with bond functions were extrapolated to the complete basis set limit (CBS). The differences between the in-

teraction energies at the CCSD and CCSDT levels were also extrapolated utilizing basis sets of up to d-aug-cc-pV6Z quality with bond functions. The contributions beyond CCSDT were calculated with the d-aug-cc-pV5Z basis set. The resulting interaction energies are in close agreement with other high level *ab initio* results from the literature. Relativistic corrections to the interaction energies were estimated within the Cowan-Griffin approximation. The diagonal Born-Oppenheimer correction (DBOC) was also determined. Its value at the potential minimum agrees very well with the most accurate one from the literature.

An analytical potential function was fitted to the calculated interaction energies. At small distances additional values from the literature supplemented with the DBOCs and the relativistic corrections of the present paper were incorporated into the fit. The large number of helium-helium distances used for the fit made it possible to use a more flexible analytic representation for the potential than was previously possible. The errors originating from the fit are practically negligible.

In the second paper of this series we will use this potential function to determine the most important two-body and three-body properties of helium which are accurate enough to be used as standard values over a wide range of temperatures.

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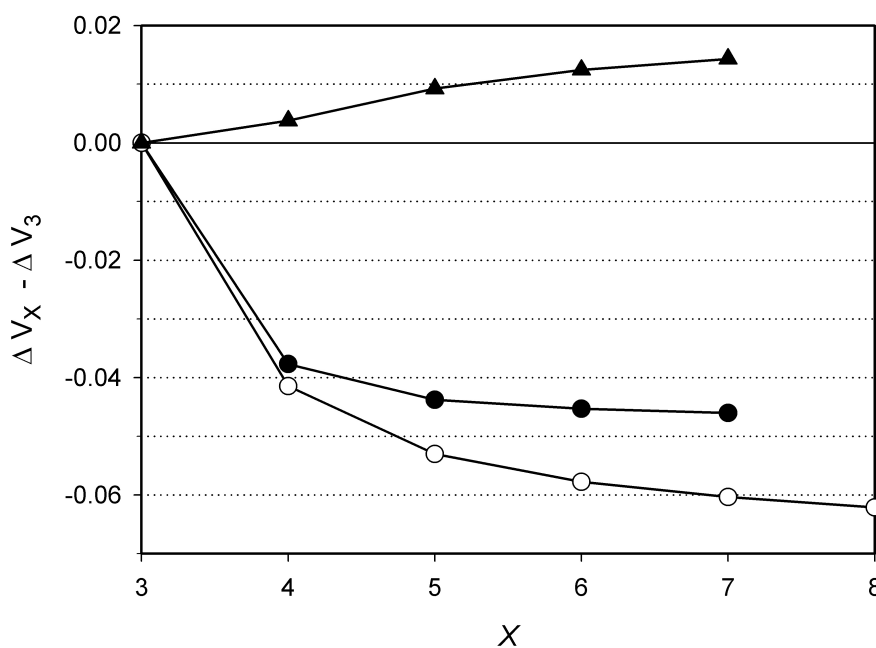


Figure 1. Convergence of the differences CCSDT-CCSD, CCSD(T)-CCSD and CCSDT-CCSD(T) at $R = 5.6 a_0$ with the daVXZ+(44332) basis sets with X ranging from 3 to 8. The energy differences were shifted so that the $X = 3$ value of each contribution gives zero for better comparability. (●) CCSDT-CCSD, (○) CCSD(T)-CCSD, (▲) CCSDT-CCSD(T).

Table 1. CCSD correlation energy $V(\text{CCSD}_{\text{corr}})$ obtained with the daVXZ+(44332) basis sets. All energies are in Kelvin.

R/a_0	$V(\text{CCSD}_{\text{corr}})$				
	X=4	X=5	X=6	X=7	X=8
2.25	-1278.3832	-1299.3072	-1308.4305	-1313.5367	-1316.7730
2.50	-897.6723	-911.8263	-917.9003	-921.2374	-923.3969
2.75	-632.9536	-642.3037	-646.2734	-648.4541	-649.8389
3.00	-449.1651	-455.2035	-457.7645	-459.1552	-460.0542
3.25	-321.0761	-324.8855	-326.5090	-327.3779	-327.9482
3.50	-231.1453	-233.4965	-234.5045	-235.0390	-235.4191
3.75	-167.4621	-168.8840	-169.4958	-169.8210	-170.0425
4.00	-122.0022	-122.8490	-123.2109	-123.4070	-123.5306
4.25	-89.3391	-89.8378	-90.0466	-90.1627	-90.2358
4.50	-65.7544	-66.0441	-66.1620	-66.2288	-66.2717
4.75	-48.6567	-48.8222	-48.8870	-48.9243	-48.9494
5.00	-36.2165	-36.3095	-36.3439	-36.3640	-36.3788
5.25	-27.1322	-27.1829	-27.2002	-27.2105	-27.2194
5.50	-20.4714	-20.4971	-20.5051	-20.5101	-20.5154
5.60	-18.3284	-18.3475	-18.3531	-18.3567	-18.3610
5.75	-15.5636	-15.5751	-15.5783	-15.5803	-15.5834
6.00	-11.9273	-11.9311	-11.9320	-11.9324	-11.9342
6.25	-9.2164	-9.2162	-9.2161	-9.2157	-9.2167
6.50	-7.1817	-7.1794	-7.1790	-7.1783	-7.1789
7.00	-4.4717	-4.4680	-4.4677	-4.4668	-4.4671
8.00	-1.9048	-1.9022	-1.9021	-1.9015	-1.9017

Table 2. Differences between $V(\text{CCSDT})$ and $V(\text{CCSD})$ obtained with daVXZ+(44332) basis sets as well as differences between $V(\text{Full CI})$ and $V(\text{CCSDT})$ obtained with daVXZ basis sets. All energies are in Kelvin.

R/a_0	$\Delta V(\text{CCSDT} - \text{CCSD})$			$\Delta V(\text{Full CI} - \text{CCSDT})$	
	$X = 4$	$X = 5$	$X = 6$	$X = 4$	$X = 5$
2.25	-79.1379	-79.5787	-79.7566	-0.1949	-0.2218
2.50	-62.6064	-62.9095	-63.0273	-0.1907	-0.2100
2.75	-49.1100	-49.3202	-49.3980	-0.1894	-0.2031
3.00	-38.0467	-38.1923	-38.2443	-0.1801	-0.1897
3.25	-29.0855	-29.1863	-29.2214	-0.1623	-0.1691
3.50	-21.9650	-22.0357	-22.0593	-0.1393	-0.1442
3.75	-16.4238	-16.4742	-16.4899	-0.1148	-0.1185
4.00	-12.1932	-12.2298	-12.2403	-0.0918	-0.0946
4.25	-9.0145	-9.0414	-9.0486	-0.0717	-0.0738
4.50	-6.6553	-6.6752	-6.6804	-0.0551	-0.0567
4.75	-4.9192	-4.9341	-4.9379	-0.0420	-0.0432
5.00	-3.6482	-3.6595	-3.6624	-0.0318	-0.0327
5.25	-2.7197	-2.7284	-2.7305	-0.0241	-0.0247
5.50	-2.0410	-2.0478	-2.0495	-0.0183	-0.0187
5.60	-1.8235	-1.8296	-1.8312	-0.0164	-0.0168
5.75	-1.5437	-1.5489	-1.5503	-0.0139	-0.0142
6.00	-1.1775	-1.1815	-1.1827	-0.0107	-0.0109
6.25	-0.9063	-0.9094	-0.9104	-0.0082	-0.0084
6.50	-0.7040	-0.7064	-0.7072	-0.0064	-0.0065
7.00	-0.4364	-0.4379	-0.4385	-0.0040	-0.0040
8.00	-0.1853	-0.1859	-0.1862	-0.0017	-0.0017

Table 3. SCF and extrapolated CCSD interaction energies, extrapolated triple contributions, Full CI–CCSDT contributions, and the final nonrelativistic potential without the DBOC. All energies are in Kelvin.

R/a_0	$V(\text{SCF})$ daV8Z+(44332)	$V(\text{CCSD})$ daV(78)Z+(44332)	$\Delta V(\text{CCSDT} - \text{CCSD})$ daV(456)Z+(44332)	$\Delta V(\text{Full CI} - \text{CCSDT})$ daV5Z	$V(\text{final, nonrel BO})$
2.25	22313.06	20987.96	−79.9916	−0.2218	20907.75
2.50	12952.24	12023.29	−63.1718	−0.2100	11959.91
2.75	7461.939	6808.536	−49.4856	−0.2031	6758.848
3.00	4268.348	3805.981	−38.2993	−0.1897	3767.492
3.25	2425.108	2095.693	−29.2568	−0.1691	2066.267
3.50	1369.077	1132.680	−22.0813	−0.1442	1110.454
3.75	768.3004	597.6879	−16.5031	−0.1185	581.0663
4.00	428.7828	304.9345	−12.2481	−0.0946	292.5918
4.25	238.0540	147.6302	−9.0535	−0.0738	138.5028
4.50	131.5339	65.1517	−6.6837	−0.0567	58.4113
4.75	72.3585	23.3444	−4.9403	−0.0432	18.3610
5.00	39.6448	3.2278	−3.6641	−0.0327	−0.4689
5.25	21.6407	−5.6015	−2.7319	−0.0247	−8.3580
5.50	11.7727	−8.7563	−2.0506	−0.0187	−10.8255
5.60	9.2200	−9.1520	−1.8322	−0.0168	−11.0010
5.75	6.3844	−9.2072	−1.5512	−0.0142	−10.7727
6.00	3.4523	−8.4866	−1.1836	−0.0109	−9.6811
6.25	1.8619	−7.3576	−0.9113	−0.0084	−8.2773
6.50	1.0016	−6.1790	−0.7081	−0.0065	−6.8936
7.00	0.2880	−4.1799	−0.4393	−0.0040	−4.6232
8.00	0.0233	−1.8789	−0.1868	−0.0017	−2.0675

Table 4. Relativistic Cowan-Griffin correction at the CCSD(T)/daV5Z and CCSD(T)/daV6Z levels as well as the DBOC at the CISD/daV5Z, CISD/daVQZ, and CISDT/daVQZ levels and the final estimate of the DBOC. All energies are in Kelvin.

R/a_0	Cowan-Griffin correction		Diagonal Born-Oppenheimer correction (DBOC)			
	CCSD(T)/daV5Z	CCSD(T)/daV6Z	CISD/daV5Z	CISD/daVQZ	CISDT/daVQZ	final estimate
1.00	−22.8753	−23.1946	157.2975	157.4258	158.1839	158.0556
1.25	−19.0499	−19.0923	71.9284	71.9926	72.2730	72.2087
1.50	−13.8452	−13.8878	36.2596	36.2888	36.4554	36.4263
1.75	−9.2750	−9.2735	20.1249	20.1490	20.2810	20.2570
2.00	−5.9138	−5.8830	11.7220	11.7410	11.8473	11.8283
2.25	−3.6376	−3.6126	6.9292	6.9425	7.0253	7.0120
2.50	−2.1779	−2.1640	4.0826	4.0918	4.1540	4.1449
2.75	−1.2763	−1.2700	2.3742	2.3814	2.4269	2.4197
3.00	−0.7328	−0.7315	1.3535	1.3598	1.3923	1.3860
3.25	−0.4115	−0.4126	0.7516	0.7565	0.7794	0.7746
3.50	−0.2256	−0.2272	0.4032	0.4068	0.4229	0.4193
3.75	−0.1202	−0.1218	0.2059	0.2090	0.2203	0.2172
4.00	−0.0617	−0.0632	0.0971	0.1001	0.1081	0.1051
4.25	−0.0300	−0.0313	0.0393	0.0416	0.0472	0.0450
4.50	−0.0133	−0.0142	0.0100	0.0109	0.0150	0.0141
4.75	−0.0048	−0.0055	−0.0037	−0.0041	−0.0012	−0.0008
5.00	−0.0007	−0.0011	−0.0095	−0.0104	−0.0083	−0.0073
5.25	0.0011	0.0009	−0.0111	−0.0118	−0.0103	−0.0096
5.50	0.0017	0.0015	−0.0107	−0.0109	−0.0098	−0.0096
5.60	0.0018	0.0017	−0.0103	−0.0103	−0.0093	−0.0093
5.75	0.0018	0.0017	−0.0095	−0.0093	−0.0084	−0.0086
6.00	0.0016	0.0016	−0.0081	−0.0076	−0.0069	−0.0074
6.25	0.0014	0.0015	−0.0068	−0.0060	−0.0055	−0.0063
6.50	0.0012	0.0012	−0.0056	−0.0047	−0.0043	−0.0052
7.00	0.0008	0.0009	−0.0035	−0.0031	−0.0028	−0.0033
8.00	0.0003	0.0003	−0.0014	−0.0020	−0.0019	−0.0013

Table 5. *Ab initio* calculated and fitted He-He interaction energies without retardation for the potentials of the present paper and of Hurly and Mehl [2] as well as the retardation correction. All energies are in Kelvin.

R/a_0	this work		Hurly and Mehl		$\Delta V(\text{retardation})$
	$V(ab\ initio)$	$V(\text{fitted})$	$V(ab\ initio)$	$V(\text{fitted})$	
1.00	286570.1*	286542.4	286593.0	286597.0	0.1
1.25	173854.3*	173947.2		174085.7	0.1
1.50	104342.9*	104291.2	104356.0	104356.0	0.1
1.75	61787.46*	61756.89		61786.88	0.09
2.00	36150.54*	36143.86	36148.7	36158.94	0.10
2.25	20911.15	20914.80		20921.81	0.11
2.50	11961.89	11963.96	11966.1	11966.32	0.10
2.75	6759.997	6760.387		6760.539	0.082
3.00	3768.146	3767.974	3769.37	3767.467	0.064
3.25	2066.629	2066.434		2066.005	0.050
3.50	1110.646	1110.670	1111.41	1110.509	0.040
3.75	581.1617	581.1887		581.2313	0.0331
4.00	292.6337	292.6195	292.74	292.7471	0.0328
4.25	138.5165	138.5169		138.6437	0.0278
4.50	58.4111	58.4128	58.409	58.5017	0.0236
4.75	18.3547	18.3550		18.4029	0.0199
5.00	-0.4774	-0.4775	-0.513	-0.4585	0.0168
5.10		-4.5592	-4.534	-4.5477	0.0157
5.25	-8.3667	-8.3665		-8.3624	0.0142
5.50	-10.8336	-10.8333		-10.8339	0.0120
5.60	-11.0085	-11.0084	-11.003	-11.0092	0.0112
5.75	-10.7796	-10.7795		-10.7796	0.0101
6.00	-9.6869	-9.6871	-9.682	-9.6850	0.0086
6.25	-8.2821	-8.2824		-8.2782	0.0072
6.50	-6.8976	-6.8976	-6.895	-6.8924	0.0062
6.60		-6.3832	-6.347	-6.3778	0.0058
7.00	-4.6257	-4.6256	-4.624	-4.6209	0.0046
7.50		-3.0758	-3.077	-3.0727	0.0034
8.00	-2.0684	-2.0684	-2.068	-2.0668	0.0026
9.00		-0.9907	-0.991	-0.9904	0.0016
10.00		-0.5130	-0.514	-0.5130	0.0010
12.00		-0.1660	-0.166	-0.1661	0.0005
15.00		-0.0424	-0.0423	-0.0424	0.0002

* Values by Komasa [3] including relativistic corrections and DBOCs.

Table 6. Potential parameters (ε/k_B , R_ε , and σ for the retarded potential).

A (K)	$0.307092338615E + 07$
a_1 (a_0^{-1})	$-0.201651289932E + 01$
a_{-1} (a_0)	$-0.431646276045E + 00$
a_2 (a_0^{-2})	$-0.459521265125E - 01$
a_{-2} (a_0^2)	$0.138539045980E + 00$
d_1	$0.167127323768E - 02$
d_2 (a_0^{-1})	$0.178284243205E + 01$
d_3	$0.176635702255E + 01$
b (a_0^{-1})	$0.203625105759E + 01$
C_6 (K a_0^6)	$0.4616213781E + 06$
C_8 (K a_0^8)	$0.4460565781E + 07$
C_{10} (K a_0^{10})	$0.5803352873E + 08$
C_{12} (K a_0^{12})	$0.1031677697E + 10$
C_{14} (K a_0^{14})	$0.2415716766E + 11$
C_{16} (K a_0^{16})	$0.7191492488E + 12$
ε/k_B (K)	10.997898
R_ε (a_0)	5.608068
σ (a_0)	4.990672

Appendix A: d-aug-cc-pV7Z and d-aug-cc-pV8Z basis sets for helium

Table A1. d-aug-cc-pV7Z and d-aug-cc-pV8Z basis sets for helium. Diffuse functions are separated by a blank line.

d-aug-cc-pV7Z:								
contracted 12s set		correlation function exponents						
exponent	contr. coeff.	s	p	d	f	g	h	i
18090.1201	0.00001142	8.0089	21.770	17.744	13.956	10.569	7.588	4.911
2709.1179	0.00008877	3.2991	9.466	7.757	5.962	4.277	2.780	
616.5260	0.00046646	1.4073	4.116	3.391	2.547	1.731		1.3070
174.6204	0.00196311	0.6121	1.790	1.482	1.088		0.8701	0.3478
56.9629	0.00706669	0.2702	0.7782	0.6481		0.5418	0.2723	
20.5602	0.02227400	0.1186	0.3384		0.3406	0.1696		
8.0089	0.06086507			0.2029	0.1066			
3.2991	0.13869491	0.03712	0.1059	0.06352				
1.4073	0.25156787	0.01162	0.03314					
0.6121	0.34077009							
0.2702	0.27715625							
0.1186	0.07272833							

d-aug-cc-pV8Z:									
contracted 14s set		correlation function exponents							
exponent	contr. coeff.	s	p	d	f	g	h	i	k
69636.5762	0.00000212	12.7483	28.215	23.624	19.487	15.405	11.787	8.605	5.654
10421.3753	0.00001649	5.5248	13.263	11.240	9.159	7.007	5.054	3.336	
2369.7889	0.00008683	2.4714	6.235	5.348	4.304	3.187	2.167		1.681
670.7140	0.00036718	1.1247	2.931	2.544	2.023	1.450		1.078	0.4997
218.7325	0.00133582	0.5167	1.378	1.211	0.9508		0.6999	0.3483	
78.9727	0.00433716	0.2393	0.6476	0.5759		0.4684	0.2261		
30.7962	0.01277297	0.1094	0.3044		0.3071	0.1513			
12.7483	0.03409673			0.1860	0.09919				
5.5248	0.08050425	0.03534	0.09832	0.06007					
2.4714	0.16153434	0.01142	0.03176						
1.1247	0.26378403								
0.5167	0.32460548								
0.2393	0.23597951								
0.1094	0.05426079								

