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Accurate Pair Interaction Energies for Helium from Supermolecular Gaussian Geminal Calculations†

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Nonrelativistic clamped-nuclei pair interaction energy for ground-state helium atoms has been computed for 12 interatomic separations ranging from 3.0 to 9.0 bohr. The calculations applied the supermolecular approach. The major part of the interaction energy was obtained using the Gaussian geminal implementation of the coupled-cluster theory with double excitations (CCD). Relatively small contributions from single, triple, and quadruple excitations were subsequently included employing the conventional orbital coupled-cluster method with single, double, and noniterative triple excitations [CCSD(T)] and the full configuration interaction (FCI) method. For three distances, the single-excitation contribution was taken from literature Gaussian-geminal calculations at the CCSD level. The orbital CCSD(T) and FCI calculations used very large basis sets, up to doubly augmented septuple- and sextuple-zeta size, respectively, and were followed by extrapolations to the complete basis set limits. The accuracy of the total interaction energies has been estimated to be about 3 mK or 0.03% at the minimum of the potential well. For the attractive part of the well, the relative errors remain consistently smaller than 0.03%. In the repulsive part, the accuracy is even better, except, of course, for the region where the potential goes through zero. For interatomic separations smaller than 4.0 bohr, the relative errors do not exceed 0.01%. Such uncertainties are significantly smaller than the expected values of the relativistic and diagonal Born−Oppenheimer contributions to the potential.

I. Introduction

An accurate knowledge of the potential curve for two interacting ground-state helium atoms is of obvious significance for a variety of theoretical and experimental investigations. Examples include simulations of the condensed phase of helium,[1] computational spectroscopy of helium-solvated molecules[2] (the subject of great recent experimental interest[3−11]), or predictions of thermophysical properties of helium gas.[12,13] In the latter field, current *ab initio* predictions are more accurate than measurements, even for properties that can be measured with high precision, such as viscosity.[14] The main motivation for the present study comes from the work of the metrology groups aimed at creation of new pressure and temperature standards based on measurements of the helium dielectric constant using capacitors,[15−18] microwave techniques,[19] or Fabry−Perot interferometers at optical frequencies.[20] The technique of dielectric constant gas thermometry can also be used to determine a more accurate value of the Boltzmann constant, k_B, which could lead to a new definition of kelvin.[21] The current temperature standard, ITS-90, defines the temperature scale using a set of fixed points and interpolating between these points with platinum thermometers. The discrepancies between the standard and the thermodynamics measurements are five times the assumed uncertainty of ITS-90 in some regions.[22] Therefore, the creation of a new temperature standard is one of the high-priority goals in metrology.[21,23]

The relation connecting the temperature, T, with the pressure and the dielectric constant involves the density and dielectric virial coefficients, which must be known to sufficiently high accuracy if T is to be determined to a better precision than given by ITS-90. The second density virial coefficient, $B(T)$, contributes to the uncertainties with the highest weight and must be known with greatest precision. The current most accurate values of $B(T)$ are those from first-principle calculations and have been obtained by Janzen and Aziz[24] using the SAPT96 potential[25,26] and by Hurly and Moldover[13] using a modification of SAPT96. By comparing with predictions of other *ab initio* calculations, which gave the depth of the potential about 100 mK or about 1% different from SAPT96, Hurly and Moldover estimated the uncertainty of the theoretical $B(T)$ at 300 K to be 2200 ppm.[13] The needs of the metrology community call for a determination of the helium pair potential with relative uncertainties less than 0.05% both in the attractive and in the repulsive region. Such a potential can be expected to give values of $B(T)$ accurate to about 100 ppm, which should be more than sufficient for the new temperature or pressure standards. The pair potential can also be used to obtain accurate values of the dielectric virial coefficient, $b(T)$, and of the third density virial coefficient, $C(T)$, provided, of course, that accurate values of the collision-induced polarizability and of the three-body part of the interaction energy are known, respectively. It is expected that virtually all thermodynamics properties of helium can now be predicted from first principles with uncertainties smaller than the experimental ones. The availability of highly accurate thermodynamic functions for helium may also lead, via relative measurements, to improved accuracy of analogous functions for other rare gases like argon.[27]

There exists vast literature on *ab initio* calculations of the interaction energy of two ground-state helium atoms in the nonrelativistic Born−Oppenheimer approximation; for reviews

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of this work, see refs 26 and 28−31. With a few notable exceptions,[25,26,32−36] older calculations (prior to year 2000) did not involve any estimations of error bounds. As we know now, the best work of this period was accurate to about 100 mK in the region around the minimum. In the early 2000s, the well depth of the potential could be predicted[28,37] with an error of about 20 mK, although calculations claiming higher accuracy were also reported.[38] In the most recent calculations,[29,30,39] error bars smaller than 10 mK at the minimum were obtained, but these calculations were performed for only a few interatomic separations. The goal of the present paper is to improve the method used in refs 29 and 30 and to extend the calculations reported in these references to a sufficient number of interatomic separations to enable an accurate analytic fit.

The method presented and extensively tested in refs 29 and 30 is based on the supermolecular (SM) approach, that is, involves a numerical subtraction of atomic energies from the dimer energy, all computed using the same dimer-centered basis set. The bulk of the interaction energy (about 90% at large separations R and much more than 90% in the repulsive region) is obtained using the explicitly correlated implementation[40,41] of the coupled cluster doubles (CCD) method. With the use of Gaussian-type geminals (GTGs) and extensive optimization of nonlinear parameters (separately for each value of R), this part of the interaction energy can be obtained with a basis set incompleteness error that is negligible in comparison to the error of the remaining part of the interaction energy. This remaining part, coming from the contributions of single, triple, and quadruple excitations, is recovered by employing conventional orbital basis sets containing, however, a significant fraction of functions placed on the interatomic bond, which has been shown to be critical for the recovery of the dispersion component of the interaction energy.[42] Finite basis set calculations, both geminal and orbital ones, are followed by extrapolations to the complete basis set (CBS) limit.

Since the nonlinear parameters used in the geminal CCD calculations are obtained by minimizing the second-order energy of many-body perturbation theory with the Møller−Plesset partitioning of the Hamiltonian (MP2) (via the weak-orthogonality functional[43,44]), very accurate, basis set saturated values of MP2 energies for the helium dimer are obtained as a byproduct of the geminal CCD calculations. These energies will be used in the present work in one of the extrapolation procedures needed to obtain accurate values of contributions to the interaction energy other than those obtained at the CCD level of theory.

The contribution from single excitations, denoted by E_S, can be computed very accurately from explicitly correlated CCSD theory[41,45] using GTG basis sets. Since this contribution is very small (about 1% of the interaction energy at large R and much less than 1% in the repulsive region), it is also possible[29,30] to compute it accurately using conventional, orbital-based CCSD theory.[46] Although the orbital expansion of the singles contribution converges very slowly, this contribution can be predicted with about 1% error when a suitable CBS extrapolation is employed. The efficiency of this CBS extrapolation has been verified[29,30] by a comparison with the values of E_S computed using CCSD and GTG bases.[29,30] It should be noted that the ability of obtaining E_S from purely orbital calculations is essential because Gaussian geminal CCSD calculations for all separations R would be much more time-consuming than the calculations we have performed.

The interaction energy components beyond the CCSD level can be obtained[29,30] using the conventional, orbital-based CCSD(T) approach (coupled-clusters single- and double-excitation method with a noniterative account of triple excitations)[47,48] for the bulk of the triple excitation contribution, denoted by E_T, followed by the full configuration interaction (FCI) calculation to account for the relatively small contribution, denoted by δE_{FCI}, coming from the remaining triple and all the quadruple excitations. The studies of refs 29 and 30 have shown that E_T and δE_{FCI} can be obtained with errors on the order of 0.1% and 1%, respectively, using the largest practically feasible orbital basis sets. In fact, up to doubly augmented correlation-consistent septuple-zeta bases supplemented with a large set of bond functions must be used in calculations at the CCSD(T) level, followed by CBS extrapolations, to reach this accuracy. At the FCI level, only up to quintuple-zeta basis sets could be applied in refs 29 and 30. It was not clear whether the corresponding CBS extrapolations are more reliable than the values computed in the largest basis sets, and therefore both types of results were used to determine the recommended values of δE_{FCI} and their error bars.

In refs 29 and 30, considerable effort has been made to estimate the uncertainties of the computed interaction energy components. In fact, in these studies as well as in the present work, most of the effort went not into the computation of the recommended values of the interaction energy, but into the estimation of the error bounds. One should realize that such estimates for *ab initio* electronic structure calculations are not rigorous and should be viewed as judicious but somewhat arbitrary assessments based on observed rates of convergence. Rigorous upper bounds can be computed variationally using the four-electron explicitly correlated Gaussian (ECG) basis,[49−51] and we will make comparisons with these results. On the other hand, rigorous lower bounds are much more difficult to compute and have not yet been obtained with useful accuracy even for simplest atomic systems.

In the present work, we adopt the general strategy of calculations outlined in refs 29 and 30, with several elements of this strategy improved. We report here calculations for a wide range of interatomic separations, which enables analytical fitting of the potential (in refs 29 and 30, only three typical interatomic separations were considered). The major improvements of the computational strategy include new methods for the optimization of the SCF orbitals, very accurate calculations of the nonfactorizable part of the CCD interaction energy using only orbital basis sets, and increased number of CBS extrapolations. Furthermore, we extended the FCI code[52] so that basis sets with cardinal numbers larger than previously could be used. This increase in the quality of FCI calculations combined with a better understanding of the CBS extrapolations have enabled us to significantly reduce the error bars compared with those reported in refs 29 and 30.

In parallel to the SM calculations, our group was working on improvements of the SAPT interaction energies of refs 25 and 26. These developments will be described in a separate paper,[53] where we will also present an analytic fit of the potential performed using a combination of SM and SAPT interaction energies, supplemented at very small R by results of variational calculations with the ECG basis.[51]

II. Method of Calculations

The interaction energy of the helium dimer, E_{int}, can be computed using the following partitioning:

$$E_{int} = E_{SCF} + E_{CCD}^{cr} + E_S + E_T + \delta E_{FCI} \qquad (1)$$

where E_{SCF} is the Hartree–Fock interaction energy, $E^{\mathrm{cr}}_{\mathrm{CCD}}$ is the correlation part of the interaction energy computed at the CCD level of theory, E_{S} is the single-excitation contribution to the interaction energy as predicted by the CCSD method,

$$E_{\mathrm{S}} = E_{\mathrm{CCSD}} - E_{\mathrm{CCD}} \tag{2}$$

E_{T} is the triple-excitation contribution to the interaction energy accounted for by the CCSD(T) method,

$$E_{\mathrm{T}} = E_{\mathrm{CCSD(T)}} - E_{\mathrm{CCSD}} \tag{3}$$

and δE_{FCI}, defined as

$$\delta E_{\mathrm{FCI}} = E_{\mathrm{FCI}} - E_{\mathrm{CCSD(T)}} \tag{4}$$

collects the remaining triple-excitation effects and the whole quadruple-excitation contribution obtained using the FCI approach. The symbols E_{CCD}, E_{CCSD}, $E_{\mathrm{CCSD(T)}}$, or E_{FCI} always refer here to the interaction energies obtained using the indicated level of theory and not to the total dimer energies. For example,

$$E_{\mathrm{FCI}} \equiv E^{\mathrm{FCI}}_{\mathrm{int}} = E^{\mathrm{FCI}}_{\mathrm{AB}} - E^{\mathrm{FCI}}_{\mathrm{A}} - E^{\mathrm{FCI}}_{\mathrm{B}} \tag{5}$$

where $E^{\mathrm{FCI}}_{\mathrm{X}}$ is the total energy of system X: dimer AB, monomer A, or monomer B. The total monomer energies in both geminal- and orbital-based approaches are computed using the full dimer basis set; that is, the interaction energies include the counterpoise correction (CP) for the basis set superposition error (BSSE).

In the explicitly correlated CCD theory, the correlation part of the CCD interaction energy, $E^{\mathrm{cr}}_{\mathrm{CCD}}$, splits naturally into the factorizable, $E^{\mathrm{cr}}_{\mathrm{FCCD}}$, and nonfactorizable (NF) contribution, E_{NF},[40]

$$E^{\mathrm{cr}}_{\mathrm{CCD}} = E^{\mathrm{cr}}_{\mathrm{FCCD}} + E_{\mathrm{NF}} \tag{6}$$

the latter expressible entirely through nonfactorizable four-electron integrals and for this reason very time-consuming to compute. In the context of purely orbital calculations, the FCCD approximation is known as the ACP-D45 method[54,55] or the ACCSD approximation.[56] As shown in ref 30, the nonfactorizable contribution converges very fast with orbital bases, and therefore, its evaluation with Gaussian geminals, although rapidly convergent as well, would be unnecessarily time-consuming. Thus, we restricted the GTG calculations to the FCCD level and added the E_{NF} contribution obtained in orbital bases. This procedure does not lead to any loss of accuracy since the error of $E^{\mathrm{cr}}_{\mathrm{CCD}}$ is dominated by the error of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$. With this splitting, the final decomposition of the interaction energy becomes

$$E_{\mathrm{int}} = E_{\mathrm{SCF}} + E^{\mathrm{cr}}_{\mathrm{FCCD}} + E_{\mathrm{NF}} + E_{\mathrm{S}} + E_{\mathrm{T}} + \delta E_{\mathrm{FCI}} \tag{7}$$

The GTG coupled-cluster methodology was presented in detail in ref 30 and in earlier papers[40,41,45] so that only the most essential information will be repeated here. The total FCCD correlation energy of a closed-shell N-electron system is expressed as

$$E^{\mathrm{cr}}_{\mathrm{FCCD}} = \sum_{\alpha=1}^{N/2} \epsilon^{1}_{\alpha\alpha} + \sum_{\alpha<\beta}^{N/2} (\epsilon^{1}_{\alpha\beta} + \epsilon^{3}_{\alpha\beta}) \tag{8}$$

The pair contributions $\epsilon^{s}_{\alpha\beta}$ are defined by

$$\epsilon^{s}_{\alpha\beta} = \frac{s}{(1+\delta_{\alpha\beta})} \langle \phi_\alpha \phi_\beta | r_{12}{}^{-1} | \tau^{s}_{\alpha\beta} \rangle \tag{9}$$

where ϕ_α, $\alpha = 1, 2, ..., N/2$, are occupied Hartree–Fock orbitals and $\tau^{s}_{\alpha\beta}$ are two-electron spinless cluster functions (pair functions), which are symmetric ($s = 1$, "singlet") or antisymmetric ($s = 3$, "triplet") with respect to the exchange of electron coordinates and are assumed to be strongly orthogonal (SO) to the occupied orbital space. The cluster functions are expanded in a basis set of GTGs

$$\tau^{s}_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = \hat{A}^{s} \hat{\Pi}_{\alpha\beta} \sum_{i=1}^{K} c_i^{\alpha\beta s} g_i(\mathbf{r}_1,\mathbf{r}_2) \tag{10}$$

$$g_i(\mathbf{r}_1,\mathbf{r}_2) = \exp(-\gamma_{1i}|\mathbf{r}_1 - \mathbf{A}_i|^2 - \gamma_{2i}|\mathbf{r}_2 - \mathbf{B}_i|^2 - \delta_i|\mathbf{r}_1 - \mathbf{r}_2|^2) \tag{11}$$

The operator $\hat{A}^s = 1 + (2 - s)\hat{P}_{12}$, where $\hat{P}_{12}$ permutes the electron coordinates, ensures the appropriate exchange symmetry in eq 10. Similarly, the operator $\hat{\Pi}_{\alpha\beta} = 1 \pm \hat{\imath}$, where $\hat{\imath}$ is the inversion through the molecular midpoint, ensures the *gerade* ($\alpha = \beta$) or *ungerade* ($\alpha \neq \beta$) symmetry of a pair function with respect to the inversion. When the Gaussian centers $\mathbf{A}_i$ and $\mathbf{B}_i$ are distributed along the molecular axis, the set of functions of the form $(1 \pm \hat{\imath})g_i(\mathbf{r}_1,\mathbf{r}_2)$ becomes complete (for $K \to \infty$) in the space of two-electron functions of $\Sigma_g{}^+$ or $\Sigma_u{}^+$ symmetry.[57,58] The linear coefficients of the expansion (eq 10) are found by solving iteratively the first-quantized FCCD equations.[40] Instead of the very time-consuming explicit SO projection, the so-called superweak orthogonality plus projection (SWOP) method is used, which is exact (ensures the exact strong orthogonality) in the complete GTG basis set limit.[59] Following the recommendation of ref 60 (see also ref 30), we use the same GTG basis set for all four pair functions. This is necessary to apply the CP correction in geminal calculations.[60] The interaction energies in explicitly correlated geminal bases are becoming CP-corrected if the subtracted helium monomer energies are computed using an expansion analogous to eq 10 for the singlet state, with the terms resulting from the operator $\hat{\imath}$ having independent linear coefficients (see ref 30).

The nonlinear parameters of the GTGs are found by minimizing the total MP2 energy of the helium dimer with the Powell method, as described in ref 30. The positions of geminals were placed both inside and outside the dimer but in the latter case were restricted to be within 10 bohr of the nearest nucleus. Although methods of avoiding complete optimizations of all the parameters have been developed,[61−64] the complete optimizations are needed at the level of accuracy aimed at in the present work. The MP2 calculations used the weak-orthogonality (WO) approach.[43,65] Although a GTG basis set optimized at the MP2 level is not fully optimal for expanding the FCCD pair functions, this deficiency can be to a large extent made up by the linear coefficients if the expansion length, K, is large enough. In practice, the helium dimer FCCD interaction energies obtained in this way converge almost as fast to the $K = \infty$ limit as the MP2 interaction energies.

When using the SWOP method, the cost of the GTG FCCD calculations scales as $aM^4K + bM^2K^2$, where M is the size of the SCF basis set and a and b are some prefactors. Therefore, M should be as small as possible to avoid prohibitive calculation times. On the other hand, in deriving the first-quantized MP2 and CC equations, we assume that the Hartree–Fock equations are solved exactly. To fulfill these two contradictory requirements as closely as possible, we use compact yet highly accurate basis sets of floating spherical Gaussian functions to expand molecular SCF orbitals

$$\phi_\alpha(\mathbf{r}) = \hat{\Pi}_\alpha \sum_{i=1}^{M} c_i^\alpha \exp(-\gamma_i |\mathbf{r} - \mathbf{C}_i|^2) \qquad (12)$$

where $\hat{\Pi}_1 = 1 + \hat{\imath}$, $\hat{\Pi}_2 = 1 - \hat{\imath}$, and the orbital positions $\mathbf{C}_i$ were constrained to the molecular axis. The nonlinear parameters γ_i and $\mathbf{C}_i$ are carefully optimized with respect to the helium dimer SCF energy (with similar restrictions on the maximum distance from nuclei as in the case of geminal calculations). As shown in ref 30, basis sets of this type require only a few dozen terms to give a more accurate E_{SCF} than standard expansions containing hundreds of terms.

Out of the broad spectrum of basis sets investigated in refs 29 and 30, we have selected two sequences of bases. One of them was the augmented correlation-consistent polarized-valence X-tuple zeta family (aug-cc-pVXZ) developed by Dunning et al.[66–69] for $X = 3$, 4, 5, and 6 and by Gdanitz[70] for $X = 7$, supplemented by a 6s6p6d3f1g1h set of 95 midbond functions originally developed by Partridge and Bauschlicher;[71] this sequence will be denoted as aXZb95. The other sequence used by us was the doubly augmented family, d-aug-cc-pVXZ (denoted here by dXZ), without any midbond functions added. These two sequences have been used here to obtain the CBS-extrapolated values of all interaction energy contributions beyond the FCCD level.

The components computed using orbital bases can be sufficiently accurate only with extrapolations to the CBS limit. A detailed description of various possible CBS extrapolations of results obtained with sequences of basis sets differing in the cardinal number X has been presented in ref 29. In this work, we have used two kinds of extrapolation schemes, referred to in ref 29 as the X^{-n} extrapolation and the E_{H} vs E (or $E_{\mathrm{H}}(E)$) extrapolation. Within the X^{-n} scheme, it is assumed that the difference between the CBS value of some energy contribution $E(\infty)$ and its approximation $E(X)$ computed using a basis set with the cardinal number X vanishes like AX^{-n}, where A is a constant. Various choices of the exponent n have been studied: in this work, we employed the X^{-3} extrapolation, that is, $n = 3$. This choice is supported by rigorous theoretical derivations in the case of atomic MP2 energies,[72–74] as well as by extensive numerical studies for molecules.[75,76]

The second class of extrapolations, denoted as E_{H} vs E or $E_{\mathrm{H}}(E)$ in ref 29, approximates the CBS value of a hard-to-calculate energy, E_{H}, utilizing the convergence pattern of a different energy contribution, E, which is easier to calculate and for which the CBS limit is known to a good accuracy. This extrapolation technique assumes that the quantities E_{H} and E exhibit the same convergence pattern when X goes to infinity. More precisely, one assumes that, for the sequence $\mathcal{B}_X$ of basis sets employed, $E_{\mathrm{H}}(\mathcal{B}_X)$ is a linear function of $E(\mathcal{B}_X)$. In our case, E can be any contribution that we are able to calculate using the Gaussian geminal basis sets. Because in our study E_{H} will always be a correlation contribution, E should also result entirely from electron correlation since the SCF energies exhibit a completely different (exponential) convergence behavior in X.[77] We have employed as E three different quantities available in our Gaussian geminal programs:

- the MP2 correlation energy for a single helium atom: the resulting scheme will be referred to as an extrapolation versus $E_{\mathrm{A}}^{\mathrm{MP2,cr}}$ (where A stands for monomer and "cr" reminds one that only the correlation part of the MP2 energy is taken into account)
- the correlation component of the MP2 interaction energy of two helium atoms: the resulting scheme will be referred to as an extrapolation versus $E_{\mathrm{MP2}}^{\mathrm{cr}}$ [recall that with the subscripted symbols like E_{SCF} or E_{CCD} we denote the interaction energies, while the superscipts are used for the total energies, cf. eqs 1 and 5]
- the correlation component of the factorizable CCD interaction energy of two helium atoms: the resulting scheme will be referred to as an extrapolation versus $E_{\mathrm{FCCD}}^{\mathrm{cr}}$.

The specific formulas for an approximation $\tilde{E}_{\mathrm{H}}(\infty)$ to the CBS limit of E_{H} employing the values $E_{\mathrm{H}}(X)$ and $E_{\mathrm{H}}(X-1)$ calculated in X-tuple zeta and $(X-1)$-tuple zeta basis sets, respectively, are[29,76]

$$\tilde{E}_{\mathrm{H}}(\infty) = E_{\mathrm{H}}(X) + \frac{(1 - 1/X)^n}{1 - (1 - 1/X)^n}(E_{\mathrm{H}}(X) - E_{\mathrm{H}}(X-1)) \qquad (13)$$

for the X^{-n} extrapolation and

$$\tilde{E}_{\mathrm{H}}(\infty) = E_{\mathrm{H}}(X) + \frac{E(\infty) - E(X)}{E(X) - E(X-1)}(E_{\mathrm{H}}(X) - E_{\mathrm{H}}(X-1)) \qquad (14)$$

for the E_{H} vs E extrapolation. It is worth noting that if the differences $E(X) - E(\infty)$ behave exactly as AX^{-n}, the extrapolation versus E is equivalent to the X^{-n} extrapolation. This observation explains the fact that the extrapolation versus $E_{\mathrm{A}}^{\mathrm{MP2,cr}}$ usually performs very similarly to the X^{-3} extrapolation: indeed, the MP2 correlation energy for the helium atom converges to its CBS value in a nearly perfect accordance with the X^{-3} law. It is also worth noting that the numerical values of the coefficients multiplying the energy differences in eq 13 for $n = 3$ range from 0.42 for $X = 3$ through 1.05 for $X = 5$ to 1.7 for $X = 7$.

The contributions E_{NF}, E_{S}, and E_{T} have been calculated in bases aXZb95 and dXZ for $X = 5$, 6, and 7. The basis set sequences aXZb95 and dXZ have been chosen as providing the most reliable results based on the investigations of refs 29 and 30. The most expensive contribution, the δE_{FCI} term, was calculated using the same basis set sequences but with $X = 4$, 5, and 6, that is, one cardinal number less than it was possible for the lower-level contributions, but, at the same time, with one cardinal number more than in refs 29 and 30. Because the uncertainty of δE_{FCI} was the leading contribution to the total uncertainty of the results reported in refs 29 and 30, the availability of the δE_{FCI} values calculated in sextuple-zeta basis sets is the main reason for the higher accuracy achieved in the present work.

III. Details of Computations

Calculations using the approach described in the previous section have been performed for 12 internuclear distances: $R = 3.0$, 3.5, 4.0, 4.5, 5.0, 5.3, 5.6, 6.0, 6.5, 7.0, 8.0, and 9.0 bohr. The contributions obtained by us at $R = 4.0$, 5.6, and 7.0 bohr are generally different but very close to those previously published in refs 29 and 30. The explicitly correlated calculations at the FCCD level have been performed using the geminal coupled-cluster code developed in our group.[78] The orbital values of the FCCD interaction energies, necessary for the computation of the E_{NF} term, were obtained using a suitably modified CCSD program from the SAPT suite of codes,[79] based on the implementation proposed in ref 80. The CCD, CCSD, and CCSD(T) energies were calculated using the MOLPRO package.[81] Finally, the FCI interaction energies have been obtained with the LUCIA program,[52] modified by us to allow for more than 255 basis functions and to reduce memory requirements.

In all tables below, the distances are given in atomic units and the energies in kelvins (the conversion factor 1 hartree = 315 774.65 K has been used).

To illustrate our extrapolation techniques, we will present the results from all the basis sets at five internuclear distances: 3.0, 4.0, 5.6, 7.0, and 8.0 bohr. For the complete set of points, only the final (extrapolated) values for all the components appearing in eqs 1−7 will be given, along with the corresponding uncertainties. The complete data for all the distances are available as Supporting Information associated with this paper.

A. SCF Calculations. In ref 30, we noted that a systematic nonlinear optimization of the SCF wave functions with floating centers was not easy, which manifested itself in somewhat irregular convergence patterns with respect to the expansion length, M. Such patterns make precise extrapolations of E_{SCF} and $E_{\mathrm{FCCD}}^{\mathrm{cr}}$ to their $M = \infty$ limits rather difficult. In fact, the main source of the estimated error of $E_{\mathrm{FCCD}}^{\mathrm{cr}}$ was the residual inaccuracy of the SCF orbitals (rather than the inaccuracy of the pair functions) at all three internuclear distances considered in ref 30. The source of the problem is a tendency of the optimization process to lower the total SCF energy of the dimer by improving the description of the orbitals in the vinicity of nuclei rather than in the region between the nuclei important for the interaction energies.

To address this problem, in the present work we used a new strategy for the SCF wave function optimization. The basis functions in the expansion of eq 12 were divided into two subsets with M_1 and $M_2 = M - M_1$ terms, respectively. Note that we are counting the symmetry-adapted basis functions. The M_1 functions from the first subset were located at the nuclei and their exponents were thoroughly optimized on the SCF energy of the helium atom. These M_1 terms were kept frozen in further calculations, while the nonlinear parameters in the remaining M_2 terms (exponents and centers), as well as all the M linear parameters c_i^{α}, were optimized by minimizing the SCF energy for the dimer. We carefully optimized a 24-term helium atom SCF orbital, obtaining an error of only 0.089 mK for the sum of the two monomer SCF energies, and used the resulting exponents for the first subset. The near-saturation of the monomer description ensures that the optimization of the remaining M_2 exponents in the basis is almost entirely directed toward the interaction energy, which now converges fairly smoothly with M_2. The only disadvantage of this approach is the fact that the resulting SCF expansions are somewhat longer than those obtained when all nonlinear parameters were optimized on the dimer SCF energy. Therefore, in the time-consuming optimizations of the GTG pair functions of eq 10, the SCF functions of ref 30 with $M = 16$ and $M = 24$ were used. This is a reasonable procedure since at the optimization stage the accuracy of the SCF orbitals is less critical.

TABLE 1: Convergence of the SCF Interaction Energies, E_{SCF}, with the Size of the Interaction Part of the Basis Set, M_2[a]

	R				
M_2	3.0	4.0	5.6	7.0	8.0
8	4268.36201	428.783021	9.219985	0.287971	0.023266
12	4268.35474	428.782585	9.219982	0.287971	0.023263
16	4268.35229	428.782553	9.219982	0.287971	0.023266
extr.	4268.3498	428.78252	9.21998	0.28797	0.02327
σ[b]	0.0025	0.00003	0.00001	0.00001	0.00001

[a] The total SCF basis set contains also $M_1 = 24$ terms taken from an accurate helium atom orbital. [b] The estimated uncertainty of the extrapolated result, see the text.

Table 1 contains the SCF interaction energies, E_{SCF}, as functions of M_2. The convergence is very fast and, except for the three shortest distances (see the extended table in Supporting Information), the last two results agree to at least 10^{-5} K. Whenever this was the case, we assumed the $M_2 = 16$ result to represent the basis set limit and the uncertainty of this value was taken to be 10^{-5} K (a lower uncertainty neither is needed nor can be safely assumed due to restrictions of numerical precision). In the other cases, the limit was estimated as

$$E_{\mathrm{SCF}}(\infty) = E_{\mathrm{SCF}}(16) + [E_{\mathrm{SCF}}(16) - E_{\mathrm{SCF}}(12)] \qquad (15)$$

where the numbers in parentheses denote the value of M_2. The error of such an estimation was taken as

$$\sigma_{\mathrm{SCF}} = |E_{\mathrm{SCF}}(16) - E_{\mathrm{SCF}}(12)| \qquad (16)$$

As it is known,[77,82] the SCF energies converge exponentially with the basis set size. This means that if the values of M_2 form an arithmetic sequence with a step ΔM_2, one should observe the energy increments to form a geometric sequence with a quotient $e^{\alpha \Delta M_2}$, where α is a constant. Formula 15 corresponds to the assumption that with $\Delta M_2 = 4$, the quotient is $^1/_2$. In fact, the convergence for the three shortest distances is faster than this since the ratio of the differences $E_{\mathrm{SCF}}(16) - E_{\mathrm{SCF}}(12)$ and $E_{\mathrm{SCF}}(12) - E_{\mathrm{SCF}}(8)$ is at most $^1/_3$ (see all the short distances in Table 1 of Supporting Information). Therefore, the extrapolation scheme of eq 15 overshoots, and eq 16 gives error estimates that are probably too conservative. However, since these estimates are anyway much tighter than the uncertainties of all the other components of the potential, we have not tried more sophisticated extrapolations.

The present results can be compared at $R = 4$, 5.6, and 7 bohr to those from ref 30. One can see that the final values from Table 5 of ref 30 agree to within their error bars with the present limits. In fact, all the discrepancies amount to only one in the last place given there, for example, to 0.1 mK at $R = 5.6$ bohr. Table 1 of ref 30, which lists more digits, shows that the agreement is even better, for example, to within 0.02 mK at $R = 5.6$ bohr. The estimated uncertainties of E_{SCF} from ref 30 have been drastically reduced by the present work, by a factor of 10 at $R = 5.6$ and 7.0 bohr and a factor of over 30 at $R = 4.0$ bohr. The reason the error bars were overestimated in ref 30 was an erratic convergence of E_{SCF}. We now see that the results obtained with the largest basis sets were more accurate than the convergence had indicated. In contrast, the current optimizations converge very fast and, with minor exceptions, smoothly. Clearly, the new strategy works better than the previous one. One has to remember, however, that some of the improvement is due to larger sizes of the basis sets used here: the largest basis set used in ref 30 contained $M = 32$ symmetry-adapted functions, the same number as the smallest, $M_2 = 8$, basis set used here. However, for all three distances, the current $M = 32$ SCF energies are more accurate than those obtained in ref 30 with basis sets of the same size.

TABLE 2: Convergence of the Correlation Part of the FCCD Interaction Energies, $E^{\mathrm{cr}}_{\mathrm{FCCD}}$, with the Pair Function Length, K, and with the Size of the Interaction Part of the SCF Basis Set, M_2

	R				
K, M_2	3.0	4.0	5.6	7.0	8.0
300, 8	−461.91046	−123.58201	−18.208804	−4.418319	−1.881085
300, 12	−461.91093	−123.58209	−18.208804	−4.418319	−1.881085
300, 16	−461.91139	−123.58208	−18.208804	−4.418319	−1.881092
600, 8	−461.96090	−123.59598	−18.211131	−4.419708	−1.881622
800, 8	−461.96408	−123.59697	−18.211454	−4.419768	−1.881644
extr.	−461.9682	−123.5980	−18.21178	−4.41983	−1.88167
σ	0.0032	0.0010	0.00032	0.00006	0.00002

B. GTG Calculations. To evaluate the $E^{\mathrm{cr}}_{\mathrm{FCCD}}$ energies, we optimized, at each value of R, pair functions with three expansion lengths: $K = 300$, 600, and 800. The results for different values of K and M_2 are listed in Table 2. To estimate the limits, we used observations from our extensive tests reported in ref 30. One of these observations was that the errors associated with the pair function expansion and the SCF function expansion are practically independent; that is, the difference $E^{\mathrm{cr}}_{\mathrm{FCCD}}(K,M_2) - E^{\mathrm{cr}}_{\mathrm{FCCD}}(K',M_2)$ does not depend on the value of M_2. Therefore, the limit values for expansion lengths going to infinity can be calculated independently and the resulting increments added to the best computed energy. In calculations of ref 30, the length of the expansion used for the SCF orbital had a small but significant effect on $E^{\mathrm{cr}}_{\mathrm{FCCD}}$: the contribution to the estimated uncertainty of the final value coming from this source was 0.15 mK at $R = 5.6$ bohr. The results presented in Table 2 (and in the Supporting Information) show that with our new expansions these errors are negligible: at $R = 5.6$ bohr, the $E^{\mathrm{cr}}_{\mathrm{FCCD}}$ energy does not change on the microkelvin place as M_2 changes from 8 to 16. In fact, for all distances larger or equal 5.3 bohr, the variations are within a few microkelvin. For the smallest separation considered, the increments are about 1 mK and remain negligible relative to the total interaction energy. In view of this behavior, investigated for $K = 300$, we have performed the calculations for larger K using only $M_2 = 8$. We have then added to the value computed with $K = 800$ the difference $E^{\mathrm{cr}}_{\mathrm{FCCD}}(300,16) - E^{\mathrm{cr}}_{\mathrm{FCCD}}(300,8)$. Since this term is nearly negligible, we have not included any contribution due to the SCF basis set truncation in the estimation of the uncertainty of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$.

The other important observation made in ref 30 was that the convergence of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$ in K resulted in a reduction of the error by a constant factor when the size of the geminal basis set was doubled. This means that the energies change approximately as

$$E_K = E_\infty + A/K^\gamma \tag{17}$$

For $R = 5.6$ bohr, the data of Table 2 are recovered with $E_\infty = -18.211\,846$ K and $\gamma = 2.1$. The CBS limit can also be approximated by just adding the difference $E_{800} - E_{600}$ to E_{800}, resulting in the value of $E_\infty = -18.211\,777$ K, only 0.069 mK different from the more sophisticated estimate. This simple approximation is, in fact, exact for $\gamma = 2.4$. For the other values of R, γ ranges from 2.9 to 4.7 (for $R = 9.0$ bohr, γ could not be determined, see below). Thus, the simple estimate probably overshoots the exact magnitude of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$ for these distances. Nevertheless, we have adopted this method to obtain CBS limits for all R. To account for the overshot, we have used the difference $|E_{800} - E_{600}|$ as our estimate of the uncertainty of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$. Since the uncertainties of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$ are negligible compared with those of some other components, more sophisticated extrapolations of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$ would be inconsequential for the final results. This method of obtaining the CBS limit is the same as that used in ref 30 (note that the quantity ΔE_K defined in ref 30 was *twice* the difference $E_{800} - E_{600}$). In summary, our best, recommended values of $E^{\mathrm{cr}}_{\mathrm{FCCD}}$ were computed from the formula

$$E^{\mathrm{cr}}_{\mathrm{FCCD}}(\infty,\infty) = E^{\mathrm{cr}}_{\mathrm{FCCD}}(800,8) + [E^{\mathrm{cr}}_{\mathrm{FCCD}}(300,16) - E^{\mathrm{cr}}_{\mathrm{FCCD}}(300,8)] + [E^{\mathrm{cr}}_{\mathrm{FCCD}}(800,8) - E^{\mathrm{cr}}_{\mathrm{FCCD}}(600,8)] \tag{18}$$

and the uncertainties of these values were assumed to be given by

$$\sigma_{\mathrm{FCCD}} = |E^{\mathrm{cr}}_{\mathrm{FCCD}}(800,8) - E^{\mathrm{cr}}_{\mathrm{FCCD}}(600,8)| \tag{19}$$

The only exception is $R = 9.0$ bohr, where our (300,8), (600,8), and (800,8) results are very close to each other but not monotonic: −0.892 925, −0.892 985, and −0.892 954 K, respectively. We chose the point halfway between the last two results and the difference of the last two results as our recommended value and its uncertainty: −0.892 97 ± 0.000 03 K.

The current extrapolated results are fully consistent (i.e., well within the error bars) with those given in ref 30 for $R = 4.0$, 5.6, and 7.0 bohr but have smaller uncertainties due to the better saturation of the SCF functions in the current work. In particular, at $R = 5.6$ bohr, the new result of −18.211 78 ± 0.000 32 K can be compared with the old value of −18.211 91 ± 0.000 47 K.

C. Orbital Calculations. *1. E_{NF}.* In ref 30, the recommended values of the nonfactorizable CCD contribution, E_{NF}, were computed in the geminal approach. Orbital calculations of the same quantity gave very close results already in the aXZ sequence ending at $X = 6$. The agreement was so close that there was no need for using larger basis sets. On the basis of these findings, we have computed here the values of E_{NF} using only orbital bases. For consistency with other components, we have used the dXZ and aXZb95 sequences of basis sets, $X = 5$, 6, and 7. The results of these calculations, as well as the X^{-3}-extrapolated energies, are presented in Table 3. The FCCD iterations at $R < 5.0$ bohr diverged for the a7Zb95 basis set, so the extrapolations at those distances are based only on the $X = 5$ and $X = 6$ values. As seen in Table 3, E_{NF} converges very fast with respect to the basis set size, and the absolute uncertainty of this term, unlike the uncertainties of the other orbital contributions discussed below, is smaller than the estimated error of the geminal FCCD calculations. The X^{-3} extrapolations from the dXZ and aXZb95 basis set families, denoted by a(X−1,X) and d(X−1,X), respectively, give almost identical results. In fact, for R larger than 5.6 bohr, the CBS extrapolations are not really necessary since the results for $X = 7$ are already converged to within 0.01 mK. It is gratifying to find out that the extended

TABLE 3: Dependence of the Nonfactorizable CCD Contribution, $E_{NF} = E_{CCD} - E_{FCCD}$, on the Orbital Basis Set[a]

	R				
X	3.0	4.0	5.6	7.0	8.0
			dXZ bases		
5	1.17264	0.48913	0.01819	−0.00340	−0.00224
6	1.16992	0.48846	0.01819	−0.00339	−0.00224
7	1.16858	0.48807	0.01819	−0.00339	−0.00224
d(56)	1.16618	0.48754	0.01820	−0.00338	−0.00223
d(67)	1.16631	0.48741	0.01819	−0.00338	−0.00223
			aXZb95 bases		
5	1.17149	0.48914	0.01824	−0.00340	−0.00224
6	1.16943	0.48836	0.01820[b]	−0.00339	−0.00224
7			0.01820[b]	−0.00339	−0.00224
a(56)	1.16660	0.48729	0.01816	−0.00338	−0.00223
a(67)			0.01818[b]	−0.00338	−0.00223
σ[c]	0.00029	0.00013	0.00003	0.00001	0.00001

[a] The empty places are due to the divergence of the FCCD iterations. [b] With one more significant digit, these $X = 6$, $X = 7$, and a(67) results amount to 0.018202, 0.018195, and 0.018183, respectively. [c] The estimated uncertainty (see text) of the value of E_{NF} obtained from the a(67) extrapolation (when available, otherwise from the a(56) extrapolation).

orbital basis sets used in the present work and the application of extrapolations improved the agreement of the orbital and geminal values of E_{NF} in comparison to that achieved in ref 30: the relevant differences are now reduced from 1.32 and 0.03 mK to 0.11 and 0.02 mK for $R = 4$ and 5.6 bohr, respectively (and are unchanged at $R = 7$ bohr). Although discrepancies of this size are not relevant for the current potential, their decrease confirms the very high quality of geminal CCD calculations. Since the extrapolated results from the aXZb95 sequence are closest to the geminal ones, we will use them as the recommended values. The error estimates σ for E_{NF} were obtained as the differences between the a(56) and a(67) extrapolations. If this difference was less or equal 0.01 mK, we assumed $\sigma = 0.01$ mK. For R smaller than or equal to 4.5 bohr, where the a7Zb95 calculations did not converge, we have used the difference between the a(56) and d(67) extrapolations.

2. E_S. In ref 30, the contribution of the single excitations to the interaction energy, E_S, was computed for $R = 4.0$, 5.6, and 7.0 bohr using both geminal and orbital basis sets. In the present work, the calculations have been extended to other distances, but only using the orbital approach with the dXZ and aXZb95 sequences of basis sets up to $X = 7$. Therefore, for the distances included in ref 30, we do not present any new results (except for some additional extrapolations). Accordingly, the estimates of E_S and their uncertainties proposed in ref 30 will remain unchanged for these distances. We now have to answer the question of how to estimate these values for other R, based on the restricted set of numerical data available. To improve the predictions, we have tested a broader range of extrapolation techniques than in refs 29 and 30. The computed and extrapolated values of E_S are shown in Table 4.

For the distances larger than 6.5 bohr, the MP2 interaction energies calculated in bases d6Z and d7Z are extremely close to each other. The same is true for the FCCD energies. Consequently, some of the results extrapolated versus E^{cr}_{MP2} and E^{cr}_{FCCD} using these two bases were completely unphysical due to subtractions in eq 14 leaving insufficient number of significant digits, and we had to list for these distances the results extrapolated from bases d5Z and d6Z, as noted in the tables.

The a(67) and d(67) extrapolations agree well with the values recommended in ref 30, their average being within the error bars of ref 30 for all three separations. Although these (67)-level extrapolated results were included in the CBS limit procedure of ref 30, there was a large number of other data contributing as well (in particular the geminal results were heavily weighted) so that such agreement could not be taken for granted. The results of the three other extrapolations, namely, the extrapolations versus $E^{MP2,cr}_{A}$, E^{cr}_{MP2}, and E^{cr}_{FCCD}, are much worse, resulting in the magnitudes of E_S generally smaller than the recommended values from ref 30. For example, for $R = 5.6$ bohr, these three schemes give the values of E_S between 172.0 and 176.8 mK, compared with the recommended limit of 177.1 ± 0.5 mK.[30] These findings agree with the observations of refs 29 and 30 concerning the extrapolations versus E_{CCD} and E^{cr}_{CCD}, which also performed worse than the X^{-3} extrapolations. Based on this evidence, we have not used the extrapolations versus $E^{MP2,cr}_{A}$, E^{cr}_{MP2}, and E^{cr}_{FCCD} in determining the limit values of E_S but relied exclusively on the X^{-3} extrapolations, taking the average of the a(67) and d(67) extrapolations as our best estimate of E_S.

The (67)-level extrapolated results from the dXZ and aXZb95 sequences are very close to each other for all R. Thus, their difference cannot be used as a measure of the uncertainties of E_S. Therefore, we decided to use the difference between the average values from the (56) and (67) extrapolations as such a measure. This procedure gives for $R = 4.0$, 5.6, and 7.0 bohr, respectively, −0.732 ± 0.009, −0.1767 ± 0.0009, and −0.04412 ± 0.00032 K, which can be compared with the corresponding values from ref 30 (our recommended values) amounting to −0.734 ± 0.002, −0.1771 ± 0.0005, and −0.0442 ± 0.0005 K. This agreement is quite satisfactory, and we believe that our orbital-only-based predictions will perform equally well for other R.

In ref 29, it has been observed that the use of bond functions does not lead to improved predictions for the single-excitations contribution. Our present results confirm this observation, as the results of both the calculated and extrapolated values from the dXZ sequence appear to be slightly more accurate than those from the aXZb95 sequence. However, the differences are very small, so one can say that the use of bond functions is not counterproductive.

3. E_T. For the noniterative triple-excitation contribution, E_T, there are no geminal results to guide us in choosing the best way of estimating the limit values. At the same time, since this contribution is by far the largest one calculated using only orbital basis sets, its reliable CBS extrapolation is crucial for the accuracy of the total interatomic potential. The most accurate calculation of the E_T contribution has been reported in refs 29 and 30 for the interatomic separation of 5.6 bohr. This calculation employed the sequence dXZb135, where b135 denotes a 6s6p6d3f3g3h set of midbond functions developed in ref 71, with the largest $X = 7$ basis containing 611 functions (the largest basis used in the present work, d7Z, contains 476 orbitals). We will therefore reanalyze the dXZb135 results and assume the limit predicted by this sequence as the best estimate of E_T. Subsequently, we will try to get as close as possible to this estimate using only the information given by the dXZ and aXZb95 sequences.

The E_T energies computed using the sequence dXZb135 are presented in Table 5. We have not performed FCCD calculations for this sequence, so instead of the extrapolations vs E^{cr}_{FCCD}, we present ones vs E^{cr}_{CCD}, which should give nearly identical results. One should note first that already the computed energies for high X provide a good approximation to E_T, amounting to −1.530 K for $X = 7$. Next, all the extrapolations give results

TABLE 4: Dependence of the Singles Contribution, $E_S = E_{CCSD} - E_{CCD}$, on the Orbital Basis Set[a]

	R									
	3.0	3.0	4.0	4.0	5.6	5.6	7.0	7.0	8.0	8.0
	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95
$X = 5$	−1.49256	−1.54718	−0.81271	−0.83777	−0.19417	−0.19860	−0.04949	−0.04992	−0.02032	−0.02038
$X = 6$	−1.38990	−1.41495	−0.77635	−0.78789	−0.18675	−0.18868	−0.04707	−0.04736	−0.01922	−0.01929
$X = 7$	−1.35172	−1.36353	−0.75992	−0.76712	−0.18300	−0.18425	−0.04593	−0.04621	−0.01869	−0.01881
(56)	−1.24888	−1.23332	−0.72640	−0.71937	−0.17656	−0.17506	−0.04375	−0.04384	−0.01771	−0.01779
(67)	−1.28678	−1.27608	−0.73198	−0.73179	−0.17662	−0.17672	−0.04399	−0.04425	−0.01779	−0.01799
$E_S(E_A^{MP2,cr})$	−1.28153	−1.26495	−0.72965	−0.72763	−0.17607	−0.17596	−0.04382	−0.04407	−0.01771	−0.01792
$E_S(E_{MP2}^{cr})$	−1.28848	−1.24406	−0.73155	−0.71336	−0.17684	−0.17201	−0.04473[e]	−0.04386	−0.01730[e]	−0.01804
$E_S(E_{FCCD}^{cr})$	−1.29373		−0.73372		−0.17677	−0.17435	−0.04491[e]	−0.04457	−0.01749[e]	−0.01819
E_S[b]		−1.281		−0.734[d]		−0.1771[d]		−0.0442[d]		−0.01789
σ[c]		0.040		0.002[d]		0.0005[d]		0.0005[d]		0.00014

[a] The symbol $(X - 1, X)$ is used here for both the a$(X - 1, X)$ and d $(X - 1,X)$ extrapolations. Unless otherwise noted, the extrapolations versus $E_A^{MP2,cr}$, E_{MP2}^{cr}, and E_{FCCD}^{cr} are based on the results obtained with $X = 6$ and $X = 7$ bases. [b] Our final approximations to the singles contribution to the interaction energy, defined as average values of the (67) extrapolations. [c] The uncertainties of E_S calculated as the differences between the averages of the (56) and (67) extrapolations. [d] Result from ref 30, which includes both geminal and orbital CCSD energies. The purely orbital results obtained using the method proposed in the present work (and employed for distances other than 4.0, 5.6, and 7.0 bohr) are $E_S = -0.732 \pm 0.009$, -0.1767 ± 0.0009, and -0.04412 ± 0.00032 K for $R = 4.0$, 5.6, and 7.0 bohr, respectively. [e] Extrapolated from d5Z and d6Z bases. The extrapolations from bases d6Z and d7Z were unreliable for this distance.

TABLE 5: Convergence of the Triple Excitations Contribution, $E_T = E_{CCSD(T)} - E_{CCSD}$, for the d$XZ$b135 Basis Sets at $R = 5.6$ bohr

X	E_T	X^{-3}	$E_T(E_A^{MP2,cr})$	$E_T(E_{MP2}^{cr})$	$E_T(E_{CCD}^{cr})$
4	−1.51541				
5	−1.52380	−1.53260	−1.53286	−1.53632	−1.53469
6	−1.52757	−1.53275	−1.53308	−1.53503	−1.53422
7	−1.52985	−1.53372	−1.53411	−1.53569	−1.53491

very close to each other, in the range −1.533 to −1.536 K. The average of the four (67)-level extrapolations is −1.534 61 K, in excellent agreement with the recommended value of E_T from refs 29 and 30 equal to -1.535 ± 0.002 K. This average differs at the most by 0.0011 K from the individual extrapolated results. Thus, we will adopt $E_T = -1.5346 \pm 0.0011$ K as our best estimate for $R = 5.6$ bohr.

The computed and extrapolated values of E_T in the dXZ and aXZb95 sequences for $R = 3$, 4, 5.6, 7, and 8 bohr are presented in Table 6. For $R = 5.6$ bohr, we have tried several methods of averaging these results. The result closest to the one inferred from the dXZb135 sequence was obtained by considering all eight results extrapolated from the $X = 6,7$ bases using the X^{-3}, vs $E_A^{MP2,cr}$, vs E_{MP2}^{cr}, and vs E_{FCCD}^{cr} schemes and taking the midpoint of the range spanned by these results. We will use this number as our recommended value of E_T and half of the width of the range as the uncertainty σ. This procedure gives at $R = 5.6$ bohr $E_T = -1.5344 \pm 0.0018$ K, in good agreement with the best estimate listed above and with the estimate of refs 29 and 30. For $R = 8.0$ and 9.0, we had to employ for the E_T vs E_{MP2}^{cr} and E_T vs E_{FCCD}^{cr} extrapolations the results calculated in bases d5Z and d6Z instead of d6Z and d7Z since the latter choice led to unreasonable values of some extrapolated energies, for the same reasons as in the case of the single-excitation contribution. For the aXZb95 sequence, there were no such problems.

In refs 29 and 30, it has been observed that the extrapolations of E_T from the bases containing bond functions appear to work better than those without such functions. This observation is confirmed by the $R = 5.6$ results in Table 6: the average of the dXZ extrapolations, equal to −1.532 97 K, is farther from our recommended value than the average of the aXZb95 extrapolations equal to −1.534 50 K. Thus, another reasonable choice for determining the CBS limits for other R could be to base it only on the aXZb95 sequence.

4. δE_{FCI}. The values of the contribution δE_{FCI}, collecting the effect of the triple excitations beyond the CCSD(T) level and the whole connected quadruple excitations effect, computed in the dXZ and aXZb95 sequences of basis sets for $X = 4$, 5, and 6, as well as the values of δE_{FCI} extrapolated to the CBS limit using the same four schemes as for E_S and E_T, are presented in Table 7. This contribution is obviously the most expensive one both in terms of the CPU time and memory required, and its calculation in $X = 7$ basis sets is presently not feasible. Nevertheless, the FCI calculations performed by us used basis sets up to 349 functions (the a6Zb95 set), much larger than in any earlier FCI calculation for the helium dimer, including our previous work[29,30] employing up to 255 basis functions (the a5Zb95 set) and the calculations with bases up to 159 functions published by van Mourik and van Lenthe.[33] The total dimer energy at $R = 5.6$ bohr obtained in refs 33, 29, and the present work is −5.805 755 67, −5.806 441 87, and −5.806 956 12 hartree, respectively. This can be compared with the lowest variational energy of −5.807 483 584 hartree from the very recent ECG calculation of ref 50. Thus, the error of the total energy has been reduced almost four times relative to ref 33. The values of E_{FCI} from the same works are −10.947, −10.974, and −10.983 K, about a factor of 3 reduction in the error compared with our current recommended value (to be discussed in the next section).

On the basis of the results from various Dunning-type basis set sequences restricted to $X \leq 5$ (except the aXZ sequence used up to $X = 6$) and from some interaction-energy optimized basis sets, the authors of refs 29 and 30 could not consider the extrapolations to be reliable due to a significant spread of the extrapolated values. For $R = 5.6$ bohr, the values of δE_{FCI} computed in the largest basis sets, containing between 210 and 255 orbitals, ranged from −321 to −328 mK, whereas the extrapolated results ranged from −318 to −324 mK. The recommended best estimate of δE_{FCI} was chosen as -323 ± 5 mK, to cover both ranges. With the $X = 6$ results now available, the conclusions from Table 7 are more clear, at least for larger distances. In all cases, the computed values of δE_{FCI} increase monotonically with X (i.e., become less negative). At $R = 5.6$ bohr, the computed values in the d6Z basis (326 orbitals) and a6Zb95 basis (349 orbitals) are −324 and −322 mK, respectively. This suggests that the CBS limit should be still smaller in magnitude, as indicated also by the X^{-3} extrapolations. These extrapolations cover the range −318 to −321 mK, with the

TABLE 6: Dependence of the Triple Excitations Contribution, $E_{\mathrm{T}} = E_{\mathrm{CCSD(T)}} - E_{\mathrm{CCSD}}$, on the Orbital Basis Set[a]

	R									
	3.0	3.0	4.0	4.0	5.6	5.6	7.0	7.0	8.0	8.0
	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95
$X = 5$	−32.51461	−32.93700	−10.24122	−10.39049	−1.50133	−1.52159	−0.35704	−0.35921	−0.15134	−0.15168
$X = 6$	−32.88820	−33.06351	−10.35513	−10.42336	−1.51870	−1.52633	−0.35950	−0.36063	−0.15210	−0.15240
$X = 7$	−33.06162	−33.14053	−10.40435	−10.44243	−1.52396	−1.52893	−0.36040	−0.36135	−0.15243	−0.15274
(56)	−33.40137	−33.23729	−10.51160	−10.46851	−1.54256	−1.53284	−0.36288	−0.36258	−0.15314	−0.15339
(67)	−33.35657	**−33.27152**	−10.48806	**−10.47486**	−1.53291	−1.53335	**−0.36193**	−0.36257	**−0.15299**	−0.15332
$E_{\mathrm{T}}(E_{\mathrm{A}}^{\mathrm{MP2,cr}})$	**−33.38046**	−33.28819	**−10.49504**	−10.47868	−1.53368	−1.53379	−0.36206	−0.36269	−0.15304	−0.15337
$E_{\mathrm{T}}(E_{\mathrm{MP2}}^{\mathrm{cr}})$	−33.34887	−33.31948	−10.48933	−10.49179	**−1.53260**	**−1.53612**	−0.36291	−0.36282	**−0.15343**[b]	−0.15328
$E_{\mathrm{T}}(E_{\mathrm{FCCD}}^{\mathrm{cr}})$	−33.32504		−10.48285		−1.53270	−1.53474	**−0.36305**	−0.36238	−0.15329[b]	−0.15318
E_{T}		−33.326		−10.485		−1.5346[c]		−0.36249		−0.15321
σ		0.054		0.010		0.0011[c]		0.00056		0.00022

[a] The notation is similar to that of Tables 3 and 4. The bold numbers are those that determine the ranges for the recommended results; see text. [b] Extrapolated from d5Z and d6Z bases. The extrapolations from bases d6Z and d7Z were unreliable for this distance. [c] Extrapolated from the dXZb135 sequence; see text. The value obtained using the method proposed in the present work is −1.5344 ± 0.0018 K.

TABLE 7: Dependence of the Contribution beyond the CCSD(T) Level, $\delta E_{\mathrm{FCI}} = E_{\mathrm{FCI}} - E_{\mathrm{CCSD(T)}}$, on the Orbital Basis Set[a]

	R									
	3.0	3.0	4.0	4.0	5.6	5.6	7.0	7.0	8.0	8.0
	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95	dXZ	aXZb95
$X = 4$	−5.77084	−5.54987	−2.02626	−1.96790	−0.33357	−0.33120	−0.08430	−0.08425	−0.03647	−0.03643
$X = 5$	−5.55905	−5.44215	−1.97039	−1.93384	−0.32758	−0.32525	−0.08266	−0.08264	−0.03576	−0.03576
$X = 6$	−5.42732	−5.37349	−1.93395	−1.91285	−0.32372	−0.32208	−0.08186	−0.08185	−0.03541	−0.03543
(45)	−5.33684	−5.32913	−1.91177	−1.89810	−0.32130	−0.31901	−0.08094	−0.08095	−0.03502	−0.03506
(56)	−5.24637	−5.27918	−1.88390	−1.88402	−0.31842	−0.31772	−0.08076	−0.08076	−0.03493	−0.03498
$\delta E_{\mathrm{FCI}}(E_{\mathrm{A}}^{\mathrm{MP2,cr}})$	**−5.23981**	−5.26983	−1.88214	−1.88201	−0.31822	−0.31746	−0.08072	−0.08071	−0.03491	−0.03496
$\delta E_{\mathrm{FCI}}(E_{\mathrm{MP2}}^{\mathrm{cr}})$	−5.25955	−5.24506	−1.88592	**−1.87200**	−0.32050	**−0.31552**	−0.08109	**−0.08053**	**−0.03480**	−0.03506
$\delta E_{\mathrm{FCI}}(E_{\mathrm{FCCD}}^{\mathrm{cr}})$	**−5.28070**	−5.25869	**−1.89350**	−1.87808	**−0.32118**	−0.31659	**−0.08115**	−0.08083	−0.03486	**−0.03512**
δE_{FCI}		−5.260		−1.883		−0.3183		−0.08084		−0.03496
σ		0.020		0.011		0.0028		0.00031		0.00016

[a] The notation is similar to that of Table 6.

average of the (56)-level extrapolations equal to −318 mK. Thus, we can now base our recommended values on the results of extrapolations. However, the X^{-3}-extrapolated values, similarly to the computed results, tend to decrease in magnitude with X, indicating that the convergence of the δE_{FCI} contribution deviates from the X^{-3} law. Thus, for this contribution the inclusion of other types of extrapolations may be particularly important. As shown in Table 7, at $R = 5.6$ bohr, the results of such extrapolations (of the same types as in the case of single and triple excitations contributions) range from −316 to −321 mK, in a reasonable agreement with the X^{-3} predictions. We have therefore determined the CBS limits and their error bars in the same way as for E_{T}, that is, as the midpoint and half of the width, respectively, of the range of all the (56) extrapolations. At $R = 5.6$ bohr, this leads to $\delta E_{\mathrm{FCI}} = -318.3 \pm 2.8$ mK, as much as 5 mK higher than the value recommended in ref 29, but within its error bars. Table 7 shows that the recommended CBS values would be virtually identical if we have taken them as the average of the X^{-3} extrapolations at the (56) level, that is, only the a(56) and d(56) extrapolations. This is an indication of the reliability of our recommended values.

One of the conclusions of ref 29 was that the bond functions are inefficient or even counterproductive in recovering the δE_{FCI} contribution. This conclusion has to be somewhat revised since Table 7 shows that the X^{-3} extrapolations from the aXZb95 sequence are only negligibly less accurate (relative to the recommended values) than those from the dXZ sequence. Since the aXZ sequence extrapolates to too negative values (ranging from −323 to −324 mK[29]), supplementing this series with either the second diffuse shell or the bond functions has practically the same effect (at about the same costs).

We inspected the R dependence of the relative errors of the orbital contributions computed by us. This dependence is rather weak since none of these contributions goes through zero in the considered range of distances. In relative terms, the most accurate is the E_{T} contribution with errors of the order of 0.1%, except for $R = 9$ bohr where the error is somewhat larger (0.3%). The E_{S} and δE_{FCI} contributions are significantly less accurate with relative errors of the order of 0.5−1.0%, except for the singles contribution at $R = 3$ bohr which has a 3% error. These uncertainties are significantly larger than the uncertainties of the correlation contribution at the CCD level, which has been obtained with relative errors of the order of 0.001%.

D. Total Potential. As stated in the previous section, our final supermolecular helium dimer interaction energies, which will be used as the grid points for the potential fit,[53] are the sums of the terms listed in eq 7. The term E_{SCF} is calculated using bases of floating spherical Gaussian orbitals, $E_{\mathrm{FCCD}}^{\mathrm{cr}}$ is taken from Gaussian geminal calculations including simple extrapolations, E_{NF} is extrapolated from calculations in the aXZb95 sequence of orbital bases using $X = 6{,}7$ and the X^{-3} scheme, E_{S} is the average of the (67)-level X^{-3} extrapolations from the dXZ and aXZb95 sequences, and E_{T} and δE_{FCI} are obtained from extrapolations (each term separately) using the sequences dXZ and aXZb95 with four extrapolation schemes (at the (67) level for E_{T} and at the (56) level for δE_{FCI}). The recommended contributions are listed in Tables 8 and 9 for all 12 separations. The total helium dimer interaction energies obtained in this way (Table 9), as well as their CCD-level (Table 8) and CCSD(T)-level (Table 9) approximations, are also

TABLE 8: Contributions to the Interaction Energies up to the CCD Level (Extrapolated to the CBS Limits) and Their Corresponding Uncertainties, σ

R	E_{SCF}	σ	E^{cr}_{FCCD}	σ	E_{NF}	σ	E_{CCD}	σ
3.0	4268.3498	0.0025	−461.9682	0.0032	1.16660	0.00029	3807.5482	0.0041
3.5	1369.12255	0.00013	−236.1091	0.0017	0.88767	0.00009	1133.9011	0.0017
4.0	428.78252	0.00003	−123.5980	0.0010	0.48729	0.00013	305.6718	0.0010
4.5	131.53383	0.00001	−66.1020	0.0011	0.21745	0.00009	65.6493	0.0011
5.0	39.64473	0.00001	−36.17927	0.00023	0.08152	0.00007	3.54698	0.00024
5.3	19.16486	0.00001	−25.52899	0.00024	0.04093	0.00005	−6.32320	0.00025
5.6	9.21998	0.00001	−18.21178	0.00032	0.01818	0.00003	−8.97362	0.00032
6.0	3.45233	0.00001	−11.82323	0.00017	0.00365	0.00001	−8.36725	0.00017
6.5	1.00165	0.00001	−7.10599	0.00022	−0.00239	0.00001	−6.10673	0.00022
7.0	0.28797	0.00001	−4.41983	0.00006	−0.00338	0.00001	−4.13524	0.00006
8.0	0.02327	0.00001	−1.88167	0.00002	−0.00223	0.00001	−1.86063	0.00002
9.0	0.00183	0.00001	−0.89297	0.00003	−0.00119	0.00001	−0.89233	0.00003

TABLE 9: The Contributions beyond the CCD Level (Extrapolated to the CBS Limits), the Total Interaction Energies, E_{int}, and the Estimated Uncertainties, σ, of These Quantities

R	E_S	σ	E_T	σ	$E_{CCSD(T)}$	σ	δE_{FCI}	σ	E_{int}	σ
3.0	−1.281	0.040	−33.326	0.054	3772.941	0.068	−5.260	0.020	3767.681	0.071
3.5	−0.982	0.010	−19.040	0.023	1113.879	0.025	−3.230	0.013	1110.649	0.028
4.0	−0.734[a]	0.002[a]	−10.485	0.010	294.453	0.010	−1.883	0.011	292.570	0.015
4.5	−0.497	0.004	−5.681	0.005	59.470	0.006	−1.074	0.008	58.397	0.010
5.0	−0.3175	0.0018	−3.0929	0.0031	0.1366	0.0036	−0.6120	0.0055	−0.4754	0.0065
5.3	−0.2379	0.0012	−2.1673	0.0024	−8.7284	0.0027	−0.4397	0.0040	−9.1681	0.0048
5.6	−0.1771[a]	0.0005[a]	−1.5346[b]	0.0011[b]	−10.6853	0.0013	−0.3183	0.0028	−11.0037	0.0031
6.0	−0.1182	0.0006	−0.9863	0.0013	−9.4718	0.0014	−0.2101	0.0017	−9.6819	0.0023
6.5	−0.07173	0.00046	−0.58681	0.00078	−6.76527	0.00093	−0.12832	0.00082	−6.89359	0.00124
7.0	−0.0442[a]	0.0005[a]	−0.36249	0.00056	−4.54193	0.00075	−0.08084	0.00031	−4.62277	0.00081
8.0	−0.01789	0.00014	−0.15321	0.00022	−2.03173	0.00026	−0.03496	0.00016	−2.06669	0.00031
9.0	−0.00807	0.00006	−0.07267	0.00021	−0.97308	0.00022	−0.01669	0.00016	−0.98977	0.00028

[a] Values from refs 29 and 30. [b] Extrapolated from the d*X*Zb135 sequence; see text.

TABLE 10: Extrapolations of the FCI Correlation Contribution to the Interaction Energy, $E^{cr}_{FCI} = E_{FCI} - E_{SCF}$

	R									
	3.0	3.0	4.0	4.0	5.6	5.6	7.0	7.0	8.0	8.0
	d*X*Z	a*X*Zb95	d*X*Z	a*X*Zb95	d*X*Z	a*X*Zb95	d*X*Z	a*X*Zb95	d*X*Z	a*X*Zb95
$X = 4$	−469.41587	−487.38951	−128.78287	−134.27751	−19.57885	−20.18599	−4.85671	−4.91464	−2.08045	−2.09092
$X = 5$	−487.28567	−493.44511	−133.30156	−135.14325	−19.96284	−20.19617	−4.88607	−4.90996	−2.08494	−2.08884
$X = 6$	−493.61586	−496.09663	−134.68537	−135.53056	−20.12207	−20.20355	−4.89922	−4.91022	−2.08673	−2.08964
(45)	−506.03431	−499.79853	−138.04248	−136.05157	−20.36571	−20.20685	−4.91687	−4.90505	−2.08965	−2.08666
(56)	−502.31118	−499.73883	−136.58621	−136.06258	−20.34079	−20.21369	−4.91728	−4.91058	−2.08919	−2.09074
$E^{cr}_{FCI}(E^{MP2,cr}_{A})$	−502.62666	−500.09972	−136.65303	−136.09969	−20.34876	−20.21429	−4.91795	−4.91060	−2.08928	−2.09079
$E^{cr}_{FCI}(E^{cr}_{MP2})$	−501.67797	−501.05619	−136.50925	−136.28436	−20.25474	−20.21881	−4.91193	−4.91065	−2.08986	−2.09053
$E^{cr}_{FCI}(E^{cr}_{FCCD})$	−500.66164	−500.52993	−136.22132	−136.17207	−20.22675	−20.21630	−4.91095	−4.91056	−2.08954	−2.09038
E^{cr}_{FCI}	−501.644	−500.398	−136.437	−136.173	−20.2878	−20.2162	−4.91445	−4.91060	−2.08952	−2.09058
σ	0.983	0.659	0.216	0.111	0.0610	0.0026	0.00350	0.00005	0.00034	0.00021
E_{FCI}[a]	3766.752	3767.999	292.362	292.615	−11.0675	−10.9961	−4.62636	−4.62260	−2.06622	−2.06731

[a] The total FCI interaction energies were obtained by adding E_{SCF} computed in $X = 6$ bases.

presented, together with their estimated uncertainties σ obtained by quadratically adding the uncertainties of the contributions,

$$\sigma^2(E_{int}) = \sigma_{SCF}{}^2 + \sigma_{FCCD}{}^2 + \sigma_{NF}{}^2 + \sigma_S{}^2 + \sigma_T{}^2 + \sigma_{FCI}{}^2 \qquad (20)$$

and similarly for E_{CCD} and $E_{CCSD(T)}$. This formula for the total uncertainty is consistent with the conventional scheme of adding experimental uncertainties. The uncertainties of E_{int} defined in this way, listed in Table 9, are significantly smaller than the uncertainties reported in refs 29 and 30 for $R = 4.0$, 5.6, and 7.0 bohr. For example, the interaction energy at $R = 5.6$ bohr obtained in this work is equal to −11.0037 ± 0.0031 K, compared with the value −11.009 ± 0.008 K recommended in ref 30. One of the reasons is that uncertainties of several contributions have been decreased in the present work. In particular, at $R = 5.6$ bohr, the uncertainties of E^{cr}_{FCCD}, E_T, and δE_{FCI} have been reduced from 0.47 to 0.32 mK, from 2 to 1.2 mK, and from 5 to 2.8 mK, respectively. However, another significant decrease results from the fact that in refs 29 and 30 the uncertainties were added linearly, rather than quadratically (with errors added linearly, our current result would have been −11.0037 ± 0.0049 K). With the use of eq 20, our total uncertainties should be viewed more like standard deviations obtained in experimental measurements rather than more or less rigorous bounds for the interval in which the true interaction energy lies.

Since the interaction energies computed using the FCI method are fairly accurate, one may wonder how good would be predictions based only on our FCI calculations. Table 10 shows the results of FCI calculations and extrapolations using the same extrapolations schemes as discussed above. Since the dXZ and a*X*Zb95 sequences give dramatically different results, the recommended values of $E_{\mathrm{FCI}}^{\mathrm{cr}}$ and their uncertainties were computed separately for each sequence as the midpoint of the range spanned by all four extrapolations from $X = 5$ and 6 and half of this range, respectively. As one can see in Table 10, the interaction energies extrapolated from the aXZb95 sequence are very accurate. At $R = 5.6$ bohr, the error compared to our best value is only 7.6 mK or 0.08%. However, the estimated uncertainty of this result, amounting to 2.6 mK, is too small. At $R = 3.0$ bohr, the agreement is even better as the relative discrepancy is only 0.008% and the error estimate is now consistent with the accurate value. Thus, although the FCI calculations constituted a major part of computer costs in the present work, such calculations by themselves would lead to a significantly less accurate potential than that presented in Table 9. In contrast to the aXZb95 sequence, the predictions from the dXZ sequence are poor. In particular, the error at $R = 5.6$ bohr is as large as 64 mK. Only at very small and very large R, where the effects of midbond functions become negligible, the predictions of this sequence are comparable to those from aXZb95. Since the two sequences performed comparably for the δE_{FCI} contribution, the difficult to extrapolate component is probably contained in $E_{\mathrm{FCCD}}^{\mathrm{cr}}$. The use of midbond functions alleviates this difficulty fairly effectively.

IV. Comparison with Literature and Conclusions.

The present work reports a calculation of interaction energies for the helium dimer using the CCSD(T) and FCI methods for R ranging from 3.0 to 9.0 bohr. Some results at $R = 4.0$, 5.6, and 7.0 bohr were taken from refs 29 and 30. The present calculations introduced several improvements to the method developed in refs 29 and 30. These methods are based on optimized floating Gaussian orbitals at the SCF level, optimized Gaussian geminals up to the FCCD level, and extrapolated orbital calculations beyond the FCCD level. For $R = 4.0$, 5.6, and 7.0 bohr, also geminal calculations up to the CCSD level performed in refs 29, 30 contributed to the present results. We found it advantageous to combine these very different techniques, and we expect similar schemes to be universally applicable to very high-accuracy calculations on small and medium-size systems.

The method was applied to nine new separations in addition to the three considered before in refs 29 and 30. For the three distances considered in ref 30, the calculations have been improved and the error bars have been significantly reduced. For example, at $R = 5.6$ bohr, these bars were reduced from 8 to 3.1 mK. The reduction of errors results partly from a more realistic, quadratic summation of errors and partly from more accurate predictions of the post-CCSD(T) effects. We were now able to use the $X = 6$ basis sets in the FCI calculations, which lowered the uncertainty of this part of the interaction energy, δE_{FCI}, from 5 to 2.8 mK at 5.6 bohr. While in the calculations of ref 30 the uncertainty of δE_{FCI} strongly dominated the overall uncertainty of the interaction energies, now this uncertainty is more comparable to the ones for the other two slowly convergent orbital contributions, E_{S} and E_{T}. Another change in our calculation scheme is relying only on extrapolated orbital values of the terms E_{NF} and (for the distances not considered in ref 30) E_{S}. In the first case, the reason is that the nonfactorizable term converges extremely well, and in the present work, we used larger basis sets than before ($X = 7$ vs $X = 6$) to completely saturate this component without using geminal results. In the second case, we did not use our GTG CCSD program to calculate the effect of the single excitations for purely economical reasons. The calculation of saturated geminal CCSD energies (with the same quality as those obtained in ref 30 for three distances) for the whole potential, while certainly feasible, would be very expensive and would not reduce significantly the overall error bars. For example, at 5.6 bohr, taking the GTG/orbital value of E_{S} from ref 30 yields the total uncertainty of the potential $\sigma = 3.1$ mK (our recommended result), while using instead the extrapolated orbital-only value (see footnote to Table 4) results in $\sigma = 3.2$ mK.

The relative accuracy of the present interaction energies is about 0.03% or better for the attractive part of the potential and as high as 0.002% on the repulsive wall at $R = 3.0$ bohr. An obvious exception is the weakly repulsive region around $R = 5.0$ bohr where the potential goes through zero. In this region, the absolute error is about 7 mK, only twice as large as that at the well minimum.

We have used several methods to extrapolate the orbital calculations. Whereas the choices of the methods are to some extent arbitrary, our recommended results are based on several types of extrapolations and the uncertainties are determined by the spread of the extrapolated results. This should make our final interaction energies fairly independent of the types of the extrapolations chosen. On the other hand, our error estimates may be somewhat too large. It is possible that a more detailed analysis of the convergence patterns in X may lead to a decrease of these estimates.

A detailed comparison with other high-quality *ab initio* interaction energies for the helium dimer was presented in ref 30. Therefore, in the present work we concentrate on new results, which appeared after ref 30 was published. For the equilibrium distance, $R = 5.6$ bohr, there exists now an improved upper bound to the interaction energy, −10.9985 K,[50] obtained from four-electron “monomer contracted” ECG calculations. Very recent unpublished calculations[83] lowered it further to −11.0003 K. Our present prediction, −11.0037 ± 0.0031K, is fully consistent with this upper bound. Let us further note that for all the distances considered here, the upper bounds given by Komasa[49] are above our error bars. The same is true in comparison to the significantly improved ECG upper bounds from ref 51.

Recently, several points of the helium dimer potential were calculated by Anderson[39] using the exact (flexible nodes) quantum Monte Carlo (QMC) method. These results, for the three distances where a comparison is possible, are consistent with ours, that is, the error bars overlap. At $R = 5.6$ bohr, Anderson’s result of −10.998 ± 0.005 K has only slightly wider error bars than ours. However, at 4.0 (9.0) bohr, our bars turn out to be 13 (4) times narrower. The agreement with the 2001 Anderson’s results[28] is not as good. At 3.0 bohr, the discrepancy is 38 K, 1.5 times the QMC error bar. Our results are also outside the QMC error bars at 5.6 and 9.0 bohr.

The present interaction energy at $R = 5.6$ bohr is in good agreement with the SAPT result from ref 53, equal to −11.000 ± 0.011 K, although the estimated uncertainty of the latter result is significantly larger. For $R = 7.0$ bohr and larger, the SAPT uncertainties become, however, equal to or smaller than those of the present work.

The results of the present work were combined with the results of SAPT calculations in ref 53 to fit an analytic potential for the helium dimer. This potential is much more accurate than the widely used potential of refs 25 and 26 and is expected to replace the latter. This potential approximates the helium−helium interaction at the nonrelativistic Born−Oppenheimer level. Some work on relativistic, quantum electrodynamics, and adiabatic (diagonal Born−Oppenheimer) contributions to the

TABLE 11: The Extrapolated Correlation Part of the MP2 Interaction Energy, $E^{\mathrm{cr}}_{\mathrm{MP2}}$, Its Uncertainty, σ, and Its Upper Bound, $E^{\mathrm{cr,UB}}_{\mathrm{MP2}}$

R	$E^{\mathrm{cr}}_{\mathrm{MP2}}$	σ	$E^{\mathrm{cr,UB}}_{\mathrm{MP2}}$
3.0	−461.93983	0.00081	−461.93762
3.5	−231.06465	0.00042	−231.06395
4.0	−117.49916	0.00026	−117.49840
4.5	−61.02283	0.00017	−61.02248
5.0	−32.55997	0.00011	−32.55961
5.3	−22.68541	0.00006	−22.68507
5.6	−16.01194	0.00008	−16.01157
6.0	−10.27955	0.00007	−10.27924
6.5	−6.11771	0.00008	−6.11742
7.0	−3.78141	0.00007	−3.78113
8.0	−1.60018	0.00006	−1.59987
9.0	−0.75788	0.00002	−0.75769

potential has been published[50,84,85] and a more extensive set of calculations is underway.[51] Some of these contributions are significantly larger than the uncertainty of our Born−Oppenheimer potential. Thus, one can hope that these contributions can be detected in the most accurate experiments. The availability of such an accurate pair potential opens also a possibility of a reliable experimental determination of the very subtle three-body pairwise nonadditive interactions of helium atoms.[83,86,87]

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Appendix A. MP2 Interaction Energies with Upper Bounds

As a byproduct of our GTG FCCD calculations, we have obtained very accurate MP2 interaction energies, $E^{\mathrm{cr}}_{\mathrm{MP2}}$, which were subsequently extrapolated to the basis set limit in exactly the same way as in the case of the FCCD interaction energies. The extrapolated values are listed in Table 11. Since the $E^{\mathrm{cr}}_{\mathrm{MP2}}$ interaction energies are the best converged quantities computed by us, it is of interest whether one can also obtain useful upper bounds to these values. Although the total MP2 energies converge from above upon enlarging the basis set (assuming that exact SCF orbitals are used), such behavior is not guaranteed for the interaction energy because this quantity is computed as a difference of dimer and monomer MP2 energies calculated with the same basis set. It is possible, however, to calculate a strict upper bound to the MP2 interaction energy by subtracting the *exact* energies of the monomers. To obtain the “exact” MP2 energy of the helium atom, which is of interest by itself, we optimized various GTG expansions, ranging from $K = 75$ to $K = 600$, using the same procedure as that for the He_2 calculations. During the optimization, a very accurate 24-term SCF orbital was used, expanded in a basis of 1s Gaussian functions (the same set as that used to construct the He_2 SCF orbitals), which yields the helium atom SCF energy 0.14 nhartree above the HF limit.[88] As seen in Table 12, the helium atom MP2 correlation energies converge fast and smoothly. Similarly as in the case of MP2 and FCCD interaction energies discussed earlier, the doubling of the basis set size increases the accuracy by about one digit. Thus, since the $K = 300$ result is different from the $K = 600$ result by 0.14 nhartree, the $K = 600$ value should be within about 0.01−0.02 nhartree of the exact value. Consequently, we have estimated the latter value to be −37.377 474 54(2) mhartree. This value is 3 orders of magnitude more accurate than the previous best MP2 correlation energy for helium.[60] The final results listed in Table 12 were checked by recalculating the $K = 600$ MP2 energies with an even more accurate 32-term SCF function, corresponding to the SCF energy of −2.861 679 995 59 hartree, just 0.02 nhartree above the limit. All the digits listed were unchanged, which proves that the results are saturated with respect to the zeroth-order function.

TABLE 12: Helium Atom MP2 Energies (in Millihartrees) Computed Using Different Length GTG Expansions and a 24-Term SCF Orbital

K	MP2
75	−37.377397
150	−37.377469
300	−37.37747438
600	−37.37747452
extrap.	−37.37747454(2)
ref 60, 150-term GTG	−37.37744

The last column of Table 11 contains the MP2 interaction energies of the helium dimer calculated by subtracting the monomer energies of −37.377 474 56 mhartree (the estimated lowest possible value for the monomer) from the ($K = 800$, $M_2 = 8$) dimer energies (see the discussion of the FCCD energies for the explanation of the construction of the basis sets). A closer analysis shows that either the results for $M_2 = 8$ are saturated with respect to the SCF interaction basis set size, M_2, or at least the difference between the values for $M_2 = 8$ and $M_2 = 16$ is small compared with the difference between the results (for a fixed M) for $K = 800$ and $K = 600$. Hence, the results for $M_2 = 8$ and $K = 800$ represent, to the number of digits given, strict upper bounds to the MP2 interaction energies. The extrapolated values in Table 11 are fully consistent with the upper bounds and lie below the latter a few values of σ away. This provides a valuable consistency check for our extrapolation procedures.

Supporting Information Available: Extended versions of the tables, including the values of all the interaction energy components at each internuclear distance considered. This material is available free of charge via the Internet at http://pubs.acs.org.

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