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Three-Body Contribution to the Helium Interaction Potential[†]

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Two nonadditive three-body analytic potentials for helium were obtained: one based on three-body symmetry-adapted perturbation theory (SAPT) and the other one on supermolecular coupled-cluster theory with single, double, and noniterative triple excitations [CCSD(T)]. Large basis sets were used, up to the quintuple-zeta doubly augmented size. The fitting functions contain an exponentially decaying component describing the short-range interactions and damped inverse powers expansions for the third- and fourth-order dispersion contributions. The SAPT and CCSD(T) potentials are very close to each other. The largest uncertainty of the potentials comes from the truncation of the level of theory and can be estimated to be about 10 mK or 10% at trimer's minimum configuration. The relative uncertainties for other configurations are also expected to be about 10% except for regions where the nonadditive contribution crosses zero. Such uncertainties are of the same order of magnitude as the current uncertainties of the two-body part of the potential.

I. Introduction

Helium is one of the most extensively studied systems due to its unique properties at low temperatures related to extremely weak interactions between helium atoms. At the same time, the relative simplicity of the electronic structure of the helium atom makes it an ideal target for high-accuracy quantum chemical calculations. Consequently, in the past decade there has been a rapid progress in ab initio studies of helium, and since the mid-1990s[1−4] the accuracy of theoretical pair potentials for helium surpasses the accuracy of potentials based on empirical data. Later these results were improved in refs 5−9. The pair interaction energy is currently known with a relative accuracy of 0.03% (or 3 mK at the minimum),[10] which is remarkable taking into account that at the minimum this energy amounts to as little as −11 K. This quest for ultrahigh accuracy in the description of helium interactions is driven by the requirements of the metrology community related to the creation of new standards for thermophysical properties;[11−16] see discussions of these issues in refs 17 and 10. Recently, various small effects usually neglected in electronic structure studies, such as the diagonal nuclear motion,[18] and relativistic,[19] and quantum electrodynamics[20] contributions, have been calculated for the helium pair interaction.

With the highly increased accuracy of the helium dimer potential, the neglect of the three-body nonadditive helium interactions becomes the next largest source of uncertainties. The three-body nonadditive potential is needed to determine the third virial coefficient for helium. Surprisingly, no accurate nonadditive potential is available in the literature, except for the potential of ref 21 which has, however, a very complicated form. The older three-body nonadditive helium potentials[22−24] are simple but of rather low accuracy compared to more recent results (see the discussion of these potentials in ref 21) and have been found to deteriorate the agreement with experiment[25] when used in simulations of condensed helium.

The potentials of refs 22−24 were fitted to supermolecular ab initio calculations, whereas the potential of ref 21 was based on nonadditive interaction energies computed using symmetry-adapted perturbation theory (SAPT). The latter method gives the nonadditive contribution as a sum of components with a clear physical interpretation.[26] Although most of such contributions were derived and implemented only fairly recently,[21,27−29] some lower-order components have been known for the helium trimer already for some time.[30,31]

The three-body implementation[21,27] of SAPT was used in ref 21 to calculate nonadditive interaction energies for 39 configurations of the helium trimer. A potential energy fit was generated,[21] but as just mentioned, its rather complicated mathematical form limited its usefulness in applications such as molecular simulations. In this work, we present a new, simpler fit based on different physical characteristics of various components of the SAPT potential, similar to the argon trimer fit from ref 32. To achieve a high quality of the fit throughout the physically relevant region, it turned out to be necessary to calculate additional points on the potential energy surface, bringing the total number of points to 95.

For two-body interactions, the current level of SAPT is in most cases giving results competitive to those obtained using the supermolecular coupled-cluster method with single, double, and noniterative triple excitations [CCSD(T)]. In fact, for the helium dimer near the minimum separation the accuracy of SAPT is somewhat higher than that of CCSD(T).[33] However, the three-body SAPT is not yet as highly developed as the two-body one, and in general the CCSD(T) three-body nonadditive interaction energies should be more accurate. In view of the helium metrology accuracy requirements discussed above, we have decided to perform also CCSD(T) calculations and fit the computed data using the same functional form.

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II. Three-Body Nonadditive Energy

The total interaction energy of three atoms or molecules A, B, and C can be decomposed as a sum of two-body (pairwise additive) and three-body (nonadditive) contributions

$$E_{\mathrm{int}}^{\mathrm{ABC}} = E_{\mathrm{int}}[2] + E_{\mathrm{int}}[3] \tag{1}$$

These contributions can be obtained from the supermolecular approach (by proper subtractions of the total energies of the trimer, E_{ABC}, constituent dimers, E_{AB}, E_{AC}, and E_{BC}, and monomers, E_{A}, E_{B}, and E_{C}), or from SAPT. The latter approach has two main advantages: avoiding the subtraction of quantities with the same orders of magnitude and yielding terms with a clear physical interpretation. For a recent review of three-body nonadditive interactions see ref 26.

A. SAPT Calculations. In SAPT, the three-body contribution to the interaction energy is expanded in a sextuple perturbation series

$$E_{\mathrm{int}}^{\mathrm{SAPT}}[3] = \sum_{K=1}^{\infty}\sum_{N=0}^{\infty}\sum_{ijk}\sum_{lmn} E^{(ijk;lmn)}[3], \quad i+j+k=K, \quad l+m+n=N \tag{2}$$

where i, j, and k are orders of the perturbations with respect to the dimer interaction operators V_{AB}, V_{BC}, V_{AC} and l, m, n with respect to the correlation operators of the monomers A, B, C (with the zeroth-order description of monomers at the Hartree−Fock level). Each of the corrections $E^{(ijk;lmn)}[3]$ can be further decomposed into a component given by the Rayleigh−Schrödinger (RS) perturbation theory and an exchange component resulting from permutations of electrons between interacting systems. It is convenient to discuss the sums of all corrections of the same type and with the same value of K or N, for example,

$$E_{\mathrm{exch}}^{(K;lmn)}[3] = \sum_{ijk} E_{\mathrm{exch}}^{(ijk;lmn)}[3], \quad i+j+k=K \tag{3}$$

Finally, the indices corresponding to the intramonomer correlation are omitted if the correction was calculated to the infinite order, for example,

$$E_{\mathrm{disp}}^{(3)}[3] = \sum_{N=0}^{\infty} E_{\mathrm{disp}}^{(3;N)}[3] \tag{4}$$

In the present study of the helium trimer, $E_{\mathrm{int}}^{\mathrm{SAPT}}[3]$ is represented by the following expression[21,27]

$$E_{\mathrm{int}}^{\mathrm{SAPT}}[3] = E_{\mathrm{exch}}^{(1;0)}[3] + \epsilon_{\mathrm{exch}}^{(1)}(2)[3] + E_{\mathrm{ind}}^{(2;0)}[3] + E_{\mathrm{exch-ind}}^{(2;0)}[3] + E_{\mathrm{exch-disp}}^{(2;0)}[3] + E_{\mathrm{disp}}^{(3)}[3] + E_{\mathrm{disp}}^{(4;0)}[3] + \delta E_{\mathrm{int}}^{\mathrm{HF}}[3] \tag{5}$$

The term $\epsilon_{\mathrm{exch}}^{(1)}(2)[3]$ contains first-order exchange effects up to the second order in the intramonomer correlation operators

$$\epsilon_{\mathrm{exch}}^{(1)}(2)[3] = E_{\mathrm{exch}}^{(1;1)}[3] + E_{\mathrm{exch}}^{(1;2)}[3] \tag{6}$$

The term $E_{\mathrm{ind}}^{(2;0)}[3]$ is the induction part of the second-order RS component (the second-order nonadditive dispersion energy, similarly as the first-order electrostatic energy, are exactly zero), and $E_{\mathrm{exch-ind}}^{(2;0)}[3]$ is its exchange counterpart. Next, $E_{\mathrm{exch-disp}}^{(2;0)}[3]$ is the second-order exchange−dispersion nonadditive contribution. The nonadditivive third-order dispersion energy, $E_{\mathrm{disp}}^{(3)}[3]$, is calculated as

$$E_{\mathrm{disp}}^{(3)}[3] = E_{\mathrm{disp}}^{(3;0)}[3] + E_{\mathrm{disp}}^{(3;1)}[3] + \epsilon_{\mathrm{disp}}^{(3)}[3] \tag{7}$$

where $\epsilon_{\mathrm{disp}}^{(3)}[3]$ is an approximate sum of all $E_{\mathrm{disp}}^{(3;N)}[3]$ from $N = 3$ to $N = \infty$.[21,32] Its evaluation will be discussed in section IV,A. $E_{\mathrm{disp}}^{(4;0)}[3]$ is the fourth-order nonadditive dispersion energy. The term $\delta E_{\mathrm{int}}^{\mathrm{HF}}[3] = E_{\mathrm{int}}^{\mathrm{HF}}[3] - E_{\mathrm{exch}}^{(1;0)}[3] - E_{\mathrm{ind}}^{(2;0)}[3] - E_{\mathrm{exch-ind}}^{(2;0)}[3]$, where $E_{\mathrm{int}}^{\mathrm{HF}}[3]$ is the Hartree−Fock supermolecular nonadditive energy

$$E_{\mathrm{int}}^{\mathrm{HF}}[3] = E_{\mathrm{ABC}}^{\mathrm{HF}} - (E_{\mathrm{AB}}^{\mathrm{HF}} + E_{\mathrm{AC}}^{\mathrm{HF}} + E_{\mathrm{BC}}^{\mathrm{HF}}) + (E_{\mathrm{A}}^{\mathrm{HF}} + E_{\mathrm{B}}^{\mathrm{HF}} + E_{\mathrm{C}}^{\mathrm{HF}}) \tag{8}$$

collects mostly third- and higher-order induction and exchange−induction effects. For three helium atoms, all terms in eq 5 decay exponentially with the interatomic distances R, except for the dispersion terms which decay as inverse powers of R.

B. CCSD(T) Calculations. The three-body nonadditive contribution to the interaction energy calculated at the CCSD(T) level of theory can be decomposed as

$$E_{\mathrm{int}}^{\mathrm{CCSD(T)}}[3] = E_{\mathrm{int}}^{\mathrm{HF}}[3] + E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}[3] \tag{9}$$

where the correlation part, $E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}[3]$, is defined analogously to eq 8. If this quantity is evaluated in the correlation-consistent basis sets developed by Dunning et al.,[6,34−36] one can extrapolate the results to the complete basis set (CBS) limit using the approximate formula

$$E(X) - E(\infty) = AX^{-3} \tag{10}$$

where X is the basis set cardinal number, A is a constant, and $E(X)$ stands for $E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}[3](X)$. Equation 10 leads to the following expression for the "two-point" extrapolated value

$$E(\infty) = E(X) + \frac{(1-1/X)^3}{1-(1-1/X)^3}[E(X) - E(X-1)] \tag{11}$$

The good performance of the X^{-3} extrapolation is extensively documented in the literature, in particular in recent studies of the two-body helium interaction.[5,10,33,37]

III. Fitting Formulas

A. SAPT Potential. The fitting procedure for SAPT three-body energies follows that described in ref 32. Here we briefly recapitulate the essential formulas. For the purpose of the fitting, eq 5 was rewritten as

$$E_{\mathrm{int}}^{\mathrm{SAPT}}[3] = E_{\mathrm{int}}^{\mathrm{HF}}[3] + \epsilon_{\mathrm{exch}}^{(1)}(2)[3] + E_{\mathrm{exch-disp}}^{(2;0)}[3] + E_{\mathrm{disp}}^{(3)}[3] + E_{\mathrm{disp}}^{(4;0)}[3] \tag{12}$$

Each of the terms in eq 12 is fitted separately, and the total three-body potential is therefore a sum of five independent potential functions (a part of $E_{\mathrm{disp}}^{(3)}[3]$ is obtained without fitting, see below). Note that the first-order exchange correction of eq 6 was not included in ref 32 as it was derived later.[21]

1. Exponentially Decaying Components. Each of the first three terms in eq 12 is represented as

$$V_{\mathrm{exp}}(R_{\mathrm{AB}}, R_{\mathrm{BC}}, R_{\mathrm{AC}}) = \sum_{k_1 \le k_2 \le k_3}^{K} A_{k_1k_2k_3} \mathrm{e}^{-\beta_{k_1k_2k_3}(R_{\mathrm{AB}}+R_{\mathrm{BC}}+R_{\mathrm{AC}})} \times \mathscr{P}[P_{k_1}(\cos\theta_{\mathrm{A}})\, P_{k_2}(\cos\theta_{\mathrm{B}})\, P_{k_3}(\cos\theta_{\mathrm{C}})] \tag{13}$$

where θ_X is the internal angle at atom X and P_k are the kth order Legendre polynomials. The operator $\mathscr{P}$ generates the sum of six terms with all the permutations of the angles θ_X.

2. Third-Order Dispersion Energy. The first two components of $E^{(3)}_{\mathrm{disp}}[3]$ in eq 7 were calculated for each grid point of our potential and then fitted together as a single term, which we will denote as $E^{(3)}_{\mathrm{disp}}(1)[3]$

$$E^{(3)}_{\mathrm{disp}}(1)[3] = E^{(3;0)}_{\mathrm{disp}}[3] + E^{(3;1)}_{\mathrm{disp}}[3] \tag{14}$$

The last term of eq 7, $\epsilon^{(3)}_{\mathrm{disp}}[3]$, was obtained as a correction to the final fit, which is described in section IV,A. $E^{(3)}_{\mathrm{disp}}(1)[3]$ was represented as a sum of the exponential function of eq 13 and of a damped asymptotic expansion of the form

$$\sum_{\substack{k,l,m=1\\ k+l+m\le 6}}^{3}{}' D(\beta_{klm}, R_{\mathrm{AB}}, R_{\mathrm{BC}}, R_{\mathrm{AC}}) W^{(3)}_{klm} Z^{(3)}_{klm} \tag{15}$$

where the prime indicates that the sum does not contain (klm) = (123) and its permutations. The damping function has the product form

$$D(\beta_{klm}, R_{\mathrm{AB}}, R_{\mathrm{BC}}, R_{\mathrm{AC}}) = D(\beta_{klm}, R_{\mathrm{AB}})\, D(\beta_{klm}, R_{\mathrm{BC}})\, D(\beta_{klm}, R_{\mathrm{AC}}) \tag{16}$$

where the individual factors are chosen as[38]

$$D(\beta_{klm}, R_{XY}) = 1 - \exp(-\beta_{klm} R_{XY}) \sum_{n=0}^{n^{klm}_{XY}} (\beta_{klm} R_{XY})^n / n! \tag{17}$$

In the equation above, n^{klm}_{XY} is the inverse power to which R_{XY} is raised in the term $W^{(3)}_{klm}$ of eq 15. The lowest such term, resulting from the triple-dipole interaction of the monomers [the Axilrod−Teller−Muto term[39,40] (ATM)] has the form

$$W^{(3)}_{111} = 3 R_{\mathrm{AB}}{}^{-3} R_{\mathrm{BC}}{}^{-3} R_{\mathrm{AC}}{}^{-3} (1 + 3 \cos\theta_{\mathrm{A}} \cos\theta_{\mathrm{B}} \cos\theta_{\mathrm{C}}) \tag{18}$$

The higher terms contain higher negative powers of the distances and more complicated functions of the angles. The explicit formulas derived in[41,42] are collected in eqs A5−A9 of ref 43.

The expansion coefficients $Z^{(3)}_{klm}$ of eq 15 are obtained as

$$Z^{(3)}_{klm} = \frac{1}{\pi} \int_0^{\infty} \alpha^k(i\omega)\, \alpha^l(i\omega)\, \alpha^m(i\omega)\, \mathrm{d}\omega \tag{19}$$

where $\alpha^n(i\omega)$ is the nth polarizability of the helium atom at the frequency ω. If the polarizabilities are computed at an appropriate order with respect to the electric field, these coefficients are consistent with the level of theory used in SAPT,[32] that is, for large distances the computed SAPT energies agree very closely with the asymptotic expansion using such coefficients.

3. Fourth-Order Dispersion Energy. The component $E^{(4;0)}_{\mathrm{disp}}[3]$ was represented as a sum of the exponential function of eq 13 and of the damped asymptotic expansion of the form

$$\sum_{\substack{k,l,m,n=1\\ k+l+m+n\le 6}}^{2} D(\beta^{(220)}_{klmn}, R_{\mathrm{AB}}, R_{\mathrm{BC}}, R_{\mathrm{AC}})\, W^{(220)}_{klmn} Z^{(220)}_{klmn} + D(\beta^{(211)}_{klmn}, R_{\mathrm{AB}}, R_{\mathrm{BC}}, R_{\mathrm{AC}}) W^{(211)}_{klmn} Z^{(211)}_{klmn} + \ldots \tag{20}$$

where the dots denote permutations of the superscripts. The damping functions D have the same form as defined by eqs 16 and 17. The terms $W^{(220)}_{klmn}$ and $W^{(211)}_{klmn}$ are defined by eqs A11−A17 in ref 43. Note that ref 43 contains some misprints, as already pointed out in ref 44. In paricular, the coefficient $Z^{(211)}_{1111}$ is equal to zero so that the term $W^{(211)}_{1111}$ of eq A11 should not be listed. The sum in the square brackets in eq A12 should contain only the first term (the other two are generated by permutations), with θ_1 replaced by θ_2. Finally, all occurences of θ_3 in eqs A16 and A17 must be replaced by θ_2. The same errors are contained in eqs 20−26 of ref 32, where these formulas were originally published. The coefficients $Z^{(220)}_{klmn}$ and $Z^{(211)}_{klmn}$ were not calculated from the atomic polarizabilities but treated as linear parameters of the fit.

B. CCSD(T) Potential. The correlation part of the CCSD(T) three-body energy, $E^{\mathrm{CCSD(T),corr}}_{\mathrm{int}}[3]$, was represented by the sum of three components: the exponential contribution of eq 13, the damped third-order asymptotic expansion of eq 15, and the damped fourth-order asymptotic expansion of eq 20. Similarly as in the case of the SAPT potential, the third-order expansion coefficients of eq 15 were taken from asymptotic calculations, and the fourth-order coefficients $Z^{(220)}_{klmn}$ and $Z^{(211)}_{klmn}$ of eq 20 were treated as linear fitting parameters. The asymptotic constants corresponding to the CCSD(T) level of theory are unknown. Therefore, we have used the nearly exact constants computed by Thakkar.[45]

IV. Details of the Fits and Discussion

A. SAPT Potential. We have fitted the SAPT three-body potential to the points computed in ref 21 plus an additional set of points computed by us. Out of the 39 points (all for isosceles triangles) calculated in ref 21, we removed the four points where any of the distances R_{AB}, R_{BC}, or R_{AC} was smaller than 3.5 bohr. The reason was that the accuracy of our fit is not critical in the high-energy repulsive region (note that the two-body energy of the two helium atoms separated by 3.5 bohr is 1111 K). This set of 35 points was extended by calculating $E^{\mathrm{SAPT}}_{\mathrm{int}}[3]$ in the least populated regions of the three-dimensional space. Specifically, we defined the “distance’’ between two helium trimer geometries, $\mathbf{R}^{(i)} \equiv (R^{(i)}_{\mathrm{AB}}, R^{(i)}_{\mathrm{BC}}, R^{(i)}_{\mathrm{AC}})$ and $\mathbf{R}^{(j)} \equiv (R^{(j)}_{\mathrm{AB}}, R^{(j)}_{\mathrm{BC}}, R^{(j)}_{\mathrm{AC}})$, as

$$(\mathbf{R}^{(i)}, \mathbf{R}^{(i)}) = \min_{\{P(\mathbf{R}^{(i)})\}} \sqrt{(R^{(i)}_{\mathrm{AB}} - R^{(j)}_{\mathrm{AB}})^2 + (R^{(i)}_{\mathrm{BC}} - R^{(j)}_{\mathrm{BC}})^2 + (R^{(i)}_{\mathrm{AC}} - R^{(j)}_{\mathrm{AC}})^2} \tag{21}$$

where $\{P(\mathbf{R}^{(i)})\}$ denotes the set of six permutations of the components of $\mathbf{R}^{(i)}$. Given the set of N molecular geometries (initially, $N = 35$), the geometry $N + 1$ was selected so as to maximize the value of the expression

$$\min_{i=1,\ldots,N} (\boldsymbol{R}^{(i)}, \boldsymbol{R}^{(N+1)}) \tag{22}$$

by testing all the possible combinations of $R^{(N+1)}_{\mathrm{AB}}$, $R^{(N+1)}_{\mathrm{BC}}$, and $R^{(N+1)}_{\mathrm{AC}}$ from $R_{\min}$ to $R_{\max}$ with a step of 0.1 bohr. The new geometry was then added to the set of geometries, and the process was repeated. In this way, we added 10 geometries with $R_{\min} = 3.5$ and $R_{\max} = 15$, then 30 with $R_{\min} = 3.5$ and $R_{\max} = 8$, 10 with $R_{\min} = 3.5$ and $R_{\max} = 15$, and finally 10 with $R_{\min} = 3.5$ and $R_{\max} = 8$ bohr, to arrive at the final set of 95 fitted points. Two different values of $R_{\max}$ were used to ensure a more balanced filling of the space. Geometries with large distances turned out to be important for the description of the long-range regions of the fit, particularly to prevent an oscillatory behavior of the exponentially decaying components. On the other hand, using only $R_{\rm max} = 15$ bohr would result in an underrepresentation of the short-range region, where more points are required due to the more rapidly changing potential.

The fitting for each of the five components of eq 12 was done by the usual least-squares method. The weighting factors for the two dispersion components were chosen as V^{-2} ($V = E^{(3)}_{\rm disp}(1)[3]$ or $V = E^{(4;0)}_{\rm disp}[3]$), which favors a uniform relative accuracy of the fits at all the points. However, such weights lead to unnecessarily high accuracy of the exponentially decaying components at very large distances (where these components are negligible compared to the dispersion ones), at the expense of accuracy at shorter distances. Therefore, the first three terms in eq 12 were fitted with the weighting factors of the form $(V_{\rm exp}\tilde{V}_{\rm exp})^{-1}$, where

$$\tilde{V}_{\rm exp} = \max(V_{\rm exp}, \epsilon) \qquad (23)$$

and $\epsilon = 10^{-10}$ hartree. The supermolecular Hartree−Fock energies $E^{\rm HF}_{\rm int}[3]$ calculated from eq 8 are meaningless (because of the loss of accuracy in subtraction) below the absolute value of about 10^{-12} hartree. The long-range points turned out important, however, to prevent the $E^{\rm HF}_{\rm int}[3]$ fit from exhibiting strong unphysical oscillations at large distances. We solved this problem by replacing, for 18 points of our set, the value of $E^{\rm HF}_{\rm int}[3]$ by the quantity

$$E^{\rm HF}_{\rm SAPT}[3] = E^{(1;0)}_{\rm exch}[3] + E^{(2;0)}_{\rm ind}[3] + E^{(2;0)}_{\rm exch-ind}[3] + E^{(3;0)}_{\rm ind}[3] \qquad (24)$$

which collects those of the programed SAPT corrections that contribute to $E^{\rm HF}_{\rm int}[3]$ and, contrary to the latter, can be evaluated without any loss of accuracy at large distances.

The order K of the Legendre polynomial expansion in eq 13 was different for different components of $E^{\rm SAPT}_{\rm int}[3]$. The authors of ref 32 achieved a satisfactory accuracy of their argon trimer fit by using $K = 2$ for the $E^{\rm HF}_{\rm int}[3]$ and $E^{(2;0)}_{\rm exch-disp}[3]$ parts and purely isotropic fits ($K = 0$) for the short-range parts of the dispersion energies. In the present case, to achieve a relative accuracy of each of the components (at the fitted points) of the order of 1%, it turned out to be necessary to use $K = 4$ for $E^{(2;0)}_{\rm exch-disp}[3]$, $K = 1$ for $E^{(4;0)}_{\rm disp}[3]$, and $K = 3$ in the other cases. One reason for the difference with ref 32 is the fact that our helium trimer geometries cover a large part of the complete potential energy surface, while the argon trimer geometries were concentrated mostly in the regions important for the description of the crystal structure of solid argon.[46]

To fit the $E^{(3)}_{\rm disp}(1)[3]$ dispersion energy, we need asymptotic constants calculated in the same basis set and at the same level of theory as the current finite-separation values of this component. We used the POLCOR code[47,48] and obtained values of 0.38821, 0.69559, 3.0835, 1.2520, and 2.2642 atomic units, respectively, for $Z^{(3)}_{111}$, $Z^{(3)}_{112}$, $Z^{(3)}_{113}$, $Z^{(3)}_{122}$, and $Z^{(3)}_{222}$. These values can be compared with benchmark results obtained by Thakkar[45] using explicitly correlated wave functions: 0.49311, 0.92372, 4.1241, 1.7377, and 3.2839 atomic units. The discrepancies are partly due to the basis set incompleteness effects, but the main source is the fact that the former constants include intramonomer correlation effects to first order, whereas the latter are to infinite order. These two effects can be approximately accounted for by the term

$$\epsilon^{(3)}_{\rm disp}[3] = F(\{Z^{(3),\rm T}_{klm}\}) - F(\{Z^{(3),\rm P}_{klm}\}) \qquad (25)$$

where $Z^{(3),\rm T}_{klm}$ are the exact values of Thakkar, $Z^{(3),\rm P}_{klm}$ are the values obtained at the present level of theory and in the present basis set, and F is defined by eq 15. The exponents in the damping functions were taken from the fit to $E^{(3)}_{\rm disp}(1)[3]$.

The fitted parameters for all the components of the three-body nonadditive energy are listed in Tables 1 and 2. The accuracy of our final fit was checked by generating an additional 20 test points (10 with $R_{\rm max} = 15$ bohr and 10 with $R_{\rm max} = 8$ bohr) according to the description following eqs 21 and 22. We compared the values of the components of $E^{\rm SAPT}_{\rm int}[3]$ at all geometries (95 fitted and 20 test points) calculated from SAPT and from our fit. For most points, the errors of our total fit are a few percent or smaller. Exceptions include regions where the components of $E^{\rm SAPT}_{\rm int}[3]$ cancel to a large extent and those where $E^{\rm SAPT}_{\rm int}[3]$ is very small compared to the total interaction energy. When expressed as a percentage of the total (two-body plus three-body) interaction energy, $E^{\rm SAPT}_{\rm int}[3]$ calculated from the fit is in error by more than 0.1% at only one out of all 115 points: the error reaches its maximum value of 0.15% for the equilateral configuration $R_{\rm AB} = R_{\rm BC} = R_{\rm AC} = 5$ bohr, where the three-body contribution actually dominates the interaction because the two-body potential crosses zero in the vicinity of $R = 5$ bohr.

In absolute terms, the root-mean-square deviation (rmsd) of the total SAPT fit for all 115 calculated points amounts to 161 mK. At most points, however, the deviation of the fit is less than 1 mK and the bulk of the rmsd comes from a few short-range geometries where the absolute value of $E^{\rm SAPT}_{\rm int}[3]$ is very high. For example, removing from our set just five points with the following values of ($R_{\rm AB}$, $R_{\rm BC}$, $R_{\rm AC}$) of (4.0, 4.0, 4.0), (4.8, 4.8, 3.5), (4.8, 3.5, 3.5), (3.5, 3.5, 3.5), and (5.6, 3.5, 3.5) reduces the rmsd to 12.5 mK. The *relative* accuracies of the fit at these five points are as high as 0.3%, 1.8%, 2.5%, 0.1%, and 4.3%, respectively, so that the magnitude of the absolute deviations is inconsequential.

Figure 1 presents contour plots of the total three-body nonadditivity (in kelvin) for isosceles triangle geometries. Note that the total recommended values of $E^{\rm SAPT}_{\rm int}[3]$ are plotted; that is, the correction term $\epsilon^{(3)}_{\rm disp}[3]$ is added to the values calculated directly from the fit. In Figure 2, the absolute value of the ratio of three-body to two-body contributions is plotted. Because the two-body helium potential is currently known with a relative accuracy approaching 10^{-4}, it is seen that the full exploitation of this accuracy is possible only with a careful inclusion of the three-body nonadditive potential.

B. CCSD(T) Potential. The CCSD(T) calculations were performed using families of orbital basis sets carefully optimized by Dunning and collaborators.[6,34−36] In particular, for the whole surface we have used the doubly augmented correlation-consistent basis sets (d-aug-cc-pV*X*Z) with $X = 4$ and $X = 5$, and the correlation contributions to the three-body interaction energies were extrapolated according to eq 11. We will use short-hand notation d*X*Z for these bases (and similarly a*X*Z for the singly augmented ones). The type and size of the basis sets chosen have been determined on the basis of a series of tests presented in Table 3. We have collected in this table the correlation component of the CCSD(T) three-body nonadditive interaction energy, $E^{\rm CCSD(T),corr}_{\rm int}[3]$, computed for the equilateral triangle geometry with $R = 5.6$ bohr. We have used both the singly and doubly augmented Dunning et al. basis sets with and without bond functions. As the bond functions, we have taken the hydrogen functions from the same type basis sets. The computed value of $E^{\rm CCSD(T),corr}_{\rm int}[3]$ in the largest basis set,

TABLE 1: Parameters Defining the Exponentially Decaying Components and the Exponentially Decaying Contributions to the Dispersion Energy Components of $E_{int}^{SAPT}[3]$ in the SAPT Potential[a]

	$E_{\mathrm{int}}^{\mathrm{HF}}[3]$	$\epsilon_{\mathrm{exch}}^{(1)}[3]$	$E_{\mathrm{exch-disp}}^{(2;0)}[3]$	$E_{\mathrm{disp}}^{(3)}[3](1)$	$E_{\mathrm{disp}}^{(4;0)}[3]$
β_{000}/A_{000}	1.280182/0.907813(+3)	0.666835/−0.313318(−5)	0.918866/0.562664(+1)	0.284035/0.220152(−4)	0.596731/0.679365(−4)
β_{001}/A_{001}	0.356208/−0.104804(−5)	0.888986/0.386581(+0)	0.430311/−0.450660(−3)	0.347415/−0.390064(−4)	1.093319/−0.101889(−1)
β_{002}/A_{002}	0.654815/−0.513024(−3)	0.990042/0.190835(+1)	0.528953/−0.492291(−1)	0.313711/0.838659(−4)	
β_{003}/A_{003}	1.276779/−0.552516(+3)	0.943692/−0.360343(+0)	0.576533/−0.364171(−1)	0.504485/0.250976(−3)	
β_{011}/A_{011}	1.243689/−0.320622(+4)	1.300110/0.405432(+2)	0.459314/−0.143751(−1)	0.389926/0.204788(−3)	0.395095/0.578583(−6)
β_{012}/A_{012}	0.449472/−0.998103(−4)	0.835126/0.321931(+1)	0.612607/0.619852(+0)	0.726069/−0.127333(+0)	
β_{013}/A_{013}	0.458441/0.404275(−4)	0.834719/−0.677358(+0)	0.443412/0.184422(−1)	1.453880/0.103714(+2)	
β_{022}/A_{022}	0.476291/0.861357(−4)	0.821980/−0.182079(+1)	0.829959/0.145578(+2)	0.274347/0.441026(−4)	
β_{023}/A_{023}	0.359914/0.498951(−5)	0.811242/0.107852(+1)	0.742415/−0.503477(+1)	0.803036/0.156129(+0)	
β_{033}/A_{033}	0.540057/−0.304150(−4)	0.809187/−0.155349(+0)	0.900419/−0.221877(+2)	0.775995/−0.567419(−1)	
β_{111}/A_{111}	0.378181/0.415594(−5)	1.294033/−0.569722(+2)	1.020420/−0.148016(+2)	0.718383/−0.389968(−1)	0.632058/−0.200925(−3)
β_{112}/A_{112}	1.260332/0.519784(+4)	1.085872/0.214048(+2)	0.680885/−0.226778(+0)	0.291139/0.204761(−3)	
β_{113}/A_{113}	1.188596/−0.531730(+3)	0.909894/0.176236(+1)	0.939162/0.918403(+2)	0.272151/0.630391(−4)	
β_{122}/A_{122}	1.242953/−0.305976(+4)	0.785712/0.124689(+0)	0.999187/0.170620(+3)	0.725351/0.185298(+0)	
β_{123}/A_{123}	0.324357/0.451793(−5)	0.905605/−0.254846(+1)	0.652502/0.270092(+1)	0.253702/−0.589481(−4)	
β_{133}/A_{133}	0.330192/−0.125974(−5)	0.864110/0.478382(+0)	0.488419/0.540791(−1)	0.227952/0.253180(−5)	
β_{222}/A_{222}	0.325163/0.324438(−6)	0.842296/0.101742(+1)	0.435978/0.603488(−1)	0.756368/−0.165884(+0)	
β_{223}/A_{223}	0.354349/0.476332(−5)	0.850562/−0.888871(+0)	0.908688/0.331494(+1)	0.836110/0.304245(+0)	
β_{233}/A_{233}	0.089314/0.272360(−12)	0.772062/0.177373(−1)	0.911179/0.216738(+1)	0.269704/0.109669(−4)	
β_{333}/A_{333}	2.483728/0.343207(+8)	0.753683/−0.192478(−2)	0.408386/0.624219(−2)	0.262609/−0.253689(−5)	
β_{004}/A_{004}			0.954042/−0.269585(+2)		
β_{014}/A_{014}			0.433625/−0.711895(−1)		
β_{024}/A_{024}			0.959320/0.495924(+2)		
β_{034}/A_{034}			0.842211/0.104534(+2)		
β_{044}/A_{044}			0.552991/0.227937(−1)		
β_{114}/A_{114}			0.436585/0.655943(−1)		
β_{124}/A_{124}			0.950727/−0.778464(+2)		
β_{134}/A_{134}			0.557299/−0.441551(+0)		
β_{144}/A_{144}			0.362811/0.360400(−3)		
β_{224}/A_{224}			1.173423/0.872729(+2)		
β_{234}/A_{234}			0.413959/0.361086(−1)		
β_{244}/A_{244}			0.399888/−0.422641(−2)		
β_{334}/A_{334}			0.579116/−0.240274(+0)		
β_{344}/A_{344}			0.553335/0.319000(−1)		
β_{444}/A_{444}			0.325291/0.178925(−4)		

[a] All quantities are in atomic units. The numbers in parentheses denote powers of 10.

TABLE 2: Parameters Defining the Damped Long-Range Dispersion Energy Components of the SAPT Potential[a]

$E_{\mathrm{disp}}^{(3)}[3](1)$	$Z_{111}^{(3)}$	β_{111}
	0.38821	1.676268
	$Z_{112}^{(3)}$	β_{112}
	0.69559	1.875505
	$Z_{113}^{(3)}$	β_{113}
	3.0835	0.677096
	$Z_{122}^{(3)}$	β_{122}
	1.2520	4.114254
	$Z_{222}^{(3)}$	β_{222}
	2.2642	2.540250
$E_{\mathrm{disp}}^{(4;0)}[3]$	$Z_{1111}^{(220)}$	$\beta_{1111}^{(220)}$
	−0.717946(+0)	0.563965
	$Z_{1122}^{(221)}$	$\beta_{1122}^{(221)}$
	0.145713(+2)	2.013555
	$Z_{1221}^{(211)}$	$\beta_{1221}^{(211)}$
	−0.517375(+2)	1.464541
	$Z_{2112}^{(211)}$	$\beta_{2112}^{(211)}$
	0.196527(+2)	1.499416
	$Z_{2211}^{(220)}$	$\beta_{2211}^{(220)}$
	−0.530945(+3)	0.489660
	$Z_{2112}^{(220)}$	$\beta_{2112}^{(220)}$
	−0.180359(+1)	2.036807

[a] All quantities are in atomic units. The numbers in parentheses denote powers of 10.

d5Z, is 174.8 mK. The extrapolations from the largest basis sets of various types are all very close to each other, in the range 175.4−175.8 mK. On the basis of this consistency of the extrapolated results and on a generally satisfactory performance of the X^{-3} extrapolations extensively investigated in refs 5, 37, and 10, we estimate the exact correlation component of the three-body CCSD(T) interaction energy to be 175.6 ± 0.2 mK. This would be a very adequate accuracy compared to the current uncertainties of the pair potential;[10] however, the neglected effects beyond the CCSD(T) level are probably much larger (see the discussion below).

As the results of Table 3 show, bond functions have much smaller effects on the convergence rate than in the case of two-body energies.[37] In fact, results from bases with bond functions are slightly farther from the estimated limit than the values from the dXZ bases of approximatelly the same total size. Therefore, we have computed the whole surface in the dQZ and d5Z bases and extrapolated the results using the X^{-3} formula. Thus, the basis set incompleteness error of all computed CCSD(T) nonadditive interaction energies should be of the order of 0.1% compared to the exact CCSD(T) values.

Whereas the basis set incompleteness errors are negligibly small, the errors of the three-body interaction energies due to the truncation of theory at the CCSD(T) level may be substantial. There have been no published investigations of the latter errors for the helium trimer. For the helium dimer, the difference between the CCSD(T) and the exact interaction energy is 3% at the minimum.[5,10] The corresponding percentage error in the correlation part of the interaction energy is 1.6%. If the percentage error is the same in the correlation component of the three-body nonadditive contribution, this would amount to about 3 mK error for the minimum configuration of the trimer.

To better estimate the method truncation error for our potentials, we performed pilot full configuration interaction (FCI) calculations for a few geometries of He_3, using the aTZ

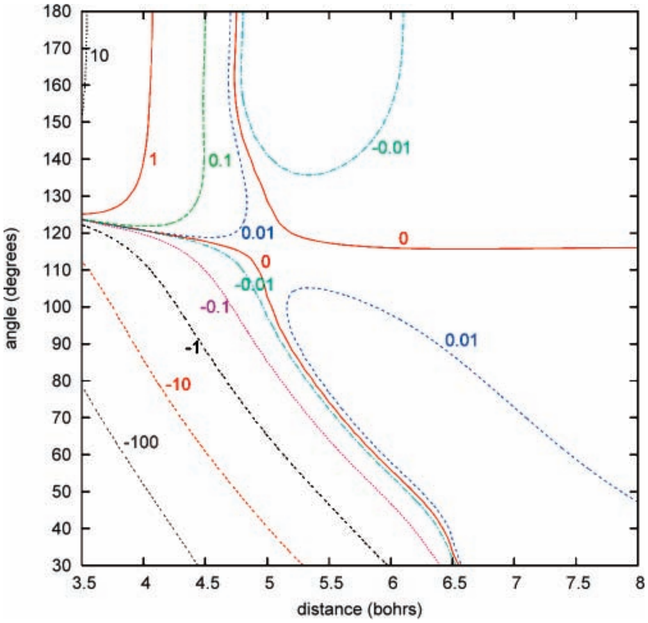

Figure 1. Total three-body contribution to the helium trimer energy, $E_{\mathrm{int}}^{\mathrm{SAPT}}[3]$, for isosceles triangle geometries (in kelvin) as a function of the interatomic distance $R_{\mathrm{AB}} = R_{\mathrm{AC}}$ (in bohr) and the angle θ_{A} (in deg).

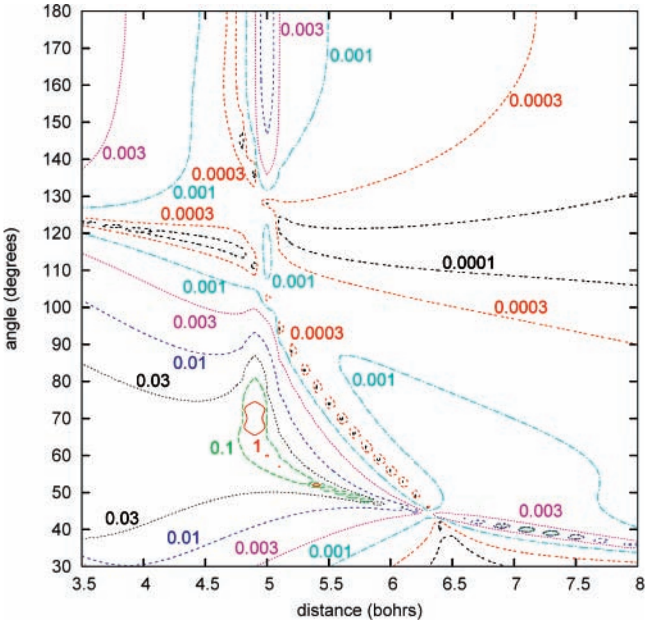

Figure 2. Absolute value of the ratio of the three-body and two-body contributions to the helium trimer energy, $|E_{\mathrm{int}}^{\mathrm{SAPT}}[3]/E_{\mathrm{int}}[2]|$, for isosceles triangle geometries as a function of the interatomic distance $R_{\mathrm{AB}} = R_{\mathrm{AC}}$ (in bohr) and the angle θ_{A} (in deg).

basis set and the Lucia program.[49] At the minimum energy configuration, (5.6, 5.6, 5.6), the correction due to the effects beyond the CCSD(T) level amounts to +10 mK, or −10% of the CCSD(T) nonadditive energy, significantly more than indicated by the two-body results. Although the fairly small aTZ basis (containing only 69 orbitals) gives for the helium dimer at the minimum separation quite an accurate value of $E_{\mathrm{int}}^{\mathrm{FCI}} - E_{\mathrm{int}}^{\mathrm{CCSD(T)}} = -320$ mK compared to the best current estimate of −318 mK,[10] this good performance may be fortuitous, and the relative error can be larger for the trimer. However, it is unlikely that it is much larger than 1−2 mK. At the other test geometries, (4.0, 4.0, 4.0), (7.0, 7.0, 7.0), and (5.6, 5.6, 11.2), the corrections were −0.5%, +9%, and +12%, respectively, relative to the CCSD(T) nonadditive interaction energies (listed in Table 6 discussed later on). Another estimate of the magnitude of the effects beyond CCSD(T) comes from a comparison between very long-range nonadditive energies calculated ab initio at the CCSD(T) level and those computed from Thakkar's asymptotic coefficients $Z_{klm}^{(3)}$ (corresponding to the FCI level of theory). For the (20.0, 20.0, 20.0) geometry, the difference amounts to +9% of the CCSD(T) energy. In summary, we believe that it is reasonable to assume that the nonadditive potentials for the helium trimer obtained in this work are accurate to within about 10% for all configurations. The uncertainty of 10 mK at the minimum separation can be compared to the total two-body uncertainty at this point amounting to 9 mK.[10]

TABLE 3: Calculated and Extrapolated Values (in Kelvin) of the Correlation Contribution to the CCSD(T) Three-Body Interaction Energy, $E_{int}^{CCSD(T),corr}[3]$, for the Equilateral Triangle Configuration of the Helium Trimer with $R = 5.6$ Bohr[a]

basis set	no. of orbitals	$E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}[3]$	X^{-3}
[7s5p3d2f]	153	0.174503	
aTZ-aTZ	138	0.170133	
aQZ-aTZ	207	0.172901	0.174921
a5Z-aTZ	309	0.174150	0.175461
aTZ-aTZ	138	0.170133	
aQZ-aQZ	276	0.173285	0.175586
dTZ	96	0.169380	
dQZ	186	0.173854	0.177119
d5Z	315	0.174792	0.175775
dTZ-dTZ	192	0.170590	
dQZ-dTZ	282	0.173349	0.175362

[a] a*XZ* and d*XZ* stand for the augmented and doubly augmented correlation consistent Dunning et al. basis sets, respectively. The symbol after the dash (if present) denotes a hydrogen atom basis set located at the midpoint of each He−He pair. [7s5p3d2f] is the basis set used in ref 21 and in the present work to calculate the SAPT energies.

The results of Table 3 also show that the [7s5p3d2f] basis set used in the SAPT calculations gives very accurate nonadditive energies. In fact, this basis is closer to the estimated limit than any other basis set in Table 3, except for the d5Z basis which is more than twice its size. Thus, the basis set incompleteness error of the SAPT results should be about 1 mK.

For the CCSD(T) potential, we used the same 115 geometries (including 20 test ones) as for the SAPT potential plus additional 90 geometries chosen in the same way as described in section IV,A (the total of 205 geometries). All the CCSD(T) calculations were performed using the Molpro package.[50] The fitting was done with $\{E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}[3]\}^{-2}$ weighting factors, and the order K of the polynomial expansion in eq 13 was set to 4. The accurate values of the third-order asymptotic constants $Z_{klm}^{(3)}$ calculated by Thakkar[45] and listed in Section IV,A were used in eq 15. Because equilateral triangles with distances R as large as 20 bohr were included in our data set, the computed CCSD(T) values are very well reproduced even for such large separations, and the fit switches smoothly to the near-exact asymptotic expansion for larger values of R, reproducing the asymptotic energies with the accuracy of 1.6% for $R = 40$ bohr and 0.6% for $R = 50$ bohr.

The fitted parameters of the correlation contribution to the CCSD(T) potential are listed in Tables 4 and 5. The total three-body CCSD(T) interaction energies can be obtained by adding to this potential the $E_{\mathrm{int}}^{\mathrm{HF}}[3]$ part defined by the parameters in Table 1.

The rmsd of our $E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}$ fit for all 225 points amounts to only 1.2 mK, that is, 2 orders of magnitude smaller error than

TABLE 4: Parameters Defining the Exponential Component of the CCSD(T) Potential, Equation 13[a]

β_{000}/A_{000}	1.02323492	−0.695777316(+01)	β_{114}/A_{114}	0.635103435	0.186994020(+00)
β_{001}/A_{001}	0.80797317	−0.240165120(+03)	β_{122}/A_{122}	0.80927299	−0.820273912(+03)
β_{002}/A_{002}	1.10178293	−0.209962434(+02)	β_{123}/A_{123}	0.63929598	−0.661072697(+00)
β_{003}/A_{003}	0.763956096	0.114539354(+02)	β_{124}/A_{124}	0.896873864	0.893167071(+02)
β_{004}/A_{004}	0.925950886	−0.142434792(+01)	β_{133}/A_{133}	0.748291484	−0.280551737(+02)
β_{011}/A_{011}	2.17319126	−0.359048753(+06)	β_{134}/A_{134}	0.711804574	0.888103360(+01)
β_{012}/A_{012}	0.803302668	−0.713175529(+03)	β_{144}/A_{144}	0.723589367	−0.224561133(+01)
β_{013}/A_{013}	0.806471155	−0.561120780(+03)	β_{222}/A_{222}	0.831727968	0.944856746(+02)
β_{014}/A_{014}	0.726925042	−0.114825345(+02)	β_{223}/A_{223}	0.402971646	−0.124087026(−03)
β_{022}/A_{022}	1.16362078	0.882505820(+02)	β_{224}/A_{224}	1.15851269	−0.206922477(+03)
β_{023}/A_{023}	0.881902884	−0.100179919(+03)	β_{233}/A_{233}	0.701733884	0.533524662(+01)
β_{024}/A_{024}	0.189609292	−0.274356610(−07)	β_{234}/A_{234}	1.33426613	0.221675594(+04)
β_{033}/A_{033}	0.833405716	0.100589843(+03)	β_{244}/A_{244}	1.56146258	−0.512062851(+04)
β_{034}/A_{034}	0.809241128	−0.561186003(+02)	β_{333}/A_{333}	0.129001943	0.745390914(−09)
β_{044}/A_{044}	0.761632375	0.406204986(+01)	β_{334}/A_{334}	1.68446878	0.246997695(+04)
β_{111}/A_{111}	0.809438727	−0.348561573(+03)	β_{344}/A_{344}	0.682184651	0.172081579(+00)
β_{112}/A_{112}	1.06217955	−0.109971735(+03)	β_{444}/A_{444}	0.625278049	−0.104329381(−01)
β_{113}/A_{113}	3.11808395	−0.432527160(+10)			

[a] All quantities are in atomic units. The numbers in parentheses denote powers of 10.

TABLE 5: Parameters Defining the Damped Long-Range Components of the CCSD(T) Potential, Equations 15 and 20[a]

$Z^{(3)}_{111}$	β_{111}
0.49311	1.60003581
$Z^{(3)}_{112}$	β_{112}
0.92372	0.00864793602
$Z^{(3)}_{113}$	β_{113}
4.1241	1.64455522
$Z^{(3)}_{122}$	β_{122}
1.7377	0.117238847
$Z^{(3)}_{222}$	β_{222}
3.2839	17.3523565
$Z^{(220)}_{1111}$	$\beta^{(220)}_{1111}$
−0.626658797(+01)	1.63422576
$Z^{(221)}_{1122}$	$\beta^{(221)}_{1122}$
−0.102499779(+03)	2.72738085
$Z^{(211)}_{1221}$	$\beta^{(211)}_{1221}$
0.182949809(+03)	17.1483776
$Z^{(211)}_{2112}$	$\beta^{(211)}_{2112}$
0.286537025(+03)	1.37893363
$Z^{(220)}_{2211}$	$\beta^{(220)}_{2211}$
0.787509100(+03)	1.05412224
$Z^{(220)}_{2112}$	$\beta^{(220)}_{2112}$
0.224706875(+02)	2.15259455

[a] All quantities are in atomic units. The numbers in parentheses denote powers of 10.

for the SAPT fit. However, the accuracy of the total $E_{\mathrm{int}}^{\mathrm{CCSD(T)}}$ fit is determined by the $E_{\mathrm{int}}^{\mathrm{HF}}[3]$ component, which has the rmsd of 186 mK. Similarly as for the total SAPT fit, large absolute deviations of the $E_{\mathrm{int}}^{\mathrm{HF}}[3]$ part are restricted to the regions where $E_{\mathrm{int}}[3]$ is very large and are therefore inconsequential. The large difference between the accuracies of the $E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}$ and $E_{\mathrm{int}}^{\mathrm{HF}}[3]$ fits might seem surprising. It stems from the fact that our procedure was optimized to obtain high quality fits for each of the five terms in eq 12. In particular, because all configurations were weighted to obtain uniform relative accuracy of the components, a lot of flexibility of the fitting function was used to reproduce the exponential tails for the exchange components. Consequently, the accuracy of these components in the short range suffered. This problem does not occur in the $E_{\mathrm{int}}^{\mathrm{CCSD(T),corr}}$ fit which is dominated by terms which decay as inverse powers of interatomic separations (the same would be true if the total SAPT nonadditive energy were fitted).

C. Comparison of SAPT and CCSD(T) Potentials. The SAPT and CCSD(T) three-body nonadditive potentials are compared in Figures 3 and 4. The former figure is for the equilateral triangle with the side varying from 5.5 to 7.1 bohr, whereas the second one is for the isosceles triangle with the angle between equal sides varied from 60 to 180°. The figures show that the agreement between the two potentials (with $\epsilon_{\mathrm{disp}}^{(3)}[3]$ added to the SAPT fit) is excellent everywhere in the ranges shown. The discrepancies are typically not exceeding 2 mK. Thus, a large part of the difference, about 1 mK, is actually due to the SAPT results not including CBS extrapolations, as discussed above. One can conclude that, compared to the uncertainty resulting from the truncation level of theory, both potentials are similarly accurate.

Let us mention that one can easily compute also the SAPT nonadditive energies in the dQZ and d5Z bases and apply the extrapolation formulas to the results. This would bring SAPT results not only closer to their CBS limits but also probably closer to the CCSD(T) results. This has not been done because of the way we started our work, that is, from the set of energies computed in ref 21.

In Table 6, we have collected the most important components of our SAPT and CCSD(T) energies (both calculated ab initio and from the fits) for five selected geometries. Note that four of these geometries were also included in the tables of ref 21. We have found several errors in the latter tables. The corrected versions are included in the Supporting Information of the present paper.[51] The literature results included in Table 6 are, with one exception, the same as in ref 21, where a detailed comparison and discussion of possible sources of discrepances can be found. Probably the most often applied nonadditive helium trimer potential is a very simple one proposed by Bruch and McGee.[52] As one can see in Table 6, this potential is relatively accurate for short-range equilateral triangles. It also performs well in the very long range because of the use of an accurate $Z_{111}^{(3)}$ coefficient. However, at the minimum configuration the accuracy is poor, with a prediction over three times larger than the true value. A more elaborate potential based on ab initio calculations was developed by Parish and Dykstra.[22,23] Unfortunately, as pointed out by Szczesniak and Chalasinski,[53] as a result of the basis set superposition errors, the predictions of refs 22 and 23 are rather inaccurate. A later potential by Cohen and Murrell[24] probably suffers from similar problems for medium and large interatomic separations; see Table 6 and the discussion in ref 21. Thus, it appears that none of the published He_3 nonadditive potentials was even single-digit accurate in the whole configuration space. An exception is the SAPT fit from ref 21, which reproduces the SAPT nonadditive interaction energies at 35 isosceles triangular geometries with

TABLE 6: Nonadditive Energy Components of the Helium Trimer at Selected Configurations (in Kelvin)[a]

	(R_{AB}, R_{BC}, R_{AC})				
	(4.0, 4.0, 4.0)	(5.6, 5.6, 5.6)	(7.0, 7.0, 7.0)	(4.0, 4.0, 8.0)	(5.6, 5.6, 11.2)
$E^{(1;0)}_{exch}[3]$	−60.582028	−0.247980	−0.001625	0.431779	0.000264
$\epsilon^{(1)}_{exch}(2)[3]$	−3.022351	−0.018379	−0.000165	−0.145203	−0.000124
$\epsilon^{(1)}_{exch}(2)[3]$ (fit)	−3.034645	−0.018277	−0.000166	−0.145279	−0.000125
$E^{(2;0)}_{ind}[3] + E^{(2;0)}_{exch-ind}[3]$	−0.523973	0.000874	0.000005	−0.239646	−0.000066
$E^{(2;0)}_{exch-disp}[3]$	5.046556	0.055925	0.000910	0.305986	0.003799
$E^{(2;0)}_{exch-disp}[3]$ (fit)	4.876265	0.057685	0.000889	0.303252	0.003677
$E^{(3;0)}_{disp}[3] + E^{(3;1)}_{disp}[3]$	2.492866	0.120563	0.014933	−0.248426	−0.016848
$E^{(3;0)}_{disp}[3] + E^{(3;1)}_{disp}[3]$ (fit)	2.492006	0.120307	0.014924	−0.251241	−0.016863
$E^{(4;0)}_{disp}[3]$	−1.092299	−0.022319	−0.001091	−0.127850	−0.003130
$E^{(4;0)}_{disp}[3]$ (fit)	−1.096135	−0.022431	−0.001089	−0.127222	−0.003151
$E^{HF}_{int}[3]$	−61.990403	−0.274273	−0.001849	1.652561	0.001524
$E^{HF}_{int}[3]$ (fit)	−61.644945	−0.273200	−0.001825	1.679323	0.001489
$\delta E^{HF}_{int}[3]$	−0.884401	−0.027167	−0.000229	1.460427	0.001327
$E^{SAPT}_{int}[3] - \epsilon^{(3)}_{disp}[3]$	−58.565631	−0.138483	0.012738	1.437068	−0.014779
$E^{SAPT}_{int}[3] - \epsilon^{(3)}_{disp}[3]$ (fit)	−58.407454	−0.135916	0.012733	1.458833	−0.014974
$E^{SAPT}_{int}[3]$ (fit)	−57.674684	−0.102952	0.016837	1.387338	−0.019347
$E^{CCSD(T),corr}_{int}[3]$	5.430413	0.175776	0.016722	0.163827	−0.018035
$E^{CCSD(T),corr}_{int}[3]$ (fit)	5.432565	0.176126	0.016719	0.163871	−0.018250
$E^{CCSD(T)}_{int}[3]$[b]	−56.559990	−0.098497	0.014873	1.816388	−0.016511
$E^{CCSD(T)}_{int}[3]$ (fit)	−56.212380	−0.097074	0.014894	1.843194	−0.016761
$E_{int}[2]$ (fit)[c]	877.717	−33.014	−13.867	583.078	−22.263
$E_{int}[3]$, ref 52	−58.4840	−0.3272	0.0099	1.0260	−0.0195
$E_{int}[3]$, ref 24[d]	−54.57	0.25	0.092		
$E_{int}[3]$, ref 30	−53.9154	−0.0821			
$E_{int}[3]$, ref 54		−0.105			
$E_{int}[3]$, ref 55	−56.7005	−0.063	0.016	1.930	

[a] The SAPT components were computed in the same basis set as used in ref 21, but some values are different because of several misprints in the tables of ref 21. The corrected set of results from ref 21 is included in the Supporting Information accompanying this paper. [b] $E^{CCSD(T)}_{int}[3] = E^{CCSD(T),corr}_{int}[3] + E^{HF}_{int}[3]$. Note that the second component was obtained in the SAPT basis set. [c] Values obtained with the fit from ref 33. [d] Values interpolated in ref 21. Note that the energies in Table 1 of ref 24 are expressed in eV, not in hartrees as mistakenly stated.

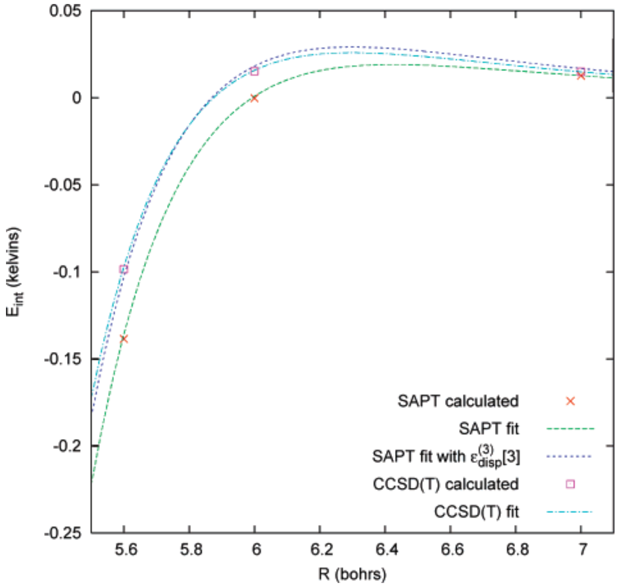

Figure 3. Comparison of SAPT and CCSD(T) potentials (in kelvin) for equilateral triangle configurations as functions of the interatomic distance (in bohr). The calculated CCSD(T) energies are obtained as sums of the calculated correlation contributions from CCSD(T) and of the calculated HF contributions in the [7s5p3d2f] basis set used in SAPT calculations (which were utilized to fit the HF part).

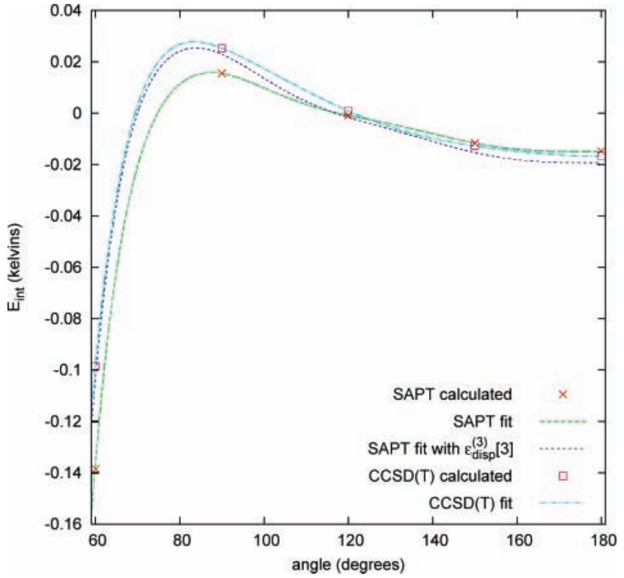

Figure 4. Comparison of SAPT and CCSD(T) potentials (in kelvin) for isosceles triangle configurations with two interatomic distances equal to 5.6 bohr as functions of the internal angle (in deg). The calculated CCSD(T) energies are obtained as sums of the calculated correlation contributions from CCSD(T) and of the calculated HF contributions in the [7s5p3d2f] basis set used in SAPT calculations (which were utilized to fit the HF part).

an rmsd of 120 mK (the corresponding value for the present SAPT fit is 27 mK). However, as mentioned earlier, this fit has a form which is too complicated for most applications.

In contrast to the discrepancies discussed above, the agreement of our results with the most elaborate literature calculations for selected points on the potential energy surface is good, in particular with the calculations of ref 54. The agreement with the SAPT calculations of refs 30 and 31 is somewhat worse but reasonable taking into account that these calculations included only the corrections $E^{(1;0)}_{exch}[3]$, $E^{(2;0)}_{exch-disp}[3]$, and a damped ATM dispersion term. The agreement is also good with the results of Roeggen and Almlof,[55] to within 9%, except for the minimum configuration where the difference amounts to 36%. Roeggen and Almlof used a method called "the extended geminal model'' supplemented by a CCSD(TQ) contribution [CCSD(T) method extended by noniterative quadruple−excitation contributions]. Roeggen and Almlof estimate the basis set incompleteness error of their result as "well below 0.01 μhartree'', and the magnitude of the level of theory truncation error as less than 0.02 μhartree. Thus, their result is -63 ± 9 mK. If the FCI contribution discussed above is added to our CCSD(T) nonadditive interaction energy, we obtain -88.5 ± 2 mK, leading to a significant discrepancy between the two calculations. The reason for this discrepancy could be, as suggested in ref 21, that for the minimum configuration the results of ref 55 were obtained by a linear interpolation from actual calculations at nearby configurations.

V. Summary

We have used SAPT and CCSD(T) methods and large basis sets to compute the three-body nonadditive contribution to the helium trimer interaction energy. The CCSD(T) results were extrapolated to the complete bases set limit. The ab initio computed energies were fitted by an analytic potential with fitting functions well representing the known physical behavior of the components of the nonadditive interaction. The SAPT and CCSD(T) potentials turned out to be very similar. The uncertainties of the potentials resulting from using finite basis sets and from fitting are about 1 mK near the trimer minimum. However, the uncertainties due to the truncation of theory can be as large as 10 mK or 10% at the minimum. We estimate that the uncertainity of the nonadditive helium trimer potential is about 10% for all configurations except for the regions where this contribution crosses zero. Thus, near the minimum, this uncertainty is of the same order of magnitude as the uncertainty of the sum of the three two-body potentials which is about 9 mK.[10,33] The uncertainty of the nonadditive component can be further reduced by performing FCI calculations for the helium trimer. Such a project is currently being pursued in our group.

The Fortran codes calculating the nonadditive three-body helium energies from the SAPT and CCSD(T) fits are available on request from the authors.

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Supporting Information Available: Full, correct versions of Tables I and II of ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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