

Helium Dimer Interaction Energies from Gaussian Geminal and Orbital Calculations[†]Wojciech Cencek,^{*,‡} Małgorzata Jeziorska,[§] Robert Bukowski,[‡] Michał Jaszuński,^{||} Bogumił Jeziorski,[§] and Krzysztof Szalewicz^{‡,⊥}

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Nonrelativistic clamped nuclei interaction energies for a pair of helium atoms have been computed using the Gaussian geminal implementation of the coupled cluster theory with single and double excitations (CCSD). Effects of triple and quadruple excitations were subsequently included employing the conventional orbital approach and very large augmented, correlation-consistent bases extended by sets of bond functions. Up to the coupled cluster doubles (CCD) level, the Gaussian geminal expansions provide nearly an order of magnitude better accuracy than orbital expansions even if the latter results are extrapolated. The recommended values of the helium dimer interaction energy are 292.54 ± 0.04 K, -11.009 ± 0.008 K, and -4.619 ± 0.007 K at the interatomic distances equal to 4.0, 5.6, and 7.0 bohr, respectively. The major contributions to the error estimates come from the orbital parts of the calculations beyond the CCSD level.

1. Introduction

Helium is an extraordinary system from the point of view of both experimental and theoretical physics. It exhibits superfluidity, one of the most striking macroscopic manifestations of the quantum character of matter. Helium also forms a new and exciting medium for high-resolution spectroscopy, the helium nanodroplets.^{1,2} Since the interactions between helium atoms are very weak, the properties of gaseous helium are closer to those of the ideal gas than properties of any other substance. Helium is therefore used as a benchmark system for thermo-physical studies of the relations between the pressure of a gas, its temperature, molar polarizability, dielectric constant, and virial coefficients.^{3,4} If the molar polarizability and the virial coefficients of helium were known with sufficient accuracy, such relations could be used to establish a new pressure standard based on capacitance measurement of the dielectric constant.^{5,6} A very accurate interatomic potential, preferably to within a few millikelvin in the well region (1 hartree = 315 774.65 K), would be required for this purpose.^{5,6} A high-quality He₂ potential is also needed to describe the very unusual bound state of this system. The depth of the potential is only about 11 K, barely accommodating one vibrational level. The wave function of this state is spread over distances of the order of 50 Å.^{7–10} Subkelvin variations in the values of the potential have a substantial impact on the binding energy, average He–He separation,^{10,11} and the scattering length. The aim of our work is to provide a He₂ potential with relative uncertainties below 0.1%, which amounts to a few millikelvin in the region of the well.

High-quality ab initio pair potentials for helium started appearing in the middle of the 1990s.¹² At that time, the accuracy

of such potentials in fact surpassed that of empirical potentials fitted to experimental data.¹³ Since 1995, more than 10 papers have been published describing large-scale calculations for He₂. These papers predicted the potential depth at the equilibrium internuclear distance $R = 5.6$ bohr ranging from -10.95 to -11.10 K, with often incompatible uncertainties.^{10–12,14–24} The lowest published rigorous upper bound to this quantity, obtained by subtracting the exact monomer energies from the variational energy of a 2400-term explicitly correlated Gaussian function,²² amounts to -10.981 K. Results with narrow error bars include the latest from a series of papers by Gdanitz,²⁰ -10.980 ± 0.004 K, the value from a previous paper from our group²⁴ equal to -11.008 ± 0.008 K, and the very recent result of unpublished Monte Carlo calculations by Anderson (cited in ref 25) amounting to -10.998 K and subject to a statistical uncertainty of $1\sigma = 0.005$ K.

The 1996 SAPT potential^{10,16} for He₂ has been used in several applications, in particular in thermal physics. As discussed by Hurly and Moldover,²⁶ quantum mechanical calculations of the second virial coefficient and of the transport properties of helium can provide more accurate results than measurements. The ab initio properties computed from the SAPT potential have been used as reference data for an acoustic viscometer,²⁷ to study helium flow properties,^{28,29} in capacitance measurements of the dielectric constant,³⁰ and to develop an interpolating and a primary low-temperature acoustic gas thermometer.³¹ Evers et al.³² have used the theoretical values of viscosities computed by Hurly and Moldover²⁶ from the SAPT potential to test the performance of their new viscometer for the case of helium gas. They found agreement to within $\pm 0.03\%$ which enabled them to calibrate viscosity and density measurements of other gases.³²

In the present paper, we report results of very accurate electronic structure calculations for the helium dimer employing the Gaussian geminal implementation^{33,34} of the coupled cluster singles and doubles (CCSD) model.^{35,36} The results for $R = 5.6$ bohr have already been utilized in ref 24 as benchmarks in

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investigations of the basis set extrapolation techniques. In addition to the CCSD energies, we have also computed the basis-set-saturated many-body perturbation theory (MBPT) energies at the second-order (MP2) and third-order (MP3) level. The interaction energies reported here have been obtained using the supermolecular approach,³⁷ that is, by subtracting the atomic energies from the total electronic energy of the dimer, both energies obtained using the same level of theory and the same basis set. This means that the basis set superposition error (BSSE) has been eliminated using the counterpoise (CP) procedure of Boys and Bernardi.³⁸

The interaction energy contributions beyond the CCSD level have been obtained by us using the conventional, orbital-based CCSD(T)^{39,40} (coupled cluster singles and doubles with non-iterative account of triple excitations) and the full configuration interaction (FCI) methods, following the approach of ref 24. Very large correlation-consistent bases (up to doubly augmented septuple-zeta in the CCSD(T) case) supplemented with large sets of bond functions have been applied. All the contributions at this level have also been CP corrected. To obtain the complete basis set limits for the triple- and quadruple-excitation contributions to the interaction energy and to estimate the error bars for these quantities, we employed extrapolation techniques tested in ref 24 for the equilibrium internuclear distance.

2. General Methodology

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

$$E_{\text{int}} = E_{\text{CCSD}} + E_{\text{T}} + \delta E_{\text{FCI}} \quad (1)$$

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

$$E_{\text{T}} = E_{\text{CCSD(T)}} - E_{\text{CCSD}} \quad (2)$$

and δE_{FCI} , defined as

$$\delta E_{\text{FCI}} = E_{\text{FCI}} - E_{\text{CCSD(T)}} \quad (3)$$

collects the remaining triple-excitation effects and the whole quadruple-excitation contribution obtained using the FCI approach. It is known that the former effects dominate δE_{FCI} .⁴¹ Unless otherwise noted, all energy symbols, such as in eqs 1–3, will always refer to the interaction energies, rather than total dimer energies. The CCSD interaction energy, E_{CCSD} , or some approximations thereto considered further on, will always include the Hartree–Fock (HF) part, obtained in the self-consistent field (SCF) procedure and denoted by E_{SCF} . The same will be assumed about $E_{\text{CCSD(T)}}$ and E_{FCI} . To denote the correlation-only part of the interaction energy predicted by method X , we shall use the symbol E_X^{cr} , for example, $E_{\text{CCSD}}^{\text{cr}} = E_{\text{CCSD}} - E_{\text{SCF}}$.

The rationale for the partitioning eq 1 are the different physical characteristics and computational requirements of the three contributions. The bulk of the (notoriously slowly convergent) correlation effects is contained in E_{CCSD} , which is ideally suited for computations employing the Gaussian-type geminals (GTGs). This basis proved to yield accuracy unreachable with orbital methods, not only in the CCSD context³³ but also at the level of the second- and third-order MBPT within the Møller–Plesset partitioning scheme (MP2 and MP3)¹⁵ and in direct variational calculations.⁴² The two remaining contributions, E_{T} and δE_{FCI} , have been calculated using orbital basis

set expansions and extrapolation techniques. These two contributions are studied separately since the dominant E_{T} term can be evaluated using much larger basis sets than those practical in FCI calculations.

The total CCSD correlation energy of a closed-shell N -electron system can be expressed as

$$E_{\text{CCSD}}^{\text{tot,cr}} = \sum_{\alpha=1}^{N/2} \epsilon_{\alpha\alpha}^1 + \sum_{\alpha<\beta}^{N/2} (\epsilon_{\alpha\beta}^1 + \epsilon_{\alpha\beta}^3) \quad (4)$$

where the pair contributions are defined by

$$\epsilon_{\alpha\beta}^s = \frac{s}{(1 + \delta_{\alpha\beta})} \langle \phi_{\alpha} \phi_{\beta} | r_{12}^{-1} | \tau_{\alpha\beta}^s + \tau_{\alpha} \tau_{\beta} + (2-s) \tau_{\beta} \tau_{\alpha} \rangle \quad (5)$$

and ϕ_{α} , $\alpha = 1, 2, \dots, N/2$, are occupied Hartree–Fock orbitals. The one- and two-electron spinless cluster functions τ_{α} and $\tau_{\alpha\beta}^s$ are defined by the set of integro-differential equations of first-quantized CCSD theory³³ and the condition of strong orthogonality to the space spanned by the occupied orbitals.⁴³ The $s = 1$ (“singlet”) and $s = 3$ (“triplet”) two-electron cluster functions (or pair functions) have definite exchange symmetry, that is, these functions are symmetric and antisymmetric, respectively, with respect to the exchange of electronic coordinates, $\tau_{\alpha\beta}^s(\mathbf{r}_2, \mathbf{r}_1) = (2-s) \tau_{\alpha\beta}^s(\mathbf{r}_1, \mathbf{r}_2)$.

The pair functions were expanded in terms of explicitly correlated Gaussian geminals $g_i(\mathbf{r}_1, \mathbf{r}_2)$, that is,

$$\tau_{\alpha\beta}^s(\mathbf{r}_1, \mathbf{r}_2) = \hat{A}^s \hat{\Pi}_{\alpha\beta} \sum_{i=1}^K c_i^{\alpha\beta s} g_i(\mathbf{r}_1, \mathbf{r}_2) \quad (6)$$

$g_i(\mathbf{r}_1, \mathbf{r}_2) =$

$$\exp(-\gamma_{1i} |\mathbf{r}_1 - \mathbf{A}_i|^2 - \gamma_{2i} |\mathbf{r}_2 - \mathbf{B}_i|^2 - \delta_i |\mathbf{r}_1 - \mathbf{r}_2|^2) \quad (7)$$

where the operator $\hat{A}^s = 1 + (2-s) \hat{P}_{12}$ (\hat{P}_{12} being the permutation operator) ensures the appropriate exchange symmetry and $\hat{\Pi}_{\alpha\beta}$ enforces the correct spatial symmetry of $\tau_{\alpha\beta}^s$, the same as the symmetry of the corresponding orbital product. For the specific case of the helium dimer, $\hat{\Pi}_{\alpha\beta} = 1 \pm \hat{i}$, where \hat{i} is the inversion in the molecular midpoint. Thus, the operators $\hat{\Pi}_{11}$ and $\hat{\Pi}_{22}$ symmetrize and the operator $\hat{\Pi}_{12}$ antisymmetrizes $g_i(\mathbf{r}_1, \mathbf{r}_2)$ with respect to the inversion. The nonlinear parameters γ_{1i} , \mathbf{A}_i , γ_{2i} , \mathbf{B}_i , and δ_i are to be determined by a nonlinear optimization procedure. To guarantee the Σ^+ symmetry of the pair functions, the vectors \mathbf{A}_i and \mathbf{B}_i are constrained to lie on the axis defined by the nuclei. The one-electron cluster functions $\tau_{\alpha}(\mathbf{r})$ are expanded in terms of the floating Gaussian orbital basis

$$\tau_{\alpha}(\mathbf{r}) = \hat{\Pi}_{\alpha} \sum_{i=1}^L c_i^{\alpha} \exp(-\gamma_i |\mathbf{r} - \mathbf{C}_i|^2) \quad (8)$$

where the operator $\hat{\Pi}_{\alpha}$ plays a similar role as $\hat{\Pi}_{\alpha\beta}$, that is, for the He dimer, $\hat{\Pi}_1$ symmetrizes and $\hat{\Pi}_2$ antisymmetrizes with respect to inversion.

In general, the functions 6 and 8 would have to contain prefactors of powers of Cartesian coordinates ensuring their proper symmetry and basis set completeness.^{44,45} In the present case, when all one-electron cluster functions are of σ symmetry and all pair functions of Σ^+ symmetry, these prefactors can be dropped without affecting the completeness of the basis set, as long as the Gaussian centers \mathbf{A}_i , \mathbf{B}_i , and \mathbf{C}_i are distributed along some finite segment of the internuclear axis and the exponents are allowed to assume all positive values.^{44,45} In our calculations

the centers were allowed to move along the axis within 10 bohr from the center of the molecule and the exponents δ_i could assume the value of zero, in addition to the positive values required by the completeness criteria. The linear coefficients c_i^α and $c_i^{\alpha\beta s}$ of eqs 8 and 6 were found by solving iteratively the first-quantized CCSD equations.³³ Accurate (or even reasonable) results can be obtained only with a suitable choice of the nonlinear parameters γ_{1i} , \mathbf{A}_i , γ_{2i} , \mathbf{B}_i , δ_i , γ_i , and \mathbf{C}_i . In the present work we followed ref 33 and optimized these parameters by minimizing the total MP2 energy of the dimer, except for γ_i and \mathbf{C}_i which were obtained by minimizing the single-excitation contribution to the fourth-order MBPT energy of the dimer. The details of the nonlinear optimization procedure are presented in section 3.

To avoid BSSE, the geminal and orbital basis sets optimized for the dimer were also used in the coupled cluster and MBPT calculations for the monomer (see section 3.2 for a detailed discussion of this issue). The only monomer pair function τ_{11}^1 was represented using the same geminals g_i as those used in eq 6 for the dimer pair functions, according to the formula

$$\tau_{11}^1(\mathbf{r}_1, \mathbf{r}_2) = \hat{A}^1 \sum_{i=1}^K (c_i g_i(\mathbf{r}_1, \mathbf{r}_2) + \tilde{c}_i \hat{g}_i(\mathbf{r}_1, \mathbf{r}_2)) \quad (9)$$

where the coefficients c_i and \tilde{c}_i are independent. Similarly, the one-electron cluster function τ_1 of the monomer was expanded in the $2L$ -term basis containing all the orbitals used in eq 8 and all the functions obtained from these orbitals by applying the inversion operation \hat{i} . Note that expansions similar to eq 9, with g_i and \hat{g}_i treated as independent basis functions, could have been used also in the case of the dimer. However, the symmetry of the dimer Hamiltonian implies that, in this case, $c_i = \pm \tilde{c}_i$ and thus the symmetry-adapted functions $\hat{\Pi}_{\alpha\beta g_i}$ were employed instead.

The number of three- and four-electron integrals in GTG calculations is significantly reduced if the so-called weak orthogonality (WO) approach⁴³ is employed. In this approach, the strong orthogonality conditions are imposed on the cluster functions approximately by means of a penalty function rather than by the explicit projection of raw geminals. Further reductions of the computational cost are achieved by the use of the approximate projection technique⁴⁴ which allows one to omit costly projectors in several terms of the CCSD equations.³³ Combination of this technique with the WO approach, referred to as the superweak orthogonality plus projection (SWOP) method, becomes exact in the limit of the complete geminal basis set. All geminal MP2 and coupled cluster calculations reported in this work have been performed using the WO and SWOP methodology, respectively. The MP3 energies were obtained using the WO first-order pair functions approximately projected before being inserted into the third-order formula.

With simplifications resulting from SWOP, the computational burden of the complete explicitly correlated CCSD method scales approximately as $M^4 K^2 + M^2 K^3$, assuming that $M = L$, where M is the number of basis functions in the expansion of the occupied Hartree–Fock orbitals and K and L are defined in eqs 6 and 8, respectively. Calculation of four-electron integrals is still required, most of them in expressions containing one-electron cluster functions. Unlike in the conventional orbital case, the geminal implementation of the coupled cluster doubles (CCD) theory⁴⁶ is computationally much less expensive than the full CCSD treatment. The scaling of computational cost of CCD in the SWOP approach is $M^2 K^3 + M^4 K$. Although typically $K \approx M^2$ and therefore the $M^4 K^2$ term dropped when going from

CCSD to CCD has the overall scaling similar to the $M^2 K^3$ term, the prefactor of the former term is much larger than that of the latter.

It has been found^{33,47} that the contribution of the nonfactorizable diagrams, which generate $\sim M^2 K^3$ four-electron integrals in the CCD equations, is very small and rather easy to converge with small geminal basis sets. The neglect of these diagrams leads to the so-called factorizable CCD (FCCD) method, defined in ref 47, which scales as $M^4 K + M^2 K^2$ in the SWOP approach and requires only two- and three-electron integrals. In the context of orbital coupled cluster theory, the FCCD method has been considered by Adams et al.^{48,49} and by Chiles and Dykstra.⁵⁰ Since the FCCD contribution to the interaction energy converges considerably slower with K , in absolute terms, than the (small) contributions from the remaining, computationally more demanding levels of the CCSD theory, the FCCD interaction energy was computed with substantially larger geminal basis sets. This strategy leads to the following partitioning of the CCSD and CCD interaction energies

$$E_{\text{CCSD}} = E_{\text{CCD}} + E_S \quad (10)$$

$$E_{\text{CCD}} = E_{\text{FCCD}} + E_{\text{NF}} \quad (11)$$

where E_{CCD} (E_{FCCD}) is the interaction energy in the CCD (FCCD) approximation, whereas E_S and E_{NF} terms, defined by the equations above, are contributions of single excitations and nonfactorizable CCD diagrams, respectively.

3. Optimization of the Nonlinear Parameters

3.1. SCF Basis Sets. The first-quantized CCSD equations are strictly valid only in the limit of the exact solution of the Hartree–Fock problem. To reduce uncertainties due to the use of approximate solutions, fairly good quality SCF bases should be used. On the other hand, since the cost of CCSD calculations in geminal bases scales as the fourth power of the SCF basis set size M , one would like to use as compact SCF basis sets as possible. With the time requirements of the current geminal codes, large traditional basis sets containing hundreds of Gaussian orbitals are impractical. In fact, it would be pointless to use such basis sets, which are mainly aimed at describing electron correlation effects, when one needs only to describe the ground-state HF orbitals. Thus, the geminal CCSD calculations usually employ compact yet accurate expansions in spherical Gaussian functions, such as those appearing in eq 8, with carefully optimized exponents and centers. The starting point for the SCF optimization was obtained by adding to atom-centered functions optimized for the SCF energy of the helium atom a number (20–80% depending on R and M) of functions scattered between the nuclei, with the more diffuse Gaussian orbitals placed closer to the center of the molecule. The whole space of the $2M$ nonlinear parameters was then optimized by the Powell method of conjugate directions,⁵¹ with the linear parameters evaluated in each step by the usual SCF procedure. The total dimer SCF energies obtained for different values of M , as well as CP-corrected SCF interaction energies are listed in Table 1. We have also calculated strict upper bounds $E_{\text{SCF}}^{\text{ub}}$ to the Hartree–Fock interaction energies by subtracting twice the accurate helium atom HF energy of $-2.861\,679\,995\,612\,21$ hartree⁵³ from the dimer energies. To further assess the quality of the optimized basis sets, we prepared a reference set in the following way. In the largest basis used in our orbital calculations (see the description of basis sets in section 5), a7Z+b135, we replaced all 15 s functions on each atom (contracted to 8 s) by a new uncontracted set of 32 s functions with exponents

TABLE 1: Total Dimer SCF Energies E (in hartrees), Interaction Energies E_{SCF} , and Strict Upper Bounds to the Interaction Energy $E_{\text{SCF}}^{\text{ub}}$ (Both in kelvin) Computed Using Basis Sets Optimized in the Present Work

M^a	E	E_{SCF}	$E_{\text{SCF}}^{\text{ub}}$
$R = 4.0$ bohr			
10	-5.721 960 737 870	436.595 66	441.848 74
16	-5.722 001 211 419	428.801 65	429.068 22
24	-5.722 002 054 475	428.782 31	428.802 00
32	-5.722 002 091 804	428.781 93	428.790 21
(a7Z+b135)+32 ^b	-5.722 002 115 291	428.782 78	428.782 80
$R = 5.6$ bohr			
10	-5.723 316 545 900	9.306 28	13.718 93
16	-5.723 330 598 175	9.233 79	9.281 58
24	-5.723 330 786 077	9.221 64	9.222 24
32	-5.723 330 792 855	9.220 00	9.220 10
(a7Z+b135)+32 ^b	-5.723 330 793 142	9.219 99	9.220 01
$R = 7.0$ bohr			
10	-5.723 345 086 007	0.294 27	4.706 69
16	-5.723 359 003 124	0.291 71	0.312 02
24	-5.723 359 077 527	0.288 39	0.288 52
32	-5.723 359 078 954	0.287 97	0.288 07
(a7Z+b135)+32 ^b	-5.723 359 079 180	0.287 97	0.288 00

^a M denotes the number of symmetry-unique basis functions (the dimension of the Fock matrix is $2M$). ^b The aug-cc-pV7Z Dunning et al. type basis set published by Gdanitz¹¹ with s functions replaced by the 32s set on each atom optimized by us plus the 6s6p6d3f3g3h set of bond functions developed by Partridge and Bauschlicher.⁵²

optimized for the Hartree–Fock energy of the helium atom. This basis, containing 561 functions, reproduces the monomer HF energy given above with an error of only 0.014 mK. The interaction energies obtained in this basis are listed in the last row of each series in Table 1. Since the monomer energy is so accurate, the upper bounds are almost equal to the regular CP-corrected values for all three distances. This equality does not mean, of course, that the values of E_{SCF} are converged to ~ 0.01 mK. Neither can we assume that the SCF interaction energies in the reference, 561-orbital basis are closer to the exact values than those computed in our largest, $M = 32$, floating s -symmetry bases. However, since the differences are only 0.85, 0.01, and 0.00 mK for $R = 4.0$, 5.6, and 7.0 bohr, respectively, for all practical purposes the two sets of bases give identical results. Since the discussed bases have been obtained by very different procedures, this agreement seems to suggest that the exact HF interaction energies are reproduced by the best results in Table 1 to within about 0.0001%. On the other hand, the convergence patterns for the floating s -symmetry bases displayed in Table 1 point to a lower accuracy. The change of E_{SCF} between $M = 24$ and $M = 32$ is 0.38, 1.64, and 0.42 mK for $R = 4.0$, 5.6, and 7.0 bohr, respectively. On the basis of these values, the accuracy of the $M = 32$ results has to be significantly downgraded. Combining both estimates, we assigned, rather conservatively, the errors of the E_{SCF} values as 1, 0.1, and 0.1 mK, respectively (relative errors of 0.0002%, 0.001%, and 0.03%). Thus, the Hartree–Fock component of the interaction energy has been computed with an error negligible compared to the errors of other components discussed later.

From the monotonically decreasing behavior of the series in M (for all R), one may expect that at the limit of infinite basis the SCF interaction energies will be a little below the lowest computed values. To account for this anticipated lowering at $R = 5.6$ and 7.0 bohr, we have decreased the lowest computed result by about 0.1 mK as suggested by the convergence rate, that is, we have chosen the limit values as 9.2199 and 0.2879 K, respectively. Then the best computed results are within the estimated error bars. We have also fitted the SCF interaction

energies for $R = 4.0$ and 5.6 bohr to the function $E(M) = E_{\infty} + \alpha e^{-\gamma M}$. For $R = 5.6$ bohr the limit value from the fit is 9.220 15 K, slightly above the upper error bar and in fact 0.05 mK above our best upper bound. We believe this is due to an incomplete optimization of the $M = 24$ function since the corresponding interaction energy lies distinctly above the fit. For $R = 4.0$ bohr the limit value from the fit was 428.7821 K, above the lowest computed value. Since the SCF interaction energy is not a variational quantity, getting below the limit value is possible, in particular if our optimizations put too much emphasis on the dimer component of the basis set at the expense of the monomer-centered part. With this insight, we took 428.782 ± 0.001 K as the best estimate of E_{SCF} for $R = 4.0$ bohr.

A clear conclusion from the results presented above is that indeed one can use floating Gaussian expansions much more compact (about 10 times shorter) than the standard bases to represent the occupied HF orbitals at a given level of accuracy.

3.2. Two- and One-Electron Cluster Functions. The parameters of the GTG functions of eq 7 were optimized with respect to the total MP2 correlation energy of the He dimer by minimizing the second-order functional being a sum of the Hylleraas-type pair functionals (see eq 13 of ref 15). Although the first-order pair functions, obtained from such minimizations, are obviously not identical with the converged CCSD cluster functions, if the geminal basis is large enough, the linear parameters can compensate for the not fully optimal nonlinear parameters, as shown by the results of ref 33. The minimizations of the functional (separately at each value of R) were performed in cycles running through all K Gaussian geminals. To optimize each geminal in a given cycle, just one iteration of the standard Powell method⁵¹ was executed. Since the parameters of all the geminals are mutually coupled through the minimized functional, it is advantageous not to fully converge the Powell procedure in each step but rather to return to each geminal more times (perform more cycles). Before performing the cycles, the initial values of the nonlinear parameters were obtained with the following “shoot-and-sort” procedure. First, for a geminal of the form of eq 7, 80 sets of parameters were randomly generated. The set giving the lowest value of the MP2 functional was then optimized with one Powell iteration. The process continued, increasing the size of the basis set by one in consecutive steps, until this size reached K . In a given step, all the geminals from previous steps were held fixed. This strategy proved extremely successful in Rayleigh–Ritz variational calculations.⁴² In almost all of the optimization cycles, the shorter SCF expansions from Table 1 were used ($M = 16$). In the final cycle, $M = 24$ was applied. To test the convergence of the results at all the levels of theory considered in this work, we generated expansions of different lengths, from $K = 300$ ($K = 75$ for $R = 5.6$ bohr) to $K = 800$. Each optimization was done independently, that is, the optimizations of larger expansions did not use any information from the shorter functions.

In Gaussian geminal computations of the MP2 energy performed in the past, different geminal basis sets (different nonlinear parameters) were usually employed for different α , β , and s , that is, for different pair functions. Since at the MP2 level each pair yields a separate contribution, this choice is optimal. In the present work we decided to represent each pair function using a universal geminal basis, as indicated by eq 6. This choice is dictated by three factors. *First*, as shown in ref 15, in calculations of the interaction energies rather than of the total energies only, the universality of the geminal basis is necessary if the interaction energy is to be made free from BSSE

by the use of the CP scheme. Although this problem ceases to be important as the basis approaches the completeness limit, calculations in smaller bases, farther from this limit, are also necessary to assess the convergence of the results. Such BSSE-free calculations would not be possible if each pair function were expanded in its own, individually optimized geminal basis.¹⁵ *Second*, from the analysis of ref 15 it is clear that, in the case of the He dimer, the geminals optimal for *each* of the singlet pair functions have to describe essentially the same physical effects, correlation within the monomers and the dispersion interaction, whereas the triplet pair τ_{12}^3 only accounts for the latter effect. It follows that the individual optimizations of singlet pairs would in fact yield three geminal bases very similar to one another, and an optimization of a basis for the triplet pair would replicate dispersion-specific geminals already present in the singlet pair bases. Because of this redundancy between different pair functions of He₂, the accuracy achieved with four individually optimized bases, each of length K , can be easily matched using just one universal basis of length only slightly larger than K , optimized to simultaneously reproduce all pair functions. Such an approach shortens the overall time spent on optimizations. *Third*, the use of universal bases dramatically reduces the time requirements of the subsequent CCSD calculations. In contrast to the MP2-level theory, the CCSD equations couple different pair functions. Therefore, when such calculations are performed in a universal geminal basis, the number of costly many-electron integrals can be an order of magnitude smaller than it would be if each pair function were expanded in its individual basis set.

The high efficiency of the CP method in the context of Gaussian geminal calculations of the interaction energy was demonstrated earlier in ref 15. In fact, it is impossible to define a non-CP-corrected interaction energy and calculate the magnitude of BSSE in an unambiguous way using a generally optimized GTG basis. This is because the Gaussian centers are distributed at many points along the internuclear axis (floating-center basis), and the monomer part of the basis cannot be uniquely defined. This is in contrast to ref 15, where the pair functions were built as combinations of monomer bases and dispersion bases, which enabled an approximate evaluation of BSSE. For $R = 5.6$ bohr, this BSSE was,¹⁵ for example, 33 and 1 mK in bases of length 120 (*D60M60*) and 340 (*D190M150*), respectively. These results show that in the largest basis sets used by us, containing 800 geminals, the BSSE would be negligible even if it were not removed by the CP approach.

The universal basis approach has also been employed in the case of the one-electron cluster functions. The nonlinear parameters of the orbital basis sets from eq 8 were determined separately for each R by optimizing the single-excitation contribution to the MP4 energy of the dimer (see ref 33 for details). Similarly to the two-electron case, this choice corresponds to finding optimal second-order single-excitation functions rather than the converged CCSD ones, an approximation which works very well in practice.³³

During the optimizations of geminal bases, the strong orthogonality condition was imposed within the WO scheme, that is, using a penalty function with the η parameter (see ref 33) ranging from 0.1 to 0.05, depending on the progress of the optimization and the internuclear distance R . The WO approach was also applied to force the orthogonality of the one-electron cluster functions during the MP4 optimizations of the corresponding bases, with $\eta = 0.01$. The first-order pair functions employed in these optimizations were obtained with $\eta = 0$ and approximately projected before insertion into the MP4 func-

TABLE 2: Convergence of Interaction Energy Contributions (in kelvin) with the SCF Basis Size M for $K = 300$ (Upper Part) and with the GTG Basis Size K for $M = 24$ (Lower Part) at $R = 5.6$ bohr

$K = 300$					
M	E_{MP2}^{cr}	E_{MP3}^{cr}	E_{FCCD}^{cr}	E_{NF}	E_S
10	-15.963 49	-2.508 20	-18.168 62	0.017 86	-0.196 40
16	-16.001 83	-2.512 44	-18.199 83	0.018 13	-0.176 36
24	-16.008 95	-2.513 37	-18.207 56	0.018 16	-0.176 92
32	-16.010 06	-2.513 54	-18.208 80		
$M = 24$					
K	E_{MP2}^{cr}	E_{MP3}^{cr}	E_{FCCD}^{cr}	E_{NF}	E_S
75	-15.818 40	-2.381 23	-17.699 94	0.000 69	-0.153 92
150	-15.976 14	-2.505 16	-18.155 24	0.018 07	-0.176 17
300	-16.008 95	-2.513 37	-18.207 56	0.018 16	-0.176 92
600	-16.010 67	-2.513 77	-18.209 89		
800	-16.010 76	-2.513 79	-18.210 21		
$M = 32$					
800	-16.011 86	-2.513 96	-18.211 44		

tional, which is consistent with the spirit of the SWOP approach. All the final coupled cluster and MBPT results reported in this work have been calculated using the parameter η set equal to 0 for the pair functions and 0.01 for the one-electron cluster functions.

The contribution E_S in eq 10 depends on three separate basis sets with the expansion lengths M , K , and L . In studying the convergence patterns of CCSD interaction energies, three degrees of freedom in expansion lengths would require too large a number of independent calculations. Therefore, we used the constraint $L = M$. In each CCSD run, defined by particular values of M and K , the nonlinear parameters in eq 8 assumed the values optimized earlier using the M -term and K -term expansions for the SCF orbitals and MP2 pair functions, respectively. The starting values of the nonlinear parameters used in the optimizations of the single-excitation basis sets were those of the SCF functions of the same length.

4. Results of Geminal Calculations

The most extensive GTG calculations, employing the largest number of combinations of M and K , were performed at the equilibrium distance $R = 5.6$ bohr. The results of these calculations had already been utilized in ref 24 to investigate extrapolations of orbital methods. These results were also used to develop a strategy which could be subsequently employed in GTG computations at the other distances, allowing us to limit the number of runs. From all the optimized GTG pair functions of the form of eq 6 ($K = 75, 150, 300, 600, 800$), the 300-term expansion is the largest one we could use within reasonable computer resources at all levels of theory up to CCSD. One full CCSD calculation with $M = 24$, $K = 300$, and $L = 24$ required about 7000 cumulative CPU hours on a Beowulf cluster with 1 GHz Athlon nodes.

4.1. Convergence with M . We first tested how fast different contributions to the interaction energy saturate with respect to M . These tests were done with $K = 300$. The results for $R = 5.6$ bohr and $M = 10, 16$, and 24 are listed in the upper part of Table 2. E_{MP2}^{cr} and E_{FCCD}^{cr} are seen to be most sensitive to the quality of the reference SCF wave function. We have calculated them also with our largest SCF expansion, $M = 32$, which changed these quantities by -1.1 and -1.2 mK, respectively, compared to the $M = 24$ results. E_{MP3}^{cr} is seen to converge much faster with M , changing only by -0.17 mK when going from $M = 24$ to $M = 32$. Since each step in our sequence of

values of M results in an increment of the interaction energy components that is several times smaller than the increment obtained in the previous step, we can predict that $M = 32$ yields the values of $E_{\text{MP2}}^{\text{cr}}$ and $E_{\text{FCCD}}^{\text{cr}}$ saturated in the size of the SCF basis at least to 0.3 mK ($E_{\text{MP3}}^{\text{cr}}$ at least to 0.1 mK). Another argument supporting this conclusion is the observation that the increments of these quantities are almost linear functions of the increments of E_{SCF} (when enlarging M for $R = 5.6$ bohr, the changes of E_{SCF} are 72, 12, and 1.6 mK, cf. Table 1, and the changes of $E_{\text{MP2}}^{\text{cr}}$ are 38, 7.1, and 1.1 mK). As discussed above, E_{SCF} for $M = 32$ should be within 0.1 mK from the infinite basis set limit. Thus, the $E_{\text{MP2}}^{\text{cr}}$ versus E_{SCF} extrapolation leads to an estimate of the uncertainty of $E_{\text{MP2}}^{\text{cr}}$ due to truncation of M amounting to about 0.1 mK, not far from the estimate given above.

The observation that the increments of the SCF and MP2 interaction energies with changing M are of similar size is different than that for the total SCF and MP2 energies in the earlier work with geminal bases. As shown in ref 54 (see Table V in that reference), the total SCF energies and the MP2 (correlation) energies have *relative* errors of similar magnitude. Therefore, since the SCF energies are about 2 orders of magnitude larger than the correlation energies, the latter have about two more significant digits than the former. It appears that the differences between this behavior and the one observed now for the interaction energies is mainly due to the greater sensitivity of the dimer MP2 energies to the quality of the SCF functions compared to the monomer energies investigated in ref 54. As an example, consider the results for $R = 4.0$ bohr, $M = 10$, and $K = 300$ (notice that the errors due to the truncation in K are not discussed here). As reference results for M becoming infinite, we will use estimates obtained in the same way as described above, although from the point of view of the present discussion the results for $M = 32$ would work equally well. The monomer total SCF and MP2 energies for $M = 10$ are in errors of 8.3 and 0.2 μ hartree, respectively, not far from the 2 orders of magnitude ratio expected from the conclusions of ref 54. However, the same quantities for the dimer are 41 and 7 μ hartree, the ratio of only 6. Furthermore, in the MP2 case, the error of the interaction energy equal to 6.4 μ hartree is almost the same as the error of the total energy (as it has to be, because of the relation between the errors of the dimer and monomer quoted above), but in the SCF case there is some cancellation of errors and the SCF interaction energy is accurate to 25 μ hartree. This leads to the errors of the SCF and MP2 interaction energies that are indeed of similar size.

For $R = 5.6$ bohr, the small term E_{NF} is fairly insensitive to the quality of the SCF function and appears to be converged to below 0.1 mK with $M = 24$. This conjecture is supported by the orbital results (see discussion in section 5.1). It is more difficult to estimate the convergence of E_{S} , because the value for $M = 10$ is far apart from those for $M = 16$ and $M = 24$, and one might even consider the small difference between the two latter results as coincidental. One may expect to see a more erratic convergence pattern for E_{S} than for other quantities in Table 2 since each step involves a changed M and L . However, the value for $M = 24$ equal to -177 mK is consistent with the extrapolations of orbital calculations described in ref 24 for $R = 5.6$ bohr and discussed later (for all three separations) in section 5.1.

Results for $R = 7.0$ and 4.0 bohr analogous to those for $R = 5.6$ bohr discussed above are presented in Tables 3 and 4, respectively. For $R = 7.0$ bohr, the convergence with M (when expressed in absolute numbers) is better than it is at $R = 5.6$

bohr: going from $M = 16$ to $M = 24$ changes $E_{\text{MP2}}^{\text{cr}}$ by -1.4 mK (compared with -7 mK) and from $M = 24$ to $M = 32$ by only -0.3 mK (compared with -1.1 mK). However, this just reflects the decreased magnitudes of all components. On the other hand, the difference between the E_{S} contributions at $M = 16$ and $M = 24$ is surprisingly large (1.3 mK), and we would have to ascribe an uncertainty of 1–2 mK to this quantity, based only on the GTG convergence in M . Furthermore, at $R = 7.0$ bohr (and also at 4.0 bohr), we have not investigated the convergence of E_{S} in K . However, as will be shown in section 5.1, extrapolated values computed in orbital basis sets agree with the $M = L = 24$, $K = 300$ geminal results and allow us to provide reliable estimates of the limits and of the error bars. The E_{NF} contribution appears to be converged to 0.01 mK at $R = 7.0$ bohr.

For $R = 4.0$ bohr (see Table 4) the difference at the $E_{\text{MP2}}^{\text{cr}}$ level between the $M = 24$ and $M = 32$ results amounts to only 0.14 mK, compared to 1.1 mK at $R = 5.6$ bohr, despite the fact that $E_{\text{MP2}}^{\text{cr}}$ is 7 times larger in magnitude at $R = 4.0$ bohr. Most likely this reflects problems with the optimization of the SCF bases for this distance and the fact that the 32-term SCF function is not as well optimized as the 24-term function, rather than the true saturation of the results with respect to M . In any case, $E_{\text{MP2}}^{\text{cr}}$ and all the other quantities in Table 4 are clearly better converged in relative terms than for $R = 5.6$ bohr.

4.2. Convergence with K . Once we have established the influence of the SCF basis size M on the MBPT and CCSD interaction energies, we can analyze the convergence of various quantities with the GTG basis expansion length K . Ideally, one should perform for this purpose a series of calculations using in all of them the most accurate SCF function, $M = 32$. This would be, however, neither practical nor necessary, because the convergence pattern with respect to K remains almost identical as long as any SCF function with a sufficiently high accuracy is used throughout the whole series. We decided to use $M = 24$ for this purpose and—only after finishing the whole K -dependent series of runs—repeat the calculations with the most accurate GTG basis ($K = 800$) and $M = 32$ for the contributions most sensitive to M ($E_{\text{MP2}}^{\text{cr}}$ and $E_{\text{FCCD}}^{\text{cr}}$) and also for $E_{\text{MP3}}^{\text{cr}}$ since this term is relatively inexpensive.

The K -dependence of the results at $R = 5.6$ bohr is presented in the lower part of Table 2. The convergence in each column is monotonic and quite smooth, with the exception of the $K = 75$ results in the last two columns. The analysis of the differences in each series reveals that $E_{\text{MP3}}^{\text{cr}}$ exhibits the fastest convergence rate, followed by $E_{\text{MP2}}^{\text{cr}}$. The increments, when going from $K = 600$ to $K = 800$, are -0.09 and -0.32 mK for $E_{\text{MP2}}^{\text{cr}}$ and $E_{\text{FCCD}}^{\text{cr}}$, respectively. Thus, $E_{\text{FCCD}}^{\text{cr}}$ saturates almost as fast as $E_{\text{MP2}}^{\text{cr}}$, which is consistent with our assumption that the first-order pair functions are rather good approximations to the fully iterated cluster functions. In all the three columns, by doubling the basis set size, one gets roughly one more significant digit, similarly as in GTG Rayleigh–Ritz variational calculations on two-electron systems.⁴² This is not surprising since in both cases the dominant effect is the two-body correlation. A perusal of the results in the lower part of Table 2 allows one to roughly estimate that the final $E_{\text{MP3}}^{\text{cr}}$ values are probably converged in K to a fraction of 0.1 mK and $E_{\text{MP2}}^{\text{cr}}$ and $E_{\text{FCCD}}^{\text{cr}}$ to about one digit less. A more rigorous discussion of the convergence will be given in section 4.3. We observe that, in all the three cases, the effect of going from $M = 24$ to $M = 32$ is, to within 0.01

TABLE 3: Convergence of Interaction Energy Contributions (in kelvin) with the SCF Basis Size M for $K = 300$ (Upper Part) and with the GTG Basis Size K for $M = 24$ (Lower Part) at $R = 7.0$ bohr

$K = 300$					
M	E_{MP2}^{cr}	E_{MP3}^{cr}	E_{FCCD}^{cr}	E_{NF}	E_S
10 ^a	-3.777 37	-0.677 68	-4.421 07	-0.003 41	-0.046 33
16	-3.778 08	-0.678 20	-4.416 47	-0.003 40	-0.042 93
24	-3.779 43	-0.678 36	-4.417 94	-0.003 39	-0.044 26
32	-3.779 78	-0.678 41	-4.418 32		
$M = 24$					
K	E_{MP2}^{cr}	E_{MP3}^{cr}	E_{FCCD}^{cr}		
300	-3.779 43	-0.678 36	-4.417 94		
600	-3.780 92	-0.678 76	-4.419 31		
800	-3.780 99	-0.678 77	-4.419 37		
$M = 32$					
800	-3.781 34	-0.678 82	-4.419 77		

^a The linear equation system not positive-definite (see text).

TABLE 4: Convergence of Interaction Energy Contributions (in kelvin) with the SCF Basis Size M for $K = 300$ (Upper Part) and with the GTG Basis Size K for $M = 24$ (Lower Part) at $R = 4.0$ bohr

$K = 300$					
M	E_{MP2}^{cr}	E_{MP3}^{cr}	E_{FCCD}^{cr}	E_{NF}	E_S
10	-115.460 19	-11.174 89	-121.506 78	0.473 77	-0.671 86
16	-117.485 44	-11.402 64	-123.574 11	0.487 11	-0.736 04
24	-117.493 31	-11.403 25	-123.582 16	0.487 18	-0.735 87
32	-117.493 45	-11.403 26	-123.582 29		
$M = 24$					
K	E_{MP2}^{cr}	E_{MP3}^{cr}	E_{FCCD}^{cr}		
300	-117.493 31	-11.403 25	-123.582 16		
600	-117.498 71	-11.404 50	-123.596 15		
800	-117.498 97	-11.404 60	-123.597 13		
$M = 32$					
800	-117.499 11	-11.403 61	-123.597 29		

mK, the same when using GTG expansions with $K = 300$ and $K = 800$. This shows that the errors in M and K are indeed cumulative.

Tables 3 and 4 present the results for $R = 7.0$ and 4.0 bohr, obtained in the same way as just discussed, with the exception that we did not use the shortest GTG expansions ($K = 75$ and 150). The convergence patterns of the E_{MP2}^{cr} and E_{MP3}^{cr} components with respect to K at 7.0 bohr are similar to those at 5.6 bohr, and E_{FCCD}^{cr} converges here as fast as E_{MP2}^{cr} . It should be noted that at $R = 7.0$ bohr the accuracy of the shortest SCF function turned out to be insufficient to ensure the positive-definite character of the system of equations used to find the linear coefficients of the pair functions of eq 6. As a result, the values in this row carry larger errors, apparent in particular in the case of E_{FCCD} .

At $R = 4.0$ bohr (see Table 4) most contributions are converged to about one significant digit less than at the two other distances. This is mainly because the helium–helium interaction is stronger and the interaction energy is about 30 times larger in magnitude for $R = 4.0$ than for $R = 5.6$ bohr. However, apparently the wave functions are more complicated at $R = 4.0$ bohr than for larger distances since we encountered more problems with optimizations in this case. Nevertheless, in relative terms the results for $R = 4.0$ bohr are actually more accurate than for $R = 5.6$ bohr, as expected in the supermolecular approach.

4.3. Recommended Values and Error Bounds. Table 5 summarizes our recommended values of the components of the interaction energy computed using GTG basis sets. In the case of E_{MP2}^{cr} , E_{MP3}^{cr} , and E_{FCCD}^{cr} , the errors of each quantity E were obtained as sums of the independent M - and K -related uncertainties. Since the convergence with respect to both M and K is monotonic, the exact values of E most likely lie below the computed ones. Let us define a quantity ΔE_N (where $N \equiv M$ or $N \equiv K$) in such a way that the unknown saturated value of E (corresponding to $N = \infty$) is contained between the most accurate calculated result (i.e., the result for $M = 32$ and $K = 800$), E_{calc} , and $E_{calc} + \Delta E_N$. The values of ΔE_N will be chosen as small as possible based on the patterns of convergence in N . The values of ΔE_M for E_{MP2}^{cr} , E_{MP3}^{cr} , and E_{FCCD}^{cr} , respectively, were assumed as -0.3 , -0.1 , and -0.3 mK at $R = 5.6$ bohr, as discussed previously. A similar analysis led us to the estimates of -0.2 , -0.06 , and -0.2 mK at $R = 7.0$ bohr and -3 , -1 , and -3 mK at $R = 4.0$ bohr, respectively. To estimate ΔE_K , we notice that doubling of the geminal basis set typically improves the accuracy by one additional digit. Thus, it seems safe to set ΔE_K equal to twice the difference between the results calculated with $K = 800$ and $K = 600$. For example, in the case of the E_{MP2}^{cr} energy, this gives -0.52 , -0.18 , and -0.14 mK for $R = 4.0$, 5.6 , and 7.0 bohr, respectively.

We next assume that the basis set converged result, E , is $0.5(\Delta E_K + \Delta E_M)$ below the $K = 800$, $M = 32$ result, denoted by E_{calc} . Thus, our recommended (complete basis set limits) values of E_{MP2}^{cr} , E_{MP3}^{cr} , and E_{FCCD}^{cr} energies and the errors of these values are given by the formula

$$E = \left[E_{calc} + \frac{1}{2}(\Delta E_M + \Delta E_K) \right] \pm \frac{1}{2}(\Delta E_M + \Delta E_K) \quad (12)$$

Although our estimation procedure may seem overly cautious, it leads to uncertainties for E_{MP2}^{cr} , E_{MP3}^{cr} , and E_{FCCD}^{cr} of the order of 0.1 mK at $R = 5.6$ and 7.0 bohr and 1 mK at $R = 4.0$ bohr, which are small compared to the uncertainties of some remaining components of the interaction energy discussed later on.

An additional argument in favor of such a simple extrapolation scheme can be obtained by extrapolating the results corresponding to the three largest basis sets ($K = 300$, 600 , and 800) for $M = 24$ with the formula $E_K = E_\infty + aK^{-\gamma}$, where a and γ are fitting parameters. We tried other extrapolation formulas but they reproduced the convergence pattern less satisfactorily. The values of E_∞ obtained in this way differ by at most 0.4 , 0.06 , and 0.04 mK for $R = 4.0$, 5.6 , and 7.0 bohr, respectively, from the results of the simple extrapolations in K only described above. These are very small differences indeed, well within the error bars of Table 5.

In the case of E_{NF} and E_S components, limited amounts of data from the geminal calculations do not allow definitive conclusions about the convergence trends, in particular for $R = 4.0$ and 7.0 bohr where the K dependence was not investigated, so the error bounds of these quantities could not be established based on such calculations alone. The limit values and error estimates of E_{NF} and E_S given in Table 5 have been inferred from comparisons with the results of orbital calculations, described in section 5.1.

One should note that in comparison with the data for $R = 5.6$ bohr reported in ref 24, the values given in Table 5 are slightly more negative and/or ascribed slightly larger uncertainties, mainly due to a more careful consideration of the dependence on M in the present work. The estimate of the CCSD contribution changed from -9.150 ± 0.001 K to -9.1509 ± 0.0012 K.

TABLE 5: Recommended (Extrapolated in Most Cases, See Text) Values of Various Gaussian Geminal Contributions to the Helium Dimer Interaction Energy (in kelvin)

	4.0 bohr	5.6 bohr	7.0 bohr
E_{SCF}	428.782 ± 0.001	9.2199 ± 0.0001	0.2879 ± 0.0001
$E_{\text{MP2}}^{\text{cr}}$	-117.5007 ± 0.0018	-16.01210 ± 0.00024	-3.78151 ± 0.00017
$E_{\text{MP3}}^{\text{cr}}$	-11.4052 ± 0.0006	-2.51403 ± 0.00007	-0.67886 ± 0.00004
$E_{\text{FCCD}}^{\text{cr}}$	-123.5996 ± 0.0025	-18.21191 ± 0.00047	-4.41993 ± 0.00016
E_{NF}	0.487 ± 0.001 ^a	0.01816 ± 0.00010 ^a	-0.00339 ± 0.00002 ^a
E_{CCD}	305.6694 ± 0.0045	-8.9738 ± 0.0007	-4.1354 ± 0.0003
E_{S}	-0.734 ± 0.002 ^b	-0.1771 ± 0.0005 ^b	-0.0442 ± 0.0005 ^b
E_{CCSD}	304.935 ± 0.007	-9.1509 ± 0.0012	-4.1796 ± 0.0008

^a Computed geminal values with error bars based on both geminal and orbital results, see text. ^b Extrapolation and error bars based on both geminal and orbital results, see text.

The current values of $E_{\text{MP2}}^{\text{cr}}$ and $E_{\text{MP3}}^{\text{cr}}$, saturated up to a fraction of a millikelvin, allow us to estimate the accuracy of the former GTG work.¹⁵ At $R = 5.6$ bohr, the $E_{\text{MP2}}^{\text{cr}}$ value reported in ref 15 is 9 mK too high, whereas $E_{\text{MP3}}^{\text{cr}}$ is 4 mK too high. The other explicitly correlated calculation by Klopper and Noga,¹⁴ using the MP2-R12 ansatz, yielded $E_{\text{MP2}}^{\text{cr}}$ too high by 52 mK and, at the same time, $E_{\text{MP3}}^{\text{cr}}$ too low by 36 mK. The interaction energy at the level of MBPT(3) = SCF + MP2 + MP3 reported in ref 14 was in error by only 16 mK, because of a cancellation of errors. Klopper and Noga also obtained the E_{CCSD} value of -9.14 K, which is about 11 mK from the current limit value.

5. Orbital Calculations

The primary goal of the orbital calculations was to provide accurate estimates of the interaction energy contributions beyond CCSD, namely, the quantities E_{T} and δE_{FCI} of eqs 2 and 3. Following ref 24, these contributions will be obtained by extrapolations of the results calculated in large orbital bases. The same technique will also be used to verify the values of E_{S} and E_{NF} obtained from the geminal coupled cluster calculations and provide error estimates of these quantities, needed in Table 5. The orbital calculations gave also the interaction energy components at MP2, MP3, and FCCD levels. These results, as discussed in ref 24, are less accurate than the geminal results and will not be reported here.

The methodology of the orbital calculations performed in the present work has been described in detail in ref 24. The core of the procedure is an extrapolation to the complete basis set limit from finite basis sets forming various systematic sequences. Two such sequences used by us were the augmented and doubly augmented correlation-consistent polarized-valence X -tuple-zeta basis sets, aug-cc-pVXZ and d-aug-cc-pVXZ, of Dunning et al.,⁵⁵⁻⁵⁸ where $X = 3, 4, 5,$ and 6 . The $X = 7$ basis was developed by Gdanitz in ref 11. These sequences will be referred to as aXZ and dXZ, respectively. Two additional sequences were obtained by combining the aXZ bases with two sets of bond functions: $6s6p6d3f1g1h$ (95-term set) and $6s6p6d3f3g3h$ (135-term set), developed by Partridge and Bauschlicher.⁵² We refer to these combined sets as aXZ+bm, where $m = 95$ or $m = 135$. Since the X -tuple-zeta basis sets give energies forming regular sequences in the cardinal number X , the results can be (approximately) extrapolated to the infinite basis set limit by assuming an inverse-power dependence of the calculated quantities on X , $E(X) = E(\infty) + AX^{-n}$. Typically, the exponent n is assumed equal to 3, although other values have been tried as well. We will use the notation X^{-n} for such two-point extrapolation based on the calculated values $E(X-1)$ and $E(X)$ and the exponent n .

In a different type of extrapolation, the quantity E is treated as a function of another quantity, $\tilde{E}(X)$, that is, $E(X) = f(\tilde{E}(X))$.

TABLE 6: Computed and Extrapolated Single-Excitation Contributions $E_{\text{S}} = E_{\text{CCSD}} - E_{\text{CCD}}$ to the Helium Dimer Interaction Energy (in kelvin) at $R = 7.0$ bohr

basis	size	E_{S}	X^{-3}	$f(E_{\text{CCD}}^{\text{cr}})^a$
aTZ+b95	141	-0.071 96		
aQZ+b95	187	-0.056 75	-0.045 65	-0.059 37
a5Z+b95	255	-0.049 92	-0.042 75	-0.011 14
a6Z+b95	349	-0.047 36	-0.043 84	-0.043 95
a7Z+b95	473	-0.046 19	-0.044 20	-0.044 46
dTZ	64	-0.066 05		
dQZ	124	-0.055 56	-0.047 91	-0.051 17
d5Z	210	-0.049 49	-0.043 12	-0.044 39
d6Z	326	-0.047 07	-0.043 75	-0.044 89
d7Z	476	-0.045 91	-0.043 94	-0.042 49
aTZ+b135	181	-0.072 05		
aQZ+b135	227	-0.056 76	-0.045 60	-0.059 25
a5Z+b135	295	-0.049 94	-0.042 78	-0.072 29
a6Z+b135	389	-0.047 38	-0.043 86	-0.044 90
a7Z+b135	513	-0.046 21	-0.044 22	-0.044 82

^a The assumed accurate (GTG) value of $E_{\text{CCD}}^{\text{cr}}$ is -4.4233 K.

If the functional dependence and the infinite basis set limit $\tilde{E}(\infty)$ are known, then the limiting value of E is readily found: $E(\infty) = f(\tilde{E}(\infty))$. In the close vicinity of $\tilde{E}(\infty)$, that is, for sufficiently large X , the function $f(\tilde{E})$ is approximately linear (from the Taylor expansion around $\tilde{E}(\infty)$). $E(\infty)$ can then be found assuming that $f(\tilde{E}(X-1))$, $f(\tilde{E}(X))$, and $f(\tilde{E}(\infty))$ lie on a straight line (cf. eq 8 of ref 24). We will refer to this extrapolation as $f(\tilde{E})$ or $E(\tilde{E})$ extrapolation. Obvious choices for \tilde{E} are $E_{\text{MP2}}^{\text{cr}}$ or $E_{\text{FCCD}}^{\text{cr}}$, because these quantities are known practically exactly from the GTG calculations.

Most of our orbital coupled cluster calculations were performed using the MOLPRO package,⁵⁹ whereas the FCI energies were obtained with the LUCIA program.⁶⁰

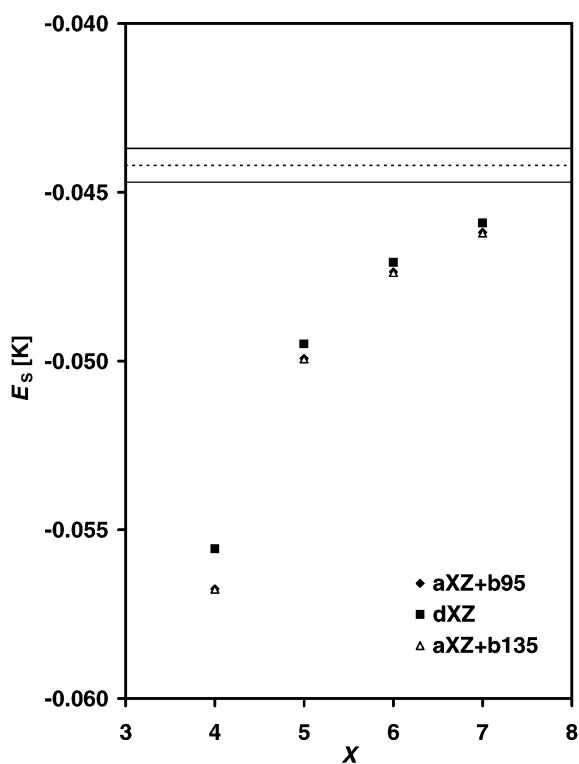
5.1. Single-Excitation and Nonfactorizable Contributions. The orbital calculations of the single-excitation contribution E_{S} at $R = 5.6$ bohr have been reported in ref 24. The results for $R = 7.0$ bohr and $R = 4.0$ bohr, obtained in the present work, are listed in Tables 6 and 7, respectively, and presented graphically in Figures 1 and 2, respectively.

Let us first estimate the limit value and its uncertainty for the single-excitation contribution at $R = 5.6$ bohr. The geminal value quoted in ref 24 was -178 ± 1 mK. This value was based on the data presented here in Table 2, except that the value for $M = L = 24$ and $K = 300$ was not known at that time. The latter value is equal to -176.9 mK and represents the current best calculated result. The data in Table 2 do not allow rigorous extrapolations; however, it is likely that the result will be lowered in the limit of infinite M , L , and K , possibly even down to -178 K as the last increments with $M = L$ and K were -0.56 and -0.75 mK, respectively. Thus, -177.5 ± 0.5 mK would be our best estimated value based only on the geminal results. Let us now consider orbital results. The best calculated values

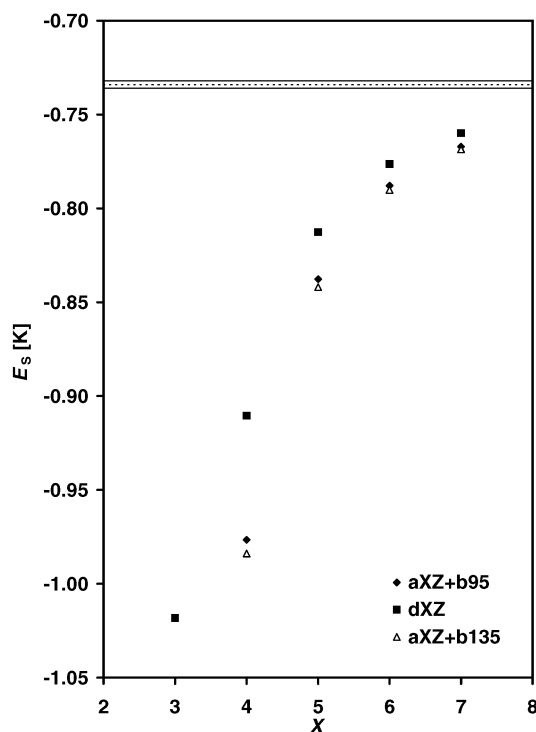
TABLE 7: Computed and Extrapolated Single-Excitation Contributions $E_S = E_{CCSD} - E_{CCD}$ to the Helium Dimer Interaction Energy (in kelvin) at $R = 4.0$ bohr

basis	size	E_S	X^{-3}	$f(E_{CCD}^{cr})^a$
aTZ+b95	141	-1.3059		
aQZ+b95	187	-0.9766	-0.7364	-0.6611
a5Z+b95	255	-0.8378	-0.6921	-0.6755
a6Z+b95	349	-0.7879	-0.7194	-0.7051
a7Z+b95	473	-0.7671	-0.7318	-0.7189
dTZ	64	-1.0183		
dQZ	124	-0.9105	-0.8318	-0.8509
d5Z	210	-0.8127	-0.7102	-0.7486
d6Z	326	-0.7764	-0.7264	-0.7359
d7Z	476	-0.7599	-0.7320	-0.7336
aTZ+b135	181	-1.3233		
aQZ+b135	227	-0.9838	-0.7362	-0.6671
a5Z+b135	295	-0.8420	-0.6932	-0.6777
a6Z+b135	389	-0.7902	-0.7191	-0.7039
a7Z+b135	513	-0.7686	-0.7317	-0.7186

^a The assumed accurate (GTG) value of E_{CCD}^{cr} is -123.1126 K.

**Figure 1.** Convergence of the computed single-excitation contribution, E_S , at $R = 7.0$ bohr. The horizontal lines denote the upper and lower bound for our recommended value (broken line), see Table 5.

from Table III of ref 24 (given there with less significant digits) and from a new series of calculations are -179.0 , -183.0 , -184.4 , and -184.4 mK in bases a7Z, d7Z, a7Z+b135, and d7Z+b135, respectively. These numbers illustrate the finding of ref 24 that the additions of a second diffuse shell or of bond functions slow the convergence (the two factors acting in similar but not additive ways). Although results of orbital calculations in such bases are 6–7 mK from the extrapolated geminal result, the orbital X^{-3} extrapolations are very close to each other: -176.7 , -176.6 , and -176.8 mK in bases d7Z, a7Z+b135, and d7Z+b135, respectively, that is, only 0.7–0.8 mK from the extrapolated geminal result. In contrast, although the a7Z computed result is closest to the geminal value (which may be, however, fortuitous²⁴), the aXZ series converges in such a way (values are nearly constant) that the extrapolated result equal to -179.5 K cannot be trusted. Since at this point we cannot

**Figure 2.** Convergence of the computed single-excitation contribution, E_S , at $R = 4.0$ bohr. The horizontal lines denote the upper and lower bound for our recommended value (broken line), see Table 5.

decide whether the geminal- or orbital-extrapolated results are more accurate, we decided to use an average of them, equal to -177.1 mK, as our recommended limit value for E_S and assign the error bar of ± 0.5 mK encompassing both results. The $E_S(E_{CCD}^{cr})$ extrapolations (with the GTG limit value of E_{CCD}^{cr} equal to -18.1938 K) give, with $X = 7$, -179.4 mK and -176.8 mK for the aXZ and dXZ sequences, respectively, and -174.5 mK for both bases with bond functions. Because of this scatter and because the extrapolations with lower X are even farther off from the geminal result, we have not used the information from the $E_S(E_{CCD}^{cr})$ extrapolations in our determination of the recommended values of E_S .

Although, as shown in ref 24, the component E_S converges fastest in the aXZ series of basis sets, the best computed result for $R = 5.6$ bohr is still 1.5 mK from the extrapolated geminal value. Despite the fact that the bases with additional diffuse functions and/or bond functions converge slower, the extrapolated results are very consistent and closer to this value. Therefore, we have decided to use only such bases for $R = 4.0$ and 7.0 bohr.

At $R = 7.0$ bohr, the X^{-3} extrapolations predict results in the range -43.9 to -44.2 mK, whereas the best computed geminal value from Table 3 is -44.3 mK. At this distance (in contrast to $R = 5.6$ bohr) we do not have enough information to perform any meaningful extrapolation of the geminal results (no variation in K is available, cf. Table 3), and therefore, we assume the computed value as the best geminal estimate. Taking the average of the average of orbital values and of the geminal result, one gets -44.2 ± 0.5 mK, with the error again encompassing all the discussed values. Table 6 and Figure 1 show that the convergence in the bases with bond functions is slower than in the dXZ basis. However, once bond functions are used the results are almost the same with single and double augmentation. The $E_S(E_{CCD}^{cr})$ extrapolations predict with $X = 7$ results in the range -42.5 to -44.8 mK, that is, as for $R = 5.6$ bohr, the scatter is larger than that of the other predictions. One can also see in

TABLE 8: Contribution from Nonfactorizable Double-Excitation Terms $E_{\text{NF}} = E_{\text{CCD}} - E_{\text{FCCD}}$ to the Helium Dimer Interaction Energy (in kelvin) from Orbital Calculations^a

basis	size	$R = 4.0$	$R = 5.6$	$R = 7.0$
aTZ	46	0.481 34	0.017 81	-0.003 473 5
aQZ	92	0.490 90	0.018 41	-0.003 410 4
a5Z	160	0.489 10	0.018 22	-0.003 378 8
a6Z	254	0.488 50	0.018 19	-0.003 378 8

^a Distances are in bohr.

Table 6 that for smaller X and bases with bond functions the predictions are very poor. This is probably related to the nonmonotonic convergence of $E_{\text{CCD}}^{\text{cr}}$. For large X , the predictions from these sequences are, however, reasonable. On the other hand, the dXZ prediction based on $X = 6$ and 7 is very inaccurate. The reasons are not clear to us; however, the plot of the dependence $E_{\text{S}}(E_{\text{CCD}}^{\text{cr}})$ is fairly nonlinear in the region of large X , so the linear extrapolation clearly cannot work well. One possible explanation for the observed behavior could be some numerical inaccuracies for this largest of the distances considered by us.

For $R = 4.0$ bohr, as for the other two separations, the X^{-3} extrapolation works very well and predicts consistent results for all basis set sequences, all equal to -0.732 K, in excellent agreement with the GTG calculations of section 4, the difference being only 4 mK, small compared to the interaction energy at this distance. We see again how powerful the extrapolation techniques are since the best computed results are about 30 mK from this range. This behavior is well illustrated by Figure 2. Following the procedure for $R = 5.6$ bohr, we take the average of the geminal and X^{-3} -extrapolated orbital results as our recommended value: $E_{\text{S}} = -734 \pm 2$ mK. The $E_{\text{S}}(E_{\text{CCD}}^{\text{cr}})$ extrapolation from dXZ sequence works very well, exactly predicting the recommended value of -734 mK. The extrapolation from sequences with bond function both predict -719 mK, fairly distant from the best estimate. Similarly as for the other two separations, we will disregard these extrapolations.

Although the convergence of the nonfactorizable contribution E_{NF} in geminal calculations was found to be very fast, we decided, as an independent check, to perform orbital calculations of this quantity in the aXZ sequence of basis sets. In particular, we wanted to verify the convergence of the geminal results for $R = 4.0$ bohr (see Table 4), where the agreement between the last two values could be accidental. The orbital results for all three distances are listed in Table 8. The components E_{NF} converged so well in the aXZ sequence that there was no point to perform calculations in doubly augmented bases or add bond functions. At $R = 4.0$ bohr, the values appear to converge to 0.488 K or slightly below, so choosing the computed geminal result of 0.487 K as the recommended value in Table 5 seems appropriate. Whereas the geminal results presented in Table 4 may appear to be converged to 0.1 mK, orbital results suggest a somewhat larger uncertainty, of about 1 mK. For $R = 5.6$ and 7.0 bohr, the values obtained in large basis sets are also in very good agreement with the corresponding geminal results. Thus, as for $R = 4.0$ bohr, we have taken the geminal values as the recommended ones. The error estimates for E_{NF} , given in Table 5, are chosen based on convergence patterns observed in Table 8. For $R = 5.6$ and 7.0 bohr, these uncertainties are consistent with those following from geminal convergence patterns.

An interesting conclusion from Table 8 is that the term E_{NF} , quite expensive to compute in Gaussian geminal bases, can easily be saturated using orbital basis sets of moderate sizes.

TABLE 9: Computed and Extrapolated Triple-Excitation Contributions $E_{\text{T}} = E_{\text{CCSD(T)}} - E_{\text{CCSD}}$ to the Helium Dimer Interaction Energy (in kelvin) at $R = 7.0$ bohr

basis	size	E_{T}	X^{-3}	X^{-2}	$f(E_{\text{CCSD}})^a$	$f(E_{\text{CCD}}^{\text{cr}})^b$
aTZ+b95	141	-0.347 07				
aQZ+b95	187	-0.356 35	-0.363 12	-0.368 28	-0.357 60	-0.354 75
a5Z+b95	255	-0.359 21	-0.362 21	-0.364 29	-0.359 53	-0.375 45
a6Z+b95	349	-0.360 63	-0.362 58	-0.363 86	-0.360 99	-0.362 52
a7Z+b95	473	-0.361 35	-0.362 57	-0.363 34	-0.358 11	-0.362 41
dTZ	64	-0.329 13				
dQZ	124	-0.351 39	-0.367 63	-0.380 01	-0.359 37	-0.360 72
d5Z	210	-0.357 04	-0.362 97	-0.367 08	-0.362 22	-0.361 79
d6Z	326	-0.359 50	-0.362 88	-0.365 09	-0.361 47	-0.361 71
d7Z	476	-0.360 40	-0.361 93	-0.362 89	-0.363 65	-0.363 05
aTZ+b135	181	-0.347 66				
aQZ+b135	227	-0.356 86	-0.363 57	-0.368 69	-0.359 18	-0.355 36
a5Z+b135	295	-0.359 41	-0.362 09	-0.363 94	-0.359 74	-0.351 05
a6Z+b135	389	-0.360 79	-0.362 69	-0.363 93	-0.368 34	-0.362 13
a7Z+b135	513	-0.361 47	-0.362 63	-0.363 35	-0.363 95	-0.362 28

^a The assumed accurate (GTG) value of E_{CCSD} is -4.1796 K. ^b The assumed accurate (GTG) value of $E_{\text{CCD}}^{\text{cr}}$ is -4.4233 K.

TABLE 10: Computed and Extrapolated Triple-Excitation Contributions $E_{\text{T}} = E_{\text{CCSD(T)}} - E_{\text{CCSD}}$ to the Helium Dimer Interaction Energy (in kelvin) at $R = 4.0$ bohr

basis	size	E_{T}	X^{-3}	X^{-2}	$f(E_{\text{CCSD}})^a$	$f(E_{\text{CCD}}^{\text{cr}})^b$
aTZ+b95	141	-10.1412				
aQZ+b95	187	-10.3203	-10.4510	-10.5506	-10.4752	-10.4919
a5Z+b95	255	-10.3905	-10.4641	-10.5153	-10.4720	-10.4725
a6Z+b95	349	-10.4234	-10.4685	-10.4981	-10.4744	-10.4779
a7Z+b95	473	-10.4424	-10.4749	-10.4952	-10.4872	-10.4867
dTZ	64	-8.6812				
dQZ	124	-9.8901	-10.7723	-11.4445	-10.5185	-10.5578
d5Z	210	-10.2412	-10.6096	-10.8654	-10.4615	-10.4716
d6Z	326	-10.3551	-10.5116	-10.6140	-10.4804	-10.4818
d7Z	476	-10.4044	-10.4881	-10.5407	-10.4810	-10.4830
aTZ+b135	181	-10.2384				
aQZ+b135	227	-10.3554	-10.4408	-10.5059	-10.4613	-10.4646
a5Z+b135	295	-10.4067	-10.4604	-10.4977	-10.4653	-10.4660
a6Z+b135	389	-10.4319	-10.4666	-10.4893	-10.4713	-10.4740
a7Z+b135	513	-10.4481	-10.4757	-10.4930	-10.4858	-10.4855

^a The assumed accurate (GTG) value of E_{CCSD} is 304.935 K. ^b The assumed accurate (GTG) value of $E_{\text{CCD}}^{\text{cr}}$ is -123.1126 K.

Thus, one can restrict the GTG calculations to the inexpensive FCCD level and still obtain very accurate CCD energies by taking the E_{NF} contribution from orbital calculations. Using extrapolated orbital single-excitation contributions, accurate CCSD energies can also be obtained in such a mixed approach, at a fraction of the costs of the all-geminal CCSD calculations.

5.2. Triple-Excitation Contribution. The values of the triple-excitation contribution, E_{T} , computed in three sequences of orbital basis sets for $R = 7.0$ and 4.0 bohr, are listed in Tables 9 and 10, respectively, along with the results of various extrapolation schemes. Convergence of E_{T} with the cardinal number X is also presented graphically in Figures 3 and 4. In contrast to the E_{S} contribution, the convergence of E_{T} is dramatically improved by using the bond functions (cf. Figures 3 and 4). The quality of extrapolations of E_{T} is difficult to assess because no accurate explicitly correlated results for this quantity are available and its functional dependence on X is not known. At $R = 5.6$ bohr we arrived²⁴ at the estimate $E_{\text{T}} = -1.535 \pm 0.002$ K by combining the X^{-3} , X^{-2} , and $E_{\text{T}}(E_{\text{CCSD}})$ extrapolations. We have repeated the $E_{\text{T}}(E_{\text{CCSD}})$ extrapolations with the current limit value of $E_{\text{CCSD}} = -9.1509$ K instead of -9.150 K used in ref 24. This increased the magnitude of the extrapolated E_{T} by 0.1 to 0.7 mK (depending on the basis set sequence), not significant enough to modify the limit value from ref 24 quoted above. We have also computed the complete

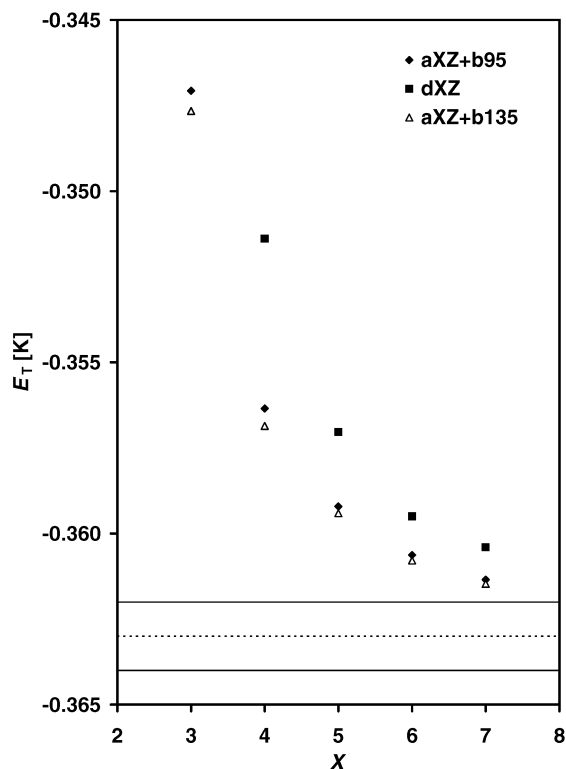


Figure 3. Convergence of the computed triple-excitation contribution, E_T , at $R = 7.0$ bohr. The horizontal lines denote the upper and lower bound for our recommended value (broken line), see Table 13.

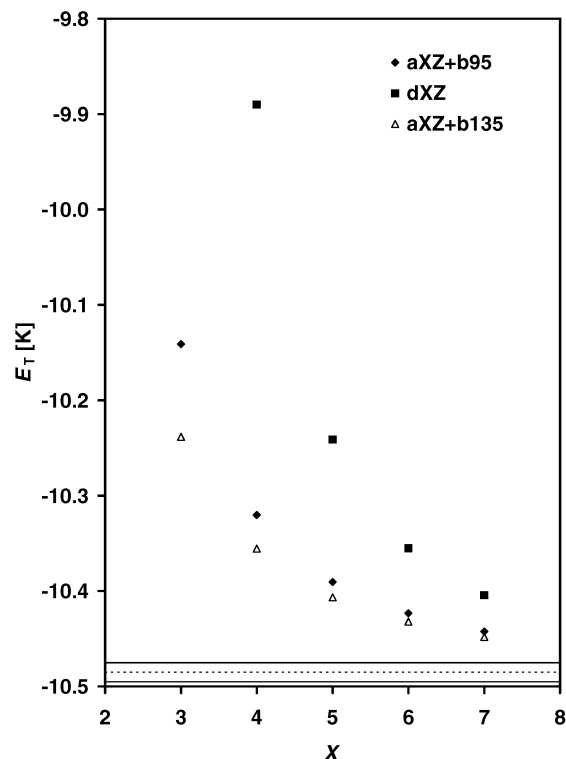


Figure 4. Convergence of the computed triple-excitation contribution, E_T , at $R = 4.0$ bohr. The horizontal lines denote the upper and lower bound for our recommended value (broken line), see Table 13.

dXZ+b135 sequence (only the d7Z+b135 value was available in ref 24), our largest size sequence. The X^{-3} , X^{-2} , and $E_T(E_{\text{CCSD}})$ extrapolations of this series gave at $X = 7$ -1.534 , -1.536 , and -1.536 K, increasing our confidence in the estimated limit value.

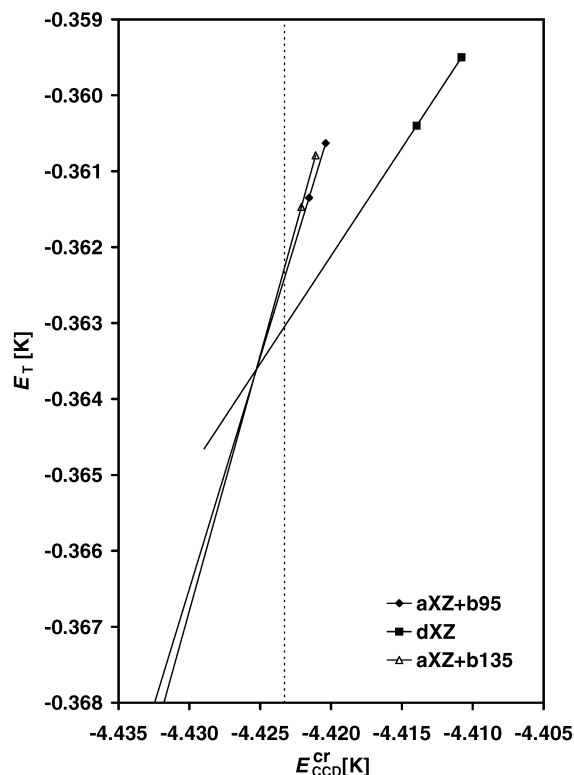


Figure 5. Extrapolation of E_T as a function of $E_{\text{CCD}}^{\text{cr}}$ at $R = 7.0$ bohr. The straight lines are drawn through the points obtained with $X = 6$ (upper) and $X = 7$ (lower). The dashed vertical line corresponds to the GTG value of $E_{\text{CCD}}^{\text{cr}} = -4.4233$ K.

At $R = 7.0$ bohr (see Table 9) the lowest computed E_T energy is -0.3615 K, the X^{-3} extrapolations range between -0.3619 K and -0.3626 K, and the X^{-2} extrapolations between -0.3629 K and -0.3634 K. The average of the extrapolated results is -0.3628 K and appears to be a reliable estimate of the limit value. The $E_T(E_{\text{CCSD}})$ extrapolations from dXZ and aXZ+b135 sequences agree to within 1 mK with this estimate, only the aXZ+b95 sequence deviates by 5 mK. We have found that even smoother extrapolation is obtained within the $E_T(E_{\text{CCD}}^{\text{cr}})$ scheme, presented graphically in Figure 5, probably due to the fact that the singles contributions included in E_{CCSD} are not sufficiently well converged for $R = 7.0$ bohr. The linearized functional dependence $E_T(E_{\text{CCD}}^{\text{cr}})$ is plotted in Figure 5 for each basis set sequence by drawing straight lines through the points corresponding to the two largest basis sets ($X = 6$ and $X = 7$) in each case. The lines cross the dashed vertical line corresponding to the (extrapolated) GTG result of -4.4233 K from Table 5 at $E_T = -0.36228$, -0.36241 , and -0.36305 K (note that even if we did not know $E_{\text{CCD}}^{\text{cr}}$ from the geminal calculations, we could still obtain a good estimate of E_T by taking the point where the three lines intersect). These values, listed at the end of each series in the last column of Table 9, are in very good agreement with the results of the X^{-n} extrapolations. By assuming $E_T = -0.363 \pm 0.001$ K, we encompass all the extrapolated results from the largest basis sets in each sequence, with the exception of the $E_T(E_{\text{CCSD}})$ result from the aXZ+b95 sequence.

At $R = 4.0$ bohr (see Table 10) the results of extrapolations are also very consistent with each other. The only exception is the X^{-2} scheme with the dXZ sequence which overshoots the average of other extrapolations by about 60 mK. This is a similar effect as observed in the X^{-2} extrapolations of E_T with bases without bond functions for $R = 5.6$ bohr in ref 24. By discarding

TABLE 11: Computed and Extrapolated Values of the FCI Contribution $\delta E_{\text{FCI}} = E_{\text{FCI}} - E_{\text{CCSD(T)}}$ to the Helium Dimer Interaction Energy (in kelvin) at $R = 7.0$ bohr

basis	size	δE_{FCI}	X^{-3}	$f(E_{\text{CCD}})^a$	$f(E_{\text{CCD}}^{\text{cr}})^b$	$f(E_{\text{MP2}}^{\text{cr}})^c$
aTZ+b95	141	-0.085 73				
aQZ+b95	187	-0.084 25	-0.083 18	-0.084 49	-0.084 51	-0.084 55
a5Z+b95	255	-0.082 64	-0.080 95	-0.070 71	-0.073 48	-0.074 95
dTZ	64	-0.084 77				
dQZ	124	-0.084 31	-0.083 97	-0.084 12	-0.084 11	-0.084 10
d5Z	210	-0.082 67	-0.080 94	-0.081 18	-0.081 29	-0.081 30

^a The assumed accurate (GTG) value of E_{CCD} is -4.1354 K. ^b The assumed accurate (GTG) value of $E_{\text{CCD}}^{\text{cr}}$ is -4.4233 K. ^c The assumed accurate (GTG) value of $E_{\text{MP2}}^{\text{cr}}$ is -3.78151 K.

TABLE 12: Computed and Extrapolated Values of the FCI Contribution $\delta E_{\text{FCI}} = E_{\text{FCI}} - E_{\text{CCSD(T)}}$ to the Helium Dimer Interaction Energy (in kelvin) at $R = 4.0$ bohr

basis	size	δE_{FCI}	X^{-3}	$f(E_{\text{CCD}})^a$	$f(E_{\text{CCD}}^{\text{cr}})^b$	$f(E_{\text{MP2}}^{\text{cr}})^c$
aTZ+b95	141	-2.0139				
aQZ+b95	187	-1.9679	-1.9343	-1.9288	-1.9238	-1.9188
a5Z+b95	255	-1.9338	-1.8981	-1.8961	-1.8941	-1.8850
dTZ	64	-2.0037				
dQZ	124	-2.0263	-2.0427	-2.0382	-2.0387	-2.0410
d5Z	210	-1.9704	-1.9118	-1.9351	-1.9337	-1.9242

^a The assumed accurate (GTG) value of E_{CCD} is 305.669 K. ^b The assumed accurate (GTG) value of $E_{\text{CCD}}^{\text{cr}}$ is -123.113 K. ^c The assumed accurate (GTG) value of $E_{\text{MP2}}^{\text{cr}}$ is -117.5007 K.

this sequence and taking $E_{\text{T}} = -10.485 \pm 0.010$ K, we are consistent with the extrapolated results from all the largest basis sets in each sequence.

We can now compare the uncertainties of the triple- and single-excitation contributions: the ratio is 5, 4, and 2 for $R = 4.0$, 5.6, and 7.0 bohr, respectively. This decreasing ratio explains why the $E_{\text{T}}(E_{\text{CCSD}})$ extrapolations are relatively less accurate at $R = 7.0$ bohr.

Our values of the interaction energies at the CCSD(T) level, equal to 294.45, -10.686 , and -4.543 K at $R = 4.0$, 5.6, and 7.0 bohr, respectively, can be compared to the corresponding values computed using the CCSD(T)-R12 approach by Klopper and Noga¹⁴ and quoted in ref 18: 294.59, -10.659 , and -4.536 K. The discrepancies amount to 140, 27, and 7 mK. The exponential extrapolations of the CCSD(T) interaction energies from bases up to d6Z by van Mourik and Dunning¹⁸ gave 295.511 and -10.672 K at $R = 4.0$ and 5.6 bohr, respectively: a much larger, 1.1 K discrepancy at the former distance but only 14 mK at the latter.

5.3. Contributions beyond the CCSD(T) Level. The results of the FCI calculations for $R = 7.0$ bohr and $R = 4.0$ bohr are presented in Tables 11 and 12, respectively. Although our FCI computations use larger basis sets than any previous work, these sets are still relatively small compared to those in CCSD(T) calculations: $X \leq 5$ versus $X \leq 7$, respectively. Thus, drawing precise quantitative conclusions about the convergence of δE_{FCI} is more difficult than for the E_{S} and E_{T} components discussed before. A perusal of the convergence patterns for the latter two components indicates that if the predictions were made based only on $X \leq 5$ results, the error bars would be a few times larger than those reported in the tables, but the estimates of complete basis set values would actually agree to within error bars.

The convergence of the computed δE_{FCI} values from Tables 11 and 12 is not very regular. For example, going from $X = 4$ to $X = 5$ at $R = 7.0$ bohr brings larger increments than going from $X = 3$ to $X = 4$ and the dXZ sequence at $R = 4.0$ bohr is not even monotonic. Generally, the extrapolations involving

TABLE 13: Interaction Energies of the Helium Dimer and Their Components (in kelvin)^a

	$R = 4.0$	$R = 5.6$	$R = 7.0$
E_{CCSD}	304.935 ± 0.007	-9.1509 ± 0.0012	-4.1796 ± 0.0008
E_{T}	-10.485 ± 0.010	-1.535 ± 0.002	-0.363 ± 0.001
δE_{FCI}	-1.91 ± 0.02	-0.323 ± 0.005	-0.076 ± 0.005
E_{int}	292.54 ± 0.04	-11.009 ± 0.008	-4.619 ± 0.007
Komasa ²³	292.784^b	-10.978^b	-4.583^b
Komasa ²²		-10.981^b	
Anderson ⁶¹		-10.98 ± 0.02	
Anderson ²⁵		-10.998 ± 0.005	
vMD ^c	293.496	-11.004 ± 0.03	
vdBvD ^d	292.72 ± 0.2	-10.99 ± 0.02	
Gdanitz ²⁰	292.75 ± 0.01	-10.980 ± 0.004	-4.620 ± 0.002
Klopper ²¹	292.6 ± 0.3	-10.99 ± 0.02	
Korona et al. ¹⁰	291.64 ± 0.87	-11.059 ± 0.03	-4.629 ± 0.03

^a Distances are in bohr. ^b Strict upper bound (variational calculation). ^c van Mourik and Dunning, ref 18. ^d van de Bovenkamp and van Duijneveldt, ref 17.

bond functions lead to higher (less negative) values (with the exception of the X^{-3} extrapolation at $R = 7.0$ bohr), particularly the $\delta E_{\text{FCI}}(\bar{E})$ schemes. Our best estimates, $\delta E_{\text{FCI}} = -0.076 \pm 0.005$ K at $R = 7.0$ bohr and $\delta E_{\text{FCI}} = -1.91 \pm 0.02$ K at $R = 4.0$ bohr, were obtained in such a way that the bounds encompass all types of extrapolations from the largest bases and the recommended result is in the middle of this range. The result for $R = 5.6$ bohr, obtained in ref 24, is $\delta E_{\text{FCI}} = -0.323 \pm 0.005$ K.

5.4. Comparison with Literature Results. The recommended total interaction energies of the helium dimer have been obtained according to eq 1 by combining the extrapolated CCSD contributions from Table 5, calculated in geminal bases (except for E_{NF} and E_{S} for which some orbital input was used), with the E_{T} and δE_{FCI} components extrapolated from the orbital calculations, as described in sections 5.2 and 5.3, respectively. The error estimates of the total interaction energies are obtained by linearly adding the errors of the components (as opposed to taking a square root of the sum of squares), which provides rather conservative estimates of the ranges where the accurate values are located. The same linear addition of errors has been applied before when assembling the CCSD values.

The interaction energies obtained in this way are compared in Table 13 to some representative literature results. Our energies are consistent with the best variational upper bounds by Komasa.^{22,23} The present estimates have the narrowest error bars at all three distances, the only exceptions being the results of Gdanitz²⁰ and the very recent quantum Monte Carlo (QMC) result of -10.998 ± 0.005 K for $R = 5.6$ bohr obtained by Anderson, quoted in ref 25. The discrepancies between our and Gdanitz's values are equal to 0.21 and 0.028 K at $R = 4.0$ and 5.6 bohr, respectively, which amounts to about 20 and 7 times the error bars of ref 20. At $R = 7.0$ bohr, the difference is 0.001 K and our result is within error bars of ref 20. The error estimate of the QMC results corresponds to one standard deviation (68% probability that the true value is within the error bars). The 2001 QMC result of Anderson⁶¹ was -10.98 ± 0.02 K. Our prediction of the interaction energy at $R = 5.6$ bohr, -11.009 ± 0.008 K, is consistent (error bars overlap) with the new QMC value, the difference being -0.011 ± 0.013 K.

The energies reported by Klopper²¹ which were obtained from extrapolated CCSD(T) and FCI calculations in orbital bases, agree with the present results if the uncertainties given by Klopper are taken into account. The extrapolated CCSD(T) values of van Mourik and Dunning¹⁸ discussed earlier were combined by these authors with nonextrapolated CCSD(T) and FCI energies. For 5.6 bohr, the agreement with our result is

very good, to within our uncertainties, but for 4.0 bohr the discrepancy is about 1 K. These authors give the error bars only for the former distance. Note that van Mourik and Dunning¹⁸ also published interaction energies computed substituting their CCSD(T) values by the CCSD(T)-R12 results from ref 14. For 5.6 bohr, this procedure significantly increased the discrepancy with our calculations, whereas for 4.0 bohr the effect was opposite. The multireference configuration interaction (MRCI) calculations by van de Bovenkamp and van Duijneveldt¹⁷ predict at $R = 4.0$ bohr the energy by over 0.1 K higher than ref 21 and almost as high as the result of Gdanitz, but the error bars are much larger than those given by Gdanitz, and therefore, our and the MRCI values differ by -0.18 ± 0.24 K, that is, are consistent.

The last row in Table 13 contains the results of the symmetry-adapted perturbation theory (SAPT) calculations. An analysis of the SAPT convergence patterns at $R = 5.6$ bohr led to an estimate of the uncertainty of the interaction energy equal to 0.03 K.^{10,16} For other distances, the error estimates for the interaction energies computed in refs 10 and 16 were 0.3% or 0.03 K, whichever was larger (notice that for the fitting purposes three times narrower uncertainties were used: 0.1% or 0.01 K). The SAPT interaction energies are the lowest of all listed. At $R = 4.0$ bohr and 7.0 bohr the SAPT error bars overlap with the current ones. Only at $R = 5.6$ bohr our current result is in a disagreement of 0.05 ± 0.04 K with the SAPT prediction. Apparently, for this distance the cancellation of errors was less favorable than for other distances. Work on improving the accuracy of the SAPT interaction energies is underway in our group. If the accuracy of the SAPT calculations matches the accuracy of the present supermolecular calculations, this method could provide a much less expensive route to the He–He potential than the present approach.

6. Conclusions

In the present work we have computed the interaction energies for the helium dimer which are believed to be more accurate than any previously published results. In the post-CCSD component, the accuracy relied on the extrapolations to the complete basis set limit using the techniques developed in ref 24. For $R = 5.6$ bohr our results are virtually the same as in ref 24 as only the geminal single-excitation contribution was now calculated using basis sets somewhat larger than before. This extension and minor revisions of the extrapolations led to the interaction energy of -11.009 ± 0.008 K, slightly different from the value of -11.008 ± 0.008 K published in ref 24. The newly obtained interaction energies for $R = 4.0$ bohr and $R = 7.0$ bohr are 292.54 ± 0.04 K and -4.619 ± 0.007 K, respectively. In a forthcoming publication from our group, these interaction energies, together with values for a few other interatomic distances, will be used to obtain an analytic potential energy fit for He₂. On the basis of the analysis of the convergence of our calculations discussed in the present work, the new potential should be accurate to better than 10 mK in the well region (0.08% at the minimum) and to about 0.02% higher on the positive wall. The potential will also be nearly exact in the asymptotic region. This will be an overall about 1 order of magnitude increase in accuracy compared to the currently widely used He₂ potential from ref 10. At the present level of accuracy, the adiabatic, relativistic, and probably even QED corrections are larger than the errors of the Born–Oppenheimer curve. The accurate adiabatic corrections are known,⁶² and work on the remaining ones is underway in our group.

We were able to significantly reduce the error bounds of helium dimer interaction energies compared to values published

before because of our use of a hybrid, geminal-orbital supermolecular approach. The magnitude of the remaining uncertainties illustrates well the mutual relation of explicitly correlated and orbital-based methods in quantum chemistry. At $R = 5.6$ bohr, the E_{CCD} contribution, constituting 82% of the total interaction energy and containing 90% of notoriously slowly convergent electron correlation component, was computed in GTG bases with an error bar over 10 times smaller than the remaining 18%, obtained with orbital methods. Stopping the GTG calculations at the CCD level seems to be a good compromise since because of the high cost of geminal CCSD runs, only relatively small geminal basis sets can be used to evaluate the effect of the singles, and the results are not dramatically more accurate than those obtained from extrapolations of large-scale orbital computations. An even more promising approach to CCSD-level calculations seems to be provided by a combination of the inexpensive geminal-based FCCD method with an orbital treatment of the nonfactorizable and the singles contributions, both easy to saturate in basis sets. Such an approach is certainly feasible for medium-size molecules containing a few dozens of electrons. The present work demonstrated that explicitly correlated bases can provide significantly higher accuracies at the CCD level than orbital calculations with extrapolations. The terms beyond the CCD level coming from orbital calculations contribute a larger absolute error to the interaction energy than that of E_{CCD} coming from the GTG calculations. This happens despite the fact that the contribution to the correlation part of the interaction energy is almost an order of magnitude smaller in the former case, that is, the required relative accuracy is about 10 times lower. The higher-order terms beyond CCD do not appear to be harder to converge than CCD energies. If the orbital calculations of E_{CCD} presented in Table II of ref 24 were assigned error bars in a similar way as we have estimated the uncertainties of the post-CCD terms, these would be about ± 5 mK, that is, as large as the errors of the post-CCD components.

Further improvements of the accuracy of the helium dimer potential depend entirely on the progress beyond the CCSD level. The most promising approach would be to perform FCI calculations involving basis sets larger than the currently used ~ 250 orbitals or full CCSDT^{63,64} calculations. Other routes include four-electron explicitly correlated computations²³ with several thousands basis functions and the SAPT calculations discussed earlier.

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References and Notes

- (1) Toennies, J. P.; Vilesov, A. F. *Annu. Rev. Phys. Chem.* **1998**, *49*, 1.
- (2) Callegari, C.; Lehmann, K. K.; Schmied, R.; Scoles, G. *J. Chem. Phys.* **2001**, *115*, 10090.
- (3) Luther, H.; Grohmann, K.; Fellmuth, B. *Metrologia* **1996**, *33*, 341.
- (4) Pendrill, L. R. *J. Phys. B* **1996**, *29*, 3581.
- (5) Moldover, M. R. *J. Res. Natl. Inst. Stand. Technol.* **1998**, *103*, 167.
- (6) Buckley, T. J.; Hamelin, J.; Moldover, M. R. *Rev. Sci. Instrum.* **2000**, *71*, 2914.
- (7) Grisenti, R. E.; Schöllkopf, W.; Toennies, J. P.; Hegerfeldt, G. C.; Kohler, T.; Stoll, M. *Phys. Rev. Lett.* **2000**, *85*, 2287.
- (8) Luo, F.; Giese, C. F.; Gentry, W. R. *J. Chem. Phys.* **1996**, *104*, 1151.
- (9) Schöllkopf, W.; Toennies, J. P. *J. Chem. Phys.* **1996**, *104*, 1155.

- (10) Korona, T.; Williams, H. L.; Bukowski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1997**, *106*, 5109.
- (11) Gdanitz, R. J. *J. Chem. Phys.* **2000**, *113*, 5145.
- (12) van Mourik, T.; van Lenthe, J. H. *J. Chem. Phys.* **1995**, *102*, 7479.
- (13) Aziz, R. A.; Janzen, A. R.; Moldover, M. R. *Phys. Rev. Lett.* **1995**, *74*, 1586.
- (14) Klopper, W.; Noga, J. *J. Chem. Phys.* **1995**, *103*, 6127.
- (15) Bukowski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1996**, *104*, 3306.
- (16) Williams, H. L.; Korona, T.; Bukowski, R.; Jeziorski, B.; Szalewicz, K. *Chem. Phys. Lett.* **1996**, *262*, 431.
- (17) van de Bovenkamp, J.; van Duijneveldt, F. B. *J. Chem. Phys.* **1999**, *110*, 11141.
- (18) van Mourik, T.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *111*, 9246.
- (19) Gdanitz, R. J. *Mol. Phys.* **1999**, *96*, 1423.
- (20) Gdanitz, R. J. *Mol. Phys.* **2001**, *99*, 923.
- (21) Klopper, W. *J. Chem. Phys.* **2001**, *115*, 761.
- (22) Komasa, J. *J. Chem. Phys.* **2001**, *115*, 158.
- (23) Komasa, J. *J. Chem. Phys.* **1999**, *110*, 7909.
- (24) Jeziorska, M.; Bukowski, R.; Cencek, W.; Jaszufski, M.; Jeziorski, B.; Szalewicz, K. *Collect. Czech. Chem. Commun.* **2003**, *68*, 463; note that the CCSD results presented in this reference as the sixth column of Table IV were obtained using the X^{-2} extrapolation rather than the X^{-3} one, as erroneously indicated in the first row of this table.
- (25) Anderson, J. B. Unpublished work; cited in: Mella, A.; Anderson, J. B. *J. Chem. Phys.* **2003**, *119*, 8225.
- (26) Hurly, J. J.; Moldover, M. R. *J. Res. Natl. Inst. Stand. Technol.* **2000**, *105*, 667.
- (27) Gillis, K. A.; Mehl, J. B.; Moldover, M. R. *J. Acoust. Soc. Am.* **2003**, *114*, 166.
- (28) Pedemonte, L.; Bracco, G. *J. Chem. Phys.* **2003**, *119*, 1433.
- (29) Moldover, M. R. et al. Work in progress following the methods developed in: Berg, R. F.; Cignolo, G. *Metrologia* **2003**, *40*, 154.
- (30) Moldover, M. R.; Buckley, T. J. *Int. J. Thermophys.* **2001**, *22*, 859.
- (31) Pitre, L.; Moldover, M. R. Work in progress.
- (32) Evers, C.; Losch, H. W.; Wagner, W. *Int. J. Thermophys.* **2002**, *23*, 1411; Evers, C.; Losch, H. W.; Wagner, W. *Chem. Ing. Tech.* **2002**, *74*, 959.
- (33) Bukowski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1999**, *110*, 4165.
- (34) Bukowski, R.; Jeziorski, B.; Szalewicz, K. In *Explicitly Correlated Functions in Molecular Physics and Quantum Chemistry*; Rychlewski, J., Ed.; Kluwer: Dordrecht, The Netherlands, 2003; p 185.
- (35) Purvis, G. D., III.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
- (36) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1987**, *86*, 2881; Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1988**, *89*, 7382.
- (37) Chafasinski, G.; Gutowski, M. *Chem. Rev.* **1988**, *88*, 943.
- (38) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (39) Urban, M.; Noga, J.; Cole, S. J.; Bartlett, R. J. *J. Chem. Phys.* **1985**, *83*, 4041.
- (40) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (41) Burda, J. V.; Zahradnik, R.; Hobza, P.; Urban, M. *Mol. Phys.* **1996**, *89*, 425.
- (42) Cencek, W.; Komasa, J.; Rychlewski, J. *Chem. Phys. Lett.* **1995**, *246*, 417.
- (43) Szalewicz, K.; Jeziorski, B.; Monkhorst, H. J.; Zabolitzky, J. G. *J. Chem. Phys.* **1984**, *81*, 2723.
- (44) Jeziorski, B.; Bukowski, R.; Szalewicz, K. *Int. J. Quantum Chem.* **1997**, *61*, 769.
- (45) Hill, R. N. *Int. J. Quantum Chem.* **1998**, *68*, 357.
- (46) Cizek, J. *J. Chem. Phys.* **1966**, *45*, 4256.
- (47) Jeziorski, B.; Monkhorst, H. J.; Szalewicz, K.; Zabolitzky, J. G. *J. Chem. Phys.* **1984**, *81*, 368.
- (48) Adams, B. G.; Jankowski, K.; Paldus J. *Chem. Phys. Lett.* **1979**, *67*, 144.
- (49) Adams, B. G.; Jankowski, K.; Paldus J. *Phys. Rev. A* **1981**, *24*, 2330.
- (50) Chiles, R. A.; Dykstra, C. E. *Chem. Phys. Lett.* **1981**, *80*, 69.
- (51) Powell, H. J. D. *Comput. J.* **1964**, *7*, 155.
- (52) Partridge, H.; Bauschlicher, C. W. *Mol. Phys.* **1999**, *96*, 705.
- (53) Szalewicz, K.; Monkhorst, H. J. *J. Chem. Phys.* **1981**, *75*, 5785.
- (54) Szalewicz, K.; Jeziorski, B.; Monkhorst, H. J.; Zabolitzky, J. G. *J. Chem. Phys.* **1983**, *78*, 1420.
- (55) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (56) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (57) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 2975.
- (58) van Mourik, T.; Wilson, A. K.; Dunning, T. H. *Mol. Phys.* **1999**, *96*, 529.
- (59) Werner, H.-J.; Knowles, P. J. *MOLPRO, A Package of ab Initio Programs*; with contributions from R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.
- (60) Olsen, J. *LUCIA, A Full CI, General Active Space Program*; with contributions from H. Larsen and M. Fulscher.
- (61) Anderson, J. B. *J. Chem. Phys.* **2001**, *115*, 4546.
- (62) Komasa, J.; Cencek, W.; Rychlewski, J. *Chem. Phys. Lett.* **1999**, *304*, 293.
- (63) Hoffmann, M. R.; Schaefer, H. F., III. *Adv. Quantum Chem.* **1986**, *18*, 207.
- (64) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041.