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Bond functions and many-body effects of the helium trimer

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Abstract. A general scheme for efficient implementation of bond functions in homonuclear triatomics is suggested and applied to the linear and triangular configurations of the helium trimer. It is found that only one set of midbond functions of size 6*s*3*p* can provide nearly all of the benefits obtainable from larger sizes as well as 100% of the energy lowering obtained with ten sets of *d*-functions added at the atom centres. They also enhance the convergence properties of the many body terms at the Hartree-Fock and electron correlation levels. Correct dissociation limits and avoiding spurious minima of potential wells as well as other linear and triangular configurations are taken into account.

Key words: Bond functions – Many-body effects – Helium trimers – Configuration interaction – Even-tempered functions

1 Introduction

In 1964, the idea of using bond functions was introduced by Preuss [1]. The aim was to replace the atom-centred higher angular momentum functions at a considerably lower cost. The utility of bond functions was then tested by the calculations of the various physical properties of molecules [2]. In 1977, Burton [3] illustrated the technique within correlated wave function computations of intermolecular forces. This involved reducing or buffering the “ghost orbital” basis set borrowing by one species with the function of a neighbouring species, when the basis set used to describe each species is not complete. This was achieved by employing Gaussian functions moved off the nuclei into the interaction region. In 1980, Cársky and Urban [4] reported on the practical use of bond functions, indicating that there was a drawback in that general rules for selecting exponents and the positions of bond functions were still lacking and it appeared [2a] that the exponents as well as the position of bond functions did not depend much on the particular bond. In 1986, Davidson and Feller [5] pointed out that for first-row diatomics the introduction of a single (s, p) set at the centre of the bond provided 90% of the energy lowering obtained with a single set of *d*-functions at the nuclear centres. In 1995, Wilson [6] reported that atom-centred basis sets had been widely used in molecular calculations designed to match the accuracy achieved in numerical Hartree-Fock studies of diatomic molecules. It has recently been shown that they can be usefully supplemented by off-centred sets [7]. Indeed, by including bond-centred functions in a systematically constructed basis set for the ground state of the nitrogen molecule, it has been possible to obtain an energy that is within a few micro-hartrees (μH) of the numerical results. The success of these calculations, and others, suggests implementation of bond functions as well as selecting exponents and positions that lack general rules. In the present study universal even-tempered basis sets were selected to guarantee well-defined basis sets of stable quality for different systems [8].

On the other hand, there has been considerable interest in the many-body effects of closed shell atoms and ions [9]. It is conventional to divide the components of the potential energy surface (PES) of three interacting atoms into three pair potentials and a three-body, non-pairwise additive potential. The pair potential is becoming well specified for many systems, but much less is known about the underlying principles governing the three-body correction to the pair potential. The non-additive part of the total interaction energy can be significant when considering the properties of bulk matter even though non-additive effects are much smaller than the additive part of the interaction energy. At both short range [10] and long range [11], the interaction potential is dominated by the two-body terms. However, at very short distances, this is no longer true [11]. Consequently, testing the convergence of the many-body effects for systems with $N \geq 3$, where N is the number of interacting particles, is a prerequisite for constructing model potentials and simulation of larger systems. To our knowledge, the effects of bond functions on many-body terms have not been outlined.

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2 Methods and calculations

2.1 Even-tempered basis sets

A set of even-tempered basis functions is defined by

$$\chi_{klm} = (r, \theta, \phi) = N \exp(-\zeta_k r^p) r^l Y_{lm}(\theta, \phi)$$

where $p = 1(2)$ for exponential (Gaussian) functions. A systematic sequence of even-tempered basis sets of Gaussian-type functions of s-, p- and d-symmetry was generated as described by Schmidt and Ruedenberg [12]. The orbital exponents were taken to form a geometric series

$$\zeta_k = \alpha_l \beta_l^k, \quad k = 1, 2, \ldots, N_l, \tag{1}$$

where α and β are dependent on the number of basis functions N_l, and the angular momentum quantum number l according to the empirical relations:

$$\ln \beta_l = b_l \ln N_l + b'_l, \tag{2}$$

$$\ln \alpha_l = a_l \ln(\beta_l - 1) + a'_l. \tag{3}$$

The following values of a_l, a'_l, b_l and b'_l for helium were employed: $a_s = 0.3966, a'_s = -3.0913$, $b_s = -0.4529$ and $b'_s = 1.0567$. The following basis sets were constructed for helium: $2ns$, $2ns\ np$, $2ns\ np\ nd$ ($n = 3 - 10$). The nomenclature $2ns$ and $2ns\ np$ for helium is used to designate atom-centred basis sets containing $2n$ functions with $l = 0$ and n functions with $l = 1$ generated according to Eq. (1). The nomenclature $20s + 2ns$ and $20s10p + 2ns\ np$ is used to designate atom-centred basis sets $20s$ and $20s10p$ to which basis sets containing $2n$ midbond functions with $l = 0$ and n midbond functions with $l = 1$ generated according to Eq. (1) have been augmented.

2.2 Many-body effects

The total energy (E) of a micro-cluster of three atoms or ions may be written as

$$E = \sum_{m \geq 1}^{3} E(m, 3)$$

$$= \sum_{i}^{3} E(1, 3)_i + \sum_{i<j}^{3} E(2, 3)_{ij} + E(3, 3)_{ijk}.$$

The total interaction energy is obtained by subtracting the monomer energies from the total energy

$$\Delta E = \sum_{m \geq 1}^{3} E(m, 3) - \sum_{i}^{3} E(1, 3)_i$$

$$= \sum_{i<j}^{3} E(2, 3)_{ij} + E(3, 3)_{ijk}.$$

The first and second terms in the last expression represent the two- and three-body contributions to the total interaction energy. There are $n(n-1)/2$, two-body terms, and $n(n-1)(n-2)/3$, three body terms, where n is the number of atoms in the finite microcluster. This expression is claimed to be convergent when the three-body term is considerably smaller than the two-body terms. Consequently, the positive value of

$$E(3, 3)_{ijk} \Bigg/ \sum_{i<j}^{3} E(2, 3)_{ij}$$

may be considered to be a measure of the convergence of the many-body terms. In Tables 1–6, the two-body terms are written as $\Sigma E^{(2)}$ and the three-body terms as $E^{(3)}$. Matrix Hartree-Fock self-consistent field (SCF), many-body perturbation theory (SDTQ-MBPT) and quadratic configuration interaction (SDT-QCI) calculations were performed for the helium trimer in the linear (optimal) ground-state configuration and the triangular configuration. Calculations were carried out with the program GAUSSIAN 92 [13].

Table 1. Basis sets, total interaction energies ΔE, two- ($\Sigma E^{(2)}$) and three-body ($E^{(3)}$) terms and the convergence rate $[E^{(3)}/\Sigma E^{(2)}] \times 100$ of the many-body terms of the linear configuration of the helium trimer at the self-consistent field (SCF) level. All energies are given in Hartrees and corrected for basis set superposition error (BSSE)

Basis set	ΔE	$\Sigma E^{(2)}$	$E^{(3)}$	$[E^{(3)}/\Sigma E^{(2)}]$ $\times 100$
$20s$	0.0000591	0.0000591	0.0	0.00
$20s + 6s$	0.0000590	0.0000592	−0.0000002	0.34
$20s10p$	0.0000582	0.0000581	0.0000001	0.17
$20s10p + 6s3p$	0.0000581	0.0000580	0.0000001	0.17

Table 2. Basis sets, total interaction energies ΔE, two- ($\Sigma E^{(2)}$) and three-body ($E^{(3)}$) terms and the convergence rate $[E^{(3)}/\Sigma E^{(2)}] \times 100$ of the many-body terms of the linear configuration of the helium trimer at the MP4SDTQ level. All energies are given in Hartrees and corrected for BSSE

Basis set	ΔE	$\Sigma E^{(2)}$	$E^{(3)}$	$[E^{(3)}/\Sigma E^{(2)}]$ $\times 100$
$20s$	0.0000714	0.0000710	0.0000004	0.56
$20s + 6s$	0.0000623	0.0000627	−0.0000004	0.64
$20s10p$	−0.0000292	−0.0000285	−0.0000007	2.46
$20s10p + 6s3p$	−0.0000425	−0.0000382	−0.0000043	11.26

Table 3. Basis sets, total interaction energies ΔE, two- ($\Sigma E^{(2)}$) and three-body ($E^{(3)}$) terms and the convergence rate $[E^{(3)}/\Sigma E^{(2)}] \times 100$ of the many-body terms of the linear configuration of the helium trimer at the quadratic configuration interaction (QCISDT) level. All energies are given in Hartrees and corrected for BSSE

Basis set	ΔE	$\Sigma E^{(2)}$	$E^{(3)}$	$[E^{(3)}/\Sigma E^{(2)}]$ $\times 100$
$20s$	0.0000726	0.0000722	0.0000004	0.55
$20s + 6s$	0.0000628	0.0000632	−0.0000004	0.63
$20s10p$	−0.0000306	−0.0000296	−0.0000010	3.38
$20s10p + 6s3p$	−0.0000442	−0.0000419	−0.0000023	5.49

Table 4. Basis sets, total interaction energies ΔE, two- ($\Sigma E^{(2)}$) and three-body ($E^{(3)}$) terms and the convergence rate $[E^{(3)}/\Sigma E^{(2)}] \times 100$ of the many-body terms of the equilateral triangular configuration of the helium trimer (bond length = 5.6 a_0) at the SCF level. All energies are given in Hartrees and corrected for BSSE

Basis set	ΔE	$\Sigma E^{(2)}$	$E^{(3)}$	$[E^{(3)}/\Sigma E^{(2)}] \times 100$
20*s*	+0.0000879	+0.0000888	−0.0000009	1.01
20*s* + 6*s*	+0.0000877	+0.0000885	−0.0000008	0.90
20*s*10*p*	+0.0000864	+0.0000873	−0.0000009	1.03
20*s*10*p* + 6*s*3*p*	+0.0000864	+0.0000870	−0.0000006	0.69

Table 5. Basis sets, total interaction energies ΔE, two- ($\Sigma E^{(2)}$) and three-body ($E^{(3)}$) terms and the convergence rate $[E^{(3)}/\Sigma E^{(2)}] \times 100$ of the many-body terms of the equilateral triangular configuration of the helium trimer (bond length = 5.6 a_0) at the MP4SDTQ level. All energies are given in Hartrees and corrected for BSSE

Basis set	ΔE	$\Sigma E^{(2)}$	$E^{(3)}$	$[E^{(3)}/\Sigma E^{(2)}] \times 100$
20*s*	+0.0001056	+0.0001065	−0.0000009	0.85
20*s* + 6*s*	+0.0000867	+0.0000999	−0.0000132	13.21
20*s*10*p*	−0.0000434	−0.0000414	−0.0000020	4.83
20*s*10*p* + 6*s*3*p*	−0.0000606	−0.0000585	−0.0000021	3.59

Table 6. Basis sets, total interaction energies ΔE, two- ($\Sigma E^{(2)}$) and three-body ($E^{(3)}$) terms and the convergence rate $[E^{(3)}/\Sigma E^{(2)}] \times 100$ of the many-body terms of the equilateral triangular configuration of the helium trimer (bond length = 5.6 a_0) at the QCISDT level. All energies are given in Hartrees and corrected for BSSE

Basis set	ΔE	$\Sigma E^{(2)}$	$E^{(3)}$	$[E^{(3)}/\Sigma E^{(2)}] \times 100$
20*s*	+0.0001074	+0.0001083	−0.0000009	0.83
20*s* + 6*s*	+0.0000876	+0.0001005	−0.0000129	12.84
20*s*10*p*	−0.0000453	−0.0000435	−0.0000018	4.14
20*s*10*p* + 6*s*3*p*	−0.0000629	−0.0000609	−0.0000020	3.28

3 Results and discussion

Van der Waals interaction potential of the helium trimer has been the subject of detailed theoretical investigations. As early as 1971, Novaro and Beltran-Lopez [14] calculated the potential of He_3 within the SCF-LCAO-MO approximation to test the pairwise additivity of intermolecular forces. In the neighbourhood of van der Waals well ($\sim 5.6a_0$) these were negligible. In 1983, Wells and Wilson [15] reported the results of an investigation (at the SCF level) of basis set superposition effects (BSSE) in the study of many-body van der Waals interactions of the helium trimer. In 1989, Ichihara and Itoh [16], calculated the interaction potential of the helium trimer using the configuration interaction method and found that BSSE could be avoided using a reference calculation approximated by a simple formula. In 1990, Mohan and Anderson [17] used the quantum Monte Carlo (random walk) method to obtain potential energies of interaction and determined three-body corrections to pairwise-additive potential energy expressions. As shown, practical use of bond functions and a general scheme of implementation for the helium trimer, and possibly other homonuclear triatomics, are still lacking.

3.1 General scheme of implementation

Based on the utility of bond functions, tested by calculations of various properties of molecules, the following general rules may be suggested for bond-function augmentation in homonuclear triatomics: (1) using the specified geometry of a homonuclear triatomic, saturate atom-centred functions to a sub μH level of accuracy at the SCF level using at least the first set of polarization functions, which have the dominant role, to minimize the BSSE, (2) once a certain size has been reached, optimize size and location of bond functions located at each bond, (3) select the exponents of the optimal bond functions so as to match the same SCF-interaction energy obtained without bond functions, (4) prior to PES scans, retain the selected bond functions at the suggested fractional position from each nucleus while continuously eliminating the BSSE of the atom-centred and bond functions at the SCF (and/or) the post-SCF levels.

3.2 Applications

The linear and triangular configurations of the helium trimer at bond length $5.6a_0$ are considered [15]. Highly accurate calculations approaching the sub μH level of accuracy have been shown to be obtainable using primitive Gaussian-type functions [18]. In general, saturation of atom-centred functions is required to minimize the BSSE attributed to bond function augmentation and large exponent functions are needed to handle the tight inner-shell orbital(s). Matrix Hartree-Fock electronic energy calculations were thus performed using atom-centred primitive Gaussian-type functions of *s*-, *p*- and *d*-symmetry designated as 2*ns*, 2ns np and 2*ns*

Table 7. Matrix Hartree-Fock electronic energies of the linear configuration of the helium trimer (bond length = 5.6 a_0) using atom-centered basis sets of primitive Gaussian-type function with *s*-, *p*-, and *d*- symmetry. All energies are given in Hartrees

Basis set	SCF	Basis set	SCF	Basis set	SCF
6*s*	−8.5817022	6*s*3*p*	−8.5817207	6*s*3*p*3*d*	−8.5817221
8*s*	−8.5844649	8*s*4*p*	−8.5844665	8*s*4*p*4*d*	−8.5844693
10*s*	−8.5848841	10*s*5*p*	−8.5848846	10*s*5*p*5*d*	−8.5848852
12*s*	−8.5849603	12*s*6*p*	−8.5849607	12*s*6*p*6*d*	−8.5849608
14*s*	−8.5849758	14*s*7*p*	−8.5849765	14*s*7*p*7*d*	−8.5849766
16*s*	−8.5849793	16*s*8*p*	−8.5849803	16*s*8*p*8*d*	−8.5849804
18*s*	−8.5849803	18*s*9*p*	−8.5849812	18*s*9*p*9*d*	−8.5849813
20*s*	−8.5849806	20*s*10*p*	−8.5849815	20*s*10*p*10*d*	−8.5849816

Table 8. Matrix Hartree-Fock electronic energies of the equilateral triangular configuration of the helium trimer (bond length = 5.6 a_0) using atom-centered basis sets of primitive Gaussian-type function with *s*-, *p*-, and *d*- symmetry. All energies are given in Hartrees

Basis set	HF	Basis set	HF	Basis set	HF
6s	−8.5816851	6s3p	−8.5817127	6s3p3d	−8.5817149
8s	−8.5844379	8s4p	−8.5844401	8s4p4d	−8.5844443
10s	−8.5848561	10s5p	−8.5848569	10s5p5d	−8.5848577
12s	−8.5849319	12s6p	−8.5849326	12s6p6d	−8.5849326
14s	−8.5849471	14s7p	−8.5849482	14s7p7d	−8.5849484
16s	−8.5849506	16s8p	−8.5849520	16s8p8d	−8.5849521
18s	−8.5849515	18s9p	−8.5849530	18s9p9d	−8.5849531
20s	−8.5849518	20s10p	−8.5849533	20s10p10d	−8.5849534

Table 9. The effect of midbond functions on the matrix Hartree-Fock electronic energies of the linear configuration of the helium trimer (bond length = 5.6 a_0). All energies are given in Hartrees and (+) stands for the addition of one set of midbond functions

Basis set	SCF	Basis set	SCF
20s + 6s	−8.5849807	20s + 6s + 6s	−8.5849808
20s + 8s	−8.5849807	20s + 8s + 8s	−8.5849808
20s + 10s	−8.5849807	20s + 10s + 10s	−8.5849808
20s + 12s	−8.5849807	20s + 12s + 12s	−8.5849808
20s + 14s	−8.5849807	20s + 14s + 14s	−8.5849808
20s + 16s	−8.5849807	20s + 16s + 16s	−8.5849808
20s + 18s	−8.5849807	20s + 18s + 18s	−8.5849808
20s + 20s	−8.5849807	20s + 20s + 20s	−8.5849808
20s10p + 6s3p	−8.5849816	20s10p + 6s3p + 6s3p	−8.5849816
20s10p + 8s4p	−8.5849816	20s10p + 8s4p + 8s4p	−8.5849816
20s10p + 10s5p	−8.5849816	20s10p + 10s5p + 10s5p	−8.5849816
20s10p + 12s6p	−8.5849816	20s10p + 12s6p + 12s6p	−8.5849816
20s10p + 14s7p	−8.5849816	20s10p + 14s7p + 14s7p	−8.5849816
20s10p + 16s8p	−8.5849816	20s10p + 16s8p + 16s8p	−8.5849816
20s10p + 18s9p	−8.5849816	20s10p + 18s9p + 18s9p	−8.5849816
20s10p + 20s10p	−8.5849816	20s10p + 20s10p + 20s10p	−8.5849816

np nd, $n = 3-10$, and the results are given in Table 7 for the linear configuration and Table 8 for the triangular configuration. As shown in these tables, an accuracy approaching the sub μH level (0.3 μH) can be achieved for the helium trimer using *s*-, *p*-, and *d*- primitive Gaussian-type functions. When we come to consider the linear configuration, the addition of 10*p* functions to the 20*s* basis contributes 0.9 μH to the Hartree-Fock energies, while the addition of 10*d* functions to the 20*s*10*p* basis set amounts to 0.1 μH. Now, for the triangular configuration, the addition of 10*p* functions to the 20*s* basis set contributes 1.5 μH to the Hartree-Fock energies, while the addition of 10*d* functions to the 20*s*10*p* basis set amount to 0.1 μH. This implies that, the first set of polarization functions play the dominant role of energy lowering and the basis sets 20*s* and 20*s*10*p* are good starting points for optimizing size and location of bond functions.

Table 10. The effect of midbond functions on the matrix Hartree-Fock electronic energies of the equilateral triangular configuration of the helium trimer (bond length = 5.6 a_0). All energies are given in Hartrees and (+) stands for the addition of one set of midbond functions

Basis set	SCF	Basis set	SCF
20s + 6s	−8.5849520	20s + 6s + 6s	−8.5849520
20s + 8s	−8.5849521	20s + 8s + 8s	−8.5849521
20s + 10s	−8.5849520	20s + 10s + 10s	−8.5849521
20s + 12s	−8.5849520	20s + 12s + 12s	−8.5849521
20s + 14s	−8.5849520	20s + 14s + 14s	−8.5849521
20s + 16s	−8.5849521	20s + 16s + 16s	−8.5849521
20s + 18s	−8.5849521	20s + 18s + 18s	−8.5849521
20s + 20s	−8.5849521	20s + 20s + 20s	−8.5849521
20s10p + 6s3p	−8.5849533	20s10p + 6s3p + 6s3p	−8.5849533
20s10p + 8s4p	−8.5849533	20s10p + 8s4p + 8s4p	−8.5849533
20s10p + 10s5p	−8.5849533	20s10p + 10s5p + 10s5p	−8.5849533
20s10p + 12s6p	−8.5849533	20s10p + 12s6p + 12s6p	−8.5849533
20s10p + 14s7p	−8.5849533	20s10p + 14s7p + 14s7p	−8.5849533
20s10p + 16s8p	−8.5849533	20s10p + 16s8p + 16s8p	−8.5849533
20s10p + 18s9p	−8.5849533	20s10p + 18s9p + 18s9p	−8.5849533
20s10p + 20s10p	−8.5849533	20s10p + 20s10p + 20s10p	−8.5849533

Bond functions have been shown to be quite efficient if their exponents and locations are optimized [19]. Since the centre of the bond is the logical selection of position in homonuclear triatomics [20], we have concentrated on size optimization. Using the atom-centred functions 20*s* the first set of midbond functions of variable size 6*s* − 20*s* were added and energy calculations were performed. This was then followed by simultaneous additions of first and second sets of midbond functions and the process was repeated with the other atom-centred functions 20*s*10*p*. The results are given in Table 9 for the linear configuration and Table 10 for the triangular configuration. As shown in these tables, the matrix Hartree-Fock electronic energies were insensitive to the size of midbond functions and the addition of the second set of midbond functions has a negligible effect. The minimal size at which midbond functions recover the most negative electronic energy is either 6*s* or 6*s*3*p*. Two more facts emerge from these tables: (1) a converged depth of a potential energy minimum can be reached using midbond functions and (2) midbond functions much smaller in size and exponents than atom-centred functions provide nearly all of the benefits obtainable from larger sizes.

A comparison of the linear configuration in Tables 7 and 9 shows that while the addition of 6*s* midbond functions to the 20*s* atom-centred basis set recovers 11% of the energy lowering obtained from the addition of 10*p* atom-centred functions to the same basis set, the addition of 6*s*3*p* midbond functions to the 20*s*10*p* basis set recovers 100% of the energy lowering obtained from the addition of 10*d* atom-centered functions. Further comparison between the triangular configuration in Tables 8 and 10 shows more or less similar behaviour. The addition of 6*s* midbond functions to the 20*s* atom-centred basis set recovers 13.3% of the energy lowering obtained from the addition of 10*p* atom-centred functions to the same basis set. The addition of $6s3p$ midbond functions to the $20s10p$ basis set has no effect on energy lowering, but the addition of $10d$ atom-centered functions amounts to only -0.1 μH. Consequently, midbond functions of low angular momentum symmetry can reproduce the matrix Hartree-Fock electronic energies normally to be achieved by use of atom-centred functions of high angular momentum symmetry with considerably lower computational effort and cost.

According to the theoretical analysis of Tao and Pan [21], bond functions are used for the improved description of molecular orbitals in the excited configurations at the correlated level and, consequently, the Hartree-Fock energies should not be affected considerably by the addition of bond functions. It is also noted that use of bond functions may be rationalized by realizing that there is an effective nucleus in the middle of the nuclei for any electrons far from the nuclei (in the excited configuration state) and so the whole system may be perceived as a Rydberg system whose states can be better described by midbond functions [21]. On this basis we examine the effect of midbond functions on the Hartree-Fock interaction energy of the helium trimer. The Hartree-Fock interaction energies ΔE of the linear configuration were calculated to be 59.1 and 58.2 μH using the basis sets $20s$ and $20s10p$. When the midbond functions $6s$ and $6s3p$ were added, these were calculated to be 59 and 58.1 μH Table 1. For the triangular configuration, the Hartree-Fock interaction energies ΔE were calculated to be 7.9 and 6.4 μH using the basis sets $20s$ and $20s10p$. When the midbond functions $6s$ and $6s3p$ were augmented, these were calculated to be 7.9 and 6.4 μH, Table 4. Clearly, the Hartree-Fock interaction energies are not significantly affected and the condition for proper use of bond functions is fulfilled.

The convergence of the many-body terms is a prerequisite for constructing model potentials and simulation of larger systems. If non-pairwise additive contributions of the helium trimer are negligible, total interaction energy will be well represented as the sum of two-body terms. We are therefore interested in the effect of bond functions on the convergence properties of the many-body expansion. Total interaction energies as well as the two- and three-body terms of the many-body effects at the Hartree-Fock (SCF) and electron correlation levels are given in Tables 1–3 for the linear configuration and Tables 4–6 for the triangular configuration. The electron correlation level includes the MBPT and QCI methods. Interaction energies were corrected for BSSE attributed to atom-centred and midbond functions using Boys and Bernardi function counterpoise method [18]. BSSE corrections were made to avoid any possible spurious minima. Several facts emerge from these tables: while midbond functions have negligible contributions to the total interaction energies and the energy terms of the many-body expansion at the SCF level, they do have significant contributions at the MBPT and QCI electron correlation levels. The total interaction energies and the two-body terms of the QCI method are significantly larger than the MBPT values. The SCF energy of the linear configuration of the helium trimer contributes to the repulsion between helium atoms, in terms of the total interaction energies and the two and three-body components. The QCI and MBPT energies contribute to the attraction when the polarization p-functions are included. The SCF energy of the triangular configuration contributes to the repulsion of helium atoms in terms of the total interaction energy and three-body terms, while the QCI an MBPT energies contribute to the attraction when the polarization p-functions are included.

In order to investigate the accuracy of interaction potentials, we consider the contributions from three-body terms. A many-body perturbation calculation of Wells and Wilson [15] indicates a three-body component of 0.00 μH for the linear configuration and $-0.43\,\mu$H for the triangular configuration at $R = 5.6a_0$. In their calculations, an even-tempered Gaussian basis set $[8s4p2d1f]$ and site-site CP method were employed. SDCI treatment of Ichihara and Itoh [16] indicates a three-body component of $-0.63\,\mu$H for the linear configuration and $8.55\,\mu$H for the triangular configuration at $R = 5.6a_0$. They used $[4s1p1d]$ basis set optimized to describe the interaction of the helium dimer system. In their comment on the discrepancy between their result and that of Wells and Wilson for the linear configuration, they considered the defect of their small basis set to be trivial, since the two helium atoms on both sides are separated and the three-body effect is expected to be quite small. For the linear configuration, Table 2, the three-body components were calculated to be 0.4 and $-0.7\,\mu$H at the SDTQ-MBPT level using the basis sets $20s$ and $20s10p$. In Table 3, these were calculated to be 0.4 and $-1.0\,\mu$H at the SDT-QCI level using the same basis sets. When midbond functions were augmented, three-body components were calculated to be -0.4 and $-4.3\,\mu$H at the SDTQ-MBPT level using the basis sets $20s + 6s$ and $20s10p + 6s3p$, respectively, as well as -0.4 and $2.3\,\mu$H at the SDT-QCI level using the same basis sets. For the triangular configuration, Table 5, the three-body terms were calculated to be -0.9 and $-2.0\,\mu$H at the SDTQ-MBPT level using the basis sets $20s$ and $20s10p$. In Table 6 these were calculated to be -0.9 and $-1.8\,\mu$H at the SDT-QCI level using the same basis set. When midbond functions were included, the three body components were calculated to be -13.2 and $-2.1\,\mu$H using the basis sets $20s + 6s$ and $20s10p + 6s3p$, respectively, as well as -12.9 and $-2.0\,\mu$H at the SDT-QCI level using the same basis sets. The present results are comparable and we may attribute any discrepancies either to the neglect of higher polarization functions or higher excitations of the electron correlation treatment.

On the other hand, the many-body expansion terms converge rapidly after the two-body terms at both the Hartree-Fock and electron correlation levels. The percentage contributions of the three-body terms $E^{(3)}$ relative to the sum of the two-body terms $\Sigma E^{(2)}$ are given in the last columns of Tables 1–3 for the linear configuration and Tables 4–6 for the triangular configuration. We may consider these contributions as a measure for the convergence rate of the many-body expansion terms. As shown, the addition of midbond functions improves the convergence properties of the many-body effects at the SCF level as well as the electron correlation levels of the triangular configuration provided that the polarization

Table 11. Matrix Hartree-Fock electronic energies of the linear configuration of the helium trimer at different bond lengths. All energies are given in Hartrees

R/a_0	$20s$	$20s+6s$	$20s10p$	$20s10p+6s3p$
2.6	−8.5162724	−8.5517437	−8.5177070	−8.5520935
3.6	−8.5779778	−8.5815327	−8.5781133	−8.5815802
4.6	−8.5843728	−8.5846799	−8.5843846	−8.5846850
5.6	−8.5849806	−8.5849807	−8.5849815	−8.5849816
6.6	−8.5850348	−8.5850077	−8.5850349	−8.5850082
7.6	−8.5850394	−8.5850100	−8.5850394	−8.5850105
8.6	−8.5850398	−8.5850102	−8.5850398	−8.5850107

Table 12. Matrix Hartree-Fock electronic energies of the equilateral triangular configuration of the helium trimer at different bond lengths (R) in a_0. All energies are given in Hartrees

R/a_0	$20s$	$20s+6s$	$20s10p$	$20s10p+6s3p$
2.6	−8.4974180	−8.4984877	−8.4998791	−8.4999742
3.6	−8.5751872	−8.5752470	−8.5753904	−8.5753952
4.6	−8.5840666	−8.5840708	−8.5840843	−8.5840845
5.6	−8.5849518	−8.5849520	−8.5849533	−8.5849533
6.6	−8.5850323	−8.5850323	−8.5850324	−8.5850324
7.6	−8.5850392	−8.5850392	−8.5850392	−8.5850392
8.6	−8.5850398	−8.5850398	−8.5850398	−8.5850398

p-functions are included. The contribution of the $E^{(2)}$ terms relative to the $\Sigma E^{(2)}$ terms at the QCI level are smaller and the corresponding interaction energies ΔE are more negative relative to the MBPT level. This implies that the QCI method provides a more accurate description of the many-body effects in the helium trimer. Since the convergence of the many-body terms is a prerequisite for constructing model potential and simulation of larger systems, it is apparent that the interaction potential of the helium trimer can be mainly described by the sum of two-body interactions.

The matrix Hartree-Fock electronic energies of the linear and triangular configurations of the helium trimer at different bond lengths are given in Tables 11 and 12. The most important output of these tables is that the contributions of bond functions to the energy lowering get smaller with increasing the interatomic distance (R) and at $R > 5.6a_0$ the energies of the triangular configurations are more negative than the corresponding linear configurations. For the two types of structures, bond functions have negative contributions to the energies at $R = 2.6 - 5.6a_0$ but at $R \geq 6.6a_0$ they have positive contributions to the energies of the linear configuration and completely negligible effects on the energies of the triangular configuration.

References

1. Preuss H (1964) Z Naturforsch 19:1335; (1965) Z Naturforsch 20:17–21
2. See e.g. (a) Russegger P, Lischka H, Schuster P (1971) Chem Phys Lett 12:392; (b) Mayer M, Pulay P (1972) J Chem Phys 56:2109; (c) Peyerimhoff SD, Buenker RJ (1972) Chem Phys Lett 16:235; (d) Vladimiroff T (1974) Chem Phys Lett 24:340; (e) Mayer M, Pulay P (1974) Theor Chim Acta 32:253; (f) Jarive J O, Rauk A, Edmiston C (1974) Can J Chem 52:2778; (g) Vladimiroff T (1976) J Chem Phys 64:433; (h) Burton PG, Markey BR (1977) Aust J Chem 30:231; (i) Burton PG (1977) Mol Phys 34: 51;(j) Carlsen NR (1977) Chem Phys Lett 51:192; (k) Urban M, Pavlik S, Kozár T (1977) Chem Zvesti 31:165; (l) Butscher W, Shih S-K, Buenker RJ, Peyerimoff SD (1977) Chem Phys Lett 52:457; (m) Neisius D, Verhaegen G (1979) Chem Phys Lett 66:358; (n) Lawlor L, Vasudevan K, Grein F (1980) Chem Phys Lett 75:79; (o) Wright J S, Williams R J (1983) J Chem Phys 78:5264; (p) Wright J S, Buenker R J (1984) Chem Phys Lett 106:570; (q) Bauschlicher Jr C W (1985) Chem Phys Lett 122:572
3. Burton PG (1977) J Chem Phys 67:4696
4. Cársky P, Urban M (1980) Ab initio calculations methods and application in chemistry. (Lecture notes in chemistry, 16) Springer Berlin Heidelberg New York
5. Davidson ER, Feller DF (1986) Chem Rev 86:681
6. Wilson S (1995) Technical Report, RAL-TR-95-018, CLRC
7. See e.g. (a) Moncrieff D, Wilson S (1993) J Phys B: Atom Mol Opt Phys 26:1605; (b) Moncrieff D, Wilson S (1993) Chem Phys Lett 209:423
8. Wilson S, Silver DM (1980) J Chem Phys 21:2159
9. See e.g. (a) Bounds DG, Hinchliffe A (1980) Mol Phys 40:989; (b) Bounds DG (1984) Mol Phys 51:1135; (c) Bruch LW, Novaro OA, Flores A (1977) J Chem Phys 67:2371; (d) Chalasinski G, Szczeniak MM, Cybulski SM (1990) J Chem Phys 92:2481; (e) Shalabi A S (1991) Chem Phys 156:359; (f) Shalabi AS (1991) J Molec Struct (THEOCHEM,) 236:371; (g) Shalabi AS, Kamel MA, Eid Kh M (1992) Int J Quantum Chem 41:281; (h) Shalabi AS, Kamel M A, Shalabi SA, Eid Kh M (1992) Mol Phys 75:1365; (i) Shalabi AS (1992) J Mol Struct (THEOCHEM)262:131; (j) Shalabi AS (1993) J Phys Chem Solids 54:765; (k) Shalabi A S, Kamel KA, Assem MM (1995) Theor Chim Acta 91:73; (l) Murrell JN (1990) Int J Quantum Chem 37:95
10. Williams DR, Schaad L T, Murrell JN (1967) J Chem Phys 47:4916
11. Kolos W, Les A (1972) Int J Quantum Chem 6:1101
12. Schmidt MW, Ruedenberg K (1979) J Chem Phys 71:351
13. Frisch M J, Trucks G W, Head-Gordon M, Gill PMW, Wong HW, Foresman JB, Johnson BG, Schlegel HB, Robb MA, Replogle ES, Comperts R, Andres JL, Ragavachari K, Binkley JS, Gonzalez C, Martin RL, Fox DJ, Defrees DJ, Baker J, Stewart JJP, Pople JA, Gaussian (1992), Gaussian Inc., Pittsburgh Pa
14. Novaro OA, Beltran-Lopez V (1971) J Chem Phys 56:815
15. Wells BH, Wilson S (1985) Mol Phys 55:199
16. Ichihara A, Itoh R (1989) Bull Chem Soc Jap 62:1410
17. Mohan V, Anderson JB (1990) J Chem Phys 92:6971
18. See e.g. (a) Shalabi AS, Wilson S (1995) J Mol Struct (Theochem) 341:165 (b) Shalabi AS (1996) Electron J Theor Chem 1: 1
19. See e.g. (a) Senff VE, Burton PG (1986) Mol Phys 58:637; (b) Gutowski M, Verbeek J, Lenthe van JH, Chalasinski G (1987) Chem Phys 111:271; (c) Lenthe, van JH, Vos RJ, van Duijneveldt JGCM, van de Rijdt, van Duijneveldt FB (1988) Chem Phys Lett 143:435 (d) Burton PG, Senff UE (1982) J Chem Phys 76:6073; (e) Senff UE, Burton PG (1985) J Chem Phys 89:797
20. See e.g. (a) Tao F-M, Pan Y-K (1994) Mol Phys 81:507; (b) Tao F-M, Pan Y-K (1992) J Chem Phys 97:4989
21. Tao F-M, Pan Y-K (1992) Chem Phys Lett 194:162