Theoretical Investigation of van der Waals Interaction Energy of Helium Trimer. Three-Body Effect

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Synopsis. Using an ab initio configuration interaction (CI) treatment, the He trimer interaction energy for the equilateral triangular configuration was calculated. The CI included all single and double electronic excitations (SD CI). The resulting three-body component was significantly larger than the third-order perturbation calculation.

There have been several reports in which the interaction energy between He atoms was calculated by the use of an ab inito MO method.[1–9] It is known that the He dimer system has a repulsive ground state, with only a van der Waals minimum. In a recent paper of our group, we presented van der Waals potential energy curves of a He trimer through the configuration interaction (CI) treatment.[10] The CI included all single and double excitations from the SCF ground state (SD CI). For a weakly bonded system the basis set superposition error (BSSE) in the He trimer energies could not be neglected and reference calculations approximated by the simple formula were performed in order to eliminate this error. As a result a reliable interaction potential of the He trimer could be obtained for the linear configuration ($D_{\infty h}$). However, the three-body component of the interaction energy for the equilateral triangular configuration (D_{3d}) was significantly larger than the many-body perturbation calculation of Wells and Wilson.[1] This discrepancy was considered to be mainly due to the defect of the basis set employed in our calculation.

In this paper we report on the results of SD CI calculations of the interaction energy of the He trimer for an equilateral triangular configuration, where two large Gaussian-type [8s4p2d1f] and [7s5p2d1f] basis sets were employed. These were chosen so as to provide an improved description of He–He interaction and to lower the BSSE in the He trimer energy. Moreover, since the third-order Møller-Plesset perturbation (MP3) energy can be obtained in the SD CI calculation process, the interaction energy of the He trimer by the MP3 treatment is also presented. The results concerning the three-body components of the He trimer interaction energies derived from the MP3 and SD CI treatments are discussed.

Details of Calculations

In the present work, two Gaussian-type basis sets, [8s4p2d1f] and [7s5p2d1f], were employed for the He atom. The [8s4p2d1f] basis set comprised (8s4p2d1f) even-tempered primitive functions. The exponents were determined by a progression ($\zeta_k = \alpha\beta^k$, $k = 1, 2, \cdots$), the values of α and β taken from the work of Schmidt and Ruedenberg[11] ($\alpha = 0.061317$, $\beta = 3.06930$). The first eight exponents given by this prescription were employed for s-type primitive functions, the first four for p-type primitives, the first two for d-type primitives and the first one for a single f-type primitive function in the [8s4p2d1f] basis set. On the other hand, the [7s5p2d1f] basis set comprised the (16s6p2d1f) primitive functions. The exponents of (16s) primitive functions were taken from Schmidt even-tempered basis set;[11] these primitives were contracted to (6,5,1,1,1,1,1). The contraction was performed so that the atomic energy with the contracted set came close to that with an uncontracted set. The exponents of the (6p) primitive functions were taken from the work of Knowles et al.,[12] and the (6p) primitives were contracted to (2,1,1,1,1). The contraction was performed in the He dimer system at an internuclear distance of 5.6 Bohr after the SCF calculation with an uncontracted (6p) set placed on the [7s] contracted set. The exponents of two d-type primitives were taken to be 1.52[12] and 0.20, and the exponent of 0.30 for the f-type primitive function. These [8s4p2d1f]and [7s5p2d1f] sets were designed so that it is possible to obtain a satisfactory description of the He interaction, while the BSSE is effectively eliminated. The SCF, MP3, and SD CI energies of the He atom (E_{He}) for these two basis sets are indicated in Table 1.

The results of MP3 and SD CI calculations for the interaction energy of the supermolecule system must be corrected in order to eliminate the BSSE.[13–17] The interaction energy for the system of n helium atoms ($E_{\mathrm{int}}^{\mathrm{He}_n}$) at some nuclear geometry may be obtained using the difference between the energy of the supersystem (E_{He_n}) and an appropriate reference energy (E_{ref}),

$$E_{\mathrm{int}}^{\mathrm{He}_n} = E_{\mathrm{He}_n} - E_{\mathrm{ref}}. \tag{1}$$

The reference energy of a He dimer system by the MP3 treatment is defined as twice the MP3 energy of the He atom which is calculated with the full basis set of the dimer system; the reference energy of a He trimer system for an equilateral triangle is defined as three times the MP3 energy of the He atom with the full

Table 1. Calculated SCF, MP3, and SD CI Energies of the He atom (E_{He})

Method	E_{He}/a.u.[a]	
	[8s4p2d1f]	[7s5p2d1f]
SCF	-2.86150709_9	-2.86167952_6
MP3	−2.89965244	−2.90082187
SD CI	−2.90073219	−2.90183194

a) 1 a.u.$=4.359814\times10^{-18}$ J.

Table 2. The He Dimer Interaction Energies ($E_{int}^{He_2}$) for the Internuclear Distance of 5.6 Bohr

Basis set	Method	E_{He_2}/a.u.$^{a)}$	E_{ref}/a.u.	BSSE/K$^{b)}$	$E_{int}^{He_2}$/K
[8s4p2d1f]	MP3	−5.79935835	−5.79933123	−8.32	−8.56
	SD CI	−5.80089249	−5.80086522	−8.26	−8.61
[7s5p2d1f]	MP3	−5.80167829	−5.80165135	−2.40	−8.51
	SD CI	−5.80305799	−5.80303110	−2.25	−8.49

a) 1 a.u.=4.359814×10^{-18} J. b) 1 K=1.380662×10^{-23} J.

Table 3. The He Trimer Interaction Energies ($E_{int}^{He_3}$) for the Equilateral Triangle of Side 5.6 Bohr

Basis set	Method	E_{He_3}/a.u.$^{a)}$	E_{ref}/a.u.	BSSE/K$^{b)}$	$E_{int}^{He_3}$/K
[8s4p2d1f]	MP3	−8.69911248	−8.69903031	−23.05	−25.95
	SD CI	−8.70050515	−8.70042617	−22.69	−24.94
[7s5p2d1f]	MP3	−8.70256898	−8.70248729	−6.84	−25.80
	SD CI	−8.70370905	−8.70363117	−6.39	−24.59

a) 1 a.u.=4.359814×10^{-18} J. b) 1 K=1.380662×10^{-23} J.

basis set of a trimer system. On the other hand, the reference energy of a He dimer system through the SD CI treatment is given by the formula of Price and Stone,[14)]

$$E_{ref} = 2[E_T + (1 - a_0^2)E_{SCF}]/(2 - a_0^2) + \varepsilon, \qquad (2)$$

where E_{SCF}, E_T, and a_0 represent the SCF energy, total SD CI energy, and the SCF ground state coefficient of He atom calculated with the full basis set of a dimer system. The constant ε is determined so that the interaction energy becomes zero when two He atoms are infinitely separated. The reference energy of the He trimer for the equilateral triangle can also be written as[10)]

$$E_{ref} = 3[E_T + 2(1 - a_0^2)E_{SCF}]/(3 - 2a_0^2) + \varepsilon. \qquad (3)$$

In this case E_{SCF}, E_T, and a_0 are the SCF energy, total SD CI energy, and the SCF ground state coefficient of the He atom with the full basis set of a trimer system.

The three-body component of the He trimer interaction energy through the MP3 and SD CI treatments is determined by the 'site–site' counterpoise method of Wells and Wilson.[1)] In this method, the three-body component ($E(3)$) for an equilateral triangle is given by

$$E(3) = E_{int}^{He_3} - 3E_{int}^{He_2'}, \qquad (4)$$

where $E_{int}^{He_2'}$ represents the interaction energy of the He dimer, which is calculated in terms of the trimer basis set.

All calculations were carried out for the He dimer and the He trimer at an internuclear distance of 5.6 Bohr (2.963392×10^{-10} m), this distance corresponding to the minimum in the van der Waals interaction potential for the dimer system. The MO calculations were performed on a HITAC M682H system at the Computer Center of the University of Tokyo using the Gaussian 86 program provided by J. A. Pople et al.

Table 4. The Three-Body Compnents ($E(3)$) of the He Trimer Interaction Energies for the Equilateral Triangle of Side 5.6 Bohr

Basis Set	$E(3)$/K$^{a)}$	
	MP3	SD CI
[8s4p2d1f]	−0.14	1.02
[7s5p2d1f]	−0.14	1.03

a) 1 K=1.380662×10^{-23} J.

Results and Discussion

Table 2 indicates the He dimer interaction energies for two different basis sets found by the MP3 and SD CI calculations. The BSSE is estimated by $E_{ref}^{(MP3)}-2E_{He}^{(MP3)}$ for the MP3 treatment, and $E_{ref}^{(SDCI)}-E_{He_2}^{(SDCI)}$ ($R=\infty$) for the SD CI treatment, where R is the internuclear distance between He atoms. The MP3 and SD CI interaction energies calculated with the same basis set are in good agreement with each other. Although these interaction energies can give only 77—79 percent of the recent empirical van der Waals well depth (10.948 K),[18)] the BSSE in the reference energies are considerably reduced, compared with our previous calculations. From Table 2 we expect that an obscure balance of the basis set for the interaction energy is removed and that the BSSE is effectively eliminated.

Table 3 indicates the He trimer interaction energies for an equilateral triangle through both the MP3 and SD CI calculations. The BSSE is estimated by $E_{ref}^{(MP3)}-3E_{He}^{(MP3)}$ for the MP3 treatment, and $E_{ref}^{(SDCI)}-E_{He_3}^{(SDCI)}$ ($R=\infty$) for the SD CI treatment. It can be seen from Table 3 that these four He trimer interaction energies are about three-times larger than the corresponding dimer interaction energies. This is due to the fact that there are three He–He interactions in the triangular configuration.

Finally, the three-body components of the He trimer interaction energies for the two basis sets by the MP3 and SD CI calculations are shown in Table 4. The three-body components are obtained using the site–site counterpoise method of Wells and Wilson. The agreement is excellent for values which are derived from the same treatment (MP3 or SD CI). The MP3 values are coincident with the third-order many-body perturbation (≡MP3) result of Wells and Wilson (-0.43×10^{-6} a.u.$=-0.14$ K).1) In the present calculations two [8s4p2dlf] and [7s5p2dlf] basis sets are defined independently and the different BSSE effects arise in E_{He_3}. From these results it is considered that the agreement of the three-body components derived from the same treatment for thses two basis sets is not fortuitous.

However, the SD CI three-body components are significantly larger than the MP3 values and of opposite sign. In the CI calculations the SD CI energy can be described by a sum of the MP3 energy and partial higher-order MP perturbation energies which are obtained by using the SD CI matrix elements.19) As shown in Table 3, E_{He_3} and E_{ref} are affected by these partial higher-order energies. The three-body components of the He trimer energies are much smaller than those $E^{(\mathrm{SDCI})}_{\mathrm{He}_3}-E^{(\mathrm{MP3})}_{\mathrm{He}_3}$ and $E^{(\mathrm{SDCI})}_{\mathrm{ref}}-E^{(\mathrm{MP3})}_{\mathrm{ref}}$ values (1 K$=3.166791\times10^{-6}$ a.u.). Thus the difference of the three-body components between the MP3 and SD CI treatments is considered to be mainly due to the effect of these partial higher-order perturbation energies.

It may be concluded from the results of this investigation that the MP3 and SD CI calculations give the different three-body components of the He trimer interaction energies for the equilateral triangular configuration. This discrepancy is considered to be mainly due to the methodological difference between the MP3 and SD CI calculations. It seems that more extensive MP and CI treatments which include triple and higher electronic excitations from the SCF ground state is necessary to determine the three-body component exactly.

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