Theoretical Investigation of the Interaction Potential of Helium Trimer

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Using the help of an ab initio calculation along with a configuration interaction treatment, the interaction potential of a He trimer has been calculated. The basis set superposition error in the He trimer system could be avoided using a reference calculation approximated by a simple formula.

There have been several reports in which the interaction potential between He atoms was calculated by the use of an ab initio MO method. It is known that the He dimer system has a repulsive ground state, with only a van der Waals minimum. We have recently calculated the interaction potential of the He dimer through the configuration interaction (CI) method.[1] For a weakly bonded system the basis set superposition error (BSSE)[2–7] in the He dimer energies could not be neglected and reference calculations had to be performed in order to correct this error. In this paper we will report on the results of CI calculations for the interaction potential of the He trimer. The CI calculations contain all single and double excitations from the SCF ground state (SD CI). A simple formula is proposed for estimating the BSSE for three-body interaction energies. The formulation was performed using a procedure described by Price and Stone.[5]

The Function Counterpoise Method for Three-Body Interactions. In principle the interaction energy (ΔE) of three closed-shell systems (atoms or molecules: A, B, and C) with energies E^{A}, E^{B}, and E^{C} can be written

$$\Delta E^{\mathrm{ABC}} = E^{\mathrm{ABC}} - E^{\mathrm{A}} - E^{\mathrm{B}} - E^{\mathrm{C}}, \tag{1}$$

where E^{ABC} is the energy of supersystem ABC at some nuclear geometry. However, this expression takes no account of the BSSE. The BSSE arises from the incompleteness of the basis set, and each of the interactuing systems can make partial use of the basis sets centered on the other systems in order to improve its own property. It leads to a nonphysical energy lowering in the supersystem. Boys and Bernardi proposed the function counterpoise (CP) method for correcting the BSSE in two-body interaction energies.[2] This is often denoted as a "full" CP method.[2–7] A generalization of the full CP method to many-body interactions was attempted by Wells and Wilson.[8–10]

In the CP method, the interaction energy for a three-body system can be calculated using the difference between E^{ABC} and an appropriate reference energy, E_{ref};

$$\Delta E^{\mathrm{ABC}} = E^{\mathrm{ABC}} - E_{\mathrm{ref}}. \tag{2}$$

The reference energy, E_{ref}, may be defined as

$$E_{\mathrm{ref}} = E^{\mathrm{AG}}{}_{\mathrm{BC}} + E^{\mathrm{BG}}{}_{\mathrm{CA}} + E^{\mathrm{CG}}{}_{\mathrm{AB}}, \tag{3}$$

where $E^{\mathrm{iG}}{}_{\mathrm{jk}}$ represents the energy for system i with "ghost" orbitals of systems j and k. The term "ghost" represents a nucleus with a nuclear charge of zero and without any electrons. In practice, system i should be calculated with the full basis set of the supersystem. Wells and Wilson called this the "site-site" CP method.[8–10] This method is valid only for both E^{ABC} and E_{ref} calculations which are size consistent.

In the present investigation, however, calculations of the interaction potential were performed using the SD CI treatment; Eq. 3 was not directly used. We therefore propose an approximate formula for calculating the true reference energy. This approach is used to describe the correct reference state by the product $\psi^{\mathrm{A}}\psi^{\mathrm{B}}\psi^{\mathrm{C}}$ of correlated wavefunctions, using ghost orbitals, for three closed shell systems. Then, since each wavefunction (ψ^{A}, ψ^{B}, and ψ^{C}) includes all single and double excitations from the SCF ground state, for size consistency, an elimination of the effect of triple and higher excitations is performed. The formulation is carried out using a procedure proposed by Price and Stone for two-body interactions[5] and the full CP technique.

Development of the Formula. The normalised wavefunction for a closed shell system A, including all single and double excitations, may be written

$$\psi^{\mathrm{A}} = a_0\psi_0^{\mathrm{A}} + a_1\psi_1^{\mathrm{A}} + a_2\psi_2^{\mathrm{A}}, \tag{4}$$

with

$$a_0^2 + a_1^2 + a_2^2 = 1, \tag{5}$$

where ψ_0^{A} is the normalised SCF function, ψ_i^{A} is the part of the normalised wavefunctions containing i-fold excitations, and the a_i's the corresponding coefficients.

The wavefunctions for closed shell systems B and C can be written similarly; these three wavefunctions are orthogonal to each other.

Then, the product wavefunction for the three separated systems with ghost orbitals is

$$\begin{aligned}\psi^{\mathrm{A}}\psi^{\mathrm{B}}\psi^{\mathrm{C}} &= (a_0\psi_0^{\mathrm{A}} + a_1\psi_1^{\mathrm{A}} + a_2\psi_2^{\mathrm{A}})(b_0\psi_0^{\mathrm{B}} + b_1\psi_1^{\mathrm{B}} + b_2\psi_2^{\mathrm{B}})\\ &\quad (c_0\psi_0^{\mathrm{C}} + c_1\psi_1^{\mathrm{C}} + c_2\psi_2^{\mathrm{C}})\\ &= a_0b_0c_0\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_0^{\mathrm{C}} + a_1b_0c_0\psi_1^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_0^{\mathrm{C}}\\ &\quad + \cdots\cdots + a_2b_2c_2\psi_2^{\mathrm{A}}\psi_2^{\mathrm{B}}\psi_2^{\mathrm{C}}.\end{aligned} \tag{6}$$

In order to obtain our estimated wavefunction for the correct reference calculation, we discard the terms which represent the triple and higher excitations, and obtain

$$\begin{aligned}\psi^{\mathrm{ABC}} = Z^{-1}(&a_0b_0c_0\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_0^{\mathrm{C}} + a_1b_0c_0\psi_1^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_0^{\mathrm{C}} + a_0b_1c_0\psi_0^{\mathrm{A}}\psi_1^{\mathrm{B}}\psi_0^{\mathrm{C}}\\ &+ a_0b_0c_1\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_1^{\mathrm{C}} + a_1b_1c_0\psi_1^{\mathrm{A}}\psi_1^{\mathrm{B}}\psi_0^{\mathrm{C}} + a_1b_0c_1\psi_1^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_1^{\mathrm{C}}\\ &+ a_0b_1c_1\psi_0^{\mathrm{A}}\psi_1^{\mathrm{B}}\psi_1^{\mathrm{C}} + a_2b_0c_0\psi_2^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_0^{\mathrm{C}} + a_0b_2c_0\psi_0^{\mathrm{A}}\psi_2^{\mathrm{B}}\psi_0^{\mathrm{C}}\\ &+ a_0b_0c_2\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_2^{\mathrm{C}}),\end{aligned} \tag{7}$$

where z^{-1} is the renormalisation factor.

This product is a CI expansion which includes all single and double excitations from the SCF ground state $\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\psi_0^{\mathrm{C}}$, though the coefficients in Eq. 7 are not variationally optimised. However, as has been noted in the previous calculations for the He–He by Dacre[4] and for the H_2–H_2 by Price and Stone,[5] the product wavefunction with the coefficients of separated systems might be a reasonable approximation to the variational function. We therefore expect that ψ^{ABC} will be a reliable estimation for the variational function.

Normalising Eq. 7, we obtain

$$\begin{aligned}Z^2 = {}& a_0^2b_0^2c_0^2 + a_1^2b_0^2c_0^2 + a_0^2b_1^2c_0^2 + a_0^2b_0^2c_1^2 + a_1^2b_1^2c_0^2\\ &+ a_1^2b_0^2c_1^2 + a_0^2b_1^2c_1^2 + a_2^2b_0^2c_0^2 + a_0^2b_2^2c_0^2 + a_0^2b_0^2c_2^2.\end{aligned} \tag{8}$$

Using the fact that terms like $a_1^2b_1^2c_0^2$ are small (because of Brillouin's theorem), Eq. 8 can be approximated as

$$Z^2 = a_0^2b_0^2 + b_0^2c_0^2 + c_0^2a_0^2 - 2a_0^2b_0^2c_0^2. \tag{9}$$

Rearranging Eqs. 6 and 7, we obtain

$$\psi^{\mathrm{A}}\psi^{\mathrm{B}}\psi^{\mathrm{C}} = Z\psi^{\mathrm{ABC}} + \text{(triple and higher excitation terms)}, \tag{10}$$

which is used to obtain the energy relationship

$$\begin{aligned}&\langle \psi^{\mathrm{A}}\psi^{\mathrm{B}}\psi^{\mathrm{C}} | H_{\mathrm{A}} + H_{\mathrm{B}} + H_{\mathrm{C}} | \psi^{\mathrm{A}}\psi^{\mathrm{B}}\psi^{\mathrm{C}} \rangle\\
&= Z^2 \langle \psi^{\mathrm{ABC}} | H_{\mathrm{A}} + H_{\mathrm{B}} + H_{\mathrm{C}} | \psi^{\mathrm{ABC}} \rangle\\
&+ a_0^2(b_1^2c_2^2 + b_2^2c_1^2 + b_2^2c_2^2)\langle\psi_0^{\mathrm{A}}|H_{\mathrm{A}}|\psi_0^{\mathrm{A}}\rangle\\
&+ a_1^2(b_1^2c_1^2 + b_0^2c_2^2 + b_2^2c_0^2 + b_1^2c_2^2\\
&+ b_2^2c_1^2 + b_2^2c_2^2)\langle\psi_1^{\mathrm{A}}|H_{\mathrm{A}}|\psi_1^{\mathrm{A}}\rangle\\
&+ a_2^2(b_0^2c_1^2 + b_1^2c_0^2 + b_1^2c_1^2 + b_0^2c_2^2 + b_2^2c_0^2\\
&+ b_1^2c_2^2 + b_2^2c_1^2 + b_2^2c_2^2)\langle\psi_2^{\mathrm{A}}|H_{\mathrm{A}}|\psi_2^{\mathrm{A}}\rangle\\
&+ 2a_2a_0(b_0^2c_1^2 + b_1^2c_0^2 + b_1^2c_1^2 + b_0^2c_2^2 + b_2^2c_0^2\\
&+ b_1^2c_2^2 + b_2^2c_1^2 + b_2^2c_2^2)\langle\psi_2^{\mathrm{A}}|H_{\mathrm{A}}|\psi_0^{\mathrm{A}}\rangle\\
&+ 2a_2a_1(b_0^2c_1^2 + b_1^2c_0^2 + b_1^2c_1^2 + b_0^2c_2^2 + b_2^2c_0^2\\
&+ b_1^2c_2^2 + b_2^2c_1^2 + b_2^2c_2^2)\langle\psi_2^{\mathrm{A}}|H_{\mathrm{A}}|\psi_1^{\mathrm{A}}\rangle\\
&+ b_0^2(c_1^2a_2^2 + c_2^2a_1^2 + c_2^2a_2^2)\langle\psi_0^{\mathrm{B}}|H_{\mathrm{B}}|\psi_0^{\mathrm{B}}\rangle\\
&+ b_1^2(c_1^2a_1^2 + c_0^2a_2^2 + c_2^2a_0^2 + c_1^2a_2^2\\
&+ c_2^2a_1^2 + c_2^2a_2^2)\langle\psi_1^{\mathrm{B}}|H_{\mathrm{B}}|\psi_1^{\mathrm{B}}\rangle\\
&+ b_2^2(c_0^2a_1^2 + c_1^2a_0^2 + c_1^2a_1^2 + c_0^2a_2^2 + c_2^2a_0^2\\
&+ c_1^2a_2^2 + c_2^2a_1^2 + c_2^2a_2^2)\langle\psi_2^{\mathrm{B}}|H_{\mathrm{B}}|\psi_2^{\mathrm{B}}\rangle\\
&+ 2b_2b_0(c_0^2a_1^2 + c_1^2a_0^2 + c_1^2a_1^2 + c_0^2a_2^2 + c_2^2a_0^2\\
&+ c_1^2a_2^2 + c_2^2a_1^2 + c_2^2a_2^2)\langle\psi_2^{\mathrm{B}}|H_{\mathrm{B}}|\psi_0^{\mathrm{B}}\rangle\\
&+ 2b_2b_1(c_0^2a_1^2 + c_1^2a_0^2 + c_1^2a_1^2 + c_0^2a_2^2 + c_2^2a_0^2\\
&+ c_1^2a_2^2 + c_2^2a_1^2 + c_2^2a_2^2)\langle\psi_2^{\mathrm{B}}|H_{\mathrm{B}}|\psi_1^{\mathrm{B}}\rangle\\
&+ c_0^2(a_1^2b_2^2 + a_2^2b_1^2 + a_2^2b_2^2)\langle\psi_0^{\mathrm{C}}|H_{\mathrm{C}}|\psi_0^{\mathrm{C}}\rangle\\
&+ c_1^2(a_1^2b_1^2 + a_0^2b_2^2 + a_2^2b_0^2 + a_1^2b_2^2\\
&+ a_2^2b_1^2 + a_2^2b_2^2)\langle\psi_1^{\mathrm{C}}|H_{\mathrm{C}}|\psi_1^{\mathrm{C}}\rangle\\
&+ c_2^2(a_0^2b_1^2 + a_1^2b_0^2 + a_1^2b_1^2 + a_0^2b_2^2 + a_2^2b_0^2\\
&+ a_1^2b_2^2 + a_2^2b_1^2 + a_2^2b_2^2)\langle\psi_2^{\mathrm{C}}|H_{\mathrm{C}}|\psi_2^{\mathrm{C}}\rangle\\
&+ 2c_2c_0(a_0^2b_1^2 + a_1^2b_0^2 + a_1^2b_1^2 + a_0^2b_2^2 + a_2^2b_0^2\\
&+ a_1^2b_2^2 + a_2^2b_1^2 + a_2^2b_2^2)\langle\psi_2^{\mathrm{C}}|H_{\mathrm{C}}|\psi_0^{\mathrm{C}}\rangle\\
&+ 2c_2c_1(a_0^2b_1^2 + a_1^2b_0^2 + a_1^2b_1^2 + a_0^2b_2^2 + a_2^2b_0^2\\
&+ a_1^2b_2^2 + a_2^2b_1^2 + a_2^2b_2^2)\langle\psi_2^{\mathrm{C}}|H_{\mathrm{C}}|\psi_1^{\mathrm{C}}\rangle\end{aligned} \tag{11}$$

where H_{i} is the Hamiltonian for system i.

On the other hand, the SCF energy (E_{SCF}) and the total SCF CI energy (E_{T}) of the individual system A can be written as

$$E_{\mathrm{SCF}}^{\mathrm{A}} = \langle\psi_0^{\mathrm{A}}|H_{\mathrm{A}}|\psi_0^{\mathrm{A}}\rangle, \tag{12}$$

$$\begin{aligned}E_{\mathrm{T}}^{\mathrm{A}} &= \langle\psi^{\mathrm{A}}|H_{\mathrm{A}}|\psi^{\mathrm{A}}\rangle = a_0^2E_{\mathrm{SCF}}^{\mathrm{A}}\\ &+ 2a_2a_0\langle\psi_2^{\mathrm{A}}|H_{\mathrm{A}}|\psi_0^{\mathrm{A}}\rangle + a_1^2\langle\psi_1^{\mathrm{A}}|H_{\mathrm{A}}|\psi_1^{\mathrm{A}}\rangle\\ &+ 2a_2a_1\langle\psi_2^{\mathrm{A}}|H_{\mathrm{A}}|\psi_1^{\mathrm{A}}\rangle + a_2^2\langle\psi_2^{\mathrm{A}}|H_{\mathrm{A}}|\psi_2^{\mathrm{A}}\rangle,\end{aligned} \tag{13}$$

and similarly for systems B and C.

Then, taking into account the relationships

$$\begin{aligned}&a_0^2b_1^2 + a_1^2b_0^2 + a_0^2b_2^2 + a_2^2b_0^2\\ &\quad = a_0^2(1 - b_0^2) + b_0^2(1 - a_0^2)\end{aligned} \tag{14}$$

and

$$a_1^2b_1^2 + a_1^2b_2^2 + a_2^2b_1^2 + a_2^2b_2^2 = (1 - a_0^2)(1 - b_0^2), \tag{15}$$

and ignoring terms like $a_1^2b_1^2c_0^2\langle\psi_1^{\mathrm{A}}|H_{\mathrm{A}}|\psi_1^{\mathrm{A}}\rangle$, the reference energy can be approximated as

$$\begin{aligned}E_{\mathrm{ref}} &= \langle\psi^{\mathrm{ABC}}|H_{\mathrm{A}} + H_{\mathrm{B}} + H_{\mathrm{C}}|\psi^{\mathrm{ABC}}\rangle\\ &= [\{b_0^2c_0^2E_{\mathrm{T}}^{\mathrm{A}} + a_0^2(b_0^2 + c_0^2 - 2b_0^2c_0^2)E_{\mathrm{SCF}}^{\mathrm{A}}\}\\ &\quad + \{c_0^2a_0^2E_{\mathrm{T}}^{\mathrm{B}} + b_0^2(c_0^2 + a_0^2 - 2c_0^2a_0^2)E_{\mathrm{SCF}}^{\mathrm{B}}\}\\ &\quad + \{a_0^2b_0^2E_{\mathrm{T}}^{\mathrm{C}} + c_0^2(a_0^2 + b_0^2 - 2a_0^2b_0^2)E_{\mathrm{SCF}}^{\mathrm{C}}\}]\\ &\quad \times (a_0^2b_0^2 + b_0^2c_0^2 + c_0^2a_0^2 - 2a_0^2b_0^2c_0^2)^{-1}.\end{aligned} \tag{16}$$

The error made in this approximation depends on the values of a_1, b_1, and c_1, as well as a_2, b_2, and c_2. Moreover, changes in these coefficients depend only on the position of the ghost orbitals. As noted by Dacre[4] and by Price and Stone,[5] however, these coefficients vary slightly between different relative positions of the interacting systems. Therefore, we also expect the error in Eq. 16 to be nearly constant.

On the other hand, if three systems are to be infinitely separated, both the interaction energy and the BSSE must be zero. In this case the reference energy becomes equal to the total energy of supersystem (E^{ABC}). Thus, we can estimate the error in Eq. 16 as a constant ε. A final formula is given by adding the constant ε:

$$\begin{aligned} E_{\mathrm{ref}} = [&\{b_0^2c_0^2E_{\mathrm{T}}^{\mathrm{A}} + a_0^2(b_0^2 + c_0^2 - 2b_0^2c_0^2)E_{\mathrm{SCF}}^{\mathrm{A}}\} \\ &+ \{c_0^2a_0^2E_{\mathrm{T}}^{\mathrm{B}} + b_0^2(c_0^2 + a_0^2 - 2c_0^2a_0^2)E_{\mathrm{SCF}}^{\mathrm{B}}\} \\ &+ \{a_0^2b_0^2E_{\mathrm{T}}^{\mathrm{C}} + c_0^2(a_0^2 + b_0^2 - 2a_0^2b_0^2)E_{\mathrm{SCF}}^{\mathrm{C}}\}] \\ &\times (a_0^2b_0^2 + b_0^2c_0^2 + c_0^2a_0^2 - 2a_0^2b_0^2c_0^2)^{-1} + \varepsilon. \end{aligned} \tag{17}$$

The reference energy can be calculated using the SCF, total (SD CI) energies, and the corresponding SCF ground state coefficients of separated systems with the ghost orbitals.

For reference, let $E_{\mathrm{SCF}}^{\mathrm{C}}$ and $E_{\mathrm{T}}^{\mathrm{C}}$ be zero and c_0 one. We then obtain E_{ref} for two-body interactions:

$$\begin{aligned} E_{\mathrm{ref}} = [&b_0^2E_{\mathrm{T}}^{\mathrm{A}} + a_0^2E_{\mathrm{T}}^{\mathrm{B}} + a_0^2(1 - b_0^2)E_{\mathrm{SCF}}^{\mathrm{A}} \\ &+ b_0^2(1 - a_0^2)E_{\mathrm{SCF}}^{\mathrm{B}}] \times (a_0^2 + b_0^2 - a_0^2b_0^2)^{-1} + \varepsilon, \end{aligned} \tag{18}$$

which is equivalent to the formula proposed by Price and Stone.[5)]

Results and Discussion

In all ab initio calculations, a Gaussian-type basis set [4s1p1d][1)] for the He atom was employed. This [4s1p1d] set could give an improved description for the interaction potential of the He dimer by the use of the SD CI treatment and the CP method of Price and Stone.[1)]

The MO calculations were performed by using the Gaussian 82 program provided by J.A. Pople et al. and the graphical unitary group approach (GUGA) program of our group.

Tables 1 and 2 indicate the interaction potentials ($E_{\mathrm{int}}^{\mathrm{He_3}}$) of the He trimer for two different spatial configurations: (i) an equilateral triangle and (ii) a linear configuration. The BSSE was estimated by $E_{\mathrm{ref}}(R) - E_{\mathrm{SD\,CI}}^{\mathrm{He_3}}(\infty)$. R in Tables 1 and 2 designates the internuclear distance between nearest-neighbour He atoms. For a triangular configuration, Eq. 17 can be simplified to

$$E_{\mathrm{ref}} = 3[E_{\mathrm{T}} + 2(1 - a_0^2)E_{\mathrm{SCF}}]/(3 - 2a_0^2) + \varepsilon, \tag{19}$$

where E_{SCF}, E_{T}, and a_0 represent the SCF, total (SD CI) energy, and the SCF ground state coefficient of the He atom with ghost orbitals. For a linear configuration, Eq. 17 can also be simplified to

$$\begin{aligned} E_{\mathrm{ref}} = [&b_0^2E_{\mathrm{T}}^{\mathrm{A}} + 2a_0^2E_{\mathrm{T}}^{\mathrm{B}} + 2a_0^2(1 - b_0^2)E_{\mathrm{SCF}}^{\mathrm{A}} \\ &+ 2(a_0^2 + b_0^2 - 2a_0^2b_0^2)E_{\mathrm{SCF}}^{\mathrm{B}}]/(2a_0^2 + b_0^2 \\ &- 2a_0^2b_0^2) + \varepsilon, \end{aligned} \tag{20}$$

where suffix A represents a He atom fixed at the

Table 1. The He Trimer Interaction Potential ($E_{\mathrm{int}}^{\mathrm{He_3}}$) for the Triangular Configuration

R/Bohr[a)]	$E^{\mathrm{He_3}}$/a.u.[b)]		E_{ref}		$E_{\mathrm{int}}^{\mathrm{He_3}}$/K	$E_{\mathrm{int}}^{\mathrm{He_3}}$[e)]/K
	SCF	correlation	E_{ref}[c)]/a.u.	$E_{\mathrm{ref}}(R)-E^{\mathrm{He_3}}(\infty)$/K[d)]		
5.0	−8.5846669	−0.0608697	−8.6455975	−1149.0	19.2	5.5
5.3	−8.5848581	−0.0600871	−8.6448892	−925.4	−17.7	−7.0
5.6	−8.5849514	−0.0594304	−8.6442898	−736.1	−29.0	−10.6
6.0	−8.5850058	−0.0587151	−8.6436302	−527.8	−28.7	−10.1
7.0	−8.5850359	−0.0575822	−8.6425718	−193.6	−14.6	−5.1
8.0	−8.5850384	−0.0571179	−8.6421364	−56.1	−6.3	−2.2
10.0	−8.5850386	−0.0569353	−8.6419697	−3.4	−1.3	−0.4
15.0	−8.5850386	−0.0569202	−8.6419588	0.0	0.0	0.0

a) R is the internuclear distance between He atoms. 1 Bohr=0.529177×10^{-10} m. b) 1 a.u.=4.359814×10^{-18} J. c) ε in E_{ref} is −3.43 K. d) 1 K=1.380662×10^{-23} J. e) See Ref. 1.

Table 2. The He Trimer Interaction Potential ($E_{\mathrm{int}}^{\mathrm{He_3}}$) for the Linear Configuration

R/Bohr[a)]	$E^{\mathrm{He_3}}$/a.u.[b)]		E_{ref}		$E_{\mathrm{int}}^{\mathrm{He_3}}$/K
	SCF	correlation	E_{ref}[c)]/a.u.	$E_{\mathrm{ref}}(R)-E^{\mathrm{He_3}}(\infty)$/K[d)]	
5.0	−8.5847862	−0.0600077	−8.6448236	−904.7	9.4
5.3	−8.5849166	−0.0593530	−8.6442227	−714.9	−14.8
5.6	−8.5849799	−0.0588114	−8.6437230	−557.1	−21.6
6.0	−8.5850166	−0.0582370	−8.6431889	−388.5	−20.4
7.0	−8.5850368	−0.0573815	−8.6423863	−135.0	−10.1
8.0	−8.5850384	−0.0570546	−8.6420794	−38.1	−4.3
10.0	−8.5850386	−0.0569302	−8.6419661	−2.3	−0.9
15.0	−8.5850386	−0.0569201	−8.6419587	0.0	0.0

a) R is the internuclear distance between nearest-neighbor He atoms. 1 Bohr=0.529177×10^{-10} m. b) 1 a.u.= 4.359814×10^{-18} J. c) ε in E_{ref} is −3.40 K. d) 1 K=1.380662×10^{-23} J.

midpoint of the linear system, and a_0 is the corresponding SCF ground state coefficient. Similarly, suffix B represents the He atom at each side and b_0 the corresponding coefficient.

It can be seen from Tables 1 and 2 that the SCF energy of the He trimer system contributes to the repulsion between He atoms and that the correlation contributes to the attraction. A He dimer interaction potential ($E_{\mathrm{int}}^{\mathrm{He}_2}$) is also indicated in Table 1. In the dimer calculation the same [4s1p1d] basis set was employed and the BSSE was avoided using the reference calculation of Price and Stone. For the triangular configuration, the interaction energies were found to be about three-times larger than those of dimer calculations. On the other hand, the interaction energies in the linear configuration were almost twice the corresponding dimer energies. This difference is due to the fact that there are only two He–He nearest-neighbor interactions in the linear configuration, as opposed to three in the triangular configuration. It is appearant that the interaction potentials of the He trimer can be mainly described by the sum of two-body interactions.

Then, in order to investigate the accuracy of the interaction potentials, we calculated the three-body components of these potentials. The Three-body component could be calculated using $E_{\mathrm{int}}^{\mathrm{He}_3}(R)-3E_{\mathrm{int}}^{\mathrm{He}_2}(R)$ for the triangular configuration, and $E_{\mathrm{int}}^{\mathrm{He}_3}(R)-2E_{\mathrm{int}}^{\mathrm{He}_2}(R)-E_{\mathrm{int}}^{\mathrm{He}_2}(2R)$ for the linear configuration. The results are indicated in Table 3.

As can be seen from Table 3, the three-body component in the triangular configuration is positive for the whole range of calculated R. A many-body perturbation calculation of Wells and Wilson indicates a three-body component of −0.43 μa.u. (−0.14 K) at R=5.6 Bohr.[9] In their calculation, an even-tempered Gaussian basis set [8s4p2d1f] was employed and the site-site CP method was applied. Our calculated value (2.7 K at R=5.6 Bohr) is significantly larger than the many-body perturbation calculation and of opposite sign. This discrepancy is considered to be mainly due to our small [4s1p1d] basis set used in the interaction calculation. In fact, this [4s1p1d] set was optimised just to describe the interaction of the He dimer system. Therefore, the contribution of the three-body component was not included sufficiently in the trimer calculations. Thus, the $E_{\mathrm{SD\,CI}}^{\mathrm{He}_3}$ was smaller than expected.

On the other hand, the three-body component of the interaction potential for the linear configuration is much less than that for the triangular configuration. For the linear configuration, Wells and Wilson obtained a value of 0.00 μa.u. (0.0 K) at R=5.6 Bohr.[9] Since two He atoms of both sides are far separated, the three-body effect is expected to be quite small. Then, the defect of the basis set may become trivial. From Table 3 we assume that the error in the interaction potential is less than ±0.1 K; the three-body component was estimated to be −0.1—−0.3 K at R=5.6 Bohr. This result is comparable with the calculation of Wells and Wilson.

Finally, we discuss the error made in the reference calculation. It may be pointed out that the error appears in Eq. 17 in two ways. First, we consider that the error made in the approximation is almost constant and substituted it for ε, though the error is not exactly constant. Secondly, Eq. 17 overestimates the BSSE in the trimer system.[6,7] However, a serious error in the reference calculaton is not expected from the interaction calculation of the linear system. Thus, the error in Eq. 17 can be considered to be small.

Conclusion

It has been shown that a reliable interaction potential of the He trimer for the linear configuration can be obtained by the use of the SD CI treatment and a reference calculation approximated by a simple formula. This result indicates that our reference calculation for deriving the interaction potential of the three-body system from the SD CI calculation can be used in general. On the other hand, the interaction potential for the triangular configuration is less reliable compared with the linear configuration. It seems that the difference between these potentials is mainly due to the defect of the basis set employed here.

Table 3. The Three-Body Component of the Interaction Potentials

R/Bohr[a]	Equilateral triangle	Linear
	$E_{\mathrm{int}}^{\mathrm{He}_3}(R)-3E_{\mathrm{int}}^{\mathrm{He}_2}(R)/\mathrm{K}$[b]	$E_{\mathrm{int}}^{\mathrm{He}_3}(R)-2E_{\mathrm{int}}^{\mathrm{He}_2}(R)-E_{\mathrm{int}}^{\mathrm{He}_2}(2R)/\mathrm{K}$
5.0	2.8	−2.0
5.3	3.2	−0.6
5.6	2.7	−0.2
6.0	1.7	−0.1
7.0	0.6	0.1
8.0	0.2	0.0
10.0	0.0	0.0

a) R is the internuclear distance between nearest-neighbor He atoms. 1 Bohr=0.529177×10^{-10} m. b) 1 K=1.380662×10^{-23} J.

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