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Ab Initio Calculation for Interaction Potential of He-He

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Synopsis. Using the help of an ab initio calculation with a configuration interaction (CI) treatment, the potential energy of a He dimer system could be calculated in due consideration of a correction for the basis set superposition error. In evaluating CI matrix elements, the graphical unitary group approach was adopted.

There have been several reports in which the interaction potential of a He dimer system was calculated by the use of an ab initio MO method with a limited CI treatment.[1-6] In this paper, our results concerning SD and full CI calculations for the potential energy of the He dimer, comprising a small basis set, are compared with the results of calculations for the same system with a large basis set by Dacre[5] and Tatewaki.[6]

In an LCAO-MO-SCF-CI calculation, the introduction of a large basis set in order to increase the level of the approximation results in a rapid increase of CI matrix elements and computer time. Consequently, a limited CI treatment is generally adopted. It appears to be of interest to investigate the description of the interaction potential for a system with a small basis set. On the other hand, it is possible to adopt a treatment in which many electron excited configurations are introduced instead of employing a large basis set. It is, therefore, possible to further investigate the effect of many excited electron configurations on the CI treatment of the interaction potential for a system with a small basis set.

By using a graphical unitary group approach (GUGA)[7-11] to evaluate the CI matrix elements, it can be expected to facilitate a CI calculation while considering many electron excited configurations. As a first step, we provided our own computer program for the application of GUGA to the many electron excited correlation problem according to a treatment introduced by Shavitt.[10]

In this CI calculation, three different Gaussian basis sets [4S1P], [4S4P], and [4S1P1D] for a He atom were employed. These Gaussian basis sets comprised Schmidt (16s) primitive functions[12] augmented by Wells (4p) primitives.[13-14] The [4S] contraction was performed so that the atomic energy with the contracted set came close to that with an uncontracted set. In practice, the Schmidt (16s) primitives were contracted to the (6;5;4;1). The [1P] contraction was performed in the He dimer system at an internuclear distance of 5.6 Bohr after an SCF calculation with an uncontracted (4p) set placed on the [4S] contracted set. The [4S1P1D] basis set comprised the [4S1P] set augmented with an optimized single Gaussian d-type function.

It has already been pointed out that the result of CI calculations for the interaction energy of the supermolecule system must be corrected in order to eliminate the type error called a "basis set superposition error".[15-17] Boys first introduced the function counterpoise method[15] in order to overcome this error. In this method, the He dimer interaction energy (E_{int}) is calculated using the difference between the CI energy of the He dimer (E_{He_2}) and an appropriate reference energy (E_{ref}):

$$E_{\text{int}}(R) = E_{\text{He}_2}(R) - E_{\text{ref}}(R), \qquad (1)$$

where R is the internuclear distance of the He dimer. The reference energy E_{ref} is defined as twice the CI energy of the He atom, with "ghost" orbitals at the expected location of the other He atom. The term "ghost" represents an atom with a nuclear charge zero and without any electrons. We employed this method in the case of a full CI calculation. Also, the counterpoise method introduced by Price[16] was used in for a SD CI calculation. Here, E_{ref} in Eq. 1 is defined as

$$E_{\text{ref}}(R) = \{2E^{\text{T}}_{\text{ref}}(R) - 2(1 - a_0^2)[E^{\text{CORR}}_{\text{ref}}(R) + (1 - a_0^2)E^{\text{SCF}}_{\text{ref}}(R)]\}/[a_0^2(2 - a_0^2)] + \varepsilon, \qquad (2)$$

where $E^{\text{SCF}}_{\text{ref}}$, $E^{\text{CORR}}_{\text{ref}}$, $E^{\text{T}}_{\text{ref}}$, and a_0 represent the SCF, SD CI correlation, total (SCF and SD CI correlation) energy and the SCF ground-state coefficient of the He atom with ghost orbitals at an internuclear distance R. The constant ε was determined so that the interaction energy becomes zero at $R=\infty$.

In the present work, the spatial symmetry considered in the calculation of the He dimer system is $D_{\infty h}$. The MO calculation was performed by using the Gaussian 82 program provided by Pople and HITAC M680H system of the Computer Center of the University of Tokyo.

Results and Discussion

Tables 1 and 2 indicate the interaction potentials for the [4S1P] and [4S4P] basis sets by the SD CI calculation. It can be seen from Tables 1 and 2 that the SCF energy contributes to the repulsion between the He atoms, and that the correlation energy contributes to the attraction.[1-6] Each interaction potential predicts a minimum of 7.0 K at 5.8—6.0 Bohr. Reliable experimental values are 10.57—11.01 K at 5.6—5.63 Bohr.[5,18-21] From these results, it can be seen that the SD CI treatment for the [4S1P] and [4S4P] basis set is insufficient for describing a reliable interaction potential of the He dimer. On the other hand, it is obvious that the interaction potential curve is little affected by the [1P] contraction of Wells (4p)

Table 1. The He Dimer Interaction Potential (E_{int}) for the [4S1P] Basis by the SD CI Calculation

$R/\mathrm{Bohr}^{c)}$	$E_{\mathrm{He_2}}/\mathrm{a.u.}^{a)}$		E_{ref}		$E_{\mathrm{int}}/\mathrm{K}^{b)}$
	SCF	correlation	$E_{\mathrm{ref}}{}^{d)}/\mathrm{a.u.}$	$E_{\mathrm{ref}}(R)-E_{\mathrm{He_2}}(\infty)/\mathrm{K}$	
5.0	−5.7232327	−0.0390468	−5.7623344	−261.1	17.3
5.5	−5.7233216	−0.0387617	−5.7620716	−178.1	−3.7
6.0	−5.7233481	−0.0385461	−5.7618722	−115.1	−7.0
7.0	−5.7233581	−0.0382936	−5.7616385	−41.3	−4.2
8.0	−5.7233590	−0.0381944	−5.7615474	−12.6	−1.9
10.0	−5.7233591	−0.0381527	−5.7615103	−0.9	−0.4
∞	−5.7233591	−0.0381485	−5.7615076	0.0	0.0

a) 1 a.u.$=4.359814\times10^{-18}$ J. b) 1 K$=1.380662\times10^{-23}$ J. c) 1 Bohr$=0.529177\times10^{-10}$ m. d) ε in E_{ref} is −0.56 K.

Table 2. The He Dimer Interaction Potential (E_{int}) for the [4S4P] Basis by the SD CI Calculation

$R/\mathrm{Bohr}^{c)}$	$E_{\mathrm{He_2}}/\mathrm{a.u.}^{a)}$		E_{ref}		$E_{\mathrm{int}}/\mathrm{K}^{b)}$
	SCF	correlation	$E_{\mathrm{ref}}{}^{d)}/\mathrm{a.u.}$	$E_{\mathrm{ref}}(R)-E_{\mathrm{He_2}}(\infty)/\mathrm{K}$	
5.0	−5.7232330	−0.0564875	−5.7797617	−326.2	13.1
5.5	−5.7233216	−0.0562450	−5.7795513	−259.7	−4.8
6.0	−5.7233481	−0.0560454	−5.7793713	−202.9	−6.9
7.0	−5.7233581	−0.0557695	−5.7791151	−122.0	−3.9
8.0	−5.7233590	−0.0556127	−5.7789660	−75.0	−1.8
10.0	−5.7233591	−0.0554235	−5.7787811	−16.6	−0.5
∞	−5.7233591	−0.0553696	−5.7787287	0.0	0.0

a) 1 a.u.$=4.359814\times10^{-18}$ J. b) 1 K$=1.380662\times10^{-23}$ J. c) 1 Bohr$=0.529177\times10^{-10}$ m. d) ε in E_{ref} is −0.98 K.

Table 3. The He Dimer Interaction Potential (E_{int}) for the [4S1P] Basis by the Full CI Calculation

$R/\mathrm{Bohr}^{c)}$	$E_{\mathrm{int}}/\mathrm{a.u.}^{a)}$	E_{ref}		$E_{\mathrm{int}}/\mathrm{K}^{b)}$			
	correlation	$E_{\mathrm{ref}}/\mathrm{a.u.}$	$E_{\mathrm{ref}}(R)-2E_{\mathrm{He}}{}^{d)}/\mathrm{K}$	This work	Dacre[e)]	Tatewaki[f)]	Experimental[g)]
5.0	−0.0392868	−5.7625707	−263.7	16.2	7.3	0.5	0.2
5.5	−0.0389979	−5.7623053	−179.9	−4.5	−7.0	(−9.6)[h)]	(−10.4)[i)]
6.0	−0.0387794	−5.7621039	−116.3	−7.5	−7.7	−8.6	−9.6
7.0	−0.0385236	−5.7618679	−41.7	−4.4	−4.0	−4.0	−4.6
8.0	−0.0384230	−5.7617759	−12.7	−1.9	−1.8	−1.8	−2.1
10.0	−0.0383808	−5.7617385	−0.9	−0.5	−0.5	—	−0.5
∞	-0.0383765_2	-5.7617355_5	0.0	0.0	—	—	—

a) 1 a.u.$=4.359814\times10^{-18}$ J. b) 1 K$=1.380662\times10^{-23}$ J. c) 1 Bohr$=0.529177\times10^{-10}$ m. d) The SCF and correlation energies of the He atom without ghost orbitals are −2.86167953 and −0.01918825 a.u., respectively. e) From Ref. 5. f) From Ref. 6. g) From Ref. 21. h) Estimated from a graphical plot. i) Estimated from a graphical plot.

primitive functions. We then investigated the effect of triple and higher excitation configurations on the CI treatment for the [4S1P] basis set.

Table 3 indicates the interaction potential for the [4S1P] basis set through a full CI calculation. There are 857 configurations which can contribute to the full CI calculation. The results of the limited CI calculation by Dacre[5)] and Tatewaki[6)] are also indicated in Table 3. In Dacre's work, a large Gaussian-type basis set including polarization functions was employed. He removed the triple and higher excitation effect from the reference energy. On the other hand, a Slater-type basis set was employed in Tatewaki's calculation. He performed first-order CI in which the triple and higher excitation configurations were effectively included. The basis set superposition error was considered to be almost negligible for his interaction potential.

The interaction potential given in Table 3 predicts a minimum of 7.8 K at 5.9 Bohr. These data are in good agreement with those results (8.4 K at 5.7 Bohr) by Dacre. In comparison with the results of our SD CI calculation, the full CI calculation lowers the potential depth by about 0.8 K. However, these calculated potential well depths are shallower than the experimental results. Tatewaki's results (9.8 K at 5.61 Bohr) reproduce the experimental values well.

Table 4 indicates the results of the interaction potential for the [4S1P1D] basis set by the SD CI calculation. This [4S1P1D] basis set for the He atom is composed of the [4S1P] basis and the single Gaussian d function. The exponent of the d function was optimized in order to describe the reliable interaction potential in the range 5 to 10 Bohr. The

Table 4. The He Dimer Interaction Potential (E_{int}) for the [4S1P1D] Basis by the SD CI Calculation

R/Bohr$^{c)}$	E_{He_2}/a.u.$^{a)}$		E_{ref}		E_{int}/K$^{b)}$
	SCF	correlation	$E_{\text{ref}}{}^{d)}$/a.u.	$E_{\text{ref}}(R)-E_{\text{He}_2}(\infty)$/K	
5.0	−5.7232328	−0.0396326	−5.7628827	−427.9	5.5
5.5	−5.7233216	−0.0391572	−5.7624473	−290.4	−9.9
5.71	−5.7233366	−0.0389983	−5.7623007	−244.2	−10.8
6.0	−5.7233481	−0.0388111	−5.7621271	−189.3	−10.1
7.0	−5.7233581	−0.0383993	−5.7617415	−67.6	−5.1
8.0	−5.7233590	−0.0382362	−5.7615884	−19.2	−2.2
10.0	−5.7233591	−0.0381735	−5.7615312	−1.2	−0.4
∞	−5.7233591	−0.0381684	−5.7615275	0.0	0.0

a) 1 a.u.$=4.359814\times10^{-18}$ J. b) 1 K$=1.380662\times10^{-23}$ J. c) 1 Bohr$=0.529177\times10^{-10}$ m. d) ε in E_{ref} is −0.61 K.

Table 5. The He Dimer Interaction Potential (E_{int}) for the [4S1P1D] Basis by the Full CI Calculation

R/Bohr$^{c)}$	E_{He_2}/a.u.$^{a)}$	E_{ref}		E_{int}/K$^{b)}$
	correlation	E_{ref}/a.u.	$E_{\text{ref}}(R)-2E_{\text{He}}{}^{d)}$/K	
5.0	−0.0398799	−5.7631227	−431.8	3.1
5.5	−0.0393981	−5.7626837	−293.1	−11.4
5.71	−0.0392371	−5.7625359	−246.5	−11.9
6.0	−0.0390475	−5.7623607	−191.2	−11.0
7.0	−0.0386303	−5.7619713	−68.2	−5.4
8.0	−0.0384650	−5.7618167	−19.4	−2.3
10.0	−0.0384016	−5.7617591	−1.2	−0.5

a) 1 a.u.$=4.359814\times10^{-18}$ J. b) 1 K$=1.380662\times10^{-23}$ J. c) 1 Bohr$=0.529177\times10^{-10}$ m. d) The SCF and correlation energies of the He atom without ghost orbitals are −2.86167953 and −0.01919811 a.u., respectively.

optimum exponent was found to be 0.20. The potential minimum of this calculation is 10.8 K at 5.71 Bohr; this potential is in good agreement with the experimental results[21] of this range. From these results, it is obvious that the d-type function makes an important contribution to the interaction potential of the He dimer.

Finally, we investigated the interaction potential for the [4S1P1D] basis set by a full CI calculation in order to confirm the effect of triple and higher excitation configurations. There are 5944 configurations which can contribute to a full CI calculation. The new interaction potential appeared lower than the experimental results. This result may have been caused by using a d function which is not optimum for a full CI calculation.

It may be concluded from the results of this investigation that a small basis set [4S1P1D] can give the interaction potential of the He dimer by the aid of the CI calculation and the function counterpoise method.

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