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Ab Initio Calculation for the Interaction Energy of He-H

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Using the help of an ab initio calculation with a configuration interaction (CI) treatment, the potential energies of a HeH system in the ground ($X^2\Sigma^+$) and the first three ($A^2\Sigma^+$, $B^2\Pi$, $C^2\Sigma^+$) excited electronic states were calculated, making due correction for the basis set superposition effect.

In recent years there have been several reports in which the radiative dissociation and predissociation of HeH were investigated.1–8) Molecular calculations predict that the HeH system has a repulsive ground state, with only a van der Waals minimum,9,10) and a series of bound Rydberg excited states.11–13) Using a MRD-CI treatment, Theodorakopoulos et al.11,12) calculated the potential energy curves of the ground and some excited electronic states of HeH. The theoretical radiative life times calculated by Petsalakis et al.13) were in good agreement with the experimental values.2,3)

In this paper we will report the results of full CI calculations of the potential energies of HeH in the ground ($X^2\Sigma^+$) and the first three ($A^2\Sigma^+$, $B^2\Pi$, $C^2\Sigma^+$) excited states, and the basis set superposition effect for these potential energies will be discussed. Then our results concerning the $A^2\Sigma^+ \rightarrow X^2\Sigma^+$ predissociation energy and the $B^2\Pi$ binding energy will be compared with the experimental values.5–7)

In all the ab initio calculations, Gaussian basis sets [6S4P] for a H atom and [6S2P1D] for a He atom were employed. The hydrogen [6S4P] Gaussian basis set was composed of Schmidt (10s/4s) functions14) augmented with the polarization and diffuse functions employed by Römelt et al.15) and Theodorakopoulos et al.11,12) The (10s/4s) contraction was performed so that the atomic energy with the contracted set came close to that with an uncontracted set. The Schmidt (10s) primitive functions were contracted to (6,2,1,1). The exponents of the polarization and diffuse functions were 0.025 and 0.01 for s-type orbitals and 0.7, 0.2, 0.035, and 0.01 for p-type orbitals. Moreover, the helium [6S2P1D] Gaussian basis set was composed of Schmidt (16s/6s) functions14) augmented with the polarization functions employed by Römelt et al.15) The Schmidt (16s) primitives were contracted to (6,5,2,1,1,1). The exponents of the polarization functions were 1.0 and 0.2 for p-type orbitals and 0.8 for the d-type orbital.

It has already been pointed out that the results of CI calculations for the interaction energy of the supermolecule system must be corrected in order to eliminate the type of error called a "basis set superposition error".16–18) Boys et al. introduced the function counterpoise method16) in order to overcome this error. In this method, the He–H interaction energy in the ground ($X^2\Sigma^+$) state ($E_{\text{int}}^{X^2\Sigma^+}$) is calculated using the difference between the full CI energy of HeH ($E_{\text{HeH}}^{X^2\Sigma^+}$) and an appropriate reference energy (E_{ref}):

$$E_{\text{int}}^{X^2\Sigma^+}(R) = E_{\text{HeH}}^{X^2\Sigma^+}(R) - E_{\text{ref}}(R), \tag{1}$$

where R is the internuclear distance of HeH. The reference energy is defined as the sum of the full CI energies of the ground H(1s) and ground He(1s^2), with "ghost" orbitals at the expected location of the other atom:

$$E_{\text{ref}}(R) = E_{\text{ghost}}^{\text{H(1s)}}(R) + E_{\text{ghost}}^{\text{H(1s}^2\text{)}}(R). \tag{2}$$

The term "ghost" represents an atom with a nuclear charge zero and without any electrons.

We also employed this method in the case of the $A^2\Sigma^+$, $B^2\Pi$, and $C^2\Sigma^+$ states of HeH in order to evaluate the "basis set superposition effect". As has been noted in the previous work by Theodorakopoulos et al.,11,12) these three states are mainly described by a single configuration, the same one for the whole range of the internuclear distance, R, from 0.5 to 20.0 Bohr. These excited states have dissociation limits H(2s)+He(1s^2) ($A^2\Sigma^+$) and H(2p)+He(1s^2) ($B^2\Pi$ and $C^2\Sigma^+$) over R=20.0 Bohr. The interaction and reference energies may then be defined as:

$$\begin{aligned} E_{\text{int}}^{\text{EXCITE}}(R) &= E_{\text{HeH}}^{\text{EXCITE}}(R) - E_{\text{ref}}(R),\ \text{EXCITE} \\ &= A^2\Sigma^+,\ B^2\Pi,\ C^2\Sigma^+ \qquad (3) \\ E_{\text{ref}}(R) &= E_{\text{ghost}}^{\text{H(2s)}}(R) + E_{\text{ghost}}^{\text{H(1s}^2\text{)}}(R) \quad \text{for } A^2\Sigma^+ \\ &= E_{\text{ghost}}^{\text{H(2p}\Pi\text{)}}(R) + E_{\text{ghost}}^{\text{H(1s}^2\text{)}}(R) \quad \text{for } B^2\Pi \\ &= E_{\text{ghost}}^{\text{H(2p}\Sigma\text{)}}(R) + E_{\text{ghost}}^{\text{H(1s}^2\text{)}}(R) \quad \text{for } C^2\Sigma^+ \end{aligned}$$

when there is the ghost He; the 2p orbitals of the H atom split into parallel (2pΣ) and perpendicular (2pΠ) elements for the H—ghost He axis.

In the present work, the spatial symmetry considered in the CI treatment of the HeH system is $C_{\infty v}$. The CI calculations contain 6472 configurations for the $^2\Sigma$ symmetry and 7084 configurations for the $^2\Pi$ symmetry. These calculations were performed by using the graphical unitary group approach (GUGA) program of our group19) and the HITAC M680H system of the Computer Center of the Institute for Molecular Science (IMS).

Results and Discussion

Table 1 indicates the CI energies (E_{H}, E_{He}) of H(1s, 2s, 2p) and He(1s^2), without ghost orbitals. These energies are equal to $E_{\mathrm{ghost}}^{\mathrm{H(1s)}}$, $E_{\mathrm{ghost}}^{\mathrm{H(2s)}}$, $E_{\mathrm{ghost}}^{\mathrm{H(2p\Sigma,2p\Pi)}}$, and $E_{\mathrm{ghost}}^{\mathrm{He(1s^2)}}$ at the internuclear distance of R=20.0 Bohr.

Tables 2—5 indicate the interaction energies of He-H in the ground $X^2\Sigma^+$ and excited $A^2\Sigma^+$, $B^2\Pi^+$, and $C^2\Sigma^+$ states, where the basis set superposition effect is evaluated by $E_{\mathrm{ref}}-E_{\mathrm{H}}-E_{\mathrm{He}}$. It can be seen from Tables 2—5 that the basis set superposition effect grows with the electronic excitation level ($X^2\Sigma^+<A^2\Sigma^+<B^2\Pi^+<C^2\Sigma^+$). For the $X^2\Sigma^+$, $A^2\Sigma^+$, and $B^2\Pi$ states, the basis set superposition effect is less than 10^{-3} a.u. for the whole range of the R values

Table 1. Full CI Energies (E_{H}, E_{He}) of H(1s, 2s, 2p) and He(1s^2)

		CI Energy/a.u.[a]
Hydrogen	(1s)	−0.4999954
	(2s)	−0.1249863
	(2p)	−0.1228372
Helium	(1s^2)	−2.8965174

a) 1 a.u.=4.359814×10^{-18} J.

Table 2. The He-H Interaction Energies ($E_{\mathrm{int}}^{X^2\Sigma^+}$) for the $X^2\Sigma^+$ State

R/Bohr[a]	$E_{\mathrm{HeH}}^{X^2\Sigma^+}$/a.u.[b]	E_{ref}/a.u.		$E_{\mathrm{int}}^{X^2\Sigma^+}$/a.u.
		E_{ref}	$E_{\mathrm{ref}}(R)-E_{\mathrm{H(1s)}}-E_{\mathrm{He(1s^2)}}$[c]	
1.0	−3.0917058	−3.3969760	−0.0004632	0.3052702
1.25	−3.2006385	−3.3968722	−0.0003594	0.1962337
1.5	−3.2632018	−3.3967590	−0.0002462	0.1335572
1.75	−3.3044846	−3.3966722	−0.0001594	0.0921876
2.0	−3.3330069	−3.3966110	−0.0000982	0.0636041
3.0	−3.3831444	−3.3965374	−0.0000246	0.0133930
4.0	−3.3941643	−3.3965274	−0.0000146	0.0023631
5.0	−3.3962007	−3.3965219	−0.0000091	0.0003212
6.0	−3.3965015	−3.3965181	−0.0000053	0.0000166

a) 1 Bohr=0.529177×10^{-10} m. b) 1 a.u.=4.359814×10^{-18} J. c) $E_{\mathrm{H(1s)}}$ and $E_{\mathrm{He(1s^2)}}$ are the CI energies of the H(1s) and He(1s^2), without ghost orbitals. See Table 1.

Table 3. The He-H Interaction Energies ($E_{\mathrm{int}}^{A^2\Sigma^+}$) for the $A^2\Sigma^+$ State

R/Bohr[a]	$E_{\mathrm{HeH}}^{A^2\Sigma^+}$/a.u.[b]	E_{ref}/a.u.		$E_{\mathrm{int}}^{A^2\Sigma^+}$/a.u.
		E_{ref}	$E_{\mathrm{ref}}(R)-E_{\mathrm{H(2s)}}-E_{\mathrm{He(1s^2)}}$[c]	
1.0	−3.0440455	−3.0219687	−0.0004650	−0.0220768
1.25	−3.1066316	−3.0218640	−0.0003603	−0.0847676
1.5	−3.1124843	−3.0217504	−0.0002467	−0.0907339
1.75	−3.0994893	−3.0216635	−0.0001598	−0.0778258
2.0	−3.0819853	−3.0216022	−0.0000985	−0.0603831
3.0	−3.0355106	−3.0215285	−0.0000248	−0.0139821
4.0	−3.0242437	−3.0215184	−0.0000147	−0.0027253
5.0	−3.0219179	−3.0215129	−0.0000092	−0.0004050
6.0	−3.0212573	−3.0215091	−0.0000054	−0.0002518

a) 1 Bohr=0.529177×10^{-10} m. b) 1 a.u.=4.359814×10^{-18} J. c) $E_{\mathrm{H(2s)}}$ and $E_{\mathrm{He(1s^2)}}$ are the CI energies of the H(2s) and He(1s^2), without ghost orbitals. See Table 1.

Table 4. The He-H Interaction Energies ($E_{\mathrm{int}}^{B^2\Pi}$) for the $B^2\Pi$ State

R/Bohr[a]	$E_{\mathrm{HeH}}^{B^2\Pi}$/a.u.[b]	E_{ref}/a.u.		$E_{\mathrm{int}}^{B^2\Pi}$/a.u.
		E_{ref}	$E_{\mathrm{ref}}(R)-E_{\mathrm{H(2p)}}-E_{\mathrm{He(1s^2)}}$[c]	
1.0	−3.0210546	−3.0198763	−0.0005217	−0.0011783
1.25	−3.0872280	−3.0197615	−0.0004069	−0.0674665
1.5	−3.0978919	−3.0196542	−0.0002996	−0.0782377
1.75	−3.0893517	−3.0195785	−0.0002239	−0.0697732
2.0	−3.0755452	−3.0195271	−0.0001725	−0.0560181
3.0	−3.0351654	−3.0194452	−0.0000906	−0.0157202
4.0	−3.0235834	−3.0193957	−0.0000411	−0.0041877
5.0	−3.0207334	−3.0193660	−0.0000114	−0.0013674
6.0	−3.0198897	−3.0193620	−0.0000074	−0.0005277

a) 1 Bohr=0.529177×10^{-10} m. b) 1 a.u.=4.359814×10^{-18} J. c) $E_{\mathrm{H(2p)}}$ and $E_{\mathrm{He(1s^2)}}$ are the CI energies of the H(2p) and He(1s^2), without ghost orbitals. See Table 1.

Table 5. The He-H Interaction Energies ($E^{C^2\Sigma^+}_{int}$) for the $C^2\Sigma^+$ State

R/Bohr[a)]	$E^{C^2\Sigma^+}_{HeH}$/a.u.[b)]	E_{ref}/a.u.		$E^{C^2\Sigma^+}_{int}$/a.u.
		E_{ref}	$E_{ref}(R)-E_{H(2p)}-E_{He(1s^2)}$[c)]	
1.0	−2.9656669	−3.0215125	−0.0021579	0.0558456
1.25	−3.0387007	−3.0213759	−0.0020213	−0.0173248
1.5	−3.0555992	−3.0211734	−0.0018188	−0.0344258
1.75	−3.0518279	−3.0209459	−0.0015913	−0.0308820
2.0	−3.0413713	−3.0207156	−0.0013610	−0.0206557
3.0	−3.0042729	−3.0200137	−0.0006591	0.0157408
4.0	−2.9939696	−3.0197653	−0.0004107	0.0257957
5.0	−2.9986434	−3.0197020	−0.0003474	0.0210586
6.0	−3.0066117	−3.0195035	−0.0001489	0.0128918
8.0	−3.0161292	−3.0194566	−0.0001020	0.0033274

a) 1 Bohr=0.529177×10^{-10} m. b) 1 a.u.=4.359814×10^{-18} J. c) $E_{H(2p)}$ and $E_{He(1s^2)}$ are the CI energies of the H(2p) and He(1s^2), without ghost orbitals. See Table 1.

Table 6. $A^2\Sigma^+$ ($v'=0$) → $X^2\Sigma^+$ Predissociation and $B^2\Pi$ Binding Energies of HeH

	This work	Theodorakopoulos[a)]	Experimental
	eV[b)]		
$A^2\Sigma^+$ ($v'=0$) → $X^2\Sigma^+$ Predissociation	7.96[c)]	7.91	7.9[d)]
$B^2\Pi$ Binding	2.13	2.20	2.19±0.03[e)]

a) From Ref. 12. b) 1 eV=1.6021892×10^{-19} J. c) The vibrational zero-point energy for the $A^2\Sigma^+$ state was estimated to be 0.2272 eV. d) Estimated from Fig. 3 in Ref. 5. e) From Ref. 7.

calculated and little effect on the shape of the interaction energy curves. This superposition effect changes the energy well depth by only 0.3—0.4 percent in the $A^2\Sigma^+$ and $B^2\Pi$ states. From these results, the basis set superposition effect can be said to be negligible for the $X^2\Sigma^+$, $A^2\Sigma^+$, and $B^2\Pi$ states. On the other hand, as may be seen in Table 5, the basis set superposition effect in the $C^2\Sigma^+$ state is about 0.002 a.u. in the energy minimum region and changes the well depth about 5 percent; therefore, it can not be neglected. The $C^2\Sigma^+$ state also has an upper boundary in the region of R=4.0 Bohr, where the basis set superposition effect is negligible.

Table 6 indicates the $A^2\Sigma^+(v'=0)\rightarrow X^2\Sigma^+$ predissociation and $B^2\Pi$ binding energies of HeH. In our calculation, the vibrational zero-point energy (E_{vib}-(v'=0)) for the $A^2\Sigma^+$ state was estimated to be 0.2272 ev. The predissociation energy was calculated by the use of:

$$A^2\Sigma^+(v'=0)\rightarrow X^2\Sigma^+ \text{ predissociation energy}$$
$$=[\{E_{H(2s)}+E_{He(1s^2)}+E^{A^2\Sigma^+}_{int}(R=1.5\text{ Bohr})$$
$$+E_{vib}(v'=0)\}-\{E_{H(1s)}+E_{He(1s^2)}\}].$$

The results of the MRD-CI calculation by Theodorakopoulos et al.[11,12)] and the experimental results reported by Peterson et al.[5)] and by Möller et al.[7)] are also listed in Table 6. Our calculated values are in good agreement with these other calculated and experimental values.

It may be concluded from the results of this investigation that our potential energies for the $X^2\Sigma^+$, $A^2\Sigma^+$, and $B^2\Pi$ states of the HeH system can give the $A^2\Sigma^+\rightarrow X^2\Sigma^+$ predissociation and $B^2\Pi$ binding energies. Moreover, the basis set superposition effect changes the interaction potential minimum about 5 percent for the $C^2\Sigma^+$ state.

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