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Ab Initio Calculation for the Interaction Energy of He-He$^+$

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Synopsis. Using an ab initio calculation with a configuration interaction (CI) treatment, the interaction energy of a He-He$^+$ system in the ground ($X^2\Sigma_u^+$) electronic state was calculated. For $X^2\Sigma_u^+He_2^+$ calculations, the Gaussian-type [6s3pld] basis set of Khan and Jordan was employed, and the effect of the basis set superposition error was estimated.

From a theoretical point of view, He$_2^+$ is a comparatively simple homonuclear ion, and there have been a number of reports in which the interaction energy of He$_2^+$ in the ground ($X^2\Sigma_u^+$) state has been calculated by the use of an ab initio MO method.[1-6] Recently Khan and Jordan utilized the multi-configuration self-consistent field (MC SCF) procedure to calculate the potential energy curve of $X^2\Sigma_u^+He_2^+$.[5] A contracted Gaussian-type [6s3pld] basis set was employed for their MC-SCF calculation. They determined the vibrational and rotational energy levels from the potential energy curve; the resulting spectroscopic constants were in excellent agreement with the experimental values. This result indicates that the [6s3pld] Gaussian set can give a significantly improved description of the potential energy curve of $X^2\Sigma_u^+He_2^+$.

On the other hand, we have calculated the interaction energies for the He-He[7] and He-H[8] systems in the ground and several electronic excited states. For these simple systems, the full CI treatment could be performed, and the basis set superposition error[9,10] was eliminated correctly from the interaction energies. Thus, it appears to be of interest to investigate the effect of the basis set superposition error on the interaction energy of $X^2\Sigma_u^+He_2^+$, itself calculated with the basis set of Khan and Jordan. In this paper we will report the results of full CI calculations of the interaction energy of $X^2\Sigma_u^+He_2^+$, and the basis set superposition error for these energies will be discussed. Our results concerning the vibrational and rotational energy levels will then be compared with the experimental and theoretical values.

Computational Details

In the CI treatment, $X^2\Sigma_u^+He_2^+$ is mainly described by a single configuration ($1\sigma_g{}^2 1\sigma_u$) for the whole range of internuclear distances calculated here; it has a dissociation limit, He(1s^2) +He$^+$(1s), at an infinite separation. The results of full CI calculations for the interaction energy of $X^2\Sigma_u^+He_2^+$ were corrected in order to eliminate the basis set superposition error. We employed the function counterpoise method of Boys and Bernardi[9] to avoid this error. In this method, the He-He$^+$ interaction energy (E_{int}) is calculated using the difference between the full CI energy of $X^2\Sigma_u^+He_2^+$ ($E_{\mathrm{He_2^+}}$) and an appropriate refference energy (E_{ref}):

$$E_{\mathrm{int}}(R) = E_{\mathrm{He_2^+}}(R) - E_{\mathrm{ref}}(R), \qquad (1)$$

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

$$E_{\mathrm{ref}}(R) = E_{\mathrm{ghost}}^{\mathrm{He(1s^2)}}(R) + E_{\mathrm{ghost}}^{\mathrm{He^+(1s)}}(R) \qquad (2)$$

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

Then the calculated interaction energy curve was interpolated in order to determine the vibrational and rotational energy levels of $X^2\Sigma_u^+He_2^+$. The vibrational analysis was given by the Störmer-Levy difference method, while the vibrational eigen functions were utilized to determine the rotational constants. The detailed procedure has been described elsewhere.[11,12] This method gives an accurate solution in a numerical form with a great number of mesh points and with the proper selection of position to make an initial guess from outside of the potential well.

In the present work, the spatial symmetry considered in the CI treatment of the $X^2\Sigma_u^+He_2^+$ is $D_{\infty h}$. The CI calculations contain 4562 configurations for the $^2\Sigma_u^+$ symmetry. The number of calculated interaction energy values was 18 points in the range of internuclear distances from 0.7 to 5.0 Å; the interpolated mesh width was taken to be 0.001 Å. The MO calculations were performed by using the graphical unitary group approach (GUGA) program of our group[7] and the HITAC M680 system of the Computer Center of the Institute for Molecular Science (IMS).

Results and Discussion

Table 1 indicates the interaction energies of $X^2\Sigma_u^+He_2^+$. The full CI energies of He(1s^2) and He$^+$(1s) (E_{He}, $E_{\mathrm{He^+}}$), without ghost orbitals, are −2.9016276 and −1.9998712 a.u. respectively. These energies are equal to $E_{\mathrm{ghost}}^{\mathrm{He(1s^2)}}$ and $E_{\mathrm{ghost}}^{\mathrm{He^+(1s)}}$ at the internuclear distance of R=5.0 Å. The basis set superposition error is evaluated by the use of $E_{\mathrm{ref}}-E_{\mathrm{He}}-E_{\mathrm{He^+}}$ in Table 1. It can be seen from Table 1 that the basis set superposition error is less than 2.0×10^{-4} a.u. for the whole range of R values calculated and that it decreases rapidly as the internuclear separation is increased. In the present CI calculations, the interaction energy minimum was found to be −0.0902342 a.u. at R=1.080 Å. (The resulting dissociation energy (D_e) is 56.585 kcal mol^{-1}, while the D_e value calculated by Khan and Jordan is 56.52 kcal mol^{-1}.[5]) The basis set superposition error changes the energy well depth by only 0.06 percent. From these results, the basis set superposition error can be said to be negligible for $X^2\Sigma_u^+He_2^+$ in the range from 0.7 to 5.0 Å. On the other hand, it seems that the basis set superposition error can not be neglected in the strongly repulsive region.

Table 1. The He-He$^+$ Interaction Energies (E_{int}) in the $X^2\Sigma_u^+$ State

R/Å	$E_{\mathrm{He_2^+}}$/a.u.[a]	E_{ref}/a.u.		E_{int}/a.u.
		E_{ref}	$E_{\mathrm{ref}}(R)-E_{\mathrm{He(1s^2)}}-E_{\mathrm{He^+(1s)}}$	
0.7	−4.859992	−4.901645	−0.000146	0.041654
0.8	−4.935025	−4.901615	−0.000116	−0.033410
0.9	−4.972956	−4.901590	−0.000091	−0.071365
1.0	−4.988745	−4.901569	−0.000070	−0.087176
1.05	−4.991386	−4.901560	−0.000061	−0.089826
1.08	−4.991789	−4.901555	−0.000056	−0.090234
1.1	−4.991654	−4.901552	−0.000053	−0.090102
1.2	−4.987432	−4.901540	−0.000041	−0.085892
1.3	−4.979609	−4.901532	−0.000033	−0.078077
1.4	−4.970316	−4.901526	−0.000028	−0.068790
1.5	−4.960798	−4.901521	−0.000023	−0.059277
1.6	−4.951749	−4.901518	−0.000019	−0.050232
1.8	−4.936269	−4.901513	−0.000014	−0.034757
2.0	−4.924721	−4.901509	−0.000010	−0.023212
2.5	−4.909330	−4.901503	−0.000004	−0.007827
3.0	−4.904088	−4.901501	−0.000002	−0.002587
4.0	−4.901824	−4.901499	−0.000001	−0.000325
5.0	−4.901568	−4.901499	0.0	−0.000070

a) 1 a.u.=4.359814×10^{-18}J.

Table 2. Calculated Vibrational Energy Levels ($G(v)$) for $X^2\Sigma_u^+$ He$_2^+$

v	$\langle R\rangle$/Å	$G(v)$/cm^{-1}[a]	$G(v+1/2)$/cm^{-1}
0	1.096546	839.878	1627.108
1	1.128439	2466.986	1557.640
2	1.161817	4024.626	1490.595
3	1.198047	5515.221	1421.905
4	1.235369	6937.126	1351.234
5	1.275629	8288.360	1282.191
6	1.317454	9570.551	1208.296
7	1.361299	10778.847	1139.739
8	1.410699	11918.586	1068.203
9	1.464292	12986.789	998.855
10	1.519420	13985.644	930.631
11	1.585618	14916.275	852.483
12	1.652376	15768.758	794.190
13	1.722394	16562.948	710.226
14	1.825547	17273.174	614.392
15	1.942362	17887.566	516.692
16	2.074584	18404.258	452.057
17	2.198430	18856.315	366.460
18	2.440572	19222.775	253.959
19	2.716176	19476.734	188.738
20	3.054041	19665.472	105.743
21	3.864818	19771.215	—

a) 1 cm^{-1}=1.986481×10^{-23}J.

Table 3. Calculated Rotational Constants (B_v) for $X^2\Sigma_u^+$ He$_2^+$

v	$\langle 1/R^2\rangle$/Å^{-2}	B_v/cm^{-1}
0	0.842382	7.096153
1	0.815831	6.872489
2	0.789154	6.647765
3	0.760736	6.408374
4	0.733318	6.177407
5	0.704796	5.937140
6	0.677290	5.705432
7	0.650155	5.476849
8	0.619915	5.222110
9	0.588833	4.960278
10	0.559436	4.712640
11	0.525021	4.422731
12	0.493997	4.161388
13	0.464803	3.915460
14	0.421702	3.552381
15	0.379868	3.199975
16	0.338387	2.850543
17	0.307814	2.592998
18	0.250046	2.106366
19	0.202450	1.705421
20	0.161017	1.356393
21	0.094637	0.797214

Table 2 indicates the vibrational energy levels ($G(v)$[13]) of $X^2\Sigma_u^+$He$_2^+$ with the vibrational quantum number v. The difference in successive $G(v)$ values ($\Delta G(v+1/2)$[13]) and the mean values of R ($\langle R\rangle$) are also indicated in Table 2. In the present calculation, we obtained a $G(21)$ value about 41 cm^{-1} higher than the result calculated by Khan and Jordan.[5] The first four $G(v)$ values in Table 2 were then used in order to determine the vibrational constants ω_e and $\omega_e\chi_e$.[13] The resulting ω_e and $\omega_e\chi_e$ values are 1697.85 and 35.97 cm^{-1} respectively. These ω_e and $\omega_e\chi_e$ values are in significantly better agreement with both the experimental values (1698.5, 35.3 cm^{-1})[14] and the values calculated by Khan and Jordan (1697.4, 35.35 cm^{-1}).[5]

Table 3 indicates the rotational constants B_v[13] at each vibrational energy level, where the mean values of $1/R^2$ ($\langle 1/R^2\rangle$) are also indicated. It can be seen from Tables 2, 3 that the calculated $\langle 1/R^2\rangle$ values are always larger than the corresponding $1/\langle R\rangle^2$ values. The rotational constant, α_e[13]$=0.2580$ cm^{-1}, was obtained from the first four B_v values and from the equilibrium distance, $R_e=1.080$ Å ($B_e=7.22214$ cm^{-1}). Our α_e value is different from both the experimental value (0.224 cm^{-1})[14] and the value calculated by Khan and Jordan (0.224 cm^{-1}).[5] This discrepancy is mainly due to our smaller B_0 value, i.e., to the smaller

$<1/R^2>_{v=0}$ value.

It may be concluded from the results of this investigation that the basis set superposition error of the $X^2\Sigma_u^+ He_2^+$ system calculated by the use of [6s3p1d] basis of Khan and Jordan is almost negligible in the range from 0.7 to 5.0 Å. The present interaction energy curve can give the vibrational energy levels. On the other hand, a rotational constant α_e larger than the experimental value was obtained.

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