

**The ground state of $(\text{He-H-He})^+$
from correlated ab initio calculations***

Jacek Komasa

Department of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Jacek Rychlewski

Department of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland and

Poznań Supercomputing and Networking Center, Wieniawskiego 17/19, 61-713 Poznań, Poland

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Short title: Correlated calculations on $(\text{He-H-He})^+$

*Dedicated to the memory of Włodzimierz Kołos

Abstract

He_2H^+ ion in its ground state is studied by means of ab initio methods taking into account the electron correlation. Geometry optimization at the CCSD(T)/cc-pV5Z level of theory has been performed and the potential energy hypersurface scan is presented. The optimum conformation is linear and symmetric with the proton at the He–He midpoint and the He–H distance equal to 1.75 bohr. Stabilization energy with respect to the $\text{He}_2\text{H}^+ \longrightarrow \text{HeH}^+ + \text{He}$ dissociation channel has been computed. Additionally, a single point variational calculations with the use of the Exponentially Correlated Gaussian wave functions have been performed. They supply an upper bound to both the total electronic (-5.903505 hartree) and the stabilization energy (-13.224 kcal/mol). A comparison of the results from both the perturbational coupled cluster and variational methods is presented.

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I. INTRODUCTION

Exceptionally weak binding appearing in the helium dimer has drawn a lot of attention recently [1–5]. The potential energy curve describing interaction of the two helium atoms has a very shallow van der Waals minimum. It is so shallow that the potential barely supports one vibrational level. He₂ has also quite large equilibrium distance (5.6 bohr) and there seems to be enough room between the two helium atoms to accommodate a proton. Interesting questions arise at this moment. What happens to the system if the proton is inserted into the helium dimer molecule? Can this system serve as a model of a hydrogen bond?

Two completely different methods are used and compared in the present study: the standard Coupled Cluster (CC) method as implemented in the popular quantum-chemical Gaussian 94 package [6] and the method of the Exponentially Correlated Gaussian (ECG) functions. The latter method is based on variational solutions to the Schrödinger equation, represented in the form of the Ritz expansion in multi-electron basis functions. Every basis function has the spatial part, ψ_k , expressed in the form of an exponential function introduced by Singer [7]:

$$\psi_k(\vec{r}_1, \dots, \vec{r}_n) = \exp \left[- \sum_{i=1}^n \sum_{j=1}^n A_{ij,k} (\vec{r}_i - \vec{s}_{i,k}) (\vec{r}_j - \vec{s}_{j,k}) \right], \quad (1)$$

where \vec{r}_i is the position vector of the i -th electron, $A_{ij,k}$ and $\vec{s}_{i,k}$ are nonlinear parameters optimized variationally. The ECG method has been successfully applied to several few-electron systems. To date, it yields the most accurate variational results for two- [8–16], three- [16–18], and four-electron systems [5,16,19,20]. The details of the method are given in the above references. Throughout, the Born-Oppenheimer approximation has been assumed.

II. RESULTS AND DISCUSSION

The calculations with the one-electron bases have been performed with Gaussian 94 program. Four different, commonly available, one-electron basis sets have been used to in-

investigate the total energy convergence with growing basis set size. The correlation consistent polarized valence bases were obtained from the ECCE Basis Set Database [21]. They were designed by Dunning [22] for H and by Woon and Dunning [23] for He. The characteristics of the basis sets used and the results of the total energy calculations (in units of hartree, $1 E_H \approx 6.35975 \cdot 10^{-18} \text{ J}$) are presented in Table I. The error resulting from the basis set incompleteness can be estimated as 1-2 mE_H. ⇐ Table I

Table II contains values of the total energy computed with the cc-pV5Z basis set. They were obtained from several levels of theory with increasing amount of the electron correlation taken into account. Although, the post-Hartree-Fock methods are not variational, the energies they yield form a monotonic sequence approaching the exact value from above. The most sophisticated CCSD(T) method recovers almost 99 % of the correlation energy. This number is only a rough estimate as neither the Hartree-Fock limit nor the total energy are known exactly. The former has been approximated by the SCF/cc-pV5Z energy, the latter from the explicitly correlated calculations discussed below. ⇐ Table II

The geometry optimization has been performed at the CCSD(T)/cc-pV5Z level of theory. The global minimum corresponds to the linear (He-H-He)⁺ conformation with two symmetric He-H bonds ($R_1 = R_2 = 1.75 \text{ bohr}$) and the CCSD(T)/cc-pV5Z energy equal to $-5.902185 E_H$. The harmonic vibrational analysis yielded no imaginary frequencies. Also the Hessian eigenvalues were all positive. Since now, we shall concentrate on the stability of the (He-H-He)⁺ in this linear conformation.

When constrained to C_{∞v} geometry the (He-H-He)⁺ ion has two degrees of freedom which can be represented by two He-H bond lengths, R_1 and R_2 . Figure 1 represents qualitatively results of two dimensional scan performed at CCSD(T)/cc-pV5Z level. The energy has been evaluated on 21×21 grid. The potential energy surface exhibits one minimum around $R_1 = R_2 = 1.75 \text{ bohr}$. There are also clearly seen two symmetric dissociation channels, each leading to HeH⁺($R = 1.46 \text{ bohr}$) and He in their ground states as the products. ⇐ Figure 1

For the equilibrium geometry variational computations with the use of the ECG wave functions were performed. To assess the ECG basis set incompleteness effect, the calculations

were done for several expansion lengths, K . The total energy, E_K , has been obtained in an extensive optimization process, separately for each K listed in Table III. The sequence of $\{E_K, K \rightarrow \infty\}$ converges from above to the exact Born-Oppenheimer energy. The extrapolation to the infinite K yields an estimated total energy:

$$E_\infty = -5.90353(1) E_H. \quad (2)$$

This number, however, is no longer an upper bound, contrary to all E_K with the finite K . The E_∞ has been used to estimate the correlation energy, $E_{corr} = 90.84 \text{ mE}_H$, and hence, the entries in the last column of Table II. \Leftarrow Table III

Several atomic and diatomic species can be imagined as stable products of the dissociation of the He_2H^+ :

$$\text{He}_2\text{H}^+ \longrightarrow \left\{ \begin{array}{llll} \text{He}_2 & X^1\Sigma_u^+, R = 5.6 \text{ bohr} & -5.8074837 E_H & [5, 20] \\ \text{He}_2^+ & X^2\Sigma_u^+, R = 2.042 \text{ bohr} & -4.99464087 E_H & [16] \\ \text{HeH}^+ & X^1\Sigma^+, R = 1.46 \text{ bohr} & -2.978706591 E_H & [13] \\ \text{He} & 1^1S & -2.9037243770341 E_H & [24-26] \\ \text{He}^+ & 1^2S & -2.0 E_H & \\ \text{H} & 1^2S & -0.5 E_H & \\ \text{H}^+ & & 0.0 E_H & \end{array} \right.$$

Among all these products of the decomposition, the energetically lowest dissociation channel leads to HeH^+ and He :

$$\text{He}_2\text{H}^+ \longrightarrow \text{HeH}^+ + \text{He}, \quad (3)$$

with the product energy threshold of $-5.88243097 E_H$. This threshold is known very accurately from variational Born-Oppenheimer calculations on both the products. The nonrelativistic energy of the ground state helium atom is known to at least 14 significant figures [24–26]. The variational energy of HeH^+ ($X^1\Sigma^+$, $R = 1.46 \text{ bohr}$) is accurate to about 0.01 cm^{-1} [13]. Both this numbers were obtained from explicitly correlated wave functions.

The stabilization energy of He_2H^+ with infinite nuclear masses, ΔE , was computed from

$$\Delta E = E^{(\text{He-H-He})^+} - E^{\text{HeH}^+} - E^{\text{He}}, \quad (4)$$

where both ions were in their equilibrium geometries. $E^{(\text{He-H-He})^+}$ has been approximated by E_{800} from Table III whereas E^{HeH^+} and E^{He} are practically exact. Hence, the stabilization energy obtained from Eq. (4) is contaminated only by the errors introduced by E_{800} . The ΔE obtained this way has the advantage that it may be recognized as a variational upper bound to the exact stabilization energy. If the experience learned from another 4-electron system, He_2 , is valid [5,20], then the ECG total energy of $(\text{He-H-He})^+$ obtained from the 800-term wave function is about $25 \mu E_H \approx 0.016 \text{ kcal/mol}$ ($1 E_H \approx 627.51 \text{ kcal/mol}$) in error and the same error concerns also the stabilization energy. The upper bound to ΔE obtained from the 800-term ECG amounts to -13.224 kcal/mol . ΔE predicted by the extrapolation to infinite basis set size equals to $-13.240(7) \text{ kcal/mol}$.

The supermolecular calculations of the stabilization energy were performed also by means of the coupled cluster method with the cc-pV5Z basis set. Contrary to the ECG approach, in calculations involving one-electron approximation the basis set superposition error (BSSE) has to be taken into account [27]. Therefore first, the counterpoise corrected interaction energy has been computed

$$E_{\text{int}} = E^{(\text{He-H-He})^+}(\text{D},\text{D}) - E^{\text{HeH}^+}(\text{D},\text{D}) - E^{\text{He}}(\text{D},\text{D}), \quad (5)$$

with $E^X(\text{G},\text{B})$ being the total energy of the system X in given geometry G calculated with the basis set B. Both G and B can have two values, M or D, referring to monomer or dimer, respectively. The geometries (D) of the $(\text{He-H-He})^+$ and HeH^+ used in Eq. (5) are those of the global minimum ($R_1 = R_2 = 1.75 \text{ bohr}$). The dimer geometry used for a monomer describes not only the positions of its nuclei but also defines the coordinates of the other monomer site, where the ghost functions are to be centered. The CCSD(T)/cc-pV5Z calculations yield $E_{\text{int}} = -18.606 \text{ kcal/mol}$. However, a significant change in the He-H bond length during the supermolecule formation is not accounted for in Eq. (5). It can be taken into account by the addition of the energy resulting from the relaxation of the monomers geometry, yielding an equivalent of the stabilization energy of Eq. (4):

$$\Delta E = E_{\text{int}} + E^{\text{rel}}, \quad (6)$$

where

$$E^{\text{rel}} = E^{\text{HeH}^+}(\text{D}, \text{M}) - E^{\text{HeH}^+}(\text{M}, \text{M}). \quad (7)$$

Such a relaxed CP interaction energy amounts to -13.187 kcal/mol, which is in good agreement with the accurate ΔE obtained from the ECG method. It is closer to the exact ΔE than -13.163 kcal/mol derived by Lee and Secrest [28] from Dykstra potential energy surface [29]. Still, a small discrepancy of about 0.1 kcal/mol is observed. The final results of the CCSD(T)/cc-pV5Z and ECG computations of ΔE are assembled in Table IV. \Leftarrow Table IV

To enable a comparison with possible experimental dissociation energy, the zero-point energy, E^0 , for both $(\text{He-H-He})^+$ and HeH^+ should also be taken into account. These values have been computed by Lee and Secrest [28]. For $(\text{He-H-He})^+$ they calculated E^0 from analytic fits to the potential energy points calculated by Dykstra [29]. Two separate treatments, variational and perturbational, yield $E^0 = 6.525$ kcal/mol and 6.543 kcal/mol, respectively. For HeH^+ Lee and Secrest fitted a tenth-order polynomial to accurate Kołos and Peek potential energy curve [30] and obtained $E^0 = 4.491$ kcal/mol. In comparison, the CCSD(T)/cc-pV5Z harmonic vibrational analysis yields $E^0 = 4.63$ kcal/mol for HeH^+ and 6.62 kcal/mol for $(\text{He-H-He})^+$. The values reported in [28] account for the anharmonicity of the potential energy surfaces and seem to be more reliable. On the other hand, in the vicinity of the equilibrium, the energies obtained by Dykstra, are as much as $6 \text{ mE}_H \approx 3.8$ kcal/mol in error. However, to estimate the dissociation energy, D_0 , we need only the difference in E^0 of $(\text{He-H-He})^+$ and HeH^+ . It amounts to 2.034 and 2.052 kcal/mol in the case of the variational and perturbational results of Lee and Secrest, and to 1.99 kcal/mol for CCSD(T)/cc-pV5Z calculations. Using the best estimate of $\Delta E = -13.240(7)$ kcal/mol we can predict that D_0 falls into the range of $11.18 \div 11.25$ kcal/mol.

The investigated system fulfills some criteria of being called the hydrogen bond: it is linear and has sufficiently large dissociation energy. Bonds with $D_0 > 9$ kcal/mol are classified as the strong hydrogen bonds. Also the short He-He equilibrium distance, equal to

3.5 bohr, allows to call this bond a strong one. Additionally, an electron charge distribution shift resulting from the bond formation can be observed. The Mulliken population analysis obtained from the SCF/cc-pV5Z density gives the following atomic charges: +0.48 on H and +0.26 on He in $(\text{He-H-He})^+$ and +0.70 on H and +0.30 on He in HeH^+ . It is an evidence of a significant electron charge transfer from the neutral helium atom to the deshielded proton in HeH^+ .

III. SUMMARY

Ab initio methods with a rigorous treatment of the electron correlation have been applied to investigate the stability of the $(\text{He-H-He})^+$ ion. The upper bound to the total electronic energy obtained from 800-term ECG wave function is $-5.903505 E_H$. It is approximately $25 \mu E_H$ in error and lies about $6 \text{ m}E_H$ lower than previous calculations. The stabilization energy, computed from this value combined with the accurate energies of the interacting fragments, supplies an upper bound to the exact ΔE and amounts to -13.224 kcal/mol . An extrapolation to the infinite basis set size limit yields $-5.90353(1) E_H$ for the total energy and $-13.240(7) \text{ kcal/mol}$ for the stabilization energy.

The total energies obtained from CCSD(T)/cc-pV5Z calculations are as much as $1.3 \text{ m}E_H$ for He_2H^+ , $0.6 \text{ m}E_H$ for HeH^+ , and $0.7 \text{ m}E_H$ for He, in error. The mutual cancellation of these errors enables to obtain the right approximation to the ΔE equal to -13.187 kcal/mol .

Insertion of the proton into the system of two helium atoms has significant stabilizing effect: ΔE in the helium dimer is -0.022 kcal/mol whereas in the $(\text{He-H-He})^+$ ion equals to -13.240 kcal/mol .

This system can be viewed as a model for the hydrogen bond with helium atoms acting as both proton-donor and -acceptor.

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TABLES

TABLE I. Convergence of the CCSD(T) energy with the basis set extent. $(\text{He-H-He})^+$ in $D_{\infty h}$ conformation with $R_1 = R_2 = 1.75$ bohr.

Basis set label	Contraction scheme (He/H)	Size	Energy in E_H
cc-pVDZ	$(5s,1p/4s,1p) \rightarrow [2s,1p]$	15	-5.870050
cc-pVTZ	$(6s,2p,1d/5s,2p,1d) \rightarrow [3s,2p,1d]$	42	-5.896571
cc-pVQZ	$(7s,3p,2d,1f/6s,3p,2d,1f) \rightarrow [4s,3p,2d,1f]$	90	-5.900994
cc-pV5Z	$(8s,4p,3d,2f,1g) \rightarrow [5s,4p,3d,2f,1g]$	138	-5.902185

TABLE II. Convergence of the energy with the level of theory in cc-pV5Z basis set. (He-H-He)⁺ in D_{∞h} conformation with $R_1 = R_2 = 1.75$ bohr.

Method	Energy in E_H	% of correlation energy
SCF	-5.812692	0.0
MP2	-5.890431	85.6
MP3	-5.899547	95.6
MP4(SDQ)	-5.901416	97.7
MP4(SDTQ)	-5.901591	97.9
CCSD	-5.901925	98.2
CCSD(T)	-5.902185	98.5

TABLE III. Convergence of the total energy, E_K , and the stabilization energy, ΔE_K , with the ECG basis set size (K). Both sequences, E_K and ΔE_K converge from above to the exact values. $(\text{He-H-He})^+$ in $D_{\infty h}$ conformation with $R_1 = R_2 = 1.75$ bohr.

K	E_K/E_H	$\Delta E_K/\frac{\text{kcal}}{\text{mol}}$
50	-5.900591	-11.396
100	-5.902874	-12.828
200	-5.903321	-13.109
400	-5.903474	-13.205
800	-5.903505	-13.224
∞	-5.90353(1)	-13.240(7)

TABLE IV. Comparison of the total and stabilization energies obtained from different methods. (He-H-He)⁺ in D_{∞h} conformation with $R_1 = R_2 = 1.75$ bohr. E^X(G,B) is the total energy of the system X in given geometry G calculated with the basis set B. Both G and B can have two values, M or D, referring to monomer or dimer, respectively.

System	Total energy in E _H	
	CCSD(T)/cc-pV5Z	Explicitly correlated, variational
E ^{(He-H-He)⁺} (D,D)	−5.902185	−5.903505 ^a
E ^{HeH⁺} (M,M)	−2.978077	−2.978706591 ^b
E ^{HeH⁺} (D,M)	−2.969442	
E ^{HeH⁺} (D,D)	−2.969453	
E ^{He} (·,M)	−2.903038	−2.9037243770341 ^c
E ^{He} (D,D)	−2.903081	
ΔE in kcal/mol	−13.187 ^e	−13.224 ^d

^a This work — 800-term ECG wave function.

^b Ref. [13] — 600-term ECG wave function.

^c Ref. [24–26].

^{d,e} Evaluated according to the Eqs. (4) or (6), respectively.

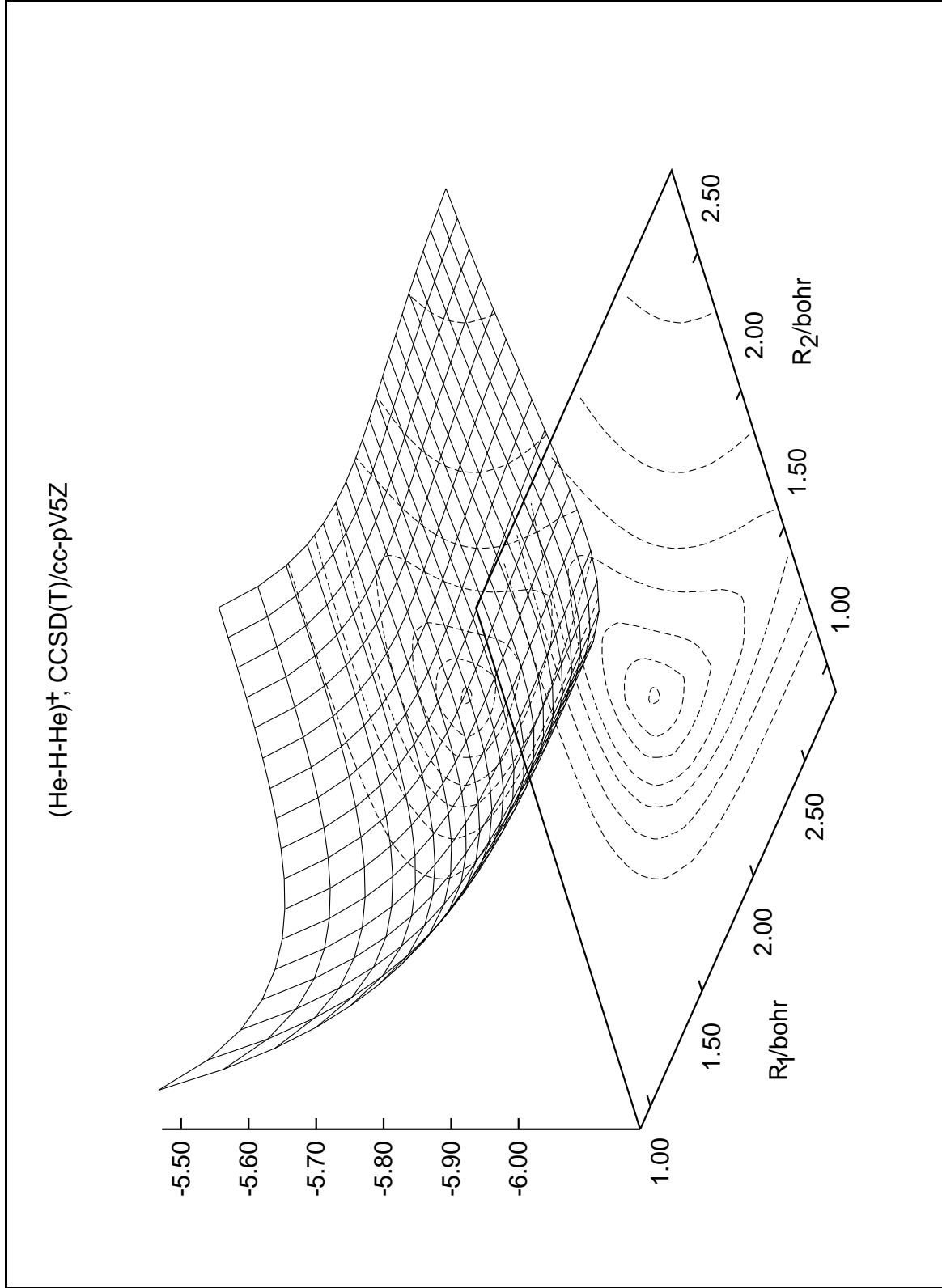


FIG. 1. Potential energy surface scan for the $C_{\infty v}$ conformation of the $(\text{He-H-He})^+$ ion. R_1 and R_2 are the He-H distances in units of bohr.

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