

# Electronic Potential Energy of $\text{H}_2^-$ and $\text{CHe}^{4+}$ Diatomic Ions

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## Abstract

Accurate electronic potential energy curves have been computed for the  ${}^{\infty}\text{H}_2^-(^2\Sigma_u^+)$  negative ion state and the singlet manifold of  $\text{CHe}^{4+}$  positive ion, including radial derivative couplings. Along with reporting the ab initio results obtained at the coupled cluster and configuration interaction level of theory, 1-D diabatization and some implications to low-energy collision processes at edge plasmas are discussed.

## Keywords:

hydrogen molecular anion, double electron capture, coupled cluster calculation, multi-reference single- and double- configuration interaction, diabatic representation

## 1. Introduction

The electronic structure of diatomic molecules has been a well established and understood problem [1-2]. Still, calculation of accurate electronic structures of diatomic ions has been far from a routine. Bound-state crossing with continuum of the form electron + neutral molecule, in case of anionic systems, or long-range series of localized electron transfer transitions, in case of cationic system, can serve as an example.

Here we report two calculations of diatomic-ion electronic structures relevant to processes in fusion edge plasmas. First, an accurate potential energy curve is computed for hydrogen molecular anion,  ${}^{\infty}\text{H}_2^-(^2\Sigma_u^+)$ . By employing the coupled cluster method up to the triples (perturbatively) for the 3-electron  $\text{H}_2^-$  system, we gain additional accuracy over the older benchmark calculation by Senekowitsch *et al.* [3] or the frozen core method in ref. [4]. Next, the case of  $\text{CHe}^{4+}$  diatomic cation is briefly discussed. Multi-reference single- and double- configuration interaction method (MRD-CI) is employed to obtain the singlet manifold of ground and excited states. Finally, the assumptions underlying the adiabatic to diabatic transform and basis set completeness for the use of ab initio results in scattering calculations are reviewed. Concluding remarks close the paper.

## 2. ${}^{\infty}\text{H}_2^-(^2\Sigma_u^+)$ diatomic anion

Accurate details of the molecular hydrogen anion po-

tential energy curve (PEC) in the range of meV have practical and measurable implications in processes such as dissociative attachment (DA),  $e + \text{H}_2 \rightarrow \text{H} + \text{H}^-$ , associative detachment (AD),  $\text{H} + \text{H}^- \rightarrow e + \text{H}_2$ , collisional detachment (CD),  $\text{H} + \text{H}^- \rightarrow \text{H} + \text{H} + e$ , and charge transfer (CT),  $\text{H} + \text{H}^- \rightarrow \text{H}^- + \text{H}$  [5]. Packing of hydrogen electron plasma in confined space can also be an example. Although  $\text{H}_2^-$  is the simplest negative molecular ion, there exist only a few ab initio studies in the literature [3,4].

We have therefore decided to eliminate the need for empirical correction on the asymptotic electron affinity of atomic hydrogen employed previously [3] by using the coupled cluster with including up to the *triple* (i.e., all) excitations. The d-aug-cc-pv5z basis proved sufficient for accuracy increase in the order of about 0.5 millihartree [3]. Complete basis set extrapolation with respect to the maximum angular momentum  $l$  represented in the basis,  $\Delta E_l \sim 1/(l+c)^3$  ( $c = 0.75$ ), was employed for the d-aug-cc-pvNz basis sets with  $N = 4, 5$ . The results are given in Fig. 1 and Table 1. Figure 2 and Table 1 also show the difference from the older calculation by Senekowitsch *et al.* [3], and the estimated contribution arising from the truncated part of the basis for  $l > 5$ .

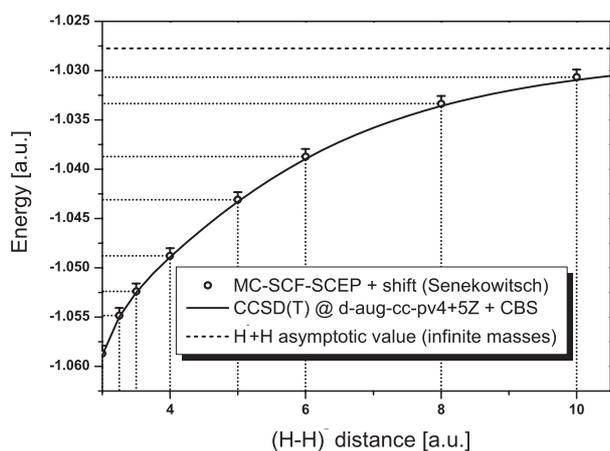


Fig. 1  $\infty\text{H}_2^-(^2\Sigma_u^+)$  potential energy curve. The circles denote the calculation of Senekowitsch *et al.* [3] corrected for asymptotics by vertical shifts. The upper error bars show the variational limit in ref. [3].

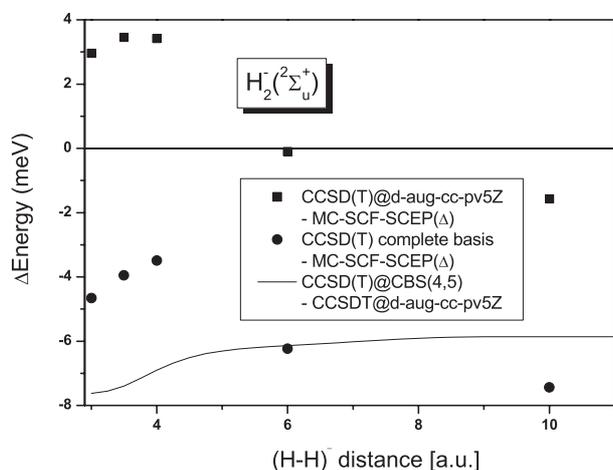


Fig. 2 Differences in  $\infty\text{H}_2^-(^2\Sigma_u^+)$  energy (meV). The full line shows the contribution of complete basis set extrapolation to energy lowering relative to CCSD(T) method with d-aug-cc-pv5Z basis. The full squares and circles indicate the differences of the two methods from the calculation in ref. [3].

### 3. $\text{CHe}^{4+}$ diatomic cation

Positively charged molecular ions often function as electron capture intermediates in charge transfer collisions. Their ab initio treatment by the MRD-CI method has been well established [6], including the excited states and computation of nonadiabatic couplings. We have decided to investigate the singlet manifold of  $\text{CHe}^{4+}$  because of recent charge transfer measurements [7], implications of this process to edge plasma description, and theoretical motivation in the long-range series of single and double electron capture crossings (the C-He distance ranges up to 100 a.u. in the present calculation). A standard gaussian basis set, [5s4p3d2f1g] for C and [4s3p2d1f] for He, has been used and augmented by diffuse functions. The results are shown

Table 1  $\infty\text{H}_2^-(^2\Sigma_u^+)$  PEC at different levels of theory. Index 5 stands for d-aug-cc-pv5Z basis set and CBS for complete basis set extrapolation ( $c = 0.75$ ) based on d-aug-cc-pv4, 5Z results.

$R$	CBS(0.75)*	CCSD(T) <sub>5</sub>	$\Delta_5$	$\Delta_{CBS}$
3.00	-1.05885323	-1.05857312	2.96	-4.66
3.25	-1.05497351	-1.05469596		
3.50	-1.05250305	-1.05223105	3.45	-3.95
3.75	-1.05058499	-1.05032183		
4.00	-1.04891901	-1.04866521	3.42	-3.48
4.25	-1.04738877	-1.04714321		
4.50	-1.04595050	-1.04571127		
4.75	-1.04459014	-1.04435536		
5.00	-1.04330558	-1.04307384		
5.25	-1.04209862	-1.04186904		
5.50	-1.04097119	-1.04074323		
5.75	-1.03992379	-1.03969715		
6.00	-1.03895522	-1.03872971	-0.10	-6.24
6.25	-1.03806278	-1.03783831		
6.50	-1.03724269	-1.03701926		
6.75	-1.03649052	-1.03626816		
7.00	-1.03580153	-1.03558029		
7.25	-1.03517095	-1.03495086		
7.50	-1.03459415	-1.03437517		
7.75	-1.03406674	-1.03384877		
8.00	-1.03358458	-1.03336746		
8.25	-1.03314380	-1.03292734		
8.50	-1.03274080	-1.03252481		
8.75	-1.03237217	-1.03215649		
9.00	-1.03203486	-1.03181935		
9.25	-1.03172606	-1.03151062		
9.50	-1.03144317	-1.03122776		
9.75	-1.03118390	-1.03096848		
10.00	-1.03094616	-1.03073072	-1.57	-7.43
10.25	-1.03072804	-1.03051260		
10.50	-1.03052787	-1.03031244		
11.00	-1.03017538	-1.02995996		
$\infty$	-1.02775101	-1.02775101	-0.41	-0.41

\*Atomic units (last two columns in meV).

in Fig. 3 and Table 2; the electronic states are assigned in increasing order ( $R = 100$  a.u.) as  $1s^22s^1\text{He}^1$ ,  $1s^22s^2$  (main capture channel),  $1s^22p^1\text{He}^1$ ,  $1s^22s^12p^1$ ,  $1s^22p^2$ ,  $1s^22p^2$ ,  $1s^22s^13s^1$ ,  $1s^23s^1\text{He}^1$ , and  $1s^2\text{He}^2$  (the initial state for electron capture in  $\text{C}^{4+}|\text{He}$  collision).

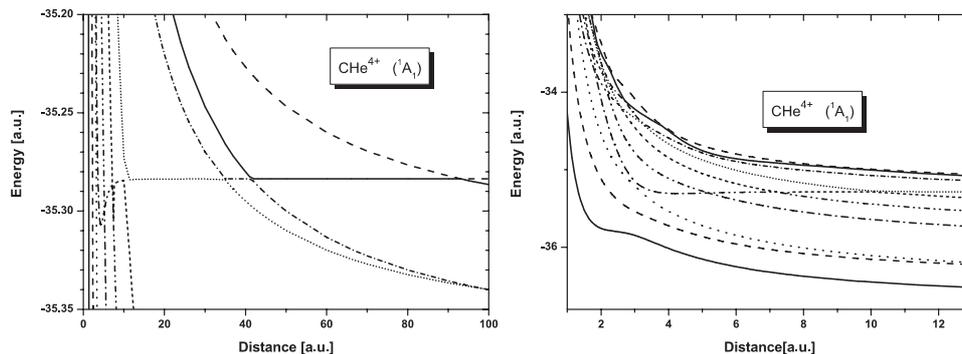
### 4. Diabatization

The ab initio adiabatic PEC above do not enter di-

Table 2 Singlet states of  $\text{CHe}^{4+}$  ordered by energy. No. 9 corresponds to  $\text{C}^{4+}|\text{He}$ . See the text for electronic state assignments.

R(a.u.)	1	2	3	4	5	6	7	8	9
0.7	-2.8141	-1.2899	0.0217	0.1536	0.3097	0.6864	0.7571	0.8836	1.0884
1.0	-4.2789	-2.8548	-1.6044	-1.5805	-1.3205	-0.9288	-0.8930	-0.7674	-0.5922
1.5	-5.5170	-4.5165	-3.6546	-3.2948	-3.0746	-2.9409	-2.7479	-2.6636	-2.5712
2.0	-5.7558	-5.1166	-4.5406	-4.0870	-3.8824	-3.7226	-3.6399	-3.6170	-3.3627
2.5	-5.7990	-5.3931	-4.9683	-4.7832	-4.3964	-4.1534	-4.1280	-4.0229	-3.8436
3.0	-5.8455	-5.5380	-5.2067	-5.1483	-4.7787	-4.4557	-4.3337	-4.2878	-4.0820
4.0	-6.0138	-5.7208	-5.5351	-5.3037	-5.1110	-4.8441	-4.6659	-4.5912	-4.4791
5.0	-6.1532	-5.8600	-5.7193	-5.3013	-5.2757	-5.0482	-4.8734	-4.7828	-4.6885
6.0	-6.2504	-5.9573	-5.8454	-5.3909	-5.2918	-5.1789	-5.0067	-4.8934	-4.7974
7.0	-6.3207	-6.0275	-5.9376	-5.4779	-5.2873	-5.2726	-5.1016	-4.9587	-4.8697
8.0	-6.3738	-6.0804	-6.0076	-5.5452	-5.3432	-5.2856	-5.1731	-5.0057	-4.9220
10.0	-6.4483	-6.1547	-6.1065	-5.6416	-5.4424	-5.2844	-5.2731	-5.0742	-4.9941
20.0	-6.5981	-6.3057	-6.3041	-5.8389	-5.6414	-5.4732	-5.2837	-5.2201	-5.1405
40.0	-6.6731	-6.4057	-6.3791	-5.9387	-5.7414	-5.5734	-5.2949	-5.2837	-5.2267
60.0	-6.6981	-6.4390	-6.4041	-5.9720	-5.7747	-5.6067	-5.3199	-5.3133	-5.2599
80.0	-6.7106	-6.4557	-6.4165	-5.9886	-5.7914	-5.6234	-5.3324	-5.3300	-5.2766
100.0	-6.7180	-6.4657	-6.4240	-5.9986	-5.8015	-5.6332	-5.3400	-5.3399	-5.2837

All in atomic units; vertical shift +30 a.u.


 Fig. 3 Adiabatic potential energy curves of  $\text{CHe}^{4+}$  system. Note the series of exothermic single- and double- electron capture crossings with  $\text{C}^{4+}|\text{He}$  (flat curves with the highest asymptotic value).

rectly into the dynamical scattering calculations; non-adiabatic couplings induced by relative motion of the nuclei must be also taken into account. This involves (1) considerable requirements on basis set and number of selected configurations (smooth wave functions are needed for numerical computation of first- and second-order derivative matrix elements) and/or (2) quasi-completeness of electronic state manifold (which then allows to avoid the second-order derivatives).

Precisely, the Schrödinger equation for nuclear functions  $\chi_n^{(a)}(R)$  in the adiabatic electronic basis  $H_{el}(\vec{r}; R)\phi_n(\vec{r}; R) = \epsilon_n(R)\phi_n(\vec{r}; R)$  reads

$$\left[ -\left( \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E \right) \underline{I} + \underline{D}(R) - \frac{\hbar^2}{2\mu} \times \right.$$

$$\left. \left( 2\underline{A}(R) \frac{d}{dR} + \underline{B}(R) \right) \right] \vec{\chi}^{(a)}(R) = 0. \quad (1)$$

Here  $\mu$  is the reduced mass of the diatomic system,  $I_{ij} = \delta_{ij}$ ,  $D_{ij} = \epsilon_i \delta_{ij}$ ,  $A_{ij} = \langle \phi_i | d/dR | \phi_j \rangle$ , and  $B_{ij} = \langle \phi_i | d^2/dR^2 | \phi_j \rangle$ . In order to deal with the nuclear dynamics by standard methods, the derivative couplings (matrices  $A$  and  $B$ ) can be removed by a unitary transform in the  $\chi$  space,  $\vec{\chi}^{(a)}(R) = \underline{C}(R) \vec{\chi}^{(d)}(R)$ . If the condition for basis set completeness holds,  $B = A^2 + dA/dR$ , then eq. 1 results in

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \underline{V}(R) - E \underline{I} \right] \vec{\chi}^{(d)}(R) = 0 \quad (2)$$

$$\text{with } \underline{V}(R) \equiv \underline{C}^{-1}(R) \underline{D}(R) \underline{C}(R).$$

The unitary transform among the two representations

solves formally,

$$\underline{C}(R) = \underline{I} + \int_R^\infty \underline{A}(R')\underline{C}(R')dR'. \quad (3)$$

The  $\text{CHe}^{4+}$  calculation involved computation of all 45 radial derivative couplings in the manifold of 10 states (not shown), in which case the basis set completeness is approximated well and the relation  $B = A^2 + dA/dR$  confirms numerically.

## 5. Concluding remarks

We have reported highly accurate reference potential energy curve for the  ${}^\infty\text{H}_2^-(2\Sigma_u^+)$  negative ion in the electronic ground state. Our coupled cluster calculation using doubly-augmented cc-pv5Z basis set does not require any vertical shift correction unlike ref. [3]. The effect of basis set truncation has been estimated with the complete basis set extrapolation method. As an instance of diatomic cation, detailed potential energy curves with series of electron capture curve crossings were computed for  $\text{CHe}^{4+}$  with the MRD-CI method. Assumptions underlying the applications of the present ab initio results in scattering calculations were reviewed.

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