Revisiting the potential energy surface for the He + H$_2^+$ → HeH$^+$ + H reaction at the full configuration interaction level

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A B S T R A C T

A new potential energy surface is proposed for the title reaction. Calculations have been carried out using the full configuration interaction method and an extended basis set. The selection of geometries is based on an earlier paper [P. Palmieri et al., Mol. Phys. 98 (2000) 1835], where calculations had been made at MRCI level including all single and double excitations from the CASSCF space. Care was taken in blending the long-range two-body interactions with the short-range three-body contributions, specifically described in a hyperspherical reference frame. A many-body expansion fit is presented, with root-mean-square deviation 6 meV, adequate for further investigations of the dynamics.

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1. Introduction

The prototypical proton transfer process,

\[ \text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H} \] (1)

and its isotopic variants involving HD$^+$ and D$_2^+$ have been well investigated both experimentally [1–4] and theoretically [5–25]. Besides being a test case of methods for ion molecule reactions, the above process is also important from the astrophysical point of view [26–31]. In order to explain the collisional outcomes of this reaction in various molecular beam experiments under different conditions, an accurate potential energy surface (PESs) is required. Attempts have been made in the past to generate new PESs, exploiting theoretical and computational advances as well as increases of computer power.

Edmiston et al. reported the first PES of the above reaction [5], limited to the collinear geometry of the triatomic species. Later, Brown and Hayes generated a PES at the Hartree–Fock level for the ground state of linear HeH$_2^+$, for which they found a stable minimum [6]. Their studies coupled with the work of Polanyi and Wong [7] on the effect of the position of the potential-energy barrier suggested that vibrational energy is more effective than translational energy in promoting the reaction. By using a semi-empirical diatomics-in-molecules (DIM) formalism, Kuntz constructed a surface for nonlinear geometries [8]. With quasiclassical trajectory studies, Kuntz and Whitten showed the shortcomings of the linear configuration to describe the reaction [9]. Using a spline fit, Sathyamurthy et al. pointed out the deficiency of the DIM functional fit of the surface to explain the discrepancy with the experimental results [10].

McLaughlin and Thompson performed truncated configuration interaction (CI) calculations for 596 points which include configurations other than linear geometry [11]. These data were fitted by two different functional forms: first by Joseph and Sathyamurthy [12] and later by Aguado and Paniagua [13]. In order to make the PES for the reaction as accurate as possible, several years ago some of us modified the surface of Ref. [13] using improved CI techniques and orbital expansions [14]. They performed a complete active space self-consistent field (CASSCF) calculation and added the dynamic correlation energy by using the internally contracted multi reference configuration interaction (MRCI) including all single and double excitations from the CASSCF space. The calculations were done using the correlation consistent polarized valence cc-pV5Z basis set [32]. Later, this work was further extended by including more points [15]. Very recently, Xu et al. reported a new PES using similar methods and adding the Davidson correction to the energy values with a root mean square deviation of 4 meV [16].

Several dynamics tests and comparisons were performed in the past using all of the above surfaces both by classical and quantum mechanical methodologies [17–25]. Most of the studies reported a qualitative description between various available experimental results and those of the calculations [17–19]. Quantitative discrepancies between experimental and theoretical results still exist [20,21], and the recent MRCI surface of Ref. [16] lead to unsatisfactory agreement with vibrational state-to-state integral cross section. One yet not definitively clarified aspect of these shortcomings is the full impact of electron correlation effects, as distinct from, say, basis set or relativistic effects. In this context, here we propose a new PES computed using the full configuration interaction (FCI), thus exhausting the basis set, in order to both validate and possibly improve the previous calculated points and their fitting.
The selection of the points for a PES is very important to enable a proper description of the dynamics of a reaction. Selecting points from suitable regions which are critical to the reaction pathways permit a better description than an arbitrary choice of the points, and also helps to reduce the computational time. With the insight gained from our earlier experience on dynamics calculations, we divided the surface into eight important regions as described in a previous Letter [15].

Thus the present surface involves (1) 60 geometries with describing the stable intermediate HeH\textsuperscript{+}, (2) 105 geometries describing the insertion complex HHeH\textsuperscript{+}, (3) and (4) 35 geometries each for the entrance and exit channel of the reaction, (5) 29 geometries correspond to the dissociative asymptote of the T-shaped HHeH\textsuperscript{+} complex, (6) 245 geometries similar to the astride of the ridge of the reaction as reported in the previous surface [15], (7) 755 geometries spaced on a three-body grid of hyperspherical coordinates and (8) 247 points selected arbitrarily. All these points (1511) lie below the complete dissociation (He + H + H\textsuperscript{+}) energy level.

The bond lengths and the dissociation energies of the optimized geometries are given in Table 1. The present MRCI results are in general agreement with the corresponding ones in Ref.15, extremely small differences being possibly due to the updated version of the program used here.

### Table 2

Partial ($\Delta\alpha$) and total root mean square deviations and maximum difference ($\Delta E_{\text{max}}$) for the fitted PES in different orders of the polynomial fit obtained from MRCI and FCI levels of calculations. Energies are in meV.

<table>
<thead>
<tr>
<th>No. of points</th>
<th>$\Delta_1$</th>
<th>$\Delta_2$</th>
<th>$\Delta_3$</th>
<th>$\Delta_4$</th>
<th>$\Delta_5$</th>
<th>$\Delta_6$</th>
<th>$\Delta_7$</th>
<th>$\Delta_8$</th>
<th>$\Delta$</th>
<th>$\Delta E_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRCI M=6</td>
<td>3</td>
<td>12</td>
<td>7</td>
<td>12</td>
<td>13</td>
<td>6</td>
<td>18</td>
<td>11</td>
<td>14</td>
<td>126</td>
</tr>
<tr>
<td>MRCI M=8</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>8</td>
<td>6</td>
<td>7</td>
<td>47</td>
</tr>
<tr>
<td>FCI</td>
<td>3</td>
<td>12</td>
<td>7</td>
<td>12</td>
<td>14</td>
<td>5</td>
<td>17</td>
<td>12</td>
<td>14</td>
<td>129</td>
</tr>
</tbody>
</table>

### Table 1

Optimized distances and the dissociation energies with respect to complete dissociation for the diatomic and triatomic species considered in the present study. Distances are in atomic units (1 Bohr = 0.529 × 10\(^{-10}\) cm) and energies in eV (1 hartree = 27.211 eV). Values in brackets correspond to the experimental results.

<table>
<thead>
<tr>
<th>System</th>
<th>$R_e$ (atomic unit)</th>
<th>$D_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeH\textsuperscript{+}</td>
<td>1.9976 (1.9880)(^b)</td>
<td>1.9972</td>
</tr>
<tr>
<td>HeH\textsuperscript{2}</td>
<td>1.4639 (1.4632)(^b)</td>
<td>1.4635</td>
</tr>
<tr>
<td>HHeH\textsuperscript{-}</td>
<td>$R_{11}$ = 1.9130</td>
<td>1.9337</td>
</tr>
<tr>
<td>HHeH\textsuperscript{+}</td>
<td>$R_{11}$ = 4.1305</td>
<td>4.1628</td>
</tr>
</tbody>
</table>

\(^a\) Equivalent to Unrestricted Hartree-Fock results.

\(^b\) Ref. [35].

The next section gives an account of the calculation procedures. Section 3 provides details of the fitting of the PES, remarks and conclusions follow in Section 4.

### 2. Details of the calculations

The calculations have been carried out by the FCI method using the cc-pVQZ basis set [32] with the MOLPRO suite of programs [33].
3. Fitting of the potential energy surface

The potential energy of a triatomic system ABC can be expressed as a sum of three monoatomic terms \( V_{1}(\mathbf{q}) \), three 2-body terms \( V_{2}(\mathbf{r}_{\alpha\beta}; \mathbf{q}) \) and a 3-body term \( V_{3}(\mathbf{r}_{\alpha\beta\gamma}; \mathbf{q}) \):

\[
V_{\text{tri}} = V_{1}(\mathbf{q}) + V_{2}(\mathbf{r}_{\alpha\beta}; \mathbf{q}) + V_{3}(\mathbf{r}_{\alpha\beta\gamma}; \mathbf{q})
\]

where \( \mathbf{r}_{\alpha\beta} \) corresponds to the bond length of the diatomic systems involved.

The monoatomic energy is taken to be zero for each atom. The short-range and the other the long range potential:

\[
V_{1}(\mathbf{q}) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \rho_{\alpha\beta\gamma} \exp(-\mathbf{r}_{\alpha\beta\gamma}/\mathbf{q})
\]

where \( \rho_{\alpha\beta\gamma} = \exp(-\mathbf{r}_{\alpha\beta}/\mathbf{q}) \).

A similar definition applies for \( V_{2}(\mathbf{r}_{\alpha\beta}; \mathbf{q}) \) and \( V_{3}(\mathbf{r}_{\alpha\beta\gamma}; \mathbf{q}) \).

The diatomic part is fitted first and the fitted parameters are used for the triatomic part.

The three-body term is written as a polynomial:

\[
V_{3}(\mathbf{r}_{\alpha\beta\gamma}; \mathbf{q}) = \sum_{i,j,k} d_{ijk} \rho_{\alpha\beta} \rho_{\beta\gamma} \rho_{\gamma\alpha} \exp(-\mathbf{r}_{\alpha\beta\gamma}/\mathbf{q})
\]

where definitions of \( \rho_{\alpha\beta\gamma} \) and \( \rho_{\alpha\beta\gamma} \) are similar to that of \( \rho_{\alpha\beta} \). The indices \( i, j \) and \( k \) vary from zero to a maximum value such that \( i < j < k \) and \( i + j + k \leq M \).

As there are two identical atoms in the present case (\( \mathbf{r} = \mathbf{c} \)), it imposes additional constraints in the linear \( (d_{ijk} = d_{kji}) \) and nonlinear \( d_{ijk} \) parameters \( \rho_{\alpha\beta} = \rho_{\beta\alpha} \), thereby reducing the number of parameters in the final fit.

The surface has been fitted by using the procedure described by Aguado et al. [34]. It has been done with the polynomials of order 6 and 8, both for the MRCI/cc-pV5Z and FCI/cc-pVQZ calculated points. The partial root mean square deviations of individual regions \( \Delta \), total root mean square deviation \( \Delta \), and the maximum energy deviation \( \Delta \) from fitted surface for \( \mathbf{r} = \mathbf{c} \) are given in Table 2. These values compare favourably with those for higher \( M \) of previous work. Besides, such high \( M \) is generally not recommended for danger of unstable behavior [34].

The representative features of the reaction for the surface fit at \( M = 8 \) with the corresponding calculated values in MRCI and FCI methods are plotted in Figs. 1 and 2 respectively. These include the collinear and T-shaped geometries. The energy of the dissociative asymptote of the entrance channel is taken as zero in all of these figures. From the Table 2, it is clear that the fitting of the surface with \( M = 8 \) gives a smaller root mean square deviation (RMSD) and a smaller \( \Delta \). It is true for both FCI and MRCI methods. Thus further discussion is limited only to the surface fitted at \( M = 8 \). There is a small well of depth 0.346 eV in the left panel curves both for MRCI and FCI levels of calculations. For the central panel curves, the well depth calculated at MRCI and FCI levels are 1.576 eV and 1.574 eV respectively. There is a very shallow minimum of energy 0.032 eV for the T-shape approach in the FCI/cc-pVQZ level. The corresponding MRCI/cc-pV5Z value is 0.037 eV. The figures in the insets of Figs. 1 and 2 show the region near the equilibrium geometry within a small energy range of 0.1 eV. After comparing the well depth reported for various potential energy surfaces, Maiti and Sathyamurthy have pointed out that it can affect the number of bound state of the systems and hence the dynamics observed [22].

Comparisons of Figs. 1 and 2 along with the values given in Table 2 indicate that the fitting of FCI/cc-pVQZ surface is very accurate and suggest it as a promising potential for further dynamics studies. The parameters resulting from the fit of the FCI/cc-pVQZ surface for \( M = 8 \) are listed in Table 3. Full codes are available from the authors on request.
Table 3  
Coefficients $d_{ij} = d_{ji}$ for the $M = 8$ for FCI/cc-pVQZ level. Interatomic distances and energies are in atomic units (1 Bohr = 0.529 Å and 1 hartree = 27.211 eV).  

![Table](image)

4. Remarks and perspectives  
Our study shows that there is no dramatic difference between the FCI/cc-pVQZ surface and the MRCI/cc-pV5Z surface in their RMSD and $\Delta_{\text{max}}$ for the different regions considered here. It should be mentioned here that in the case of the H + H$_2$ reaction, Mielke et al. [36] reported that by enlarging the MRCI reference function, energies close to FCI can be achieved. Recently for the F + H$_2$ reaction Fu et al. [37] proposed a hierarchical scheme for accurate potential energy surface generation using the potential energy difference obtained from a part of two potential energy surfaces obtained by using different basis sets. The small difference in potential energy values obtained by two different methods suggests that the above scheme may be extended to this case also.

However, it should be emphasized that even a small difference in the potential energy surface can be significant for the nuclear dynamics. We hope that further calculations on the newly proposed surface with state-of-the-art methods may be able to explain the remaining anomalies with respect to available experimental results as well as to interpret the fine details that future experiments may provide. Particularly sensitive would be the comparison with the remarkably rich resonance pattern, while specifically appealing will be the calculation using the present surface of the full scattering properties by exact quantum mechanical methods for the isotopic variants of this reactions, explicitly He + HD$^+$ leading to the two channels HeH$^+$ + D and HeD$^+$ + H. Because of the presence of a small term of incorrect symmetry with respect to invariance for the exchange of hydrogen and deuterium atoms, the previous PES [15] was not suitable for these cases. With the surface presented here, such studies should be within reach in the near future, the relevant technology being available, as demonstrated for example from recent work on the F + HD reactions [38–40].

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