DECOMPOSITION PATHWAYS OF TETRAHYDROGEN

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Final Report

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FOREWORD

This final report was submitted by the University of California, Berkeley, Berkeley, CA on completion of contract F04611-87-K-0030 with the OLAC, Phillips Laboratory (AFSC), Edwards AFB CA 93323-5000. OLAC PL Project Manager was Dr. Stephen L. Rodgers.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the SF 298.

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Investigations of a variety of possible decomposition pathways using quantum Monte Carlo methods including a careful examination of nonadiabatic couplings between excited and the ground state using state-averaged multiconfiguration self-consistent field procedures lead to the conclusion that the H₄ MIES is a very short lived species.

Minimum energy paths have been computed for use in constructing improved ground and excited potential energy surfaces for the calculation of reorientation cross sections for He + H₂(B 'B').
QUANTUM MONTE CARLO STUDY OF THE DECOMPOSITION
PATHWAYS OF TETRAHYDROGEN

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PART A: QUANTUM MONTE CARLO STUDY OF THE DECOMPOSITION PATHWAYS OF TETRAHYDROGEN

I. Introduction

Bound excited states of small molecules are of both practical and theoretical interest. Stabilized and vacuum-stored excited-state molecules have been postulated as a new energy source. Nicolaides et al. have suggested an H₄ species as a candidate system. In their multireference single- and double-excitation configuration interaction (MR-SDCI) study, a species they labeled a maximum ionicity excited state (MIES) of pyramidal geometry with equilateral triangle base was found for which the coulomb attraction between the ionic fragments H⁺ and H⁻ governed stability. In their work, a local excited-state minimum was characterized that results from an avoided curve crossing between the lowest-lying 1'A' and 2'A' states.

In experiments by Moore and collaborators, however, large quenching cross sections have been measured for the interaction of excited-state H₂(B ¹Σ⁺) = H₂(B) molecule with ground-state H₂(X ¹Σ⁺) = H₂(X) molecules. This evidence could be interpreted as an argument against stability of an excited H₄ species. The correlation diagram for the interaction of two H₂ molecules shows that H₂(B) can dissociate to an unstable H₃ and H atom with subsequent decomposition to H₂ + H + H or H + H + H + H; see Fig. 1.
To ascertain the stability of various H₄ species requires determination of the possible decomposition pathways. Many ab initio potential energy surface (pes) studies of nuclear arrangements of high symmetry have appeared including investigations of the square,⁴,⁵ a rectangle,⁴,⁵ rhombus,⁴ a trapezoid,⁵,⁶ and various tetrahedra.⁴,⁵ A three-dimensional equipotential map including several of the lowest-lying states for (C_2v) tetrahedra have been provided by Michl⁵ et al. Various symmetric pathways have been investigated including the (C_2v) in-plane "T" approach,⁷ "kite" approach,¹¹ and two perpendicular plane approaches.⁵ In addition, a detailed molecular orbital correlation analysis has been reported.⁸

The major findings of those studies are: (1) the reaction of excited H₂(B) with ground state H₂(X) is exothermic with activation energy; (2) the ground state pes that correlates to H₂(X) + H₂(X) is repulsive and the excited pes that correlates to H₂(X) + H₂(B) is bound and leads to the formation of excimer H₄⁺; (3) the binding of the excimer is due to charge transfer; (4) there is either a crossing or avoided crossing between two or more lowest-lying states that provides a funnel facilitating decay of the excited state to the ground state.

Montgomery et al. pointed out that the well, implied by a one-dimensional plot in Ref. 1, for the ground 1'A' state is actually a saddle point on the multidimensional surface.⁹ Nicolaides et al. followed their earlier prediction with a new finding of a minimum
on the excited singlet surface for $C_3$ trigonal pyramidal geometry.\textsuperscript{10,11} In the latter papers, nonadiabatic coupling matrix elements that connect the excited- and ground also were reported.

To better understand stability of the excimer $H_4$ species, tetrahydrogen, a quantum Monte Carlo\textsuperscript{12} study of the system was carried out under this contract that also included state averaged multiconfiguration self-consistent field (SA-MCSCF) calculations of nonadiabatic coupling matrix elements over a range of coordinate values to enable a detailed investigation of possible decomposition pathways. Although an extended basis set is required to describe the highly ionic character of $H_4$ and its dissociation in conventional \textit{ab initio} basis set approaches, QMC routinely yields improved absolute energies with nominal dependence on basis set.\textsuperscript{12} Furthermore, our recently developed symmetry constrained optimization technique\textsuperscript{13} can easily handle degeneracies that arise in curve crossing (avoided crossing) regions without regard to the particular symmetry type.

The remainder of Part A is arranged as follows. Section II summarizes the central features of the QMC method. Section III presents findings of our MCSCF and QMC survey studies of the one-dimensional pes as a function of separation between apex $H$ and triangular base $H_3$. This is followed in Sec. IV with results of decomposition pathway explorations. Section V presents and discusses a two-dimensional pes contour map for $C_{3v}$ symmetry. Section VI describes splitting of the $^1\Sigma$ state at deformed (non $C_{3v}$)
geometries and the interaction between these lowest-lying states followed in Sec. VII with consideration of the role of nonadiabatic coupling in the subject system. Section VIII discusses our $H_4$ results and presents conclusions of the study.

II. Method

Quantum Monte Carlo

QMC is a stochastic method for solving the Schrödinger equation by a random walk process. An attractive feature of QMC is that with modest basis sets and single or small multiconfiguration wavefunctions combined with electron correlation factors that are explicit functions of interelectronic distance, one often recovers 90–100% of the correlation energy.\textsuperscript{14–25}

Because QMC is well described elsewhere,\textsuperscript{12} we present only a brief summary adequate for present purposes. Introducing $f = \psi \psi_t$, where $\psi$ is the exact eigenfunction of the $N$-electron system Hamiltonian and $\psi_t$ is a trial (approximate) wavefunction, the time-dependent Schrödinger equation in imaginary time $\tau$ can be written

$$\frac{\partial f}{\partial \tau} = -\frac{1}{2} D \nabla^2 f + D \nabla F_d f + (E_L - E_t) f \; .$$

(1)

Here $D = \hbar^2/2m_e$ where $m_e$ is the electron mass and $E_t$ is a constant shift of the zero of energy. Monte Carlo sampling of Eq. (1) in $3N$-dimensional space is governed by three factors corresponding to the three terms on the right-hand side of Eq. (1), namely, (1) diffusion, (2) particle drift under the influence of a "quantum force,"


where (3) is a first-order kinetic or branching process.

The local energy

\[ E_L = \frac{H\psi_c}{\psi_c} \]

is sampled throughout 3N-dimensional space. If one carries out random walks in the absence of the branching process, i.e., variational Monte Carlo (VMC), the usual variational energy is obtained, i.e.,

\[ \langle E \rangle_V = \frac{\langle \psi_c | H | \psi_c \rangle}{\langle \psi_c | \psi_c \rangle} \]  

Inclusion of the branching step leads to the fixed-node energy

\[ \langle E \rangle_{FN} = \frac{\langle \psi_{FN} | H | \psi_c \rangle}{\psi_{FN} | \psi_c \rangle} \]  

It is well established that Eq. (4) yields an upper bound to the ground-state energy; in Ref. 12 it is shown that Eq. (5) also provides an upper bound.

In this work, the trial function \( \psi_c \) was constructed as a product of a single determinant and symmetric two-body (electron-electron and electron-nucleon) correlation factors. These factors were determined as follows.

(a) Determinantal function: a basis set of 25 Slater-type
functions on each atom, consisting of two 1s (1.68, 0.8) and single 2s (0.9) and 2p (1.6) functions was used in a MCSCF calculation for a ten-configuration wavefunction formed by allowing two electrons to be singly and doubly excited among four molecular orbitals (MO). The term with the largest coefficient (>0.985) was selected as the independent-particle function.

(b) Two-body correlation factors: the familiar Jastrow function

\[ G = \prod_{i,a} G_{ia} \]

where

\[ G_{ia} = \exp \left( \frac{ar_{ia}}{1 + b r_{ia}} \right) \]  \hspace{1cm} (6)

was used to describe electron-nucleon (e-n) correlation. Here \( r_{ia} \) denotes the separation between the i-th electron and a-th nucleus. A related but improved form

\[ S = \prod_{i,j} \left[ 1 - a_i \exp \left( - \frac{r_{ij}}{b_1} - \frac{r_{ij}^2}{b_2} \right) \right] \]  \hspace{1cm} (7)

was introduced to represent electron-electron (e-e) correlation where \( r_{ij} \) is the separation between electrons i and j.

(c) Optimization: with the introduction of correlation factors, it is desirable to optimize the product function, i.e., the linear and nonlinear coefficients of the determinant as well as the correlation parameters \( a, b, \alpha \) as well as \( a_1, b_1, \) and \( b_2 \). This was readily achieved with a recently reported algorithm. In order
to maintain the symmetry of the state under consideration and to retain orthogonality between different states, a group theoretic symmetry constraint is enforced during optimization. This takes the form of a point group projection operator for the MOs and a Young tableaux permutation group projection operator to insure proper multiplets. (This capability was developed under support by this contract.)

III. Potential Energy Surface for C\textsubscript{3v} Symmetry

For C\textsubscript{3v} symmetry, potential curves for the three lowest-lying states, i.e., the doubly degenerate \(^1\text{E}\) state and the \(^1\text{A}\) state were computed as a function of separation \(R\) between the apex H atom and the equilateral triangle base of H atoms. The triangle side-length \(r\) was fixed for two sets of calculations at 1.70 a.u. and 1.80 a.u. These results are presented in Figs. 2 and 3, respectively. At each point the independent-particle function was taken either as the lead term from a MCSCF calculation or from a previously optimized function at an adjacent geometry. Optimization of the product of single-particle and correlation functions was carried out subject to the symmetry constraint mentioned in Sec. II. The constraint facilitates the capability of distinguishing states in the curve crossing region where near degeneracy often causes root flipping in MCSCF calculations.

The potential curves of Fig. 2 for \(r = 1.70\) a.u. were generated by a least-squares fitting procedure to 18 QMC energies. At \(R = 6.0\) a.u. the QMC ground-state (\(^1\text{E}\)) energy is \(-2.0650(30)\)
which is in good agreement with the sum of the asymptotic $H_3$
ground-state energy ($-1.565$ a.u.$^{28}$) plus $H$ atom energy ($-0.5$ a.u.).
Note that the QMC curve crossing at $R = 3.9$ occurs at a slightly
larger distance than that found in the Nicolaides et al. study$^1$
reproduced in Fig. 2 by the dotted line. In most regions the QMC
results are lower by $0.6-1.0$ eV. This considerable energy lowering
prompted us to carry out a singles and doubles configuration
interaction (SDCI) calculation which was done at $R = 3.4$ a.u. The
energy obtained was $-2.059$ a.u. which lies, as anticipated, between
the results of Nicolaides et al. and the present QMC energy and
provides a consistency check.

In Fig. 3 QMC energies are displayed resulting from QMC
calculations at 16 geometries, ranging from $R = 3.0$ to $6.0$ a.u. for
$r = 1.80$ a.u. for the doubly degenerate $^1E$ state and the $^1A_1$ states.
The components of the $^1E$ state were calculated independently using
the symmetry constraint method$^{13}$ mentioned in Sec. II. The
closeness of the energies of the components confirms that the
ground state, as the correlation diagram analysis indicates, is
doubly degenerate. Curve crossing occurs at $R = 4.3$ a.u. which is
larger than the distance found at $r = 1.70$ a.u. Compared with
results at $r = 1.70$ a.u., one finds a shift in the shape (as
characterized by the onset of repulsion) of the potential curve to
smaller $R$ as would be anticipated because of the larger separation
of the $H$ atoms forming the base of the pyramid.
IV. Approach of $H_2(B)$ and $H_2(X)$

Calculations were performed for $H_2(B)$ approach to $H_2(X)$ in which these molecules are contained initially in perpendicular bisector planes; see Fig. 4. Table 1 summarizes the sequence of geometry changes, labeled I-VIII, that were followed to carry the system from the asymptotic region to the neighborhood of the $H_4$ MIES configuration. The table also lists the energy lowerings associated with the steps which are plotted in Fig. 5. It is noteworthy that no energy barrier is encountered along this path. Further, Fig. 6 shows that when $H_2(B)$ is displaced from bisecting $H_2(X)$ in Step II, charge transfer occurs immediately. (Similar behavior has been found for the related $H_2(B) + \text{He}$ system in an independent study by the P.I.)

Calculations to explore the possibility of dissociation via paths alternative to the pyramidal MIES avenue have also been carried out. One possibility is the so called T-approach pathway in which $H_2(X)$ approaches $H_2(B)$ in a $C_2v$ T configuration. Over a wide range of geometries, no barrier was found, see Table 2. The excited state energy $E_2$, however, did drop below the MIES energy ($-2.065$ a.u.) reported in the previous section. But the interaction at shorter separations remains to be explored. The interesting finding is that charge transfer ends before curve crossing occurs.

V. Two-dimensional Energy Surface with $C_{3v}$ Symmetry

Figures 6 and 7 show contour maps constructed using a 28-
configuration MCSCF wavefunction and the basis set of Sec. II. MCSCF calculations at 125 geometries and QMC computations at 49 geometries were performed for $r = 1.55-2.00$ a.u. and $R = 3.0-5.4$ a.u. The $^1A$ state (Fig. 7) and doubly degenerate $^1E$ state (Fig. 8) surfaces were found to cross along a seam represented by the dashed line in each figure. A noteworthy feature is that the seam is nearly linear. It is described well by the relation $R = -4.7166 r + 1.2594$. In both cases the minimum energy along this seam is found at $r = 1.80$ a.u. and $R = 4.1453$ a.u., near the point where the seam is tangential to the $E = -2.00$ a.u. contour.

As shown previously, QMC calculations of this system can lead to total energies 2-2.5 eV lower than MCSCF calculations with a double-zeta plus polarization (DZP) basis set. It has also been documented that QMC results are weakly dependent on the basis set used to construct the QMC trial function. For these reasons, it was important to revisit the two-dimensional potential energy surface discussed above with the QMC method. Using the optimization algorithm and the symmetry constraint technique we constructed a MCSCF trial function for the QMC calculations. MCSCF energies and QMC energies obtained with the MCSCF trial function are listed in Table 3 at nine geometries along the seam. The QMC energies are lower than the MCSCF energies by 1.47-1.97 eV.

These results show that there is a broad crossing region of the three states where nonadiabatic coupling can be significant. Based on present findings it is clear that the excited pyramidal $H_4$...
holds the prospect of decay over a wide range of geometries besides 
$C_{3v}$ symmetry. Motions that destroy $C_{3v}$ symmetry provide additional 
pathways for decay of the system.

VI. SA-MCSCF Study of Distorted (non $C_{3v}$) Geometries

For pyramidal $H_4$, the structure of the pes's in the vicinity 
of $C_{3v}$ geometry is more complicated than a conical intersection 
because there are three, rather than two, surfaces that cross. Our 
investigation of non $C_{3v}$ geometries consisted of (1) deforming the 
$H_3$ base from an equilateral to an isosceles triangle, and (2) 
displacement of the apex H atom from the peak of the pyramid while 
retaining the isosceles base. The study proceeded in two parts: 
(1) Consideration initially of only the states of the same 
symmetry, thereby ignoring the third state which correlates with 
the antisymmetric branch of the $1E$ state for $C_{3v}$ symmetry. (2) 
Treatment of all three states at selected geometries.

Perspective view and contour map

Figure 8 provides perspective views and Fig. 9 shows the 
contour map of the ground and excited pes's at $R = 3.8$ a.u. From 
the contour map one sees (1) the local minimum of the excited state 
does not occur for $C_{3v}$ symmetry, but for an isosceles base 
arrangement with longer equal-length sides (A) and a shorter third 
side (B) and (2) the saddle point (S) of the ground state and the 
local minimum (D) of the excited state are found at different 
geometries.

These phenomena are explainable by the Jahn-Teller effect.

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When a non-symmetric displacement of the nuclei occurs, the symmetry is lowered with loss of the degeneracy. In the present case the degeneracy of the open shell $^1E$ is broken. As mentioned above Nicolaides et al. found a minimum for a deformed geometry consistent with the present findings. Our calculations also found that the energy of the excited state is lowered by a lateral displacement of the apex H atom of 0.1 a.u. along the perpendicular bisector plane of side B towards B.

**Strong interaction between three lowest-lying states**

Starting with $C_{3v}$ symmetry (see the contour map of the $^1A$ state in Fig. 6 and the $^1E$ state in Fig. 7), we calculated the three lowest-lying pes's for R fixed at 4.2 a.u., B held constant, while varying the equal side lengths (A). One-dimensional pes's for $B = 1.55-1.95$ and $A = 3.0-5.4$ a.u. were computed. The case $B = 1.6$ a.u. is plotted in Fig. 10. The calculations were done using the 28-configuration MCSCF wavefunction.

Figure 10 plots the splitting of the two $^2A'$ and $^1A''$ branches for $A \neq B$. One can observe that the symmetric $^2A'$ branch interacts strongly with the ground $^1A'$ state, as expected, since both states have the same symmetry in $C_{3v}$ symmetry. These curves are seen to approach closely at $a = 1.70$ a.u. although the energy gap between the $^1E$ and $^1A_1$ states is large (0.696 eV) for $C_{3v}$ symmetry. As the energy gap decreases with increase of b, the interaction is found to increase.

Our findings may be summarized as follows. In addition to the
seams in \( C_{3v} \) symmetry, at lower \( C_{s} \) symmetry additional regions of crossing (avoided crossing) are encountered. This is due to splitting of the doubly degenerate \(^1E\) state under geometry deformation and very strong interaction of the symmetric branch with the ground \(^1A_1\) state. These findings lend further support to our indications of the lack of stability of the tetrahydrogen system and the prediction of many decay paths.

VII. Nonadiabatic coupling

To estimate the transition probability between the \(^1A_1\) state and one of the doubly degenerate \(^1E\) states, five geometries near the crossing region in \( C_{3v} \) symmetry have been selected to examine the dependence of the nonadiabatic coupling matrix elements on nuclear displacements. Both the perturbed and unperturbed wavefunctions for these states can be written

\[
|A\rangle = \sum_{k} C_{Ak} \Psi_{k}^{CSP} \quad (8)
\]

\[
|E\rangle = \sum_{k} C_{Ek} \Psi_{k}^{CPS} \quad (9)
\]

\[
|A\rangle = |A\rangle \phi = \phi' = \sum_{k} C_{Ak} \Psi_{k}^{CPS} \quad (10)
\]

\[
|E\rangle = |E\rangle \phi = \phi' = \sum_{k} C_{Ek} \Psi_{k}^{CPS} \quad (11)
\]

where \( \phi_k^{CSP} \)'s are configuration state functions, i.e.,

-13-
\[ \Psi_{k}^{csp} = det|\phi_1 \ldots \phi_n|_k \]

and the molecular orbital function \( \phi_j \) is a linear combination of atom-centered Slater functions

\[ \phi_j = \sum_{m} d_{jm} X_m \]  

(13)

Here \( Q \) and \( Q' \) (see Eq. 10) are unperturbed and perturbed nuclear coordinates, respectively. The nonadiabatic coupling matrix elements consist of two terms, one arising from the CI coefficients and the other from the atom-centered basis functions.

\[ \langle A|v|E \rangle = D^{CI} + D^{AO} \]  

(14)

\[ D^{CI} = \sum_{kh} C_{Ak} C'_{Ek} \delta_{kh} = \sum_{k} C_{Ak} C'_{Ek} \]

(15)

\[ D^{AO} = \sum_{ij} P_{ij}^{AB} \langle \chi_i | \frac{\partial \chi_j}{\partial Q} \rangle \]

(16)

Using a triple-zeta plus polarization (TZP) basis set from a previous QMC calculation, a state-averaged MCSCF calculation was carried out to generate 24 reference MOs. A SDCI calculation consisting of 1035 configurations was carried out using both unperturbed \( (Q) \) and perturbed \( (Q') \) to obtain the CI coefficients (Eqs. 8-11). The atomic orbital term \( D^{AO} \) was found to give a very small contribution.

The nonadiabatic coupling matrix elements for each geometry were calculated for the six normal modes of nuclear motion shown in
Fig. 11. Among these modes, $Q_3$ and $Q_6$ are $A$-type (totally symmetric) motions, $Q_1$ and $Q_2$ are dissociative $E$-type motions with imaginary vibrational frequencies, and $Q_4$ and $Q_5$ are $E$-type with real vibrational frequencies.

Representative $NA$ coupling matrix elements are listed in Table 4 for selected $r$ and $R$. Because of selection rules, the two $A$-type motions $Q_3$ and $Q_6$ make no contribution to the coupling matrix elements. Among the four $E$-type motions $Q_1$ and $Q_2$ (dissociate) lead to strong couplings whereas, $Q_4$ and $Q_5$ induce relatively weak couplings.

In the region of closest approach ($r = 1.9$ a.u., $R = 4.6$ a.u.) the coupling is very strong. The calculated matrix elements roughly describable by a linear relation vs. the inverse of the energy gap between the $^1A_1$ and $^1E$ states see Fig. 12.

From our investigation, it is clear that there are a variety of regions ($C_3v$ and deformed) where the three lowest-lying pes's have crossings or avoided crossings. In this section we have shown that certain types of nuclear motions cause very strong coupling between these states which provides further evidence for strong quenching and a short lifetime for excited $H_4$.

VII. Conclusions of the $H_4$ Study

QMC and MCSCF studies of one-dimensional and two-dimensional pes's show that three states, a doubly degenerate $^1E(C_3v)$, which splits into $^1A'$ and $^1A'' (C_5)$, and a $^1A_1$ state are involved in quenching of excited $H_4$. In the vicinity of the MIES, that is for
R between 3.0-5.4 a.u. and r between 1.55-2.00 a.u., these states have many crossings or avoided crossings. The splitting of degenerate states and the interaction among these states imply high probability for electronic transitions. The nonadiabatic coupling matrix element calculations showed that the two dissociative E-type normal modes lead to very strong coupling between the \(^1\text{A}_\text{g}\) and \(^1\text{E}\) states. Collectively, these findings lead to the prediction that the H\(_4\) MIES is a very short lived species.

References


Table 1. Geometries* and energies for the approach of H$_2$(B) to H$_2$(X)

<table>
<thead>
<tr>
<th>step</th>
<th>$R'$</th>
<th>$L_1$</th>
<th>$L_2$</th>
<th>$L_2(\text{+})$</th>
<th>$L_2(\text{-})$</th>
<th>D</th>
<th>Energy Lowering*</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>5-2.2</td>
<td>1.40</td>
<td>2.43</td>
<td>1.215</td>
<td>1.215</td>
<td>0.0</td>
<td>-0.91</td>
</tr>
<tr>
<td>II</td>
<td>2.2</td>
<td>1.40</td>
<td>2.43</td>
<td>1.215-1.93</td>
<td>1.215-0.5</td>
<td>0.715</td>
<td>-0.20</td>
</tr>
<tr>
<td>III</td>
<td>2.2</td>
<td>1.60</td>
<td>2.63</td>
<td>1.93-2.13</td>
<td>0.5</td>
<td>0.865</td>
<td>-0.20</td>
</tr>
<tr>
<td>IV</td>
<td>2.2-1.75</td>
<td>1.60</td>
<td>2.63</td>
<td>2.14</td>
<td>0.5</td>
<td>0.865</td>
<td>-1.18</td>
</tr>
<tr>
<td>V</td>
<td>1.75-1.55</td>
<td>1.60</td>
<td>2.73</td>
<td>2.23</td>
<td>0.5</td>
<td>0.915</td>
<td>-0.46</td>
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<tr>
<td>VI</td>
<td>1.55</td>
<td>1.60</td>
<td>3.13</td>
<td>2.23-2.63</td>
<td>0.5</td>
<td>1.115</td>
<td>-0.69</td>
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<tr>
<td>VII</td>
<td>1.50</td>
<td>1.70</td>
<td>3.23</td>
<td>2.63-2.73</td>
<td>0.5</td>
<td>1.165</td>
<td>-0.11</td>
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</table>

*Total energy lowering for the seven steps is 3.75 eV. Distances in a.u.; energies in eV.

*aSee Fig. 4 for a diagram defining the second-seventh table headings.

$R'$ - distance between the midpoint of H$_2$(X) and the point where H$_2$(B) meets the H$_2$(X).

$L_1$ - length of H$_2$(X).

$L_2$ - length of H$_2$(B).

$L_2(\text{+})$ - length of H$_2$(B) above the H$_2$(X) plane.

$L_2(\text{-})$ - length of H$_2$(B) below the H$_2$(X) plane.

D - magnitude of shift of H$_2$(B) midpoint (above (+)/below (-)) plane of H$_2$(X).
Table 2. CI* total energies of three lowest-lying states along the T-approach pathway for H₂(B) + H₂(X)

<table>
<thead>
<tr>
<th>#</th>
<th>L₁</th>
<th>L₂</th>
<th>L₃</th>
<th>E₁</th>
<th>E₂</th>
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</tr>
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<td>01</td>
<td>2.4300</td>
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<td>-1.96950</td>
<td>-1.84546</td>
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<td>2.2624</td>
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<td>-1.97964</td>
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<td>03</td>
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<td>04</td>
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<td>2.0292</td>
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<td>-2.01944</td>
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*aSDCI results based on MC reference molecular orbitals with DZP basis set.

*bT-shape arrangement: H₃H₄ bisects and is perpendicular to H₅H₆. L₁ is the length of H₅H₆ and L₂ is the length of H₃H₄.

*cEnergies in a.u., 1 a.u. = 27.210 eV.

*dL₃ is the distance from the midpoint of H₅H₆ to the closer atom H₇. Distances in a.u.

*Curve crossing between the two geometries.
Table 3. MCSCF and QMC energies at several points along the crossing seam of the lowest-lying potential energy surfaces of pyramidal $H_4$.\(^a\)

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\(^a\) Energies in a.u. except where noted. 1 a.u. = 27.210 eV.
Table 1. Non-Adiabatic Coupling Matrix Elements

| r(a.u.) | R(a.u.) | \( <A'|E>_{1,2}^a \) | \( <A'|E>_{4,5}^b \) | \( <A'|E>_{3,6}^c \) |
|---------|---------|----------------------|----------------------|----------------------|
| 1.70    | 4.0     | 1.90                 | 0.29                 | 0.0                  |
| 1.70    | 3.8     | 2.10                 | 0.31                 | 0.0                  |
| 1.80    | 4.22    | 3.18                 | 0.52                 | 0.0                  |
| 1.80    | 4.4     | 4.59                 | 0.86                 | 0.0                  |
| 1.80    | 4.6     | 8.10                 | 1.60                 | 0.0                  |
| 1.90    | 4.6     | 13.79                | 2.67                 | 0.0                  |

\(^a\)Non-adiabatic coupling induced by the doubly degenerate dissociative modes \( Q_1 \) and \( Q_2 \).

\(^b\)Non-adiabatic coupling induced by the doubly degenerate bound modes \( Q_4 \) and \( Q_5 \).

\(^c\)Non-adiabatic coupling induced by the totally symmetric modes \( Q_3 \) and \( Q_6 \).
Figure 1
Correlation Diagram of Tetrahydrogen

One-dimensional potential energy curves of pyramidal H$_4$ as a function of R for $r = 1.70$ a.u. where R is the separation from apex H to equilateral triangle base and $r$ is the base side-length. Solid lines connect fixed node (FN) QMC calculated energies for the $^1E$ and $^1A_1$ states. The two dotted lines are the result from Ref. 1. The open triangles are VMC results.
Figure 3
One-dimensional energy curves of pyramidal H₄ for r = 1.80 a.u. Solid lines connect FNQMC energies. Dotted lines connect MCSCF energies.

Figure 4
T-Approach Geometry for interaction of H₂ (B) with H₂ (X)
Excited State Potential Energy along a C₄ Path

Figure 5
Plot of Total Energies Corresponding to the Pathway Presented in Table 1.

Contour map of ¹A₁ potential energy surface of pyramidal H₄. R is the distance between apex H and triangle base H₃. r is the side length of H₃. The dotted line is the crossing seam of the ¹A₁ state and the doubly degenerate ¹E state.
Figure 7
Same as Figure 5 except the potential energy surface is for the doubly degenerate $^1E$ state.

Figure 8
Perspective view of two of the three lowest-lying pes's of tetrahydrogen in $C_s$ symmetry, see text.
Figure 9

Contour map for $R = 4.0$ a.u. as a function of $a$ and $b$; see Figure 9 for definition.
Upper panel: ground state    Lower panel: excited state.
Three lowest-lying potential energy curves for pyramidal H₄ with isoceles triangle base as a function of A, the length of the two equal sides for R = 4.2 a.u. and B = 1.6 a.u. The \(^1E\) curve splits into two branches for A ≠ B, and the symmetric branch \(^2A'\) interacts with the ground state \(^1A'\).

Figure 11
Normal modes of H₄
Figure 12

Calculated nonadiabatic coupling matrix elements at five geometries vs the inverse of the energy difference between the pes's.
PART B: QUANTUM MONTE CARLO STUDY OF THE 1 \( ^1A' \) and 2 \( ^1A' \) POTENTIAL ENERGY SURFACES \( \text{He} + \text{H}_2 \)

I. Introduction

There is much theoretical and experimental interest in the reactions of atoms with electronically excited molecules. The \( \text{He} + \text{H}_2 \) system is particularly suitable for theoretical studies because of its simplicity: four electrons and three nuclei. Considerable effort has been made to understand the quenching of \( \text{H}_2(\text{B} \, ^1\Sigma_u^+) \) by \( \text{He}^{1-11} \) and its large effective energy transfer cross section. After unsuccessful attempts to find an avoided crossing along \( C_2v \) and \( C_w \) approaches,\(^4\) Farantos et al.\(^5\) located an avoided crossing for general \( C_5 \) approach which shed light on the quenching process. Subsequent construction of analytical \textit{ab initio} potential-energy surfaces for the 1 \( ^1A' \) and 2 \( ^1A' \) states\(^6\) made possible dynamics studies.\(^7-10\) However, Farantos's quenching cross sections were much smaller than the experimental values.\(^7\) Later Yarkony et al.\(^10-11\) extended study of the avoided crossing region using a second-order CI method and found that there is actually a crossing seam between these pes's. This development holds new promise for understanding electronic quenching in the subject system.

The QMC method\(^{12-14}\) is characterized by its high accuracy and simplicity in the calculation of energies of small molecules. It is of interest to ascertain the capability of the QMC to treat the \( \text{He} + \text{H}_2 \) system which, because of its small number of electrons, is
an ideal candidate for QMC studies. On the other hand, these studies are also challenging because the stochastic nature of QMC makes it difficult to obtain the high precision which is required for small interaction energies even though the QMC method routinely yields total electronic energies lower than basis set methods. In an attempt to minimize these considerations, special procedures were introduced in this study including total wavefunction optimization and the use of averages over independent calculations.

In Sec. I we describe the wavefunctions and optimization and computational methods. In Sec. III we present the results and discussion. Section IV contains our summary and conclusions.

II. Method

A. QMC approach

The VMC method, which evaluates the energy expectation value according to the trial wavefunction distribution \( \Psi_t \), is much more efficient than diffusion QMC because QMC has serious sample self-correlations for small time-steps. However, the VMC energy depends strongly on the quality of the trial function and it is difficult to guarantee the same quality at different geometries. In this study we use the fixed-node\(^{14}\) QMC approach because it has the advantages of simplicity, stability, and high accuracy. We note that the fixed-node depends on the nodal structure of \( \Psi_t \).

B. Wavefunction and optimization

Double-zeta-plus-polarization basis sets of atom-centered Slater-type orbitals were used. The orbital exponents are: \( \zeta_{1s} = \)
1.147, $\zeta_{1s} = 0.349$, $\zeta_{2px} = \zeta_{2py} = 1.200$ for the atom-centered functions on H and $\zeta_{1s} = 1.446$, $\zeta_{1s^*} = 2.862$, $\zeta_{2px} = \zeta_{2py} = 1.200$ for atom-centered functions on He.

The trial wavefunctions $\Psi_T$ can be expressed as

$$\Psi_T = \Phi(1,2,3,4)S_e[\{r_i\}]S_n[\{r_{ia}\}] ,$$

For the $1^1A'$ state (closed shell, the configuration is $\psi_1^2\psi_2^2$) we have:

$$\Phi(1,2,3,4) = (\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))(\psi_1(3)\psi_2(4) - \psi_4(4)\psi_2(3)) ,$$

For the $2^1A'$ state (open shell, the configuration is $\psi_1^2\psi_2\psi_3$) we have:

$$\Phi(1,2,3,4) = (\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2))(\psi_1(3)\psi_3(4) - \psi_4(4)\psi_3(3))$$

$$+ (\psi_1(1)\psi_3(2) - \psi_3(1)\psi_1(2))(\psi_1(3)\psi_2(4) - \psi_4(4)\psi_2(2)) ,$$

The electron-electron correlation function $S_e$ in this study was chosen to have the form

$$S_e[\{r_i\}] = \exp[-b\sum_{r_{ij}} \exp(-a_1r_{ij} + a_2r_{ij}^2)] ,$$

In order to reduce the variance in the local energy, $E_L = \Psi_T^{-1}H\Psi_T$, the parameter $a$ is set to $0.5/b$. This choice removes the singularity in $E_L$ due to the coalescence of electrons of opposite spin. (Satisfying the cusp condition for electrons of like spin is
not important for present purposes because $\Psi_1 \to 0$ as such electrons coalesce.) This leaves two parameters to be determined. Equation (4) is both easy to evaluate and yields a good description of electron correlation.\textsuperscript{15}

The electron-nuclear correlation function, $S_n$, further increases the flexibility of the trial function and complements the determinant in satisfying the electron-nuclear cusp condition. The form used here is the familiar Jastrow form

\[ S_n[(v_{ia})] = \exp \left[ \sum_{i,a} \frac{-\lambda r_{ia}}{1 + vr_{ia}} \right]. \tag{5} \]

The trial function specifies the nodal boundaries which ultimately determine the accuracy of computed energies, and serves as a guiding function for importance sampling during the random walk. High quality trial functions are essential not only to enhance the convergence rate of the computation but also to reduce the time-step bias in the fixed-node QMC procedure.\textsuperscript{16} In order to improve the quality of the trial function, a fixed-sample optimization is performed before each product calculation. Even though a full scale optimization of all trial function parameters, both for the basis set and correlation functions, has been proven to be useful for both VMC and QMC energies using single determinant wavefunctions,\textsuperscript{16} it is still in question for QMC energies using multideterminant wavefunctions because the optimization procedure may degrade the nodal structure of multideterminant wavefunctions.\textsuperscript{17}
Since multideterminant wavefunctions were used in the QMC calculations reported here, in order to avoid nodal structure degradation, we only optimized correlation function parameters and left the basis set parameters unchanged. Since correlation functions are nodeless, changes of parameters of those functions during optimization does not affect the nodal structure of $\Psi_t$ nor the QMC energies. However, optimized correlation parameters can still play a role in reducing energy variance, time-step bias, and in satisfying cusp conditions.

C. Computational procedure

The QMC energies are computed at points on the minimum energy pathway of Farantos's analytic pes for selected orientations. In this work $r$ is the $H_2$ internuclear separation, $R$ is the distance from He to the center of mass of $H_2$, and $\theta$ is the orientation angle formed by $r$ and $R$. Nuclear geometry is specified by the ordered triple $(R,r,\theta)$ with $R$ and $r$ in atomic units, and $\theta$ in degrees.

For each geometry, we used the HONDO program to obtain the MO coefficients, combined the resulting independent particle function with the correlation function, and then performed an unoptimized VMC calculation to create a set of configurations for use in optimization. From 1,000 to 1,500 sample points were used in the fixed-sample optimization procedure followed. The eight parameters of the correlation functions were optimized, and the resulting wavefunction used in a VMC calculation to yield 1,000 configurations which were divided equally into ten groups. These
ten sets of configurations were then used to perform ten independent QMC calculations.

The final QMC energy is the average value of these ten calculations. Using the average value of the independent runs is helpful in removing sample dependence and self-correlations. Trial function optimization appears to be a useful method of reducing time-step bias for QMC calculations. Figure 1 shows QMC energies vs time-step from which one sees that the bias vanishes for \( r < 0.01 \). On this basis all of the QMC calculations were carried out with \( r = 0.005 \). Including wavefunction optimization, the calculations for each geometry took approximately two hours of CPU time on a CRAY X-MP using vectorized codes.

III. Result and Discussion

The QMC energies for the minimum energy pathways for \( \theta = 0^\circ, 30^\circ, 45^\circ \), and \( 90^\circ \) are listed in Tables I and II. There are intersections between the \( 1^1A' \) and \( 2^1A' \) pes's around \((1.75, 4.13, 45)\) and \((1.75, 5.74, 30)\). Since the pes's should be continuous the interactions must extend over a considerable region. (On the other hand Farantos shows the closest approach of the two surfaces to be 5 kcal/mol at \((1.788, 4.44, 29.88)\).) This finding supports the extended region of crossing of the two surfaces found by Yarkony et al.\(^{10,11}\) and provides an explanation for the high quenching rate of \( \text{H}_2(\Sigma_u^+) \) by He. Furthermore, the present calculations show the energy of the \( 2^1A' \) state even lower than that of the \( 1^1A' \) state at \((1.75, 4.13, 45)\). The conditions for intersections of pes's of
polyatomic molecules have been discussed extensively.\textsuperscript{18-22} The intersection of two surfaces having the same symmetry is allowed for polyatomic molecules. As Manaa et al.\textsuperscript{11} have indicated, such intersections may play an important role in multistate electronically nonadiabatic processes.

In general, the present QMC energies are significantly lower than the energies obtained in previous studies. In particular, our computed well depth for the 2 $^1A'$ state is about 50 kcal/mol which is to be compared with previous values of 35 kcal/mol\textsuperscript{6} and 39 kcal/mol.\textsuperscript{10} As a check on the accuracy of the QMC energies we compared results at the asymptotic limit. The experimental value for the ground state of He is $-2.9037\hbar$,\textsuperscript{23} the best computed energies for $H_2(B^1\Sigma^+_u)$ and $H_2(X^1\Sigma_g^+)$ at $r = 2.43$ bohr are respectively $-0.7567\hbar$\textsuperscript{24} and $-1.0999\hbar$.\textsuperscript{25} We can infer that the exact energies for 2 $^1A'$ and 1 $^1A'$ states asymptotically should be $-3.6604\hbar$ and $-4.0036\hbar$, respectively. For comparison, Yarkony\textsuperscript{11} obtained $-3.6501\hbar$ and $-3.9962\hbar$; Farantos's value\textsuperscript{6} for $E(2^1A')$ is $-3.6499\hbar$; our QMC results are $-3.6591(14)\hbar$ and $-4.0033(11)\hbar$.

The data in Tables 1 and 2 give a rough picture of the shape of the pes for the 2 $^1A'$ state. At 45° the minimum energy path (MEP) is initially at $r = 2.4a_0$ and changes only slightly up to $R = 3.0a_0$. Around (1.75, 4.1, 45) there is a minimum which is in the vicinity of the intersection with the 1 $^1A'$ surface. There is a barrier on the MEP before the minimum and as soon as the approaching He overcomes the barrier it is quenched to the 1 $^1A'$.
state. Farantos's calculations predict this barrier to be 5.26 kcal/mol at (1.5, 4.0, 45), but Yarkony claims a barrier of 1.49 kcal/mol at (2.65, 2.52, 64.178). The recent experimental estimate of the barrier by Pibel et al.\textsuperscript{26} is only 0.715 kcal/mol. It is clear that He atom must have enough energy and proper orientation to pass the barrier and decay to 1 \textsuperscript{1}A' state.

At present, there is no QMC technique to locate the saddle point aside from estimates using other \textit{ab initio} techniques. Using Farantos's location (30, 2.4, 45), our QMC energy is \(-3.6396(9)h\) and the corresponding barrier is 12.2 kcal/mol. Using Yarkony's location (2.65, 2.52, 64.178) we obtained \(-3.6469(12)h\) and a barrier of 7.6 kcal/mol.

References


23. See, for example, I. N. Levine, Quantum Chemistry (Allyn and Bacon, Boston, 1983).


Table 1. QMC Total Energies of HeH\(_2\) for \(\theta = 0^\circ, 30^\circ, 45^\circ\).\(^*\)

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\(^*\)Energies are in hartrees and distances in bohr.

\(^\dagger\)The parenthetical quantity is the standard deviation.

Above two notes are also applicable to Table 2.
Table 2. QMC Total Energies of HeH₂ for \( \theta = 45^\circ, 65^\circ, \) and 90°

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Figure 1

The fixed-node QMC total energy at geometry (1.59, 4.18, 45) vs time step $\tau$. 

Total Energy (Hartree)

Time Step $\tau$ (Hartree $^{-1}$)