Ab initio non-adiabatic coupling elements: the conical intersection between the \( 2^2A' \) and the \( 3^2A' \) of the \( H + H_2 \) system

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Received 22 January 2002; in final form 4 February 2002

Abstract

The conical intersections between the \( 1^2A' \) and \( 2^2A' \) electronic states and the \( 2^2A' \) and \( 3^2A' \) electronic states of the \( H_2 + H \) system were characterized by line-integral calculations using \( ab \) initio non-adiabatic coupling terms. The calculations confirmed that when a contour surrounds the \( \{1^2A', 2^2A'\} \) conical intersection but does not approach, too closely, the \( \{2^2A', 3^2A'\} \) conical intersections the line-integral produces for the topological phase, the expected \( \pi \)-value [Chem. Phys. Lett., 319 (2000) 489]. Estimating the location of \( \{2^2A', 3^2A'\} \) conical intersection, the line-integral procedure was employed again – this time for the \( \{2^2A', 3^2A'\} \) system – confirming, in the same way, also the existence of the \( \{2^2A', 3^2A'\} \) conical intersections. © 2002 Published by Elsevier Science B.V.

1. Introduction

The \( H + H_2 \rightarrow H_2 + H \) exchange reaction together with its isotopic analogs is considered as the most fundamental reaction in chemistry. The interest in this reaction goes back to the early days of quantum mechanics starting with Wigner’s transition state theory [1] and it continues to be of major interest along the seventy years to follow until nowadays [2,3]. During this period major efforts were invested in developing appropriate quantum mechanical (QM) numerical methods to solve, as accurate as possible, the tri-atom Schrödinger equation (SE) [3–5]. As for the potential energy surface (PES) that govern the motion of the three atoms, here the numerical–theoretical efforts were less extensive mainly due to the original successful treatment by London [6], Eyring and Polanyi [7]. Still, along the years, the available advanced methods at a given time were also applied for this system, in particular with respect to the lowest adiabatic state, leading to more and more accurate PESs (a summary of this subject, as
well as the relevant references, can be found in [8]). Simultaneously with the theoretical development the experimental studies reached a similar level of sophistication and accuracy. This, in particularly, applies to the recent molecular beam experiments which yield state-to-state vib-rotational integral [9,10] and differential cross-sections [11]. Thus, so it seems, the time has come where theory would simulate correctly the experiments. What in fact happened was that a fit between theory and experiment was only partly achieved. In this respect we mention the detailed (integral) rotational distributions as calculated by Neuhauser et al. [10] as measured by Adelman et al. [9,10]. The fit between the two types of results was good but still not good enough as one would expect. During that period Kuppermann and coworkers [12] suggested that eventually the agreement between theory and experiment can be improved by incorporating geometrical phase effects formed by the well-known equilateral conical intersections (CI) between the two lowest adiabatic states of the H$_2$ + H system. Consequently he and his coworkers performed a series of calculations and, indeed, in most cases an improved fit was obtained [13,14]. Still, this modification did not resolved all the discrepancy. One could argue that these calculations were not exact as they were performed not employing a full two-state treatment. In fact they were single-state calculations in which some of the (nuclear) single-valued angular basis set functions were replaced by double-valued basis set functions with the aim of forming the necessary double-valued nuclear wave function. (The motivation for this is that double-valued nuclear wave functions are required to compensate for the double-valuedness of the electronic wave functions [15] to ensure single-valuedness of the total wave function.)

The relevance of such a treatment was recently contested in a two-state model study [16,17]. It was found that a single-state treatment (based on an extended Born–Oppenheimer approximation) produced transition probabilities which compare very nicely with results obtained due to the full two-state treatment. However, it was also found that extending this model to three states, namely, adding a third, energetically much higher state, and couple it with the second state via a second CI, revealed a significant discrepancy between the previous two-state results and those due to the three-state treatment [18]. Thus a third adiabatic state, coupled via a CI, cannot always be ignored, even for very low energies (namely, much below the opening of the third state) and its effect has to be incorporated in some way.

Returning now to the modified dynamic treatment of the H$_2$ + H reaction mentioned above [12–14], we claim that it could be that the discrepancy with the experiment is not due to the single-state approximation as such but because the effect of CIs between the next two adjacent states, namely, the 2$^2$A’ and the 3$^3$A’ electronic states was ignored.

Recently we started a systematic study of the CI for the H$_2$ + H system. In this process we not only revealed the existence of several additional CIs between the two lowest states of this system, namely, the 1$^1$A’ and the 2$^2$A’ electronic states but also between the above mentioned 2$^2$A’ and the 3$^3$A’ electronic states. In the present publication we concentrate on the equilateral single CI between the two lowest states (labeled as (1,2) CI) and a pair of CIs between the second and the third states, labeled as (2,3) CI, located not too far from the (1,2) CI.

2. Background information

To carry out such a study we consider a plane which contains the three atoms (A, B, C). This particular plane is formed by ‘freezing’ the interatomic distance $R_{BC}$ between the atoms B and C (each value of $R_{BC}$ forms a different plane, namely, different PESs and different NACTs). The third atom i.e., atom A, serves as a probe to examine, at a given point $(q, \varphi)$ on this plane, the NACT, $\tau(q, \varphi)$ [19]. Since we treat three surfaces we have to consider three NACTs, namely, $\tau_{13}(q, \varphi)$, $\tau_{12}(q, \varphi)$ and $\tau_{23}(q, \varphi)$. Each of the NACTs is a vector and therefore we expect each one of them to have three components. In what follows we concentrate only on one component, the angular component $\tau_{\rho}(q, \varphi)$, for reasons to be given later. Also it is well known that the NACTs between non-adjacent states are usually negligibly small so that these ones, i.e., $\tau_{13}(q, \varphi)$ will not be considered...
in the present article. Thus we are left with two NACTs i.e.: \( \tau_{12\varphi}(q, \varphi) \) and \( \tau_{23\varphi}(q, \varphi) \).

Whereas the CI for the equilateral triangle (D\(_{3h}\)) configuration between the 1\(^2\)A’ and the 2\(^2\)A’ electronic states is well studied \([20,21]\) the CIs between the next pair of states, namely, the 2\(^2\)A’ and the 3\(^2\)A’ electronic states are not known at all. Although the possible existence of such a CI was speculated no efforts were made to reveal its existence and definitely not its position. In order to carry out the study of this CI we employ the line-integral technique \([22–24]\) which was successfully applied for the H\(_2 + \) H system \([20,21]\) as well as in a recent study of the C\(_2\)H molecule \([19]\). In the present article the line-integral procedure is applied to determine the positions of the two symmetrical (2,3) CIs and to reveal the kind of interaction between the equilateral (1,2) CI and these two CIs.

The two-state line-integral takes the form \([22]\)

\[
\gamma_{jj+1}(s) = \int_{s_0}^{s} \tau_{jj+1}(s') \cdot ds', \quad j = 1, 2, \quad (1)
\]

where the integration is carried out along a contour \( \Gamma \) (the two points \( s \) and \( s_0 \) are on \( \Gamma \)), \( \gamma(s|s_0) \) is the termed the adiabatic-to-diabatic transformation (ADT) angle, \( \tau_{jj+1} \) is the relevant NACT and the dot stands for a scalar product. The topological (Berry) phase \( \alpha(\Gamma) \) is equal to \( \gamma(s_0|s_0) \), namely, to the \( \gamma \)-angle as calculated along a closed contour \( \Gamma \) \([23–25]\). Thus

\[
\alpha_{jj+1}(\Gamma) = \oint_{\Gamma} ds \cdot \tau_{jj+1}(s|\Gamma). \quad (2)
\]

It is well noticed that \( \alpha_{jj+1}(\Gamma) \) does not depend on any particular – initial or final – point along the contour \( \Gamma \) but only on the contour itself (as a whole).

Considering Eqs. (1) and (2), it is noticed that only the tangential component of the NACT contributes to the \( \gamma \)-angle integral and to the \( \alpha \)-phase integral. Thus if the contour is assumed to be a circle then only the angular component has to be considered. In the present article all contours will be circles of a given radius \( q \) at a given center. Thus, from now on \( \gamma_{jj+1}(q|\varphi) \) will be defined as

\[
\gamma_{jj+1}(q|\varphi) = \int_{\varphi_0}^{\varphi} \tau_{jj+1\varphi}(\varphi'|q) d\varphi', \quad (3)
\]

where \( \varphi \) is the angular (polar) coordinate defined for the specific plane and \( \tau_{jj+1\varphi}(\varphi|q) \) is corresponding (angular) component of the NACT along the circle. A similar expression is given for \( \alpha_{jj+1}(q) \) (see also Eq. (2)).

The calculation of the non-adiabatic coupling terms (along chosen circles) was carried out at the state-average CASSCF level using 311+(3pd) basis set \([26]\) extended with additional diffuse functions. In order to take properly into account the Rydberg states we added one s diffuse function and one p diffuse function in an even tempered manner \([28]\) with the exponents of 0.0121424 and 0.046875, respectively, to the basis set. We used the active space including all three electrons distributed on nine orbitals. Three different electronic states, namely, 1\(^2\)A’, 2\(^2\)A’ and 3\(^2\)A’ were computed by the state-average CASSCF method with equal weights. To perform the above mentioned integrations the relevant NACTs were obtained employing the MOLPRO program \([27]\) (which was also successfully applied by us for the study of the C\(_2\)H molecule). The details how to operate it for our purpose were discussed in previous publications (in particular, see Appendix of \([19]\)) and will not be repeated here.

3. Numerical results

The aim of the present study is to find out whether the H\(_2 + \) H system possesses (2,3) CIs and if so to reveal their positions. We start our treatment by studying first the (1,2) NACTs in order to expose the region in configuration space (CS) where the effect of the (2,3) CI is strongest and then, as a second step, to treat directly the (2,3) NACTs.

3.1. The (1,2) equilateral conical intersection

For our purpose we calculated the NACTs, \( \tau_{12\varphi}(\varphi|q) \) (some of them are presented in Figs. 1a,c,e,g), the ADT angles, \( \gamma_{12}(\varphi|q) \) (some of them are presented in Figs. 1b,d,f,h) and the corresponding topological phases \( \alpha_{12}(q) \) (given in Table 1) for circles with their centers at the point of the (equilateral) (1,2) CI (see Fig. 2). The results in Fig. 1 were calculated for the ‘frozen’ HH distance
i.e., $R_{HH} = 1.044$ Å and for four different $q$-values (additional calculations were performed for smaller and larger $q$-values). While tracing $\tau_{12a}(\varphi|q)$ as a function of $\varphi$ it is noticed that for the three smaller $q$-values this function is a positive tri-wigged (oscillating) smooth function. However, once $q$ becomes 0.75 Å, the $\varphi$-dependence changes significantly; the amplitudes are not equal anymore and the function flips signs (which, as we know from previous studies [19], is an indication that a CI(s) due to adjacent states perturbs these functions). A similar situation is encountered for the $\varphi$-dependence of $\gamma_{12}(\varphi|q)$. For the three smaller

Table 1

<table>
<thead>
<tr>
<th>$q$ (Å)</th>
<th>$\tau_{12}$</th>
<th>$\cos \tau_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>3.11</td>
<td>-0.9995</td>
</tr>
<tr>
<td>0.015</td>
<td>3.12</td>
<td>-0.9998</td>
</tr>
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<td>3.14</td>
<td>-1.0000</td>
</tr>
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<td>0.030</td>
<td>3.14</td>
<td>-1.0000</td>
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<tr>
<td>0.050</td>
<td>3.14</td>
<td>-1.0000</td>
</tr>
<tr>
<td>0.100</td>
<td>3.13</td>
<td>-1.0000</td>
</tr>
<tr>
<td>0.200</td>
<td>3.12</td>
<td>-0.9998</td>
</tr>
<tr>
<td>0.300</td>
<td>3.10</td>
<td>-0.9999</td>
</tr>
<tr>
<td>0.50</td>
<td>3.09</td>
<td>-0.9998</td>
</tr>
<tr>
<td>0.60</td>
<td>3.10</td>
<td>-0.9999</td>
</tr>
<tr>
<td>0.7</td>
<td>3.10</td>
<td>-0.9999</td>
</tr>
<tr>
<td>0.72</td>
<td>3.09</td>
<td>-0.9999</td>
</tr>
<tr>
<td>0.75</td>
<td>2.24</td>
<td>-0.619</td>
</tr>
<tr>
<td>0.80</td>
<td>2.27</td>
<td>-0.640</td>
</tr>
</tbody>
</table>
$q$-values these functions increase uniformly from zero to $\sim \pi$. However once $q$ becomes 0.75 Å (or larger) the $\varphi$-dependence changes significantly – the function oscillates and is not capable of reaching the $\pi$-value.

In Table 1 are summarized the $x_{12}(q)$ phases – expected to be $\pi$ [29] – and their $\cos(x_{12}(q))$ values as calculated for a several $q$-values. It is well noticed that as long as $q$ is smaller (or equal to) than 0.72 Å all $x_{12}$-values are in the vicinity of $\pi$. However once $q$ surpasses this $q$-value, the $x_{12}$-values drop, abruptly, to become 2.27 (or $\cos(x_{12}) = -0.64$). The fact that $x_{12}$ stops, from a certain $q$-value, to be a multiple of $\pi$ is an indication that the (1,2) system is not isolated anymore in the CS surrounded by this enlarged circle (although still being quasi-isolated in the smaller region surrounded by a circle of radius $q = 0.72$ Å).

In other words we encounter a strong perturbation due to higher states acting, most likely, via the (2,3) CIs located in the circular strip [0.72, 0.75 Å].

### 3.2. The (2,3) symmetrical conical intersections

Following our past experience the abrupt change in $x_{12}(q)$ (for $q > 0.72$ Å) has to be due to the existence of CIs between other states. The only ones that are capable of causing such effects – as was discussed on several occasions [30] – are CIs between the nearest states i.e., in the present case, the CI(s) between the $2^2A'$ and the $3^2A'$ electronic states. Thus our next subject is to reveal the location(s) of possible (2,3) CI(s).

From the numerical treatment reported in the previous Section it is to be expected that the (2,3) CI is located in the circular strip [0.72 < $q$ < 0.75 Å] with respect to the equilateral (1,2) CI position. To locate the $\varphi$-interval is somewhat more difficult but can be done by studying Figs. 1e and g. It is noticed that the functions $\tau_{12\varphi}(\varphi | q)$ and $\gamma_{12}(\varphi | q)$, when in the $120^\circ \leq \varphi \leq 240^\circ$ range, behave differently in these sub-figures (compared to those in the other sub-figures) and therefore the (2,3) CI, if it exists, is expected to be located in this angular region. More detailed inspections, finally locate the two symmetrical (2,3) CIs at $q \sim 0.73$ Å and at $\varphi \sim 141^\circ, 219^\circ$ (for more details see Fig. 2). It has to be emphasized that these numerical values apply only when $R_{HH} = 1.044$ Å. Varying $R_{HH}$ probably leads to different (2,3) CI locations.

In Fig. 3 are presented the NACTs terms, $\tau_{23\varphi}(\varphi | q)$ – Fig. 3a – and the corresponding ADT angles, $\gamma_{23}(\varphi | q)$ – Fig. 3b – as calculated along circles with their center at the vicinity of the (2,3) CI and with the following $q$-values i.e., $q = 0.01, 0.02, 0.05, 0.1$ Å. As can be seen we have in all four cases positive, oscillating, (almost) equi-amplitude NACTs and uniformly increasing ADT angles. Moreover they all end up (for $\varphi = 2\pi$) with $\varphi(q)$-values $\sim \pi$ (their actual values for the above mentioned radii are: 3.1415, 3.1414, 3.1403, 3.1364, respectively). Increasing $q$ to 0.2 Å produced significant disturbances due to the nearby (frozen) hydrogens.
4. Discussion and conclusions

The purpose of the present study is to examine the possibility that the $2^2A'$ and $3^2A'$ electronic states of the $H_2 + H$ system form a CI at a location nearby the equilateral $(1,2)$ CI. The calculations carried out for this purpose, namely, deriving the relevant NACT and employing the line-integral procedure to calculate the topological phase $\pi$, show unambiguously that indeed this is the case. This kind of calculation are usually performed on planes which contain the CIs. In our studies a plane is formed by freezing all internal coordinates and serves as a probe to expose the positions of CIs. The numerical procedure to expose the $(2,3)$ CI consists of two steps:

(a) First we examine what happens along circles that surround the $(1,2)$ CI – the well known equilateral CI. In general if the radii are small enough the topological angle, $\pi$, is always a multiple of $\pi$ and as is also in our case (see Table 1 where $\pi \sim \pi$). According to our theory [29–31] if no CIs are located between the second and the third states the $\pi$-value for $\pi$ is maintained for any radius immaterial how large it is. The only way deviations can be formed is due to the existence of $(2,3)$ CIs (or eventually, also, due to the frozen hydrogen atoms themselves). So the procedure is to increase the radii more and more and to find out whether during this process $\pi$ starts to deviate from $\pi$. We found that as long as $q \leq 0.72 \text{ Å}$, $\pi$ deviates only slightly from $\pi$. However once $q$ is in the range $0.72 < q < 0.75 \text{ Å}$, one encounters an abrupt change in $\pi$ (see Table 1). Once such a deviation appears, we can, by examining the angular dependence of the $(1,2)$ NACT, to determine the angular range for the location of the wanted CI. In the present case it was found to be in the range: $120^\circ < \varphi < 240^\circ$.

(b) The next step consists of verifying whether indeed the cause for this deviation is a $(2,3)$ CI. This is done by considering small-radii circles with their centers in the determined region and calculating the $(2,3)$ NACTs along these circles (see Fig. 2). The final verification is obtained when along some of these circles the relevant topological phase, $\pi$, is a multiple of $\pi$. In the present case the $(2,3)$ CI was located at ($q = 0.73 \text{ Å}, \varphi = 141^\circ$) with respect to the $(1,2)$ CI (see Fig. 2). The corresponding $\pi(q)$-values are given in Section 3.2.

The $H_2 + H$ system was studied before by Yarkony [20] who confirmed the existence of the $(1,2)$ CI employing the line-integral procedure. He also found that once the radii of the circles reach a certain value the corresponding $\pi(q)$-values start to deviate significantly from the expected $\pi$-value, thus suggesting the existence of a $(2,3)$ CI. However he did not, search for it and did not confirm its existence.

The existence of the nearby $(2,3)$ CI is most important for a proper study of the dynamics related to the $H_2 + H$ system and its isotopic analogs. The main conclusion of this article is that the two lowest states of the $H_2 + H$ system do not form an isolated sub-Hilbert space and therefore at least three states have to be included in any dynamical study of this system. The same conclusion applies also to the diabatization process. The diabatization cannot, unfortunately, correctly be done employing only two states. In fact, at least, three states are necessary and eventually even more than that.

Before conclusion we refer to a subject that so far was neglected by us i.e., the energy values at the points of the CIs. The energy value of the lower potential energy surfaces at the $(1,2)$ CI location is $\sim 2.82$ eV (above the minimum energy of the separated $H + H_2$ system) and the one of the two upper potential energy surfaces at the $(2,3)$ CI location is $\sim 16.26$ eV. It could be that the second energy value is high enough justifying ignoring the second CI (or the third state). In our opinion ignoring the third state just for that reason may cause inaccuracy as was revealed in our models studies [16–18]. As for the diabatization – ignoring the relevant topological effects may be even more
severe, however this subject will be discussed in future publications.

Acknowledgements

M.B. would like to thank Professor A. Dalgarno and Dr. K. Kirby for their warm hospitality at the Institute for Theoretical Atomic and Molecular Physics at the Harvard Astrophysics Center where this study was partially carried out and to the National Science Foundation for partly supporting this work through a grant for the Institute for Theoretical Atomic and Molecular Physics. This work is also supported, in part, by the Academia Sinica and the National Science Council of ROC under Grant NSC 9002113-M-001-068 and in part by a grant FKFP 0498/2000. G.J.H. also gratefully acknowledges the grant ‘Bolyai’ from the Hungarian Academy of Sciences.

References

[27] Molpro is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions from J. Almlöf, et al.