Ab initio non-adiabatic coupling elements: Conical intersections of the C\(_2\)H\(_2\) molecule

Gábor J. Halász \(^{a}\), Ágnes Vibók \(^{b}\), Michael Baer \(^{c,\ast}\)

\(^{a}\) Faculty of Informatics, University of Debrecen, Debrecen, Hungary
\(^{b}\) Department of Theoretical Physics, University of Debrecen, Egyetem ter 1, 4010 Debrecen, Hungary
\(^{c}\) The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel

Received 2 June 2005; in final form 21 June 2005
Available online 18 August 2005

Abstract

In this Letter, we report on ab initio non-adiabatic coupling terms, the relevant conical intersection (ci)-points and the corresponding adiabatic potentials as obtained for the C\(_2\)H\(_2\) (acetylene) molecule. The emphasis in this study is on the region, where the four lower \(A'\)-states of this molecule form three (in fact four) cis all located close to each other so that if the molecule is excited to the fourth state it may decay to its ground state without the intervention of spin–orbit couplings.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

A few years ago we started a systematic study of the non-adiabatic coupling terms (NACTs) and their conical intersection (ci) points in poly-atomic systems. So far all our studies concentrated on tri-atom systems of the type \{X\(_2\),Y\} systems which are characterized by two symmetry lines: one along the XX axis and one that goes through the center-of-mass point of the X\(_2\)-system and is perpendicular to the XX axis. We found that the ci points are located, either, along the symmetry lines or at symmetric points on both sides of the perpendicular-symmetry line, thus forming what we defined as ci-twins [1].

Recently, we extended the NACT studies to tetra-atomic systems, where one of the aims is to check whether symmetry considerations are, really, important for the existence of cis. Since we are acquainted with the ci structure of the [C\(_2\),H] system [1–3] it became quite natural to choose acetylene, namely, C\(_2\)H\(_2\) as the tetra-atomic system for this purpose. In this Letter, we report on a preliminary study of the NACTs and the ci-points related to the four lower states of this molecular system with symmetry of 1A'.

Other than being the natural extension of the C\(_2\)H radical, acetylene is considered one of the more fundamental molecules in chemistry and as such was exposed to numerous spectroscopic [4–8] and theoretical studies [9–15]. As far as the cis are concerned we mention the recent experiment by Wittig and co-workers [8] who studied the photo-dissociation of acetylene and verified the tendency of this process to form C\(_2\)H(A\(_2\)P). This preferred product lead Cui et al. [12] to assume that the second excited (singlet) state, assigned by them as a S\(_1\)-state and is of the 1A'-symmetry, interacts with a S\(_2\)-state which is of a 1A' symmetry (and which in our notation is the 2\(^2\)A') yields, adiabatically, the C\(_2\)H(A\(_2\)P) radical. However, Wittig’s experiments carried out with a lower energy photon also shows the formation of the C\(_2\)H(X\(^2\)Σ) radical. This fact may indicate that another state – the ground state of C\(_2\)H\(_2\) molecule, assigned by them as a S\(_0\)-state, and by us as the 1\(^2\)A' state – is involved in the spectroscopic process and yields the above mentioned radical [12,16].
In this Letter, we do not intend to study the details of the just described processes. Being a preliminary study we show, among other things, that the two mentioned cis are likely to be found close to each other in the region similar to the one discussed by Cui et al. [12]. Moreover, we show, among other things, that the two mentioned processes are viable. Being a preliminary study we break-up the five-dimensional configuration space and present it as a series of two-dimensional configuration spaces which are chosen to be planes. In what follows, we distinguish between the various planes as follows: Each plane is formed by fixing three internal coordinates: \( R \) – the distance between the two intermediate atoms (in our case the two carbons) so that \( R = R_{CC} \); \( \rho \) – the distance between one of the intermediate atoms (one of the carbons) and one external atom (in our case the nearby hydrogen) so that \( \rho = R_{CH} \); \( \beta \) – the angle formed by \( R_{CC} \) and \( R_{CH} \), thus \( \beta = \angle(R_{CC}, R_{CH}) = \angle(HCC) \). This choice leaves one atom, A (in our case a hydrogen), to move freely on that plane (see Fig. 1). As is usually the case, this free moving atom is used as a test-particle to locate cis and to examine the spatial distribution of the corresponding NACTs, \( \tau_{jj+1}(s) \), at the various points \( s \) belonging to the (planar) region just described. It is important to mention that in order to obtain the NACTs for the five-dimensional configuration space the values of \( (R_{CC}, R_{CH}, \beta) \) have to be varied, step by step, along a given grid.

In the present study, we consider four states and therefore treat the more relevant NACTs, namely, \( \tau_{jj+1}(s) \), \( j = 1, 2, 3 \). In this notation each of the NACTs is a vector.

The emphasis in this Letter is on the ADT angle, \( \gamma(s) \), formed by the following line-integral [17–19]:

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

where the integration is carried out along a contour \( \Gamma \) (the two points \( s \) and \( s_0 \) are on \( \Gamma \)) and the dot stands for a scalar product. For a closed contour the line integral yields the topological phase \( \alpha(\Gamma) \) [18–21], namely:

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

It is noticed that \( \alpha_{jj+1}(\Gamma) \) does not depend on any particular point along the contour \( \Gamma \) but on the contour itself [22,23].

The importance of studies of this kind is in revealing to what extent a two-state diabatization is valid. Two-state diabatization for a given region is feasible if and only if the line integral in Eq. (2) carried out along a (closed) contour, \( \Gamma \) that surrounds the region under consideration yields a value which is a multiple integer of \( \pi \), namely, \( \alpha(\Gamma) = n\pi \), where \( n \) is an integer (or zero). The origin for this requirement is as follows: If \( u_j(s); j = 1, 2 \) are the two adiabatic potential energy surfaces (PES) then the corresponding diabatic PESs, namely \( W_{ij}(s) \), \( W_{12}(s) \) and \( W_{12}(s) \) are given in the form:

\[
\begin{align*}
W_{11}(s) &= u_1(s)\cos^2\gamma(s|\Gamma) + u_2(s)\sin^2\gamma(s|\Gamma), \\
W_{22}(s) &= u_1(s)\sin^2\gamma(s|\Gamma) + u_2(s)\cos^2\gamma(s|\Gamma), \\
W_{12}(s) &= (1/2)(u_2(s) - u_1(s))\sin(2\gamma(s|\Gamma)).
\end{align*}
\]

\[ (3) \]
where \( \gamma(s|\Gamma) \) is the corresponding ADT angle. It is quite obvious that in order to have a single-valued diabatic potential matrix, \( W(s) \), the values of \( W_{jk}(s); j,k = 1,2 \) at the initial point of the closed contour have to be identical to their values at the final point (which is the same point along the closed contour). This condition is satisfied if and only if \( \alpha(\Gamma) \), given in Eq. (2), fulfills:

\[
\gamma_{jj+1}(s_0|\Gamma) = \gamma_{jj+1}(\Gamma) = n\pi,
\]

(4)

where \( n \) is an integer.

From Eqs. (1) and (2) it is noticed that, in fact, only the tangential component of \( s_{jj+1}(s) \) is responsible for yielding the ADT angle, \( \gamma(s|\Gamma) \). Therefore, in case of circular contours it is sufficient to consider the angular component, \( \tau_{jj+1}(\phi|q)/q \), where \( \tau_{jj+1}(\phi|q) \) is obtained from the expression:

\[
\tau_{jj+1}(\phi|q) = \left\langle \frac{\partial}{\partial \phi} \zeta_{jj+1}(\phi|q) \right\rangle.
\]

(5)

Here, \( \zeta_j(\phi|q) \) and \( \zeta_{j+1}(\phi|q) \) are two successive eigenfunctions. Since, in case of a circular contour we have \( ds = q \, d\phi \), Eq. (1) yields, for \( \gamma(s|\Gamma) \) \( (= \gamma_{jj+1}(\phi|q)) \), the result:

\[
\gamma_{jj+1}(\phi|q) = \int_0^\phi \tau_{jj+1}(\phi'|q) \, d\phi'
\]

(6)

and an analogous expression is given for \( \alpha_{jj+1}(q) \), where the upper limit of the integral in Eq. (6) is \( \phi = 2\pi \).

3. Numerical results

Like in previous cases (see for instance the study on the \{H\sb{2},O\} system [23]) the NACTs are calculated at

![Fig. 2. The angular \( \phi \)-dependent NACTs, \( \tau_{jj+1}(\phi|q); j = 1, 2, 3 \), as calculated, for acetylene along, three different equi-centered circles (characterized by different radii \( q \)) that surround the four \( cis \) presented in Fig. 1. The results for the (1,2) NACT are presented in subfigures (a–c); the results for the (2,3) NACT are presented in subfigures (d–f); the results for the (3,4) A NACT are presented in subfigures (g–i); and the results for the (3,4) B NACT are presented in subfigures (j–l). Also, in each subfigure is given the corresponding value of the topological phase, \( \alpha_{jj+1}(q) \).](image)
the state-average CASSCF level using 6-311G** basis set [24]. We used the active space including all 10 valence electrons distributed on 10 orbitals (a full valence active space). Following convergence tests, we included in the calculations, in addition to the four studied states, $1^2\text{A}', 2^2\text{A}', 3^2\text{A}'$ and $4^2\text{A}'$, also another 4–6 electronic states of the same symmetry.

As mentioned in Section 1, the study of the C$_2$H$_2$ is carried out for one fixed configuration of the HCC sub-system as described in Fig. 1. For this configuration we revealed four cis, namely one (1,2) $ci$, one (2,3) $ci$ and two (3,4) cis – all four of them shown in Fig. 1. In Fig. 2, are presented several $q$-dependent NACTs, namely, $\tau_{i,j+1}(q)$; $j = 1,2,3$, as obtained, in each case, for three different circles: one with a radius $q = 0.02$ (once, 0.05) Å, one with a radius $q = 0.1$ Å and one for $q = 0.2$ Å. In each sub-figure is also listed the relevant topological phase, $\tau_{i,j+1}(q); j = 1,2,3$ (see Eq. (6)). In most cases, we get results close enough to the expected value of $\pi$. The worst case in this respect happens for the (3,4)$_{(a)}$ $ci$ for which the decay of the $\tau$-values, as a function of $q$, is indeed, fast. We are not sure what causes this deterioration but we have some clues to believe that, close to this $ci$, is located a (4,5) $ci$ which interacts with it and consequently affects $\tau$ in a non-Abelian way.

In Fig. 3 are presented the four lower (singlet) potential energy surfaces for the configuration given in Fig. 1 as well as the corresponding $ci$ positions. All energy values are measured with respect to an energy value calculated for the ground state, collinear, configuration with the inter-atomic distances (H–C), (C–C), (C–H) = (1.076, 1.218, 1.076) Å. The values of the energies at the $ci$-points are as follows: \{$E_{12}, E_{23}, E_{34(a)}, E_{34(b)}$\} = {5.5, 9.1, 10.0, 11.2 eV).

4. Discussion and conclusion

As mentioned earlier, we report in this Letter, on results related to the four lower states of symmetry $A'_0$ of acetylene. In this section we emphasize two issues:

![Fig. 3. A three-dimensional presentation of the four ab initio lower surfaces of the A’ symmetry (namely, 1^2A, 2^2A, 3^2A and 4^2A), as calculated for acetylene for the configuration given in Fig. 1. Also noticed are the positions of the four ci-points.](image-url)
In our present study, no attempts were made to reveal the configuration(s) with the lowest \( c_i \)-energies. Still it is interesting to mention that we found the (1,2) \( c_i \) (formed by the \( 1^2A' \) and the \( 2^2A' \) states) to be at an energy 5.5 eV which is close to the energy value for which other groups \([11,12]\) found the crossing between the two first excited states with different symmetries (namely \( A' \) and \( A'' \)). However, we encountered this \( c_i \) for a somewhat different configuration determined by the angle \( \beta = 109^\circ \) (see Fig. 1) which seems to be much smaller than in Qui’s et al. angle. These and other findings will be further studied and presented in our next publication.

Acknowledgments

G.J. Halász and M. Baer acknowledge the support of the US-Israel Bi-national Science Foundation (years 2003–2007) for partially supporting this study. G.J. Halász acknowledges the Hungarian Academy of Sciences for partially supporting this research through the Grant ‘Bolyai’. Á. Víbók acknowledges the OTKA Grant T037994, the OTKA Grant M041537 and the Supercomputer Laboratory of the Faculty of Natural Sciences, University of Debrecen.

References