Conical intersection revisited: extension to an elliptic form

Michael Baer\textsuperscript{a,b,*}, Alexander M. Mebel\textsuperscript{c}, Robert Englman\textsuperscript{b}

\textsuperscript{a} Harvard–Smithsonian Center for Astrophysics, Institute for Theoretical Atomic and Molecular Physics, Cambridge, MA 02138, USA
\textsuperscript{b} Department of Physics and Applied Mathematics, Soreq NRC, Yavne 81800, Israel
\textsuperscript{c} Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 10764, Taiwan

Received 4 December 2001; in final form 22 January 2002

Abstract

In this Letter we relate to a general $2 \times 2$ diabatic potential matrix for which is derived an analytic expression for the various non-adiabatic coupling terms. Its main advantage is in leading to a simple algorithm to determine the number and the kind of conical intersections one encounters in a (planar) region defined by a closed contour. This approach was tested with respect to two models, one of them is the elliptical linear model. This model was then, further, applied to simulate ab initio results obtained for the C$_2$H molecule. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The importance of conical intersections for chemical systems was already demonstrated in the early studies of Longuet-Higgins and coworkers [1–3] molecular spectroscopy. These studies were further extended by Cederbaum, Koeppel and coworkers in a series of papers which are summarized in two excellent reviews [4,5]. As for chemical dynamics – these kind of studies took place several years later. Kuppermann and coworkers [6–8] were the first to reveal the manifestation of conical intersection in chemical exchange cross-sections for a real (three-dimensional) system, i.e. the H + H$_2$ reaction and its isotopic analogs. Significant effects, due to the existence of conical intersections, were also detected in quantum mechanical (reactive) transition probabilities as calculated for simplified models of exchange processes [9–12].

The conical intersection study is based on the following potential matrix:
\begin{equation}
W = k \begin{pmatrix} y & x \\ x & -y \end{pmatrix},
\end{equation}
where $x$ and $y$ are Cartesian coordinates and $k$ is a given constant [1–3,9,10,13–17]. One way to obtain the relevant non-adiabatic coupling term is according to the following recipe:

(1) First to derive the adiabatic eigenfunctions ($\psi_1, \psi_2$) which can be identified with the eigenvectors of the above diabatic potential matrix. Thus
\begin{equation}
\psi_1 = (\cos(\phi/2), \sin(\phi/2)),
\psi_2 = (-\sin(\phi/2), \cos(\phi/2)),
\end{equation}
where $\phi$ is the corresponding polar coordinate

$$\phi = \tan^{-1}(x/y).$$

(3)

(2) Second, to calculate the non-adiabatic coupling term employing the formula [14–20]

$$\tau_{12} = \langle \psi_1 | \nabla | \psi_2 \rangle,$$

(4)

which for the present model leads to the following results [16]:

$$\tau_\phi(q, \phi) = -\frac{1}{2} \text{ and } \tau_q(q, \phi) = 0,$$

(5)

where $q$ is the corresponding radial coordinate. It is noticed that $\tau_\phi(q, \phi)$, the angular non-adiabatic coupling term, is constant. This result is not supported by the ab initio calculations as were recently carried out for the C$_2$H molecule [21–24] as well as for numerous other molecular systems [25–27]. Fig. 1 presents $\tau_\phi(q, \phi)$, as calculated for the 3$^3$A', 4$^3$A' states of this molecule for several $q$-values, as a function of $\phi$. It is well noticed that $\tau_\phi(q, \phi)$ is a strongly $\phi$-dependent function (in fact, we found it also to be $q$-dependent but this subject is beyond the scope of the present study – cf. results from the different sub-figures). For completeness we mention that the ab initio calculations were carried out at the state-average CASSCF level [28] with the 6-311G** basis set for which the active space, including all nine valence electrons distributed on nine orbitals (full valence active space), was used [24]. The non-adiabatic coupling terms were calculated employing the MOLPRO program [29].

Fig. 1. The angular non-adiabatic coupling term $\tau_\phi(q, \phi)$ as calculated along circles which surround the (3,4) conical intersection and is defined in terms of radii $q$: (a) $q = 0.03$ Å; (b) $q = 0.05$ Å; (c) $q = 0.1$ Å; (d) $q = 0.2$ Å. The calculations were done for $r_{CC} = 1.25$ Å. In this situation the (3,4) conical intersection is located at a distance of 0.15 Å from the C$_2v$ axis and at a distance of 1.55 Å from the CC axis.
The aim of this Letter is to introduce a modified model which is capable to simulate, for small enough radii (i.e. \(q\)-values), the main features of the ab initio angular shape as shown in Fig. 1. In this process we developed, in the next section, a general expression that yields the non-adiabatic coupling terms in a most straightforward way for any assumed \(2 \times 2\) diabatic potential matrix. This expression reveals, as a by-product, a novel connection between the existence of conical intersections in a region formed by a closed contour and certain features of the diabatic potential elements along this contour (see Section 3). Examples are analyzed in Section 4. The modified Jahn-Teller model and its relevance to the ab initio results is discussed in Section 4.2 and conclusions are summarized in Section 5.

2. The non-adiabatic coupling terms for a general \(2 \times 2\) potential matrix

For this purpose we consider the following potential matrix:

\[
W = \begin{pmatrix} v(q, \varphi) & u(q, \varphi) \\ u(q, \varphi) & -v(q, \varphi) \end{pmatrix},
\]

(6)

where \(u(q, \varphi)\) and \(v(q, \varphi)\) are two general (given) potentials. Next we define two polar coordinates \((\rho, \theta)\):

\[
\theta = \tan^{-1}(u/v) \quad \text{and} \quad \rho = \sqrt{u^2 + v^2},
\]

(7)

and like in Section 1 obtain the corresponding \((\rho\) and \(\theta)\) non-adiabatic coupling terms:

\[
\tau_\rho(\rho, \theta) = -\frac{1}{2} \quad \text{and} \quad \tau_\theta(\rho, \theta) = 0.
\]

(5’)

However we are interested in \(\tau_\rho(q, \varphi)\) and \(\tau_\varphi(q, \varphi)\) and in order to obtain these we employ the chain rule for differentiation:

\[
\frac{\partial}{\partial \lambda} = \frac{\partial \rho}{\partial \rho} \frac{\partial}{\partial \rho} + \frac{\partial \theta}{\partial \rho} \frac{\partial}{\partial \theta}, \quad \text{where } \lambda = q, \varphi.
\]

(8)

Since \(\tau_\rho(q, \theta) = 0\) we get, based on Eqs. (5’) and (8), the following results:

\[
\tau_\varphi(q, \varphi) = -\frac{1}{2} \frac{\partial \theta}{\partial \varphi} \quad \text{and} \quad \tau_q(q, \varphi) = -\frac{1}{2} \frac{\partial \theta}{\partial q}.
\]

(9)

Recalling Eq. (7) it can be shown that

\[
\frac{\partial \theta}{\partial \lambda} = \frac{1}{1 + (u/v)^2} \frac{\partial (u/v)}{\partial \lambda}, \quad \text{where } \lambda = q, \varphi,
\]

(10)

which yields for the two polar non-adiabatic coupling terms the expressions:

\[
\tau_\lambda(q, \varphi) = -\frac{1}{2} \frac{1}{1 + (u/v)^2} \frac{\partial (u/v)}{\partial \lambda}, \quad \text{where } \lambda = q, \varphi.
\]

(11)

Thus Eq. (11) presents the angular and radial non-adiabatic coupling terms for any given two-state diabatic system (in fact it applies to any kind and any number of Jacobi coordinates). Usually one obtains the required non-adiabatic coupling terms employing the Hellmann–Feynman theorem [30,31]. It seems to us that the above expression is simpler and reveals more details about the topological feature of the system in a given region surrounded by a closed contour.

3. The quantization condition for a general \(2 \times 2\) potential matrix

In what follows we consider cases where \(q\) is held fixed and only \(\varphi\) is allowed to vary. For this situation the quantization condition can be expressed in terms of \(\tau_\varphi(q, \varphi)\) only, namely [17,32–34],

\[
\int_0^{2\pi} \tau_\varphi(q, \varphi) \, d\varphi = n\pi,
\]

(12)

where \(n\) is an integer (or zero). Eq. (12) is fulfilled for any \(q\)-value (in what follows we delete \(q\) in most expressions). Our aim is to employ Eq. (11) for \(\lambda = \varphi\) and to obtain the information regarding the existence of conical intersection in a given region. For this purpose we break up the interval \([0, 2\pi]\) into \(N\) sub-intervals \([\varphi_{j-1}, \varphi_j]\) so that the integration along the \([0, 2\pi]\) interval becomes

\[
\int_0^{2\pi} \tau_\varphi \, d\varphi = \sum_{j=1}^{N} \int_{\varphi_{j-1}}^{\varphi_j} \tau_\varphi \, d\varphi
\]

\[
= \frac{1}{2} \sum_{j=1}^{N} \int_{\varphi_{j-1}}^{\varphi_j} \frac{1}{1 + (u/v)^2} \frac{\partial (u/v)}{\partial \varphi} \, d\varphi.
\]

(13)
Next we select the grid points \( \{ \varphi_j \}, \ j = 0, 1, \ldots, N \) to fulfill the following criteria:

\[
\varphi_j = \begin{cases} 
  j = 0 & \text{for } v(\varphi_j) \neq 0, \\
  0 < j < N & \text{for } u(\varphi_j) = 0 \text{ or } v(\varphi_j) = 0, \\
  j = N & \text{for } v(\varphi_j) \neq 0.
\end{cases}
\]  

(14)

In what follows the grid points \( \{ \varphi_j \} \) for which \( u(\varphi_j) = 0 \) will be labeled as 'z-points' (these are the zeros of the function \( u(\varphi_j)/v(\varphi_j) \)) and the grid points \( \{ \varphi_j \} \) for which \( v(\varphi_j) = 0 \) will be designated as 'p-points' (these are the poles of the function \( u(\varphi_j)/v(\varphi_j) \) – we assume that this expression has simple poles although higher-order poles can be treated as well). As for \( j = 0 \) and \( N \), the first and the final points on the closed contour (assumed to be identical), the value of \( u(\varphi_j) \) can be arbitrary and therefore can also assumed to be zero without affecting the treatment’s generality.

Next, recalling that an integration of each term in Eq. (13) yields \( \tan^{-1}(u/v) \) we get

\[
\frac{1}{2} \int_{\varphi_j}^{\varphi_{j+1}} \frac{1}{1 + (u/v)^2} \frac{\partial(u/v)}{\partial \varphi} d\varphi = \frac{1}{2} \tan^{-1} \left( \frac{u(\varphi)}{v(\varphi)} \right) \bigg|_{\varphi_j}^{\varphi_{j+1}}
\]  

or adding up the results of two successive intervals where the midpoint (i.e. \( j = 2k + 1 \)) is a p-point and the two endpoints (i.e. \( j = 2k \) and \( j = 2k + 2 \), respectively) are z-points we get

\[
\int_{\varphi_{2k}}^{\varphi_{2k+2}} \tau_\varphi d\varphi = \frac{1}{2} \tan^{-1} \left( \frac{u(\varphi)}{v(\varphi)} \right) \bigg|_{\varphi_{2k}}^{\varphi_{2k+1}} = \pm \frac{1}{2} \pi.
\]  

(15)

(16)

Here the plus (minus) sign stands for the case that \( (u/v) \) is positive (negative) in the range \([\varphi_{2k}, \varphi_{2k+1}]\).

It is important to emphasize that in a given series of p-points and z-points it may happen that two (or more) successive points are of the same kind. In such a case the two successive p-points do not contribute to the integral in Eq. (13), as they annihilate each other (the contribution due to two successive z-points is zero by definition). This fact indicates that if along the interval \([0, \varphi_N]\) are encountered \( M \) p-points Eq. (13) becomes

\[
\int_{0}^{\varphi_N} \tau_\varphi d\varphi = \pm \frac{1}{2} m \pi,
\]  

(17)

where \( m \) is an integer (or zero) that fulfills the condition: \( m \leq M \). However the quantization condition (see Eq. (12)) requires that \( m \) be an even number (or zero). It is guaranteed to be zero if there are no \( p \) points along the considered contour. In case of a single conical intersection \( m \) has to be at least 2 \([17, 32–34]\), which implies that in order for the (diabatic) potential in Eq. (7) to yield a conical intersection the diagonal term, i.e. \( v(q, \varphi) \) has to flip its sign at least twice along any closed contour that surrounds the conical intersection.

It is important to mention that the roles of \( v(q, \varphi) \) and \( u(q, \varphi) \) can be reversed, namely, all points that were defined as poles can be defined as zeros and vice versa so that the same \( m \)-value is expected in Eq. (17).

As a final subject in this respect we would like to mention that Englman et al. \([35]\) recently, also studied the general \( 2 \times 2 \) diabatic matrix (see Eq. (6)) for the same purpose, namely, for revealing the connection between the certain features of the two diabatic potentials \( v(\varphi) \) and \( u(\varphi) \) and the number (and also the kind) of conical intersections expected in a given region in configuration space.

4. The study of various systems

In this section we analyze two systems in order to show the relevance of the analytic expressions derived in the previous sections.

4.1. The generalized linear degeneracy model: extension to the elliptic form

The most general linear conical intersection can be written in the form

\[
u(q, \varphi) = bx \quad \text{and} \quad v(q, \varphi) = y.
\]  

(18)

We start by making the connection between the existence of conical intersections (within a circle surrounding them) and the properties of \( v(q, \varphi) \) and \( u(q, \varphi) \). (1) Since \( v(q, \varphi) = y = q \cos \varphi \), it is noticed that \( v(q, \varphi) \) flips its sign twice along the interval \([0, 2\pi]\). (2) Since \( u(q, \varphi) = bx = bq \sin \varphi \), it is noticed that \( u(q, \varphi) \) flips its sign three times.
along the interval \([0, 2\pi]\). (3) Since between the two \(p\)-points we always have a \(z\)-point this implies, that in Eq. (17), \(m = 2\), namely, that we have a single conical intersection for any value of \(b \neq 0\) (just like the \(b = 1\) case).

Next we derive the explicit expression for \(\tau_\phi(q, \varphi)\). Recalling Eqs. (3), (7) and (11) we obtain
\[
\tau_\phi(q, \varphi) = -\frac{1}{2} \frac{b}{\cos^2 \varphi + b^2 \sin^2 \varphi}.
\]

In what follows the case of \(b = 1\) is termed as the circular conical intersection (the ordinary conical intersection) and the case for which \(b \neq 1\) will be termed as elliptic conical intersection. Whereas the circular case is characterized by a constant value of \(\tau_\phi(q, \varphi)\) which is equal to \(-\frac{1}{2}\) (see Eq. (5)) the elliptic case is characterized by an oscillating \(\tau_\phi(q, \varphi)\)-function (see Fig. 2). In the next section we extend the treatment of this (elliptic) case and compare Eq. (19) with ab initio calculations.

One of the more important features of the model is the invariance of Eq. (19) under the transformations \((b \rightarrow 1/b, \varphi \rightarrow \varphi \pm \pi/2)\) which is due to the basic symmetry of the model. In other words \(\sigma_\phi(q, \varphi|b) = \tau_\phi(q, \varphi + \pi/2|b^{-1})\).

Next we consider the value \(\tau_\phi(q, \varphi)\) once calculated at \(\varphi = 0\) and once \(\varphi = \pi/2\). The ratio of the two yields \(b^2\) and thus gives a direct measure for the ellipticity parameter \(b\), and their product yields \(\frac{1}{4}\) which provides a measure for the validity of the elliptic model at any actual situation (see Table 1).

4.2. The Jahn-Teller model for degenerate conical intersections

Recently, applying the line integral treatment to ab initio non-adiabatic coupling terms of the \(\text{C}_2\text{H}\) molecule, we revealed the existence of conical-intersection-twins between the \(3^2\text{A}'\) and \(4^2\text{A}'\) electronic states of this molecule [23,24]. Moreover this study indicated that these two conical intersections cancel each other in the sense that the integration along a contour that surrounds both of them is zero. Mebel et al. [24] suggested a model potential of the kind given in Eq. (6) where
\[
v(q, \varphi) = q^2 \cos^2 \varphi - a^2 \quad \text{and} \quad u(q, \varphi) = q \sin \varphi.
\]

As a second example for the theory presented in Section 3 we analyze the conical intersection situation by considering again \(v(q, \varphi)\) and \(u(q, \varphi)\) along a closed contour. For this purpose we consider two situations:

(1) The case \(a > q\): In this case \(v(q, \varphi)\) does not produce \(p\)-points along the whole defined region and therefore no conical intersections are expected.

![Fig. 2. The elliptical model angular non-adiabatic coupling term \(\tau_\phi(q, \varphi)\) (see Eq. (19)) as calculated along circles which surround the conical intersection is defined in terms of various \(b\)-values (the numbers stand for different \(b\)-values).](image-url)
we have as, indeed, is the case (see [24]). Thus for this case

$$ A \text{ comparison between the ab initio and the elliptic model parameters}$$

<table>
<thead>
<tr>
<th>$q$ (Å)</th>
<th>$T_a$</th>
<th>$T_s$</th>
<th>$T_0/T_s$</th>
<th>$T^*$</th>
<th>$\hat{r}$</th>
<th>$(\hat{T}/\hat{r})^{1/2}$</th>
<th>$\hat{T} \cdot \hat{r}$</th>
<th>$n^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>2.28</td>
<td>2.04</td>
<td>1.12</td>
<td>2.16</td>
<td>0.12</td>
<td>4.24</td>
<td>0.259</td>
<td>1.001</td>
</tr>
<tr>
<td>0.05</td>
<td>2.35</td>
<td>1.95</td>
<td>1.20</td>
<td>2.15</td>
<td>0.10</td>
<td>4.63</td>
<td>0.215</td>
<td>1.000</td>
</tr>
<tr>
<td>0.10</td>
<td>3.12</td>
<td>1.55</td>
<td>2.01</td>
<td>2.20</td>
<td>0.09</td>
<td>4.94</td>
<td>0.198</td>
<td>1.003</td>
</tr>
<tr>
<td>0.20</td>
<td>5.81</td>
<td>1.03</td>
<td>5.64</td>
<td>2.45</td>
<td>0.062</td>
<td>6.29</td>
<td>0.152</td>
<td>1.020</td>
</tr>
<tr>
<td>Model</td>
<td>$b/2$</td>
<td>$b/2$</td>
<td>1</td>
<td>$b/2$</td>
<td>$1/(2b)$</td>
<td>$b$</td>
<td>0.250</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a T_0 = \tau_0(\varphi \sim 0)$.
$^b T_s = \tau(\varphi \sim \pi)$.
$^c \hat{T} = (T_0 \cdot T_s)^{1/2}$.
$^d \hat{r} = \tau_\varphi(\varphi \sim \pi/2)$.
$^e n$ is the quantization number (see Eq. (12)).
$^f b$ is the parameter (of the model) to be fitted (see Eq. (18)).

as, indeed, is the case (see [24]). Thus for this case we have $M = m = 0$.

(2) The case $a < q$: In this case $v(q, \varphi)$ produces four $p$-points namely at $\varphi = \cos^{-1}(\pm a/q)$ and at $\varphi = \pi + \cos^{-1}(\pm a/q)$. However $u(q, \varphi)$ produces three $z$-points: two of them form the end-points and only one point is inside the $[0, 2\pi]$ interval. It is easy to see that all seven points are arranged as follows: $\{z, p, p, z, p, p, z\}$. Thus we have twice two successive $p$-points (which, as was mentioned earlier, annihilate each other) and therefore we have, indeed, $M = 4$ but nevertheless only $m = 0$ which implies that the integral in Eq. (17) is zero. It is important to emphasize that, in this case, having $m = 0$ does not rule out the existence of conical intersections in this region. It implies that the number of conical intersections, in the region surrounded by the contour, is even and that half of them are of opposite sign than the other half.

Next we derive the explicit expression for $\tau_\varphi(q, \varphi)$. Recalling Eqs. (7) and (11) it follows:

$$ \tau_\varphi(q, \varphi) = q \cos \varphi \frac{q^2 - a^2 + q^2 \sin^2 \varphi}{(q^2 \cos^2 \varphi - a^2)^2 + q^2 \sin^2 \varphi}. \quad (21) $$

This case was discussed elsewhere [24] and it was shown (as can be shown here employing Eq. (21)) that

$$ \gamma(\varphi, q) = \int_0^q \tau_\varphi(\varphi', q) d\varphi' $$

$$ = \frac{1}{2} \tan^{-1} \left( \frac{q \sin \varphi}{q^2 \cos^2 \varphi - a^2} \right), \quad (22) $$

which for $\varphi = 2\pi$ becomes zero.

5. The study of the elliptical model: comparison with ab initio treatments

The (general) linear conical intersection is expected to be valid near the intersection point namely for infinitesimal $q$-values whereas farther away it has to be modified by adding to $u(q, \varphi)$ and $v(q, \varphi)$ higher-order terms. In particular we find that the model $\tau_\varphi(q, \varphi)$ function is characterized by a strong oscillating function (see Fig. 2), namely, having two well-defined peaks of identical values – one at $\varphi \sim 0$ $(2\pi)$ and one at $\varphi \sim \pi$ (the absolute positions of the two peaks may vary from one system to another). This shape is expected to hold for the ab initio curves close to the intersection point.

The angular $\varphi$-dependence of $\tau_\varphi(q, \varphi)$ is presented in a recent publication by Mebel et al. [24] for various conical intersections arising between successive states of the $C_2H$ molecules. These non-adiabatic coupling terms were obtained, as mentioned earlier, employing the MOLPRO program. In many cases the angular dependence of $\tau_\varphi(q, \varphi)$, qualitatively, resembles the oscillatory shape which follows from the present elliptic model (cf. Figs. 4a, c; Fig. 5a, c; Fig. 7a, c, e; Fig. 8e, g; Fig. 9a, c of [24]).

In what follows a quantitative comparison is made between the predictions of the present model and the $\tau_\varphi(q, \varphi)$-function as obtained for one of the twin conical intersection points $X_{34}$ between the $3^2A'$ and $4^2A'$ states, as shown in Fig. 1 (see also Fig. 8(e) and (g) in [15]). This conical intersection is located at $\sim 1.5$ Å from the CC axis and
about 0.15 Å from the C2v line. The reason for choosing this case is that its conical intersection is located at an arbitrary point in configuration space, without having any particular symmetry features. The elliptic model applies to intersection points without specific qualifications (whereas at symmetry points it may fail), provided only that the closed contour surrounding the conical intersection is performed at sufficiently small distance from the intersection point (so that the linearity approximation holds). The data are summarized in Table 1.

In this table are presented results due to four different circular contours calculated for four \( q \)-values, i.e. \( q = 0.03, 0.05, 0.1, 0.2 \) Å. At the last row are presented the relevant values as expected from the elliptical (linear) model; five values are \( b \)-dependent but two – columns 4 and 8 – are pure numbers and immediately reflect the relevance of the model as a function of \( q \). The ab initio values for the various parameters as defined along the columns of the table are seen to converge, uniformly, to the values predicted by the model (presented in the last row). However it is also realized that the model seems to break down already at \( q = 0.2 \) Å for which all values (except for the \( n \)-value) are significantly different from the ones predicted by the (linear) model.

The model is defined in terms of a single parameter \( b \). As the table shows this value can be calculated at various points along the \( \tau_q(q, \varphi) \) curves. The converged results for \( b \) are as follows: From the 5th column we get the value, 4.32, from the 6th the value, 4.17 and the final value – in column 7 – is 4.24.

The \( n \)-value reflects the quantization requirement (see Eq. (12)). The ab initio treatment shows a very nice convergence towards the value \( n = 1 \) (as expected for a single conical intersection). This value is seen to be much less insensitive to whether the linearity condition holds or not which implies that the quantization condition is a feature independent of whether the linearity assumption is fulfilled or not.

In this discussion we did not refer to the radial non-adiabatic coupling term \( \tau_q(q, \varphi) \). If \( b \) is a constant (which does not depend on \( q \)) then \( \tau_q(q, \varphi) \) is zero. The ab initio calculations do not support this result – in fact \( \tau_q(q, \varphi) \) behaves in the vicinity of the conical intersection as \( (1/q) \). However this subject is beyond the scope of the present Letter.

As a final comment we would like to mention that a similar model will soon be applied to the \( \text{H}_2 + \text{H} \) system for which we carry out an extensive ab initio study with the aim of revealing the various conical intersections that characterize it.

6. A summary

In this publication we achieved the following:
1. For a given general \( 2 \times 2 \) diabatic potential matrix we derived an analytic expression, for the various non-adiabatic coupling terms, which can be considered as an alternative formula to the Hellmann–Feynman expression.
2. Having such an expression opens up various possibilities to study the number and the kind of conical intersections one encounters in a region defined by a closed contour. This study is done by following the series of sign flips undergone by the two diabatic potentials terms \( u(q, \varphi) \) and \( v(q, \varphi) \) while moving along the closed contour.
3. This approach was applied to study two cases: (a) an elliptic-linear-type model and (b) a potential that was employed previously [24] to study two ‘degenerate’ conical intersections.
4. Part of the article was devoted to the study of the above-mentioned elliptical linear model and relate its parameters to a real molecular system, namely the C2H molecule. As a special case we chose the \( (3, 4) \) conical intersection located at about 1.5 Å from the CC axis and probed four circular contours with \( q \)-values in the range \( 0.03 \leq q \leq 0.2 \) Å. We found that the calculated angular dependence of the angular non-adiabatic coupling term fits quite well the predicted form by the model as long as \( q \) is small enough. However significant deviations are observed already for \( q = 0.2 \) Å. The model is characterized by a single parameter \( b \). The ab initio treatment yields for this parameter the value of 4.24.
Acknowledgements

We would like to thank Dr. A. Yahalom for discussions and for his assistance in preparing the manuscript. One of the authors (MB) would like to thank Prof. 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.

References

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