A Novel Intraline of Conical Intersections for Methylamine: A Theoretical Study

C. LEVI,[1] G. J. HALÁSZ,[2] Á. VIBÓK,[3] I. BAR,[1] Y. ZEIRI,[4,5] R. KOSLOFF,[6,7] M. BAER[7]

[1]*Department of Physics, Ben-Gurion University, Beer Sheva 84105, Israel*

[2]*Department of Information Technology, University of Debrecen, P.O. Box 12, H-4010 Debrecen, Hungary*

[3]*Department of Theoretical Physics, University of Debrecen, P.O. Box 5, H-4010 Debrecen, Hungary*

[4]*Physical Chemistry Department, Nuclear Research Center Negev, P.O. Box 9001, Beer Sheva 84190, Israel*

[5]*Department of Biomedical Engineering, Ben-Gurion University, Beer Sheva 84105, Israel*

[6]*Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

[7]*The Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

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ABSTRACT: In this article the study of conical intersections (ci) related to the N—H bond in the methylamine, CH_3NH_2, molecule is extended. In a previous publication (Levi et al., J Chem Phys 2008, 128, 244302) we reported on a novel feature associated with the intersection of the two lowest states $^1A'$ and $^1A''$ of the methylamine. We established the existence of a finite (closed) line of ci located in the HC—NHH plane—a line that is formed by moving a single hydrogen on that plane while fixing the (six) other atoms. The validity of this line was proved by studying the singularities of the (angular) nonadiabatic coupling terms (NACT)—a study that was later supported by revealing the degeneracy points formed by the two interacting adiabatic potential energy surfaces (PESs). This situation led to two additional interesting features: (i) Along any (open) contour in the above plane that intersects this line is formed a narrow, spiky NACT for which the area under it is $\sim\pi/2$; (ii) In case of a closed contour the corresponding topological (Berry) phase is zero (and not an integer multiple

Correspondence to: Á. Vibók; e-mail: vibok@phys.unideb.hu
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of π as is usually the case). In the current article we present the theory to support these findings. © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 109: 2482–2489, 2009

Key words: conical intersection; nonadiabatic coupling; methylamine; topological phase

Introduction

The study of the electronic nonadiabatic coupling terms (NACT) and conical intersections (ci) concentrated, for the last two decades, mainly on small molecules, namely, triatomic and tetraatomic systems [1–17]. Our approach, which is based on ab initio treatments [1, 4–6], was recently extended to larger systems and among them we performed a detailed study of the methylamine molecule, CH_3NH_2, consisting of seven atoms [18]. The structure of the molecule is given in Figure 1 where it can be seen that the methyl group, CH_3, is separated from the amine group, NH_2 by the CN bond. This molecule is for long time an issue of interest since it comprises two strongly coupled large amplitude motions, specifically, the torsion of the methyl top and the inversion of the amine group [17]. Several experimental studies provided evidence that the principal channel for photo-dissociation in the first absorption band corresponds to the N—H bond fission [19–23]. Recently [22], it was shown that in the vibrational mediated photodissociation of CD_3NH_2 about 90% of H and D observed products are hydrogen photofragments released from the amine group and the remaining 10% are the deuterium released from the methyl group.

Early numerical treatments revealed cuts through the ab initio potential energy surfaces (PESs) for the ground, $^1A'$ and the first excited, $^1A''$ states of methylamine. Particularly, it was pointed out that the $^1A''$ state potential that leads to the breakup of the N—H bond is characterized by a small barrier (~3,000 cm^{-1}) at short range which seems to be followed, at somewhat larger bond extensions, by a ci formed by the above mentioned states—both belonging to the C_s symmetry [24, 25].

Our detailed study based on the MOLPRO, a package of ab initio programs [26], revealed one of the more interesting results, namely, that the two lowest states $^1A'$ and $^1A''$ are coupled not by a single ci (or several ci) but by a line of ci that is formed by moving a single hydrogen in a fixed plane while locking the (six) other atoms (see Fig. 2). Such lines are usually known as *seams* but this one is somewhat different. In all previous studies [1–8] the seams are located outside the planes that contain the moving test particle (which in our case is the HC—NHH plane [18]). Since this hydrogen (the test particle in our case) is moving in the HC—NHH plane, the line just described is located in that (HC—NHH) plane as well (see Fig. 2). This situation is responsible for two additional phenomena: (a) Along any (open) contour in the above plane that intersects this line (seam), a narrow, spiky NACT is formed (see Fig. 3) for which the area under it is $\sim\pi/2$ [18]. (b) It was shown, following a careful application of MOLPRO [26], that the corresponding topological phase, formed by two such spiky NACTs, is zero.

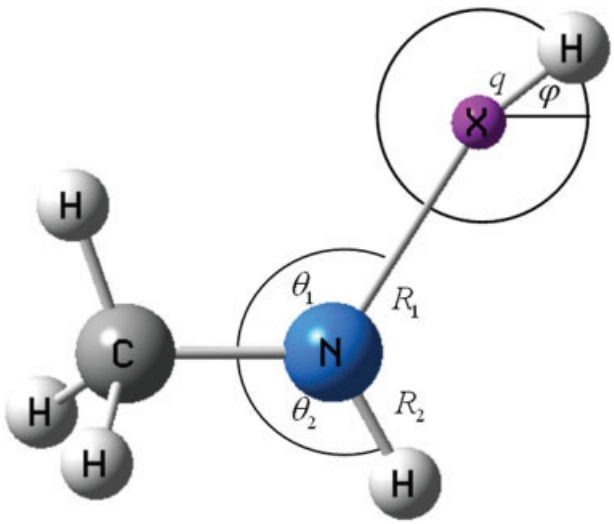

FIGURE 1. The equilibrium structure of methylamine. In the present study, five atoms, namely, the carbon, the nitrogen two amine hydrogens, and a methyl hydrogen, are assumed to form a fixed plane—the HC—NH_2 plane—and their relative motion is constrained to this plane. The coordinates θ_1 and R_1 show the position of the test hydrogen (with respect to the nitrogen) that was varied during the ci-search (the coordinates θ_2 and R_2 are held fixed during this process). The polar coordinates q and φ show the position of test hydrogen with respect to an assumed point close to a possible ci-point. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

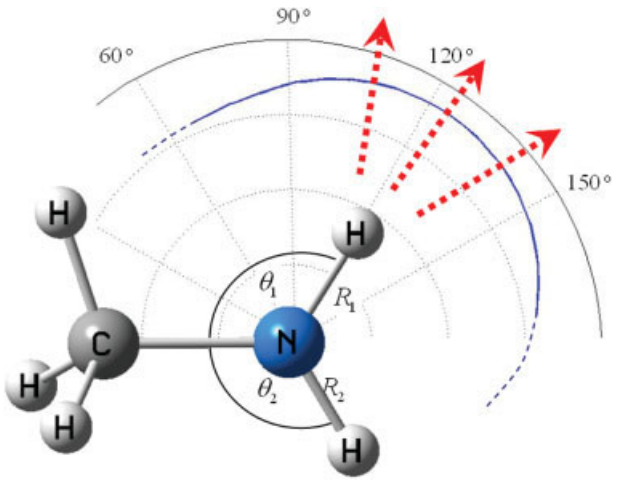

FIGURE 2. The intra (fixed configuration space) seam for the conical intersections located in the HC—NH_2 plane as calculated for R_2 = 1.0 Å and θ_2 = 120°. The curve presented is for a system of coordinates located at the nitrogen. The arrows are drawn to indicate that any photo-dissociation process is accompanied by crossing the seam. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In the current publication we present the theory that supports these two findings.

Numerical Comments

The ab initio study was carried out employing the MOLPRO package [26] with the multireference configuration interaction (MRCI) method and the 6-31+G* basis set. We used the active space, including two valence electrons distributed on five orbitals (three of them belonging to the irreducible representation of A′). Three electronic states were computed with equal weights. All seven atoms were considered, but, as was mentioned earlier, the search for ci is carried out by activating only the amine hydrogen. To follow the motion of the hydrogen we employ two (polar) coordinates, the radial coordinate, q, and the angular coordinate, φ, defined for a system of coordinates located at some point in the plane (see Fig. 1). The detection is done by calculating the angular NACT, $\tau_{\varphi jk}(\varphi,q|\mathbf{s})$, defined as

$$\tau_{\varphi jk}(\varphi,q|\mathbf{s}) = \left\langle \zeta_j(\mathbf{s}_e|\varphi,q,\mathbf{s}) \left| \frac{\partial}{\partial\varphi} \zeta_k(\mathbf{s}_e|\varphi,q,\mathbf{s}) \right\rangle \right. . \quad (1)$$

Here $\zeta_i(\mathbf{s}_e\ \varphi,\ q,\ \mathbf{s})$; $i = j,\ k$ are the electronic (adiabatic) Born–Oppenheimer (BO) eigenfunctions [27, 28], $\mathbf{s}_e$ stands for the set of electronic coordinates and $\mathbf{s}$ presents the group of all nuclear coordinates excluding φ and q. Having defined the system of coordinates the search starts by forming circular contours of different radii and calculating the angular NACTs along these contours. The next step was deriving the adiabatic-to-diabatic transformation (ADT) angle (known, also, as the mixing angle), $\gamma(\varphi,\ q)$ [29] (see also Ref. [1], chapter 3.1)

$$\gamma(\varphi,q|\mathbf{s}) = \int_0^{\varphi} d\varphi' \tau_{\varphi}(\varphi',q|\mathbf{s}). \quad (2)$$

In case of a closed contour we get the angle $\gamma(\varphi = 2\pi,\ q|\mathbf{s}) = \alpha(q|\mathbf{s})$, where $\alpha(q|\mathbf{s})$ is identified as the, so-called, topological (Berry) phase [30, 31]. It is important to emphasize that for situations where the NACT is formed by two isolated states (namely, states affected, at most, slightly by higher states), $\alpha(q\ \mathbf{s})$ is expected to be a multiple integer of π (or zero) [4a, 32, 33]. We calculated, for relative large regions, NACTs between the three lowest states of the C_s symmetry, namely, ^{1}A′, ^{1}A″, and ^{2}A″ and found that only the NACTs formed by the two lower states are nonzero, whereas the other two that involve the second excited state are practically zero (thus, guaranteeing the isolation of the two lower states in the region of interest).

Figure 3(a) presents the angular NACT, along such a circle, as a function of φ with q = 0.1 Å where the coordinates of the center are at $(R_1,\ \theta_1)$ = (1.65 Å, 80°) and $(R_2,\ \theta_2)$ = (1.0 Å, 120°) (see Fig. 1). This figure shows also two relatively sharp peaks with opposite signs. It turns out that the value of the integral under each peak is ~1.55 rad (i.e., a value close to $\pi/2$) and the value of the topological phase is $\alpha(q|\mathbf{s}) \sim 0$. It is important to emphasize that the structure of the angular NACT differs significantly from most other angular NACTs for which we usually encounter either two [1, 4b,c, 5, 6, 7b, 8] (and sometimes three [4a, 9a]) positive maxima values and the topological phase becomes, approximately, an integer multiple of π (and not zero). The only exceptions (to the best of our knowledge) are ionic systems like $(H + H_2)^+$ [34a,b] or $(H_2 + H_2)^+$ [34c] (that involve charge transfer processes).

Thus the question is what makes this particularly case so unique? As was mentioned already in the "Introduction" section, additional calculations

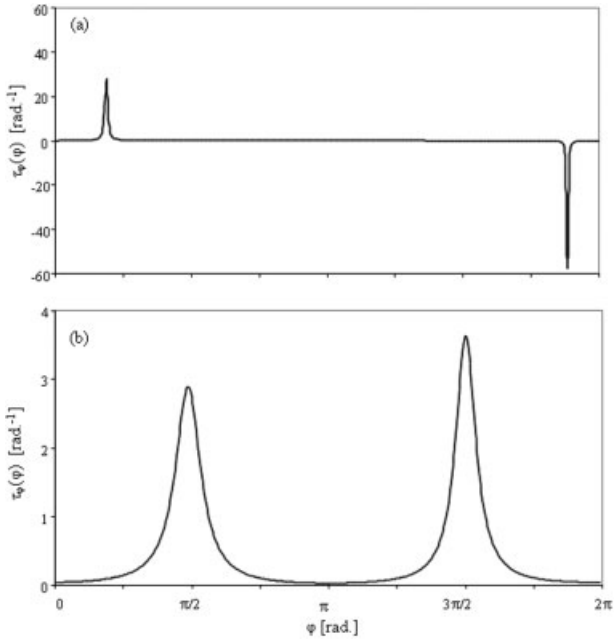

FIGURE 3. The angular nonadiabatic coupling term (NACT) presented as a function of φ for $q = 0.1$ Å as calculated at three different locations along the seam (see Fig. 3): (a) The NACT at the point (R_1, θ_1; R_2, θ_2) = (1.60 Å, 160°; 1.0 Å, 120°); (b) The NACT at the point (R_1, θ_1; R_2, θ_2) = (1.83 Å, 122°; 1.0 Å, 120°).

showed that the same plane hosts many more ci all are characterized by the same feature as discussed earlier, namely, the corresponding angular NACTs possess two sharp peaks of opposite signs. Finally it was established that these ci form a continuous (finite) line. This line, presented in Figure 2, was calculated for a center of the coordinates located at the nitrogen atom (we recall that this line is formed by holding the second amine hydrogen fixed at (R_2, θ_2) = (1.0 Å, 120°) (see Fig. 1).

This just described line can be interpreted as a seam (defined as the continuous line that connects all these infinite number of ci-points) but is characterized by additional features. Evidences were given for the fact that this line is finite (all seams encountered, so far, are infinite) and most likely a closed line [18].

Like any other seam this one is also expected to be a line that follows the degeneracy points between the two adiabatic surfaces. This line, presented in Ref. [18], was found to nearly overlap with the seam (the deviations were within the error-limit of the calculations).

Theory

In this chapter we prove two Lemmas:

LEMMA 1

A NACT calculated along a planar contour that intersects the corresponding planar seam is likely to form, at the intersection point $\varphi = \varphi_s$, a Dirac δ-function which yields in the vicinity of φ_s a topological phase of $\pi/2$.

Proof

To prove this Lemma we define a system of coordinates with its origin in the plane that contains the seam. All contours to be mentioned are circular contours with respect to this origin and with fixed radii, namely, $\varphi = \varphi(q)$. The various contours (for different q-values) intersect the seam at points defined as $\varphi = \varphi_s(q)$.

To evaluate the angular NACT (in the vicinity of the seam) we consider the following ADT angle $\gamma(\varphi, q|\mathbf{s})$ [introduced in Eq. (2)] but can be written also, in terms of diabatic potentials, as [34]:

$$\gamma(\varphi,q|\mathbf{s}) = 1/4\pi - 1/2\tan^{-1}\{\Delta W(\varphi,q|\mathbf{s})/2W_{12}(\varphi,q|\mathbf{s})\} \tag{3}$$

where we recall that ΔW is given as (see Ref. [1], section 3.1.1.3)

$$\Delta W = W_{11} - W_{22} = (V_1 - V_2)\cos 2\gamma \tag{4a}$$

and W_{12} as:

$$W_{12}(= W_{21}) = \frac{1}{2}(V_1 - V_2)\sin 2\gamma \tag{4b}$$

Here V_1 and V_2 are the adiabatic PESs, W_{11} and W_{22} are the corresponding diabatic PESs and W_{12} is the diabatic coupling term.

In what follows we delete the variable **s** which stands for the group of the nonrelevant nuclear coordinates.

In addition to the line $\varphi = \varphi_s(q)$ that defines the seam (for a given planar system of coordinates) we introduce another line $\varphi = \varphi_p(q)$ which yields for any q the value $\gamma = 1/4\pi$:

$$\gamma(\varphi_p(q),q) = 1/4\pi. \tag{5}$$

It is important to realize that the line $\varphi = \varphi_p(q)$ differs, in general, from the seam, $\varphi = \varphi_s(q)$. Next we evaluate $(\Delta W/W_{12})$ as a function of φ in the vicinity of $\varphi = \varphi_p(q)$, to a first order in $\Delta\varphi$ $(= \varphi - \varphi_p(q))$, namely:

$$\lim_{\varphi\to\varphi_p}\left(\frac{\Delta W(\varphi,q)}{W_{12}(\varphi,q)}\right) = -4\left.\frac{d\gamma}{d\varphi}\right|_{\varphi=\varphi_p}\{\varphi - \varphi_p(q)\} \quad (6)$$

where because of Eq. (5) we have $\sin[2\gamma(\varphi_p, q)] = 1$. Recalling Eq. (3), we find that in the close vicinity of $\varphi_p(q)$ the ADT angle $\gamma(\varphi(q), q)$ becomes

$$\gamma(\varphi,q) = \frac{1}{4}\pi + \frac{1}{2}\tan^{-1}\left\{2\left.\frac{d\gamma}{d\varphi}\right|_{\varphi=\varphi_p}\{\varphi - \varphi_p(q)\}\right\}. \quad (7)$$

To simplify the presentation we introduce the function $\kappa(\varphi_p, q)$:

$$\kappa(\varphi_p,q) = \left(2\left.\frac{d\gamma}{d\varphi}\right|_{\varphi=\varphi_p}\right)^{-1} \quad (8)$$

so that Eq. (7), in the close vicinity of $\varphi_p(q)$, can be written in the form:

$$\gamma(\varphi,q) = 1/4\pi + 1/2\tan^{-1}\{\{\varphi - \varphi_p(q)\}\kappa(\varphi_p,q)^{-1}\}. \quad (9)$$

Differentiating Eq. (9) with respect to φ yields the corresponding angular NACT, $[\tau_\varphi^{(\kappa)}(\varphi,q)]$, namely:

$$\tau_\varphi^{(\kappa)}(\varphi,q) = \frac{1}{2\kappa(\varphi_p,q)^2 + \{\varphi - \varphi_p(q)\}^2}. \quad (10)$$

More can be said for a situation where the ab initio angular NACT, $\tau_\varphi(\varphi, q)$, becomes a narrow function of φ in the vicinity of the seam (namely, $\varphi_s(q)$). In this situation two things happen: (a) The function $\gamma(\varphi, q)$, approaches a steep function of φ thus leading to an increasing derivative, $(d\gamma/d\varphi)$, and therefore decreasing values for $\kappa(\varphi_p, q)$; (b) The two lines $\varphi_p(q)$ and $\varphi_s(q)$ approach each other so that in the limit (of a spiky NACT) they essentially overlap.

The conclusion of this analysis is that when $\tau_\varphi(\varphi, q)$, for a given q, becomes a spiky function of φ it causes $\tau_\varphi^{(\kappa)}(\varphi,q)$ to converge in the following way:

$$\tau_\varphi^{(\kappa)}(\varphi,q) = \frac{1}{2\kappa(\varphi_s,q)^2 + \{\varphi - \varphi_s(q)\}^2} \quad (11)$$

which in the limit $\kappa \to 0$ becomes, by definition, a Dirac δ-function at $\varphi = \varphi_s$. Thus,

$$\lim_{\kappa\to 0}\tau_\varphi^{(\kappa)}(\varphi,q) = \frac{1}{2}\pi\delta(\varphi - \varphi_s(q)). \quad (12)$$

Having the analytic expression for the angular NACT, in the vicinity of the intersection point between the contour and the seam, it can be seen that the corresponding ADT angle $\gamma(\varphi_s)$ becomes

$$\gamma(\varphi_s) = \frac{1}{2}\pi\int_{\varphi_s-\Delta\varphi}^{\varphi_s+\Delta\varphi}\delta(\varphi - \varphi_s(q))d\varphi = \frac{1}{2}\pi \quad (13)$$

where $\Delta\varphi$ is finite.

As is noticed from Figure 3, the angular NACT, upon approaching the line of ci, becomes spiky with relatively large values. Moreover, the corresponding ADT angle (or topological phase) as calculated from the following expression:

$$\gamma(\varphi_s) = \int_{\varphi_s-\delta\varphi}^{\varphi_s+\delta\varphi}\tau_\varphi(\varphi|q)d\varphi \quad (14)$$

($\delta\varphi$ is a finite small value but not necessarily an infinitesimal value) becomes $\sim\pi/2$ which fits the theoretical value in Eq. (13).

Comments

1. The derivation of $\tau_\varphi^{(\kappa)}(\varphi,q)$ as given in Eq. (11) [and which lead to the Dirac δ-function; see Eq. (12)] is based on the first term of the Taylor expansion of $(\Delta W/W_{12})$. In the Appendix we extend this derivation by keeping two terms of the Taylor expansion and show that this extension does not affect the results.
2. The same proof can be given for the ratio $(W_{12}/\Delta W)$ (instead of $\Delta W/W_{12}$), but in this case the contour to be considered is $\varphi = \varphi_p(q)$ which yields for any q the value $\gamma_p = (1/2)\pi$ [see Eq. (5)].

LEMMA 2

NACTs calculated along a closed planar contour, Γ, that intersects the planar seam at two points are likely to have two spiky peaks of opposite signs so that the topological phase, $\alpha(\Gamma)$, is zero.

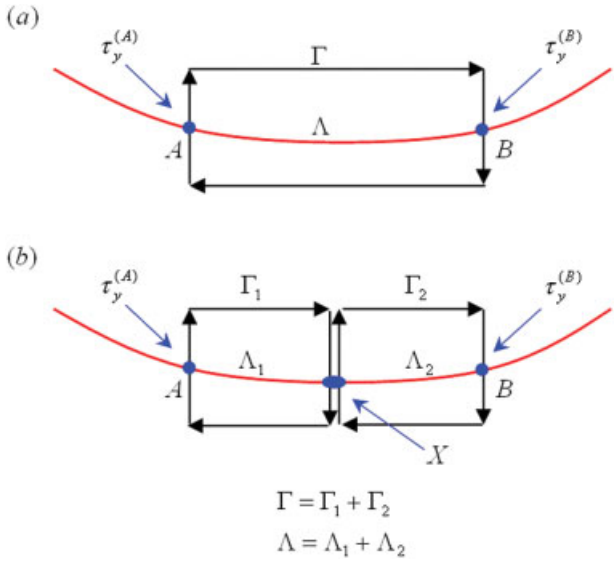

FIGURE 4. A schematic drawing showing a section of the seam and the closed contours Γ, Γ_1, and Γ_2 intersecting it at various points. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Proof

To prove the Lemma we refer the reader to Figure 4. In Figure 4(a) is presented, from left to right, the seam and a closed rectangular contour Γ which intersects this seam at two points, A and B. To prove the lemma we employ Cartesian coordinates (x, y) and concentrate on the y-components τ_y defined as

$$\tau_y(x,y) = \left\langle \zeta_1(\mathbf{s}_e|x,y) \left| \frac{\partial}{\partial y} \zeta_2(\mathbf{s}_e|x,y) \right\rangle \right. \qquad (1')$$

(the y-components of τ are the ones to become the spiky functions at the intersection points). Since we intend to show that $\tau_y(A) = -\tau_y(B)$ (to guarantee that for this particular contour $\alpha(\Gamma) = 0$) we assume that for any contour of the kind Γ we have $\tau_y(A) = \tau_y(B)$ so that $\alpha(\Gamma)$, the corresponding topological phase, is π. By making this assumption we show that it leads to an undefined value ($\neq 0$) for $\alpha(\Gamma)$.

To continue we refer to Figure 4(b) and discuss separately the situation along the two contours Γ_1 and Γ_2. For Γ_1 we have that $\tau_y(A) = \tau_y(P)$ so that $\alpha(\Gamma_1) = +\pi$. For Γ_2 we have that $\tau_y(B) = \tau_y(P)$ so that $\alpha(\Gamma_2) = +\pi$. Since $\Gamma = \Gamma_1 + \Gamma_2$ [cf. Fig. 4(b)] it is easy to see that

$$\alpha(\Gamma) = \oint_\Gamma \mathbf{ds}\tau(\mathbf{s}) = \oint_{\Gamma_1} \mathbf{ds}\tau(\mathbf{s}) + \oint_{\Gamma_2} \mathbf{ds}\tau(\mathbf{s}) \qquad (15)$$

or

$$\alpha(\Gamma) = \alpha(\Gamma_1) + \alpha(\Gamma_2) = 2\pi \qquad (16)$$

which leads to an inconsistency since we started with $\alpha(\Gamma) = \pi$. This inconsistency grows as we consider several closed contours, Γ_j, $j = \{1, n\}$ such that $\Gamma = \Gamma_1 + \cdots + \Gamma_n$.

The only way to avoid the inconsistency is to assume from the start that $\alpha(\Gamma) = 0$ for any closed contour that intersects the seam at two (or an even number) of points.

Discussion and Conclusions

This article concentrates on an exceptional continuous line of ci revealed in the methylamine molecule. This line can be interpreted as a seam, but if it is a seam it is uncommon because some of its features are different. In what follows we briefly discuss a few issues (which were already presented in [18] but are mentioned here again for completeness):

1. In all previous studies [1–9] the seams are located outside the planes that contain the moving test particle (which in the present case is the HC—NHH plane). In other words, the methylamine creates a phenomenon where the two interacting states, i.e. ^{1}A′ and ^{1}A″ are coupled by a continuous line of ci formed by one single moving atom where all other (six) atoms of the molecule are fixed in configuration space. Since this hydrogen is moving in the HC—NHH plane the line, just described, is located in that (HC—NHH) plane as well (see Fig. 2). As it stands, this situation seems to be unlikely but an analysis based on symmetry arguments justified this finding [18].
2. Once the existence of the aforementioned seam was established two questions had to be answered: (i) Is this seam a finite or an infinite line? (ii) If it is a finite line is it an open or a closed line? Again, as analyzed in the previous study [18], the answers to the two questions is positive, namely, that line is most likely finite and closed.
3. We also encountered an uncommon topological (Berry) phase which is ~0 instead of being

an integer multiple of π [18]. This finding was explained by the fact that each intersection point between the contour and the seam causes the corresponding tangential component (in our present case, the angular component) of the NACT to become a narrow, spiky function which yields, upon integration (over φ), the value of $\pi/2$. Moreover, the corresponding numerical integration along the complete closed contour revealed that the final topological phase is approximately zero. In the current article we proved, analytically, that in case the tangential NACT becomes a spiky function it has to be a δ-function of the form $(1/2)\pi\delta(\varphi - \varphi_s(q))$ (see Lemma 1) and that the corresponding topological phase has to be zero (see Lemma 2).

4. To strengthen the idea that the newly revealed continuous line of ci is indeed a seam we also studied the angular NACTs along a closed contour in a plane that is slightly tilted away (by about 30°) from the HC—NHH plane [18]. In this way the closed contour, instead of intersecting the line of ci, surrounds it and, therefore, is, as expected, characterized by two positive peaks [see Fig. 3(b)]. Careful calculations of the topological phase yielded the value 2.91 rad which is (close to) π [4–6, 8, 9a, 30–33, 35].

Appendix: Extending the Proof of Lemma 1

In this section we derive the second-order term for $(\Delta W/W_{12})$ and use it to obtain the extended expressions for $(d\gamma/d\varphi)$ and $\tau_\varphi^{(\kappa)}(\varphi,q)$:

$$\frac{\Delta W(\varphi,q)}{W_{12}(\varphi,q)} = 2\frac{d}{d\varphi}\cot(2\gamma)\Big|_{\varphi_p}(\varphi-\varphi_p) + \frac{d^2}{d\varphi^2}[\cot(2\gamma)]\Big|_{\varphi_p}(\varphi-\varphi_p)^2 + O((\varphi-\varphi_p)^3) \quad \text{(A1)}$$

where

$$\frac{d}{d\varphi}\cot(2\gamma) = -\frac{2}{\sin^2(2\gamma)}\frac{d\gamma}{d\varphi} \quad \text{(A2)}$$

$$\frac{d^2}{d\varphi^2}\cot(2\gamma) = -\frac{2}{\sin^2(2\gamma)}\frac{d^2\gamma}{d\varphi^2} + \frac{8\cos(2\gamma)}{\sin^3(2\gamma)}\left(\frac{d\gamma}{d\varphi}\right)^2. \quad \text{(A3)}$$

Next, evaluating Eqs. (A2) and (A3) at $\gamma(\varphi_p) = \pi/4$ yields

$$\frac{d}{d\varphi}\cot(2\gamma)\Big|_{\varphi_p} = -2\frac{d\gamma}{d\varphi} \quad \text{(A2′)}$$

$$\frac{d^2}{d\varphi^2}\cot(2\gamma)\Big|_{\varphi_p} = -2\frac{d^2\gamma}{d\varphi^2} \quad \text{(A3′)}$$

Thus,

$$\lim_{\varphi\to\varphi_p}\frac{\Delta W(\varphi,q)}{W_{12}(\varphi,q)} = -4\frac{d\gamma}{d\varphi}\Big|_{\varphi_p}(\varphi-\varphi_p) - 2\frac{d^2\gamma}{d\varphi^2}\Big|_{\varphi_p}(\varphi-\varphi_p)^2. \quad \text{(A4)}$$

Now, recalling the relation [see Eq. (3)]

$$\gamma(\varphi,q|\mathbf{s}) = 1/4\pi - 1/2\tan^{-1}\{\Delta W(\varphi,q|\mathrm{s})/2W_{12}(\varphi,q|\mathbf{s})\} \quad \text{(A5)}$$

we get

$$\gamma(\varphi,q|\mathbf{s}) = 1/4\pi - 1/2\tan^{-1}\left\{-2\frac{d\gamma}{d\varphi}\Big|_{\varphi_p}(\varphi-\varphi_p) - \frac{d^2\gamma}{d\varphi^2}\Big|_{\varphi_p}(\varphi-\varphi_p)^2\right\} \quad \text{(A6)}$$

Differentiating Eq. (A6) with respect to φ yields finally for, $\tau_\varphi^{(\kappa)}(\varphi,q)$ (after some rearrangements), the following second-order expression:

$$\tau_\varphi^{(\kappa)}(\varphi,q) = \frac{1}{2\kappa^{(1)}(\varphi_p,q)^2 + \{\varphi-\varphi_p(q)\}^2} \times [1 + \kappa^{(1)}(\varphi_p,q)/\kappa^{(2)}(\varphi_p,q)(\varphi-\varphi_p(q))] \quad \text{(A7)}$$

Here,

$$\kappa^{(n)}(\varphi_p,q) = \left(2\frac{d^n\gamma}{d\varphi^n}\Big|_{\varphi=\varphi_p}\right)^{-1};\ n = 1,2 \quad \text{(A8)}$$

Thus, as long as the ratio $\kappa^{(1)}/\kappa^{(2)}$ is finite we may neglect the second term in the parentheses securing the relevant expression for the Dirac δ-function.

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