Topological effects for nonsymmetrical configurations: The $C_2H_2^+$ as a case study

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During the last decade the study of topological effects formed by molecular systems became a routine but it was always carried out for configurations that were limited by symmetry conditions. To be more specific this applied to the Jahn-Teller (JT) effect formed by molecular configurations of planar symmetry [see, e.g., Baer *et al.*, Faraday Discuss. **127**, 337 (2004)] and the Renner-Teller effect formed by configurations of axial symmetry [see, e.g., Halász *et al.*, J. Chem. Phys. **126**, 154309 (2007)]. In this article we consider for the first time molecular configurations that avoid any symmetry conditions or, in other words, are characterized by the C_1 point group. We report on a detailed study of topological effects formed by such a molecular system. The study concentrates on both, the two-state (Abelian) case and the multistate (non-Abelian) case. It is shown that the theory that was originally developed to treat topological effects due the JT intersection and also applies for the study of topological effects in the most general case. The study is accompanied with numerical results. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2779035]

I. INTRODUCTION

The dynamics triggered in a molecule after absorbing a photon is usually discussed in terms of the Born-Oppenheimer (BO) theory,[1] where the fast electronic degrees of freedom are treated separately from the slow nuclei. In this picture, electrons and nuclei do not easily exchange energy. Yet, in some nuclear configurations generally termed conical intersections (CIs), energy exchange can become significant. It is widely recognized today that were it not for CIs important photobiochemical processes such as vision and photosynthesis of vitamin D could not take place.

The BO treatment may yield various kinds of intersections[1] but in the literature mainly two are discussed: (i) the Renner-Teller (RT) intersection usually characterized as a parabolic intersection;[2–16] (ii) the Jahn-Teller (JT) intersection which, in general, is characterized as a CI.[17–35] The two types differ also in two additional ways: (a) the BO-RT nonadiabatic coupling terms (NACTs) are formed by states of *opposite* symmetry and the resulting topological (Berry) phase α is equal to 2π.[2–4,7] (b) The BO-JT NACTs are formed by states of *same* symmetry and the resulting JT phase α is equal to π (Refs. 25 and 27) (see also Ref. 33, Chap. 3). It is important to emphasize that the two kinds of intersections are encountered in those cases where the system of atoms maintains planar or axial symmetry and where it is characterized by the following point groups: C_{2h}, C_{2v}, or C_2.

The natural question to be asked is what happens in case the molecular system lacks the above mentioned symmetries. Recently we faced such a situation while studying the intersections of the $C_2H_2^+$ ion.[17] In this case the two carbons form the linear axis and the two, off-axis, hydrogens (together with the two carbons) form a plane. In case we let the two hydrogens, *simultaneously*, surround the CC axis, the planar symmetry is preserved and consequently we encounter the ordinary RT case ($\alpha=2\pi$). However, if one of the hydrogens is *clamped* while the other hydrogen is allowed to surround the axis, a *nonsymmetric* C_1 point group is created, which still leads to topological effects but seem to be more characteristic of the JT effect because the value of α is found to be π (Ref. 17) and not the (typical) RT phase $\alpha=2\pi$. Although this outcome is somewhat of a surprise, it is straightforward to show that, indeed, this is the correct result.[17(a)]

Definition: In what follows we refer to the ordinary JT/RT intersections as the *symmetrical* intersections and the C_1 configuration (for which the planar/axial symmetry is not maintained) as the nonsymmetrical intersection.

The present article is devoted to the (first-of-its-kind) study of topological effects at intersections formed by nonsymmetrical configurations. This study is carried out along two lines.

(1) In the first part we concentrate on the two-state topological features as formed by the lower states $1\,^2A''$ and the $1\,^2A'$ (which in the linear, point group $D_{\infty h}$ configuration correspond to the two degenerate $X\,^2\Pi_u$ states[15(b)]) and the two upper states $2\,^2A''$ and $2\,^2A'$

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(which in the linear, point group $D_{\infty h}$ configuration, correspond to the two degenerate $X\,^2\Pi_G$ states[15(b)]). We intend to show that these two pairs of states yield, for the present nonsymmetrical case, the characteristic JT phase, namely, $\alpha=\pi$.

(2) It is well known that topological effects are formed in the vicinity of a *point of degeneracy* between two adjacent states (points of degeneracy are better known as the points of conical/parabolic intersections). However, two states may not be enough to form topological effects for larger regions in configuration space[17,25,27,34,35] (see also Ref. 33, Chaps. 1 and 4). Therefore, if we are interested in studying the number of intersections and their character in an extended *region* we have to consider numerous states simultaneously. For this purpose, some time ago, we introduced the adiabatic-to-diabatic Transformation (ADT) matrix $\mathbf{A}(\mathbf{s}|\Gamma)$ (Ref. 36) (here, $\mathbf{s}$ stands for the collection of nuclear coordinates and Γ is the *contour* that defines the boundaries of the region) and the corresponding topological matrix $\mathbf{D}(\Gamma)$ (Ref. 25) which yields the required information. As is known both matrices are calculated along the contour Γ but whereas $\mathbf{A}(\mathbf{s}|\Gamma)$ is calculated along an *open* contour, the $\mathbf{D}$ matrix is calculated along *closed* contours (as is elaborated below).

The need to treat the topological effects employing matrices forms the transition from an Abelian phenomenon (characterized by two states) to a non-Abelian phenomenon formed by several (>2) states[37] (see also Ref. 33, Chap. 1). We intend to show that the analytical tools developed for studying the JT multistate intersections[25,27] apply also for the nonsymmetrical multistate intersections.

II. THEORETICAL COMMENTS

The analytical tools that were mentioned earlier are all based on the BO-NACT, $\boldsymbol{\tau}_{jk}(\mathbf{s})$, a term that couples states j and k and is given in the form[1] (see also Ref. 33, Chap. 1)

$$\boldsymbol{\tau}_{jk}(\mathbf{s}) = \langle \zeta_j(\mathbf{s}_e|\mathbf{s})|\nabla\zeta_k(\mathbf{s}_e|\mathbf{s})\rangle. \tag{1}$$

Here $\zeta_i(\mathbf{s}_e|\mathbf{s})$; $i=j,k$ are the electronic (adiabatic) BO eigenfunctions, $\mathbf{s}_e$ and $\mathbf{s}$ stand for the collection of electronic coordinates and nuclear coordinates, respectively, and ∇ is the (nuclear) grad operator.

At this stage we have to be more specific regarding the nuclear coordinate $\mathbf{s}$. Our system is defined in terms of four atoms: two fixed carbons that form the axis and two off-axis hydrogens H_1 and H_2. Here H_1 is clamped at a distance q_1 from the CC axis and H_2, which is located at a distance q_2 from this axis, is free to move around that axis (see schematic drawing in Fig. 1). In what follows we concentrate on the polar coordinates of this, free, atom, namely, (φ,q_2). As a result $\mathbf{s}$ is written in the following form: $\mathbf{s}\equiv(\varphi,q_2|q_1,R)$, where R is the CC distance (which is fixed throughout this article).

Out of the various possible components of $\boldsymbol{\tau}_{jk}(\varphi,q_2|q_1,R)$, the only one of interest for us is the component *tangential* to the contour along which the integration is performed.[27(a)] As mentioned earlier, in our case the contour

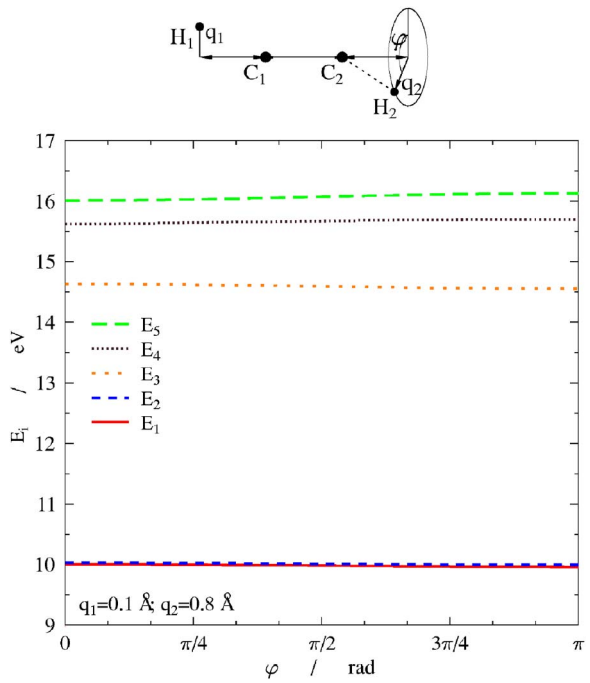

FIG. 1. (Color online) Energy curves for the five lower states of the $C_2H_2^+$ ion presented as a function φ for the case $(q_1,q_2)=(0.1,0.8)$ Å. This calculation is done for the C_1 point group where atom H_1 is clamped at a point (namely, at $q_1=0.1$ Å) and H_2 is allowed to rotate around the CC axis (see schematic drawing), where the radius of the circular contour is $q_2=0.8$ Å. The lower potential curves are for the $1\,^2A''$ and $1\,^2A'$ states (which in the linear point group, $D_{\infty h}$ configuration, correspond to the two degenerate $X\,^2\Pi_u$ states), the upper curves are for the $2\,^2A''$ and $2\,^2A'$ states (which in the linear, point group $D_{\infty h}$ configuration, correspond to the two degenerate $X\,^2\Pi_g$ states) and the third (middle) curve is for an A' state that has its origin in the isolated $D_{\infty h}$, $1\,^2\Sigma_g^+$ configuration.

is a *circle* around a center located at the CC axis, and consequently the component of interest is the relevant *angular* φ component, which can be written as $(1/q)\boldsymbol{\tau}_{\varphi jk}(\varphi,q_2|q_1,R)$, where $\boldsymbol{\tau}_{\varphi jk}(\varphi,q_2|q_1,R)$ is

$$\boldsymbol{\tau}_{\varphi jk}(\varphi,q_2|q_1,R) = \left\langle \zeta_j(\mathbf{s}_e|\varphi,q_2|q_1,R) \times \left| \frac{\partial}{\partial\varphi}\zeta_k(\mathbf{s}_e|\varphi,q_2|q_1,R) \right\rangle. \right. \tag{2}$$

In order to simplify our notation we drop the variable R but we still retain the two distances (radii) (q_1,q_2).

Having introduced the angular NACT the corresponding $\mathbf{A}$ matrix, formed along this circular contour, can be shown to be of the form [27(a)] (see also Ref. 33, Chap. 4)

$$\mathbf{A}(\varphi,q_2|q_1) = \wp\,\exp\left(-\int_0^{\varphi} d\varphi\boldsymbol{\tau}_{\varphi}(\varphi,q_2|q_1)\right), \tag{3}$$

where $\boldsymbol{\tau}_{\varphi}(\varphi,q_2|q_1)$ is the matrix for the elements $\boldsymbol{\tau}_{\varphi jk}(\varphi,q_2|q_1)$, $\wp$ is the *ordering* operator that reminds us that in order to evaluate the exponentiated matrix it has to be done in a certain order because of difficulties due to the commutation relations. It is important to pay attention that the dimension of the $\mathbf{A}$ matrix (and later, of the $\mathbf{D}$ matrix) is identical to the dimension of the $\boldsymbol{\tau}$ matrix.

Comment: In what follows we consider only the angular component of $\boldsymbol{\tau}$. Consequently we drop the subscript φ so

that $\boldsymbol{\tau}$ and $\boldsymbol{\tau}_{jk}$ stand, from now on, for $\boldsymbol{\tau}_{\varphi}$ and $\boldsymbol{\tau}_{\varphi jk}$, respectively.

Next is presented the topological matrix **D** (again details are given in Ref. 27(a)),

$$\mathbf{D}(q_2|q_1) = \wp \exp\left(-\int_0^{2\pi} d\varphi \boldsymbol{\tau}(\varphi, q_2|q_1)\right). \tag{4}$$

Our intensive interest in the **D** matrix is due to the fact that in case the above mentioned N states form a quasi-Hilbert subspace (in the region of interest), the matrix **D** is diagonal. In other words whenever a $N\times N$**D** matrix becomes diagonal (with ±1 along the diagonal in the case of real eigenfunctions), this fact implies that the N states form, approximately, an isolated (namely, decoupled) group of states (approximately) independent of the rest of the states that form the Hilbert space[25,27(a)] (see also Ref. 33, Chap. 2.1.3). It is important to realize that the dimension of the **D** matrix (as well as of the **A** matrix) is determined by the dimension of the $\boldsymbol{\tau}$ matrix. In other words, all three of them are of dimension $N\times N$.

In the case that $N=2$, Eqs. (3) and (4) simplify significantly because any 2×2 orthogonal matrix can be written in terms of[36(a)]

$$\mathbf{A}^{(2)}(\varphi, q_2|q_1) = \begin{pmatrix} \cos(\gamma_{12}(\varphi, q_2|q_1)) & \sin(\gamma_{12}(\varphi, q_2|q_1)) \\ -\sin(\gamma_{12}(\varphi, q_2|q_1)) & \cos(\gamma_{12}(\varphi, q_2|q_1)) \end{pmatrix}. \tag{5}$$

In this presentation, $\gamma_{12}(\varphi, q_2|q_1)$ is termed as the ADT angle and is given as an (line) integral,[36(a)]

$$\gamma_{12}(\varphi, q_2|q_1) = \int_0^{\varphi} \boldsymbol{\tau}_{12}(\varphi', q_2|q_1) d\varphi'. \tag{6}$$

A similar expression applies for $\alpha_{12}(q_2|q_1)$, the topological (Berry) phase. Thus,[25,27(a)]

$$\alpha_{12}(q_2|q_1) = \int_0^{2\pi} \boldsymbol{\tau}_{12}(\varphi, q_2|q_1) d\varphi. \tag{7}$$

The corresponding **D** matrix is similar to the **A** matrix as given in Eq. (5) but where $\alpha_{12}(q_2|q_1)$ replaces $\gamma_{12}(\varphi, q_2|q_1)$, namely,

$$\mathbf{D}^{(2)}(q_2|q_1) = \begin{pmatrix} \cos(\alpha_{12}(q_2|q_1)) & \sin(\alpha_{12}(q_2|q_1)) \\ -\sin(\alpha_{12}(q_2|q_1)) & \cos(\alpha_{12}(q_2|q_1)) \end{pmatrix}. \tag{8}$$

It is well noticed that the condition for the **D** matrix to be diagonal is that

$$\alpha_{12}(q_2|q_1) = 2\pi n, \tag{9}$$

where n is an integer or half an integer.

Comment: From previous studies we know that a group of N states yields a *single-valued* diabatic potential if and only if this group is approximately isolated from the rest of the states that form the complete Hilbert space. This happens when the NACTs of the type $\boldsymbol{\tau}_{jk}$, that couple any state j within the group of N states with any state k outside that group, are negligibly small, i.e., $|\boldsymbol{\tau}_{jk}| \sim O(\varepsilon)$; for $j \leqslant N$ and $k \geqslant N$. In such a case this group of N states forms a Hilbert subspace (more about this issue can be found in Refs. 27 and 33, see Chap. 1).

III. RESULTS

In accordance with the goals presented in the introduction, we consider two-state, three-state, and five-state results. (1) As for the two-state case we concentrate on the two lower states $1\,^2A''$ and $1\,^2A'$ (that originate from the two lower degenerate $X\,^2\Pi_u$ states[15(b)] and on the two upper states (the fourth and the fifth states), namely, the states that are labeled as $2\,^2A''$ and $2\,^2A'$ and have their origin in the two (higher) degenerate $X\,^2\Pi_g$ states.[15(b)] We intend to show that both the two lower states and the two upper states yield the topological phase $\alpha(q) \sim \pi$ [see Eq. (9)]. (2) As for the three-state system (which is a non-Abelian system) we concentrate on the relevant **D** matrix [see Eq. (4)] and show that in those cases where the 2×2 D matrix fails to be diagonal, the 3×3 **D** matrix takes over and satisfies the diagonality requirement. (3) Finally, we also present the diagonal elements of the 5×5 **D** matrix just to show that they are consistent with the diagonal elements of the relevant 3×3 **D** matrices.

The calculation of the energy curves and the (angular) NACTs is carried out at the state-average complete active space self-consistent field (CASSCF) level, employing the following basis functions: For the carbons as well as for the hydrogens, we applied s, p, and d functions. We used the active space, including all nine valence electrons distributed on ten orbitals. Five electronic states were computed by the state-average CASSCF level using the 6-311G** basis set with equal weights. In certain cases these calculations were repeated with three/four states to check for convergence. All calculations were done for the following collinear configuration: the C–C distance: $R=R_{CC}=1.254$ Å and the (two) H–C distances: $R_{HC}=1.080$ Å. The numerical treatment is carried out employing the MOLPRO program.[38]

Figures 1 and 2 presented the five lower potential energy curves related to the nonsymmetrical states formed by two off-axis hydrogens, H_1 and H_2. Here H_1 is clamped at a distance q_1 from the CC axis and H_2, which is located at a distance q_2 from this axis, is free to move around that axis. It is well noticed that the two lower curves are attributed to $1\,^2A''$ and $1\,^2A'$ states; the third curve is the potential energy curve for the state A' that has its origin in the isolated $D_{\infty h}$, $1\,^2\Sigma_g^+$ configuration and the two upper curves are related to the $2\,^2A''$ and $2\,^2A'$ states.

The potential curves in Fig. 1 were derived for the case that $(q_1, q_2)=(0.1, 0.8)$ Å, and those for $(q_1, q_2)=(1.0, 1.0)$ Å are presented in Fig. 2. In what follows the first set of (nonsymmetrical) q's is referred to as case 1 and the second as case 2.

For reasons of convenience we label the five states according to their energies at $\varphi=0$, as state 1, state 2, etc. Thus, for instance, $\boldsymbol{\tau}_{23}(\varphi|q_1, q_2)$ is the NACT between state 2 (in our case $1\,^2A''$) and state 3 (in our case A'), etc.

A. The topological (Berry) phases

Figure 3 presents three φ-dependent NACTs of $\tau_{45}(\varphi|q_1, q_2)$, as calculated for three different values of q

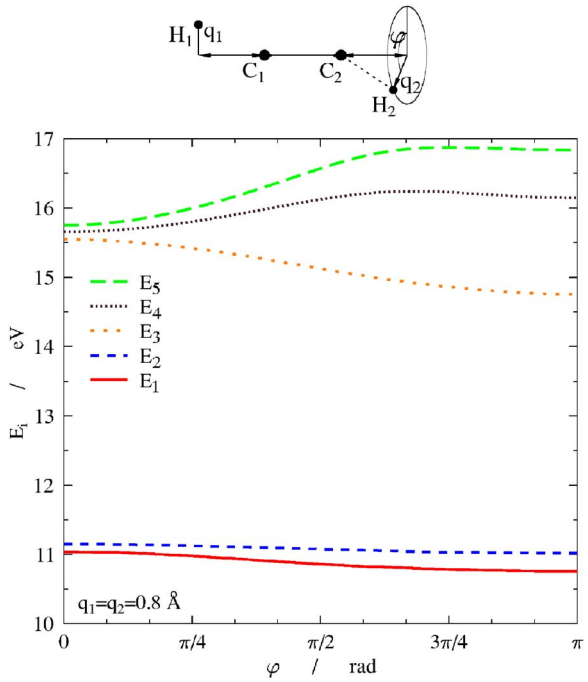

FIG. 2. (Color online) Energy curves for the five lower states of the $C_2H_2^+$ ion presented as a function φ for the case $(q_1,q_2)=(0.8,0.8)$ Å. The rest, see Fig. 1.

where $q=q_1=q_2$. A similar figure but for $\tau_{12}(\varphi|q_1,q_2)$ is given in Fig. 2(a), as published in Ref. 17(a). The calculations are carried out for $q=0.25,0.5,0.8$ Å. It is well noticed that the three curves are strongly oscillating functions (in particular, the one for $q=0.8$ Å) in the vicinity of the value $\tau_{45}(\varphi|q_1,q_2)=0.5$ rad^{-1} (a fact that implies that the corresponding topological phases are expected to be $\alpha_{45}(\varphi|q_1,q_2)\sim\pi$ even in extreme cases). The relevant Berry phases for both τ_{12} and τ_{45} are summarized in Table I. It is

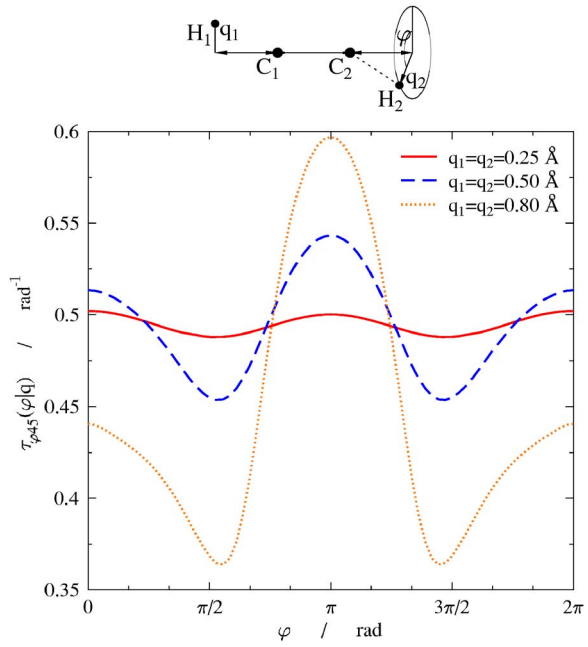

FIG. 3. (Color online) *Ab initio* C_1 φ-dependent nonadiabatic coupling term, $\tau_{\varphi 45}(\varphi|q_1,q_2)$. Results for the case $q_1=q_2$ $(=q)$; (---) $q=0.25$ Å; (- - -) $q=0.5$ Å; (···) $q=0.8$ Å.

TABLE I. The topological (Berry) phases α_{12}, as calculated for the states $1\,^2A''$ and $1\,^2A'$, and α_{45}, as calculated for the states $2\,^2A''$ and $2\,^2A'$ along circles with different radii (q).

q (Å)	α_{12} (rad)	cos α_{12}	α_{45} (rad)	cos α_{45}
0.25	3.105	−0.9993	3.109	−0.9995
0.50	3.010	−0.991	3.103	−0.9992
0.80	2.858	−0.960	2.812	−0.946

noticed that the larger the q is, the more significant is the deviation of the corresponding phase, α (α_{12} or α_{45}) from π. This dependence on q, which is typical for the symmetrical JT and RT intersections, is due to increasing disturbances caused by nearby states. It is noticed that in case of $q=0.8$ Å, the disturbances are so significant that NACTs, due to three states, have to be included in the calculations in order to restore the diagonality of the **D** matrix (see next section).

Another interesting fact that results from this study is that in both cases, the Berry phases (namely, α_{12} and α_{45}) are equal to π (like in the JT case) and not to 2π (like in the RT case which is characterized by an axial symmetry).

B. Abelian versus non-Abelian systems for nonsymmetric configurations space

As already discussed in the Introduction the main emphasis in this article is on the ability of the general theory (that was successfully applied in the symmetrical JT and RT situations) to remedy for the cases where the two-state system fails to yield topological phases close enough to an integer multiple of π (thus 2×2 diagonal **D** matrices). We intend to show that in such a situation adding a third state, just like in the symmetrical cases, improves significantly the topological features, as revealed by the **D** matrices.

We start by presenting the NACTs of the type $\tau_{ij}(\varphi|q_1,q_2)$ as a function of φ for different pairs of (q_1,q_2). Figures 4–6 present the NACTs τ_{12}, τ_{23}, and τ_{13} (namely, NACTS related to the lower states) and in Fig. 7 are presented NACTs for τ_{45}, τ_{53}, and τ_{43} (namely, NACTS for the upper states). The values of q_1 and q_2 are inserted in each figure.

It is noticed that in all four cases both τ_{12} and τ_{45} have values that oscillate in the vicinity of $\tau\sim0.5$ rad^{-1}, whereas the other τ-matrix elements, namely, τ_{13}, τ_{23}, τ_{34}, and τ_{35} have, on the average, much smaller values. Among those we see that the NACTs related to two upper states, i.e., τ_{34} and τ_{35}, are much smaller than the corresponding ones related to the lower states, i.e., τ_{23} and τ_{34}. This fact has implications regarding the possibility of the three-state **D** matrix to remedy the nondiagonality of the two-dimensional **D** matrix as discussed next.

Having the NACTs we are now in a position to calculate the diagonal elements of the various **D**-matrix elements. In Table II are compared results as calculated for the two-state case (third column) and the three-state case (columns 4, 5, and 6). It is noticed that when the elements $\mathbf{D}_{11}^{(2)}(q_1,q_2)$ $(\equiv\mathbf{D}_{22}^{(2)}(q_1,q_2))$ are significantly different from (-1), *sometimes* but not *always*, the relevant elements of the three-state

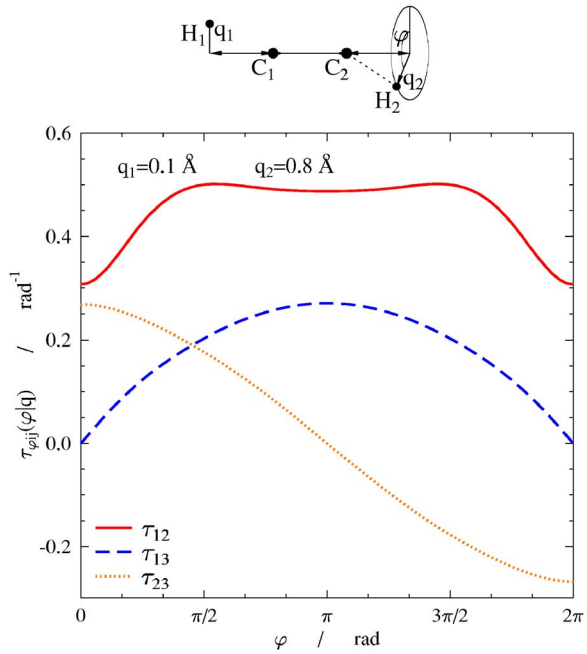

FIG. 4. (Color online) *Ab initio* C_1 φ-dependent nonadiabatic coupling term, $\tau_{\varphi ij}(\varphi|q_1,q_2)$. Results for the case $(q_1,q_2)=(0.1,0.8)$ Å: (---) $\tau_{\varphi 12}$; (- - -) $\tau_{\varphi 13}$ (·····) $\tau_{\varphi 23}$.

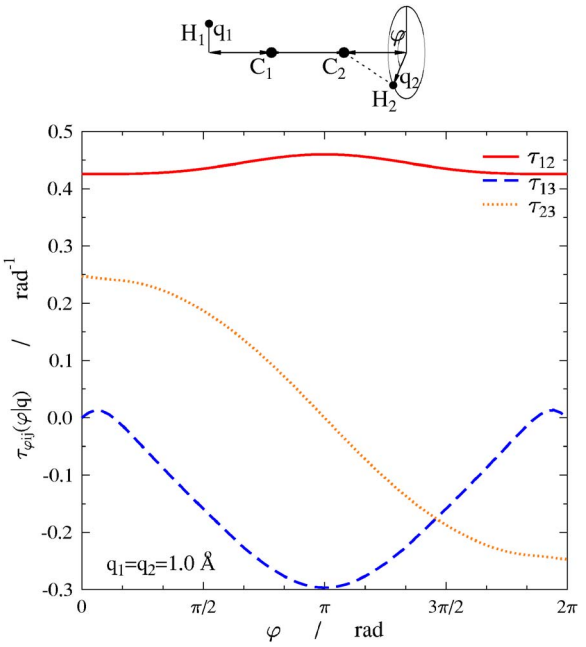

FIG. 6. (Color online) *Ab initio* C_1 φ-dependent nonadiabatic coupling term, $\tau_{\varphi ij}(\varphi|q_1,q_2)$. Results for the case $(q_1,q_2)=(1.0,1.0)$ Å: (---) $\tau_{\varphi 12}$; (- - -) $\tau_{\varphi 13}$ (·····) $\tau_{\varphi 23}$.

D matrix, namely, $\mathbf{D}_{jj}^{(3)}(q_1,q_2)$; $j=1,2,3$ are closer to ±1. We emphasize the word sometimes because this is true for the lower states but not for the upper ones. In the case of the lower states we see that the extension to three states, indeed, improved significantly the diagonality of the **D** matrix (namely, lead to diagonal values closer to ±1). The fact that in the case of the upper states no improvement is achieved is due to two reasons. (a) The two additional NACTs, $\boldsymbol{\tau}_{34}$ and $\boldsymbol{\tau}_{35}$, have, on the average, values too small to be able to affect the relevant **D** matrix. (b) It is most likely that NACTs formed by higher states (i.e., $j>5$) affect the two-dimensional NACTs, but they are not included in the calculation.

Next we comment on the positions of the *minus* signs along the diagonal of the three-state **D** matrix. It is seen that in the case of the *lower states*, the minus signs are attached to the first two elements, namely, $\mathbf{D}_{jj}$, $j=1,2$ which implies that the circular contour surrounds a degeneracy point between states 1 and 2 (the lower states out of five). In contrast

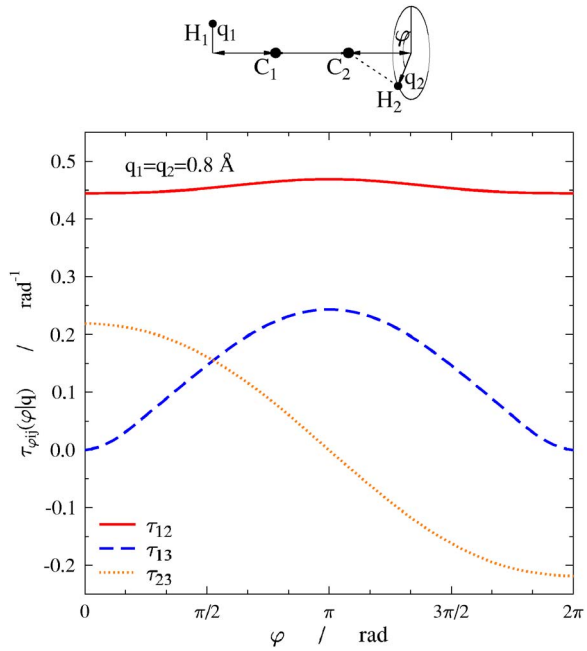

FIG. 5. (Color online) *Ab initio* C_1 φ-dependent nonadiabatic coupling term, $\tau_{\varphi ij}(\varphi|q_1,q_2)$. Results for the case $(q_1,q_2)=(0.8,0.8)$ Å: (---) $\tau_{\varphi 12}$; (- - -) $\tau_{\varphi 13}$ (·····) $\tau_{\varphi 23}$.

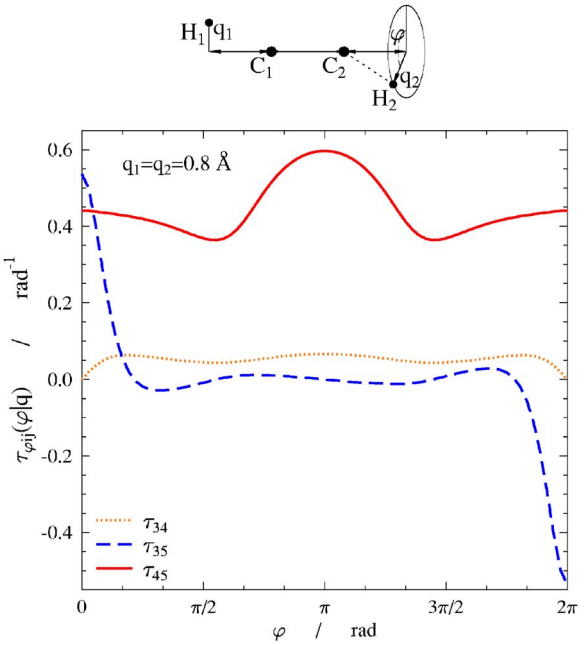

FIG. 7. (Color online) *Ab initio* C_1 φ-dependent nonadiabatic coupling term, $\tau_{\varphi ij}(\varphi|q_1,q_2)$. Results for the case $(q_1,q_2)=(0.8,0.8)$ Å: (---) $\tau_{\varphi 45}$; (- - -) $\tau_{\varphi 35}$ (·····) $\tau_{\varphi 23}$.

TABLE II. The diagonal **D**-matrix elements as calculated for two states ($\mathbf{D}_{11}^{(2)}$) and for three states $\mathbf{D}_{jj}^{(3)}$ $j=1,2,3$.

	(q_1,q_2)[a]	$\mathbf{D}_{11}^{(2)}$	$\mathbf{D}_{11}^{(3)}$	$\mathbf{D}_{22}^{(3)}$	$\mathbf{D}_{33}^{(3)}$	α (rad)[b]
Lower states	(0.1,0.8)	−0.959	−0.999	−0.999	+1.000	2.854
	(0.8,0.8)	−0.960	−0.993	−0.993	+1.000	2.858
	(1.0,1.0)	−0.927	−0.986	−0.982	+0.996	2.757
Upper states	(0.8,0.8)	−0.946	+0.998	−0.952	−0.951	2.812

[a]Units in Å.
[b]The two-state topological (Berry) phase.

to this, the minus sign in the case of the *upper states* is attached to the two last elements $\mathbf{D}_{jj}$, $j=4,5$ which implies that the circular contour surrounds a degeneracy point between states 4 and 5 (the upper states out of five).

For completeness we also calculated the diagonal elements for one corresponding 5×5 **D** matrix [a calculation based on all elements of the type $\boldsymbol{\tau}_{jk}(\varphi|q_1,q_2)$; $j,k=\{1,5\}$], and these are presented in Table III. It is noticed that the minus signs are attached to the first two elements and the last two elements consistent with positions of the minus signs in the three-state **D**-matrix elements as discussed in the previous paragraph.

IV. DISCUSSION AND CONCLUSIONS

In this article we studied, for the first time, a molecular system which is not restricted by any symmetry conditions. This fact leads to a situation where any state in the electronic manifold is coupled to any other state. Limiting ourselves to a given region in configuration space, the question is whether the approach that originally developed to treat the JT effect and recently, successfully, extended to treat the RT effect is applicable also to treat C_1 point groups, namely, configurations that are not controlled by any symmetry conditions.

To get an answer to this question we considered the tetra-atomic system $C_2H_2^+$, where the two carbons form the axis of the molecule and the two off-axis hydrogens behave as follows. One hydrogen is clamped to a fixed point, while the second hydrogen is allowed to surround the CC axis, which serves as an axis of rotation (in other words the moving hydrogen follows a circular contour). At any point along the contour—except at $\varphi=0$, π—the four atoms are not restricted by any symmetry conditions. Our studies concentrate on topological effects formed by following the just mentioned closed contours. Our main findings are as follows.

(1) Altogether we studied the five lower states of the $C_2H_2^+$ ion, all of them related to the C_1 point group: For the lower pair of states, $1\,^2A''$ and $1\,^2A'$, and the upper pair of states, $2\,^2A''$ and $2\,^2A'$, we revealed, in each case, a point of degeneracy, *most likely* located on the CC axis. In other words, we established that the CC axis which is known to contain the points of degeneracy that form the RT effect contains points of degeneracy that are formed by states belonging to the C_1 point group. The main difference between the two types is that whereas the Berry phase for the RT effect is 2π, the Berry phase for this C_1 point group is π.

(2) It is well known that for those situations where a two-state treatment (which yields the topological-Berry phase) breaks down, we are forced to employ the non-Abelian approach (the extended multistate version) which is based on the topological **D** matrix as introduced in Eq. (4) and which was successfully applied whenever we studied the (symmetrical) JT or the RT effects. In the present article we show that the same non-Abelian approach applies also for the present, nonsymmetrical, C_1 point group. We find that whenever the radius of the contour gets too large (i.e., >0.6 Å), the Abelian two-state version has to be replaced by the non-Abelian **D** matrix.

TABLE III. The diagonal **D**-matrix elements as calculated for five states ($\mathbf{D}_{jj}^{(5)}$; $j=\{1,5\}$).

(q_1,q_2)[a]	$D_{11}^{(5)}$	$D_{22}^{(5)}$	$D_{33}^{(5)}$	$D_{44}^{(5)}$	$D_{55}^{(5)}$
(0.8,0.8)	−0.986	−0.982	+0.997	−0.944	−0.946

[a]Units in Å.

The importance of this study is in revealing the fact that a theory that was devised for a symmetrical situation (a situation that is only rarely encountered in reality) applies well for the most general molecular configuration.

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[1] M. Born and J. R. Oppenheimer, Ann. Phys. **84**, 457 (1927); M. Born, Festschrift Göttingen Nach. Math. Phys. **K1**, 1 (1951); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University, New York, 1954).
[2] E. Renner, Z. Phys. **92**, 172 (1934).
[3] G. Herzberg, *Molecular Spectra and Molecular Structure* (Krieger, Malabar, 1991), Vol. III.
[4] H. C. Longuet-Higgins, Adv. Spectrosc. (N.Y.) **2**, 429 (1961).
[5] K. Dressler and D. A. Ramsay, J. Chem. Phys. **27**, 971 (1957); Philos. Trans. R. Soc. London, Ser. A **251**, 553 (1958).
[6] J. A. Pople and H. C. Longuet-Higgins, Mol. Phys. **1**, 372 (1958).
[7] M. Peric and S. Peyerimhoff, Adv. Chem. Phys. **124**, 583 (2002).

[8] Ch. Jungen and A. J. Merer, Mol. Phys. **40**, 1 (1980); **40**, 95 (1980); in *Molecular Spectroscopy, Modern Research*, edited by K. N. Rao (Academic, New York, 1977), Vol. 2, p. 127.
[9] J. M. Brown and F. Jorgenson, Adv. Chem. Phys. **52**, 117 (1983); J. M. Brown, in *Computational Molecular Spectroscopy*, edited by P. Jensen and P. R. Bunker (Wiley, New York, 2000), p. 517.
[10] S. Carter and N. C. Handy, Mol. Phys. **47**, 1445 (1982); **52**, 1367 (1984).
[11] R. Barrow, R. N. Dixon, and G. Duxbury, Mol. Phys. **27**, 1217 (1974).
[12] A. Alijah and G. Duxbury, Mol. Phys. **70**, 605 (1990); G. Duxbury, B. McDonald, M. Van Gogh, A. Alijah, Ch. Jungen, and H. Palivan, J. Chem. Phys. **108**, 2336 (1998).
[13] M. Peric, R. J. Buenker, and S. Peyerimhoff, Mol. Phys. **59**, 1283 (1986); M. Peric, S. Peyerimhoff and R. J. Buenker, Z. Phys. D: At., Mol. Clusters **24**, 177 (1992).
[14] P. R. Bunker and P. Jensen, J. Mol. Spectrosc. **118**, 18 (1986); *Molecular Symmetry and Spectroscopy* (NRC Research, Ottawa, 1998).
[15] (a) M. Peric and S. D. Peyerimhoff, J. Chem. Phys. **102**, 3685 (1995); (b) M. Peric, B. Engels and M. Hanrath, Chem. Phys. **238**, 33 (1998).
[16] G. J. Halász, Á. Vibók, R. Baer, and M. Baer, J. Chem. Phys. **125**, 094102 (2006).
[17] (a) G. J. Halász, Á. Vibók, D. K. Hoffman, D. J. Kouri, and M. Baer, J. Chem. Phys. **126**, 154309 (2007); (b) G. J. Halász, Á. Vibók, R. Baer, and M. Baer, J. Phys. A **40**, F267 (2007).
[18] H. A. Jahn and E. Teller, Proc. R. Soc. London, Ser. A **161**, 220 (1937).
[19] M. S. Child and H. C. Longuet Higgins, Philos. Trans. R. Soc. London, Ser. A **254**, 259 (1961).
[20] G. Herzberg and H. C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963); H. C. Longuet Higgins, Proc. R. Soc. London, Ser. A **344**, 147 (1975).
[21] E. R. Davidson, J. Am. Chem. Soc. **99**, 397 (1977).
[22] M. S. Child, Adv. Chem. Phys. **124**, 1 (2002); S. Adhikari and G. D. Billing, *ibid.* **124**, 143 (2002); R. Englman and A. Yahalom, *ibid.* **124**, 197 (2002); A. Kuppermann and R. Abrol, *ibid.* **124**, 323 (2002); G. A. Worth and M. A. Robb, *ibid.* **124**, 355 (2002).
[23] M. Chajia and R. D. Levine, Phys. Chem. Chem. Phys. **1**, 1205 (1999); K. L. Kompa and R. D. Levine, Proc. Natl. Acad. Sci. U.S.A. **98**, 410 (2001).
[24] A. Kuppermann, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), p. 411; R. Abrol, A. Shaw, and A. Kuppermann, J. Chem. Phys. **116**, 1035 (2002).
[25] M. Baer, S. H. Lin, A. Alijah, S. Adhikari, and G. D. Billing, Phys. Rev. A **62**, 032506 (2000).
[26] A. L. Sobolewski and W. Domcke, Chem. Phys. **259**, 181 (2000).
[27] (a) M. Baer, T. Vertsi, G. J. Halász, Á. Vibók, and S. Suhai, Faraday Discuss. **127**, 337 (2004); (b) A. M. Mebel, G. J. Halász, Á. Vibók, A. Alijah, and M. Baer, J. Chem. Phys. **117**, 991 (2002).
[28] R. Englman and T. Vertesi, Phys. Lett. A **354**, 196 (2006); E. S. Kryachko, Adv. Quantum Chem. **44**, 119 (2003); P. Barragan, L. F. Errea, A. Macias, L. Mendez, A. Riera, J. M. Lucas, and A. Aguilar, J. Chem. Phys. **121**, 11629 (2004); S. Gomez-Carrasco, A. Aquado, M. Paniaqua, and O. Roncero, *ibid.* **125**, 104105 (2006); M. B. Sevryuk, L. Y. Rusin, S. Cavalli, and V. Aquilanti, J. Phys. Chem. A **108**, 8731 (2004); V. A. Mozhayskiv, D. Babikov, and A. I. Krylov, J. Chem. Phys. **124**, 224309 (2006); K. A. Kistler and S. Matsika, J. Phys. Chem. A **111**, 2650 (2007); E. Abrahamsson, G. C. Groenenboom, and R. V. Krems, J. Chem. Phys. **126**, 184309 (2007).
[29] G. D. Billing, M. Baer, and A. M. Mebel, Chem. Phys. Lett. **1**, 372 (2003).
[30] J. C. Tully, Faraday Discuss. **127**, 463 (2004).
[31] *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004).
[32] M. Ben-Nun and T. J. Martinez, Chem. Phys. **259**, 237 (2000).
[33] M. Baer, *Beyond Born Oppenheimer: Electronic Non-Adiabatic Coupling Terms and Conical Intersections* (Wiley, Hoboken, 2006).
[34] B. Sarkar and S. Adhikari, J. Chem. Phys. **124**, 074101 (2006); P. Puzari, B. Sarkar, and S. Adhikari, *ibid.* **121**, 707 (2004).
[35] O. Godsi, C. R. Evenhuis, and M. Collins, J. Chem. Phys. **125**, 164321 (2006).
[36] (a) M. Baer, Chem. Phys. Lett. **35**, 112 (1975); (b) Mol. Phys. **40**, 1011 (1980).
[37] C. N. Yang and R. L. Mills, Phys. Rev. **96**, 191 (1954).
[38] H.-J. Werner and P. J. Knowles, J. Almlöf *et al.*, MOLPRO, a package of *ab initio* programs.