Topological effects due to conical intersections: A model study of two interacting conical intersections

Michael Baer, António J. C. Varandas, and Robert Englman

Articles you may be interested in

On the description of conical intersections—A continuous representation of the local topography of seams of conical intersection of three or more electronic states: A generalization of the two state result
J. Chem. Phys. **141**, 174109 (2014); 10.1063/1.4900631

Solvent effect on the nuclear magnetic shielding: ab initio study by the combined reference interaction site model and electronic structure theories
J. Chem. Phys. **115**, 8949 (2001); 10.1063/1.1412872

The study of conical intersections between consecutive pairs of the five lowest 2 A ′ states of the C 2 H molecule
J. Chem. Phys. **115**, 3673 (2001); 10.1063/1.1389842

Erratum: "Topological effects due to conical intersections: A model study of two interacting conical intersections" [J. Chem. Phys. 111, 9493 (1999)]
J. Chem. Phys. **112**, 6089 (2000); 10.1063/1.481181

Time-dependent and time-independent approaches to study effects of degenerate electronic states
J. Chem. Phys. **109**, 6550 (1998); 10.1063/1.477306

Topological effects due to conical intersections: A model study of two interacting conical intersections

Michael Baer[a)] and António J. C. Varandas
Departamento de Quimica, Universidade de Coimbra, P-3049 Coimbra Codex, Portugal

Robert Englman
Department of Physics and Applied Mathematics, Soreq NRC, 81800 Yavne, Israel

A model is presented to study the (weak) interaction between two conical intersections (e.g., a dimer of two loosely bound molecules each characterized by a conical intersection). The model is an extension of a previous model for a single conical intersection formed by an electron housed by a vibrating molecule [Baer and Englman, Mol. Phys. **75**, 293 (1992)]. The main result of this study is that the intermolecular coupling removes part of the degeneracy of the global system and in turn forms a new degeneracy, but will not affect the multivaluedness of the nuclear wave functions. © *1999 American Institute of Physics.* [S0021-9606(99)01344-6]

I. INTRODUCTION

The study of effects of doubly degenerate electronic states on molecular processes is becoming a major subject in molecular physics.[1–11] Within this framework Baer and Englman[7] suggested to examine such effects employing a model formed by a molecular electron coupled to the vibrational motion of the molecule, i.e., a conical intersection.[12] The electron–molecule coupling was studied within the framework of a two-state model (namely a two-dimensional Hilbert space) and it was shown[7–9] that the geometrical features of this system were solely determined by the adiabatic–diabatic transformation (ADT) angle α.[13] Among other things we also showed that the ADT angle, once calculated along a closed path around the point of degeneracy,[7–9] yields the topological phase β.[3] This was done twice:[9] Once for the resulting Jahn–Teller-type degeneracy and in this case β was found to be equal to π and once when the Jahn–Teller degeneracy was removed by a perturbation μ and then β was found to be equal to 2π (or zero). In the present work this model is extended to contain two such electrons, where each one is attached to a (different) molecule and the aim is to study a situation where two systems, each governed by a conical intersection interaction with each other. This extended system will have to be treated within a four-dimensional Hilbert space and, therefore, yields new geometrical features so far (to our knowledge) not exposed.

II. THE MODEL

Our model contains two electrons each one housed by a separate molecule and with its motion coupled to the vibra-

tional motion of the corresponding molecule. In addition, the two electrons are interacting with each other by a Coulomb force. Such a model can represent a weakly bound dimer of the form: $A_3 \cdots A_3'$.[12(b)] The aim of the present study is to analyze the effect of this external electron–electron coupling on the degeneracy of the global system and the resulting *multivaluedness* of the *nuclear* wave functions, or in other words, to study the geometrical effects that originate from such an interaction.

In what follows the motion of each of the electrons will be described in terms of one (periodic) coordinate, θ_a (θ_b) and the vibrational motion of each of the two mother molecules will be described in terms of two coordinates: A polar periodic coordinate φ_a (φ_b) [defined along the interval (0, 2π) and a radial coordinate q_a (q_b)]. In addition there are other (nuclear) coordinates responsible for the relative motion of the two molecules which will not be specified. As mentioned earlier, the Hamiltonian we apply is an extension of an electronic Hamiltonian which has been used before to describe a single electron housed by a vibrating molecule,[7–9] namely a Hamiltonian that contains a periodic potential in both θ_a (θ_b) and φ_a (φ_b). The type of the potential that was chosen for the *single* electron–molecule model yields a Schrödinger equation which is the same as the Mathieu equation.[7,12(a)] Here we choose similar potentials responsible for the two electron–molecule systems and consequently the resulting Hamiltonian can be considered as a kind of an extended-Mathieu equation

$$H = -\frac{1}{2} E_{ael} \frac{\partial^2}{\partial \theta_a^2} - \frac{1}{2} E_{bel} \frac{\partial^2}{\partial \theta_b^2} + G_a \cos(2\theta_a - \varphi_a)$$
$$+ G_b \cos(2\theta_b - \varphi_b) + G \cos[2(\theta_a + \theta_b) - (\varphi_a + \varphi_b)].$$

$$(1)$$

In this equation, E_{ael} and E_{bel} are characteristic electronic magnitudes and G_a (G_b) is the coupling coefficients usually assumed to be equal to $k_a q_a$ ($k_b q_b$) where k_a (k_b) is a force

constant of the ath (bth) molecule. The fifth term in this equation (which is chosen to be symmetrical with respect to the electronic coordinates) describes a Coulombic-type interaction between the two electrons, each attached to one molecule, and therefore, the coefficient G depends on the distance between the two molecules (and eventually on other physical magnitudes). This kind of interactions were discussed in a series of papers by Dexter et al.[12(c)–12(e)] It is important to note that in Eq. (1) the third and the fourth terms describe the intramolecular coupling within each molecule and the fifth term describes the intermolecular coupling between the two molecular systems. The present treatment will be done for the case that all three parameters namely G_a, G_b, and G are small compared to the E_{ael} and E_{bel} values. Throughout this treatment we assume both, q_a and q_b to be constants.

III. THE SOLUTION OF THE EIGENVALUE PROBLEM

The equation we are interested to solve is the following (electronic) eigenvalue equation:

$$(H - u(\varphi_a, \varphi_b))\chi(\theta_a, \theta_b | \varphi_a, \varphi_b) = 0, \qquad (2)$$

where $u(\varphi_a, \varphi_b)$ is an eigenvalue and $\chi(\theta_a, \theta_b | \varphi_a, \varphi_b)$ is the corresponding eigenvector, the bar specifies the parametric dependence of χ on the nuclear coordinates φ_a and φ_b. In a previous publication we showed that the two general adiabatic independent solutions for the single electronic–molecule, which are relevant for our purpose, have the form

$$\psi_1(\theta | \varphi) = \sum a_n(\varphi) \cos^n\left(\theta - \frac{\varphi}{2}\right) \qquad (3a)$$

and

$$\psi_2(\theta | \varphi) = \sum b_n(\varphi) \sin^n\left(\theta - \frac{\varphi}{2}\right), \qquad (3b)$$

where the summation index runs over the odd integers starting with $n=1$. These equations will be applied here as well. Consequently the general solution of Eq. (2) can be written as a product of these functions. Thus

$$\chi_{ij}(\theta_a, \theta_b | \varphi_a, \varphi_b) = \psi_i(\theta_a | \varphi_a)\psi_j(\theta_b | \varphi_b); \quad i,j = 1,2, \qquad (4)$$

where the indices a and b are used to distinguish between the two molecules. It is important to emphasize that in the present study we assume that the overlap between the eigenstates belonging to the two different centers is small, and therefore, to a good approximation we do not have to apply antisymmetrized wave function.[12(c),12(d)] Modifications due to antisymetrization (or particle exchange) and due to the electronic spin will be treated in Sec. IV. Moreover since G_a, G_b, and G are assumed to be small we may keep only the first term in each of the summations presented in Eq. (3). [It is important to note that G_a (G_b) becomes zero when q_a

(q_b) becomes zero, but G, in general is expected to differ from zero at these points.] Therefore, the following four functions will be considered:

$$\chi_{11} = \sin\left(\theta_a - \frac{\varphi_a}{2}\right)\sin\left(\theta_b - \frac{\varphi_b}{2}\right);$$

$$\chi_{12} = \sin\left(\theta_a - \frac{\varphi_a}{2}\right)\cos\left(\theta_b - \frac{\varphi_b}{2}\right),$$

$$\chi_{21} = \cos\left(\theta_a - \frac{\varphi_a}{2}\right)\sin\left(\theta_b - \frac{\varphi_b}{2}\right);$$

$$\chi_{22} = \cos\left(\theta_a - \frac{\varphi_a}{2}\right)\cos\left(\theta_b + \frac{\varphi_b}{2}\right).$$

$$(5)$$

Having the (trial) functions and recalling that

$$\cos(2\theta - \varphi) = 2\cos^2\left(\theta - \frac{\varphi}{2}\right) - 1 = 1 - 2\sin^2\left(\theta - \frac{\varphi}{2}\right), \qquad (6)$$

it can be shown[9] that these χ_{ij}-functions are the lowest order eigenfunctions with the following eigenvalues:

$$u_{11} = E_{el} + \tfrac{1}{2}(G_a + G_b + G),$$

$$u_{12} = E_{el} + \tfrac{1}{2}(G_a - G_b - G),$$

$$u_{21} = E_{el} + \tfrac{1}{2}(-G_a + G_b - G),$$

$$u_{22} = E_{el} + \tfrac{1}{2}(-G_a - G_b - G),$$

$$(7)$$

where E_{el} stands for $(\tfrac{1}{2})(E_{ael} + E_{bel})$. From the definitions of G_a and G_b it is noticed that in the extended four-dimensional space at least two pairs of the four eigenvalues namely u_{11} and u_{22} and u_{21} and u_{12} are degenerate at the (extended) origin $q_a = q_b = 0$ and one pair, u_{21} and u_{12}, is degenerate along the line formed by the equation: $q_a = (k_b/k_a)q_b$. A closer look at the possible degeneracy reveals that each point of degeneracy in the case of a single molecular electron becomes, at the moment that a second molecular electron is added to the system, a seam in the extended configuration space (for an analogous situation in the case of a realistic molecular system see Ref. 14). In our particular case the points $q_a = 0$ and $q_b = 0$ become, in the extended configuration space, two seam lines that intersect each other at the origin ($q_a = 0$, $q_b = 0$). However, we saw that introducing a coupling between the two one-electron-molecules forms two new features: It removes the degeneracy along these two seams leaving only one point of degeneracy (in the extended configuration space) but then produces a new seam defined by the equation $q_a = (k_b/k_a)q_b$. This seam is unexpected because it forms a three-dimensional surface in a four-dimensional configuration space (while a degeneracy can be at most of n-2 dimen-

sionality in an n-dimensional space). This seam is probably a special feature of the applied model and has to be considered with care (this is further discused in Chap. VI).

So far we considered the simplest case of two interacting systems each having a conical interaction, and we already encounter a complexity for which it is not clear how to construct the relevant diabatic nuclear wave function with the correct geometrical properties. It turns out that the only way to guarantee such a nuclear wave function (or vector of nuclear wave functions) is to employ the ADT matrix[13] which transforms adiabatic, i.e., single-valued functions to functions with the required geometry. The importance of the ADT matrix is due to the fact that it contains the geometrical properties of the system enforced by the electronic eigenfunctions. The existence of this particular feature was demonstrated in a series of studies[7–9]—however, all of them performed in a two-dimensional Hilbert space. In the next section we derive the ADT matrix for the present a four-dimensional Hilbert space model.

IV. DERIVATION OF THE NONADIABATIC COUPLING TERMS AND ADIABATIC–DIABATIC-TRANSFORMATION MATRIX

To derive the ADT matrix we have first to obtain the nonadiabatic coupling matrices $\tau_{\varphi a}$ and $\tau_{\varphi b}$. These are 4×4 anti-symmetrical matrices with elements $(\tau_\varphi)_{iji'j'}$ defined as[13(a)]

$$(\tau_\varphi)_{iji'j'} = \frac{1}{q} \left\langle \chi_{ij} \left| \frac{\partial}{\partial \varphi} \chi_{i'j'} \right. \right\rangle, \tag{8}$$

where the χ_{ij} are real electronic eigenfunctions. Employing the χ_{ij}-functions derived before [see Eq. (5)] it can be shown that $\tau_{\varphi a}$ and $\tau_{\varphi b}$ assume the form

$$\tau_{\varphi a} = \frac{1}{2q_a} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$

$$\tau_{\varphi b} = \frac{1}{2q_b} \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}. \tag{9}$$

Next the 4×4 ADT matrix A is obtained by solving the first-order two-component vector equation[13(a)]

$$\frac{1}{q_a} \frac{\partial}{\partial \varphi_a} A + \tau_{\varphi a} A = 0, \tag{10a}$$

$$\frac{1}{q_b} \frac{\partial}{\partial \varphi_b} A + \tau_{\varphi b} A = 0. \tag{10b}$$

The necessary condition for Eq. (10) to have a unique solution is that $\mathbf{Curl}\,\tau = [\tau \times \tau]$.[13(a),13(d)] This condition is fulfilled because τ is essentially a vector of constant matrices and because $\tau_{\varphi a}$ and $\tau_{\varphi b}$ commute so that $[\tau \times \tau] = 0$. The fact that τ is a constant vector matrix also helps in solving Eq.

(10) because in this case the solution can be presented as a product of two matrices one dependent on φ_a and the other on φ_b

$$A = A_a(\alpha_a(\varphi_a)) A_b(\alpha_b(\varphi_b)). \tag{11}$$

The matrix A will be solved subject to the boundary condition that $A(\varphi_a = 0, \varphi_b = 0) = I$. Substituting Eq. (11) into Eq. (10a) and multiplying it, from the right-hand-side by $(A_b)^{-1}$ yields the equation for A_a

$$\frac{1}{q_a} \frac{d}{d\varphi_a} A_a + \tau_{\varphi a} A_a = 0. \tag{10a'}$$

A solution will be found for the boundary condition $A_a(\alpha_a(\varphi_a = 0)) = I$. We assume that $A_a(\alpha_a)$ is of the form

$$A_a(\alpha_a) = \begin{pmatrix} \cos \alpha_a & 0 & -\sin \alpha_a & 0 \\ 0 & \cos \alpha_a & 0 & -\sin \alpha_a \\ \sin \alpha_a & 0 & \cos \alpha_a & 0 \\ 0 & \sin \alpha_a & 0 & \cos \alpha_a \end{pmatrix}. \tag{12}$$

Substituting Eq. (12) into Eq. (10a') and recalling Eq. (8) justifies this form and yields the first-order differential equation for α_a and the corresponding solution

$$\frac{d\alpha_a}{d\varphi_a} = \frac{1}{2} \Rightarrow \alpha_a = \frac{1}{2} \varphi_a \Rightarrow \alpha_a(\varphi_a = 2\pi) = \pi. \tag{13}$$

The derivation of $A_b(\alpha_b)$ needs more consideration. In order to also get in this case a separate equation the previous solution matrix $A_a(\alpha_a)$ has to commute with the $\tau_{\varphi b}$ matrix which indeed it does. Multiplying the resulting equation by $(A_a)^{-1}$ yields the equation for $A_b(\alpha_b)$

$$\frac{1}{q_b} \frac{d}{d\varphi_b} A_b + \tau_{\varphi b} A_b = 0. \tag{10b'}$$

Again we try a solution but of the form

$$A_b(\alpha_b) = \begin{pmatrix} \cos \alpha_b & -\sin \alpha_b & 0 & 0 \\ \sin \alpha_b & \cos \alpha_b & 0 & 0 \\ 0 & 0 & \cos \alpha_b & -\sin \alpha_b \\ 0 & 0 & \sin \alpha_b & \cos \alpha_b \end{pmatrix}. \tag{12'}$$

Substituting Eq. (12') into Eq. (10b') yields the first-order differential equation for α_2 and its immediate solution

$$\frac{d\alpha_b}{d\varphi_b} = \frac{1}{2} \Rightarrow \alpha_b = \frac{1}{2} \varphi_b \Rightarrow \alpha_b(\varphi_b = 2\pi) = \pi. \tag{13'}$$

From Eqs. (12') and (13') it is seen that A_b fulfills the required boundary condition: $A_b(\alpha_b(\varphi_b = 0)) = I$. It is important to mention that since A_a and A_b are orthogonal matrices the matrix A is orthogonal as well.

Since A is equal to the product $A_a A_b$ [see Eq. (11)], A will change its sign whenever either A_a or A_b does, which

happens when either φ_a or φ_b, respectively, complete a full cycle. It is interesting to note that when both complete a cycle no change of sign follows.

V. ANTISYMMETRIC ADIABATIC SPIN ORBITALS

To formulate the theory in terms of properly antisymmetric states the notation in Eq. (5) has to be extended so that we can discuss electronic coordinates without associating the electrons directly to a particular molecule. Thus Eq. (5) takes the following form

$$\chi_{ab,11}=\cos\left(\theta_1-\frac{\varphi_a}{2}\right)\cos\left(\theta_2-\frac{\varphi_b}{2}\right),$$

$$\chi_{ab,12}=\cos\left(\theta_1-\frac{\varphi_a}{2}\right)\sin\left(\theta_2-\frac{\varphi_b}{2}\right),$$

$$\chi_{ab,21}=\sin\left(\theta_1-\frac{\varphi_a}{2}\right)\cos\left(\theta_2-\frac{\varphi_b}{2}\right),$$ (5′)

$$\chi_{ab,22}=\sin\left(\theta_1-\frac{\varphi_a}{2}\right)\sin\left(\theta_2-\frac{\varphi_b}{2}\right),$$

where the first pair of indices (preceding the comma) labels the mother molecule of the respective electron (in the above equations it is electron 1 housed by molecule a and electron 2 by molecule b) and the second pair (after the comma) labels the state (state 1 is the lower state with the cos-eigenfunction and state 2 is the upper state with the sin eigenfunction). Next we include for the electrons, the (α,β) spin states. Then the proper antisymmetric states namely, the singlet and the three triplet states (we show only one triplet state) are

$$^1\chi_{11}=\tfrac{1}{2}(\chi_{ab,11}+\chi_{ba,11})(\alpha(1)\beta(2)-\beta(1)\alpha(2)),$$

$$^3\chi_{11}=\tfrac{1}{2}(\chi_{ab,11}-\chi_{ba,11})(\alpha(1)\beta(2)+\beta(1)\alpha(2)).$$ (14)

Each state of Eq. (5′) is replaced by four corresponding states given in Eq. (14). In our treatment we neglect spin orbit coupling between the singlet and the triplet states in Eq. (13) and we also neglect the overlap between $\chi_{ab,ij}$ and $\chi_{ba,ij}$ functions. As a result of these assumptions it can be shown that the formalism presented in Secs. II–IV will hold also for the antisymmetrized spin orbitals.

VI. CONCLUSIONS

Our main findings are as follows:

1. It has been shown that if each of the two interacting molecular electrons has a single point of degeneracy at q_a $(q_b)=0$, bringing the two together results in two seams in the extended configuration space. Coupling of the two interacting systems (or in other words turning on the electron–electron interaction) removes the original degeneracy almost entirely, leaving only one point of degeneracy, i.e., $(q_a=0,q_b=0)$ in the extended configuration space. However, this coupling also forms a new degeneracy defined by the relation $q_a=(k_a/k_b)q_b$. This is a three-dimensional seam in a four-dimensional space (probably a special feature of the applied model) but of minor importance as it does not create any topological effects. This was shown to be the core while analyzing the propeties of the ADT matrix.[18]

2. We showed that **A** changes sign whenever one of the electronic basis functions changes sign. This usually happens when the corresponding polar angle φ_a (φ_b) follows a close loop around its conical intersection located at its origin $q_a=0$ ($q_b=0$) (it is important to emphasize that if none of the two loops surround its point of degeneracy no change of sign appears as was discussed in Ref. 9). This fact implies that the nuclear wave functions, like the electronic ones, are multivalued. In the single molecular electron case we showed that change of sign of the ADT matrix, and therefore, also the multivaluedness of the nuclear wave function, are closely connected with the fact that the electronic eigenvalues, (namely, the nuclear potential-energy surfaces) have a degeneracy yielding the CI.[9] From the present study it follows that this feature is doubled in case a second molecular electron is added to the system. It is expected that this will, indeed, happen when the two systems do not interact. Here we turned on the electron–electron interaction thus letting the two systems to interact and found that the interaction, even being weak, affected the degeneracy scheme significantly (removing one type of degeneracy and simultaneously producing a different one). Nevertheless the multivaluedness of the nuclear wave functions remained as if no coupling was assumed. This is, to some extent, an unexpected result, because in contrast to a previous study[9] in which the degeneracy was removed by an intramolecular (weak) coupling and as a result the nuclear wave functions became single valued, here, we find that intermolecular coupling is not capable to affect the multivaluedness of the nuclear wave functions. This result is important because it is expected that sooner or later this coupling will produce topological effects and the question is only: At what stage? Therefore, this point is subject to further studies.

3. It was mentioned earlier that **A** changes sign whenever one of the polar angles, either φ_a or φ_b, follows a close loop around its conical intersection located at its own origin, $q_a=0$ or $q_b=0$, respectively. This implies that in the case the two systems do not interact **A** will not change sign when both angles, simultaneously, follow a close loops around their origins. We found that as long as the interaction is weak this feature is still maintained. Again, it is expected that when the two systems get closer so that the interaction becomes strong enough also this feature will be affected.

4. Dimerization reactions for several molecules (e.g., silaethylene,[15] formaldehyde[16,17] and others) involve potential-energy surfaces with conical intersections as well as other types of crossings. The results in this work, treating adiabatic-to-diabatic transformations should facilitate calculations of efficient pathways.

5. We would also like to point out a quasi-technical achievement namely we presented here for the first time a study of a four-dimensional system and obtained for it the ADT angles and the relevant geometrical phases. We showed that the ADT angles yield the correct symmetrical features of the system and are (also) identical, like in previous two-state models, to the corresponding Longuet-Higgins angles.[2]

Note added in proof. While this manuscript was in preparation Kendrick, Mead, and Truhlar (KMT) published a Note [J. Chem. Phys. **110**, 7594 (1999)] which objects to a claim, made by one of the present authors [see Ref. 8(c)], namely that the Longuet-Higgins phase and the ADT angle are identical for a two-dimensional Hilbert space. They could not find a two-state example to support their point and so they used two 4-dimensional eigenvectors for this purpose. In this paper a four dimensional Hilbert-space model which yields all four 4-dimensional eigenvectors to be used to form the ADT angles is treated. It is well noticed that the two properly derived ADT angles posses the features expected from the corresponding Longuet-Higgins phase.[2(e)] Since two of the four eigenvectors are identical to KMT's eigenvectors, the present treatment, in fact, shows that their ADT angles, which differ from ours, are incorrect. As a result, their objection is not supported by any example and therefore cannot be accepted.

ACKNOWLEDGMENTS

[1] H. A. Jahn and E. Teller, Proc. R. Soc. London, Ser. A **161**, 220 (1937).

[2] (a) H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, and R. A. Sack, Proc. R. Soc. London, Ser. A **244**, 1 (1958); (b) H. C. Longuet-Higgins, Adv. Spectrosc. **2**, 429 (1961); (c) M. S. Child and H. C. Longuet-Higgins, Philos. Trans. R. Soc. London, Ser. A **254**, 259 (1961); (d) G. Herzberg and H. C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963); (e) H. C. Longuet-Higgins, Proc. R. Soc. London, Ser. A **344**, 147 (1975).

[3] M. V. Berry, Proc. R. Soc. London, Ser. A **392**, 45 (1984); Y. Aharonov, E. BenReuven, S. Popescu, and D. Rohrlich, Nucl. Phys. B **350**, 818 (1990).

[4] H. Koppel, W. Domcke, and L. S. Cederbaum, Adv. Chem. Phys. **57**, 59 (1984); T. Pacher, L. S. Cederbaum, and H. Koppel, *ibid.* **84**, 293 (1993); W. Domcke and G. Stock, *ibid.* **100**, 1 (1997).

[5] B. H. Lengsfield and D. R. Yarkony, in *State Selected and State-to-State Ion-Molecule Reaction Dynamics: Part 2, Theory*, edited by M. Baer and C. Y. Ng (Wiley, New York, 1992), Vol. 82, p. 1; V. Sidis, *ibid.*, p. 73; D. Yarkony, Rev. Mod. Phys. **68**, 985 (1996); J. Phys. Chem. **100**, 18612 (1996); A. Kuppermann, in *Dynamics of Molecules and Chemical Reac-*

tions, edited by R. E. Wyatt and J. Z. H. Zhang (Marcel Dekker, New York, 1996), p. 411.

[6] J. W. Zwanziger and E. R. Grant, J. Chem. Phys. **87**, 2954 (1987); N. Markovic and G. D. Billing, *ibid.* **99**, 2674 (1993); **100**, 1089 (1994); B. Lepetit and A. Kuppermann, Chem. Phys. Lett. **166**, 581 (1990); A. Kuppermann and Y.-S. M. Wu, *ibid.* **205**, 577 (1993); Y.-S. M. Wu and A. Kuppermann, *ibid.* **235**, 105 (1995); X. Wu, R. E. Wyatt, and M. D'mello, J. Chem. Phys. **101**, 2953 (1994); R. G. Sadigov and D. R. Yarkony, *ibid.* **109**, 20 (1998); J. Schon and H. Koppel, *ibid.* **103**, 9292 (1995); D. Yarkony, *ibid.* **105**, 10456 (1996); N. Matsunaga and D. Yarkony, *ibid.* **107**, 7825 (1997); G. Chaban, M. S. Gordon, and D. Yarkony, J. Phys. Chem. A **101**, 7953 (1997); S. Xantheas, S. T. Ebert, and K. Ruedenberg, J. Chem. Phys. **93**, 7519 (1990); K. Ruedenberg and G. J. Atchity, *ibid.* **99**, 3799 (1993); T. J. Martinez, Chem. Phys. Lett. **272**, 139 (1997); A. J. Dobbyn and P. J. Knowles, Mol. Phys. **70**, 825 (1990); G. D. Billing and A. Kuppermann, Chem. Phys. Lett. **294**, 26 (1998).

[7] M. Baer and R. Englman, Mol. Phys. **75**, 293 (1992).

[8] (a) R. Baer, D. Charutz, R. Kosloff, and M. Baer, J. Chem. Phys. **105**, 9141 (1996); (b) D. M. Charutz, R. Baer, and M. Baer, *ibid.* **265**, 629 (1997); (c) M. Baer, *ibid.* **107**, 2694 (1997); (d) **107**, 10662 (1997); (e) R. Englman and M. Baer, J. Phys.: Condens. Matter **11**, 1059 (1999).

[9] M. Baer, A. Yahalom, and R. Englman, J. Chem. Phys. **109**, 6550 (1998).

[10] A. J. C. Varandas, J. Tennyson, and J. N. Murrell, Chem. Phys. Lett. **61**, 431 (1979); A. J. C. Varandas and H. G. Yu, *ibid.* **259**, 336 (1996); J. Chem. Soc., Faraday Trans. **93**, 819 (1997); A. J. C. Varandas, H. G. Yu, and Z. R. Xu, Mol. Phys. (in press).

[11] T. Bitter and D. Dubbens, Phys. Rev. Lett. **59**, 251 (1998); D. Suter, K. T. Mueller and A. Pines, *ibid.* **60**, 1218 (1988).

[12] (a) R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley Interscience, London, 1972); (b) *ibid.*, Section 7.7 and references therein; (c) D. L. Dexter, J. Chem. Phys. **21**, 836 (1953); (d) Phys. Rev. **126**, 1962 (1962); T. Miyakawa and D. L. Dexter, Phys. Rev. B **1**, 2961 (1970).

[13] (a) M. Baer, Chem. Phys. Lett. **35**, 112 (1975); (b) Z. H. Top and M. Baer, J. Chem. Phys. **66**, 1363 (1977); (c) M. Baer, Mol. Phys. **40**, 1011 (1980); (d) M. Baer, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC, Boca Raton, 1985), Vol. II, pp. 243–244.

[14] A. J. C. Varandas, A. I. Voronin, and P. J. Jimeno, Chem. Phys. **107**, 10014 (1997).

[15] F. Bernardi, A. Bottoni, M. Olivucci, M. A. Robb, and A. Venturini, J. Am. Chem. Soc. **115**, 3322 (1993).

[16] F. Bernardi, A. Bottoni, M. Olivucci, A. Venturini, and M. A. Robb, J. Chem. Soc., Faraday Trans. **90**, 1617 (1994).

[17] E. T. Seidel, R. S. Grev, and H. F. Schaefer III, J. Am. Chem. Soc. **114**, 3643 (1992).

[18] M. Baer, R. Englman, and A. J. C. Varandas, Mol. Phys. (in press). In this publication an extended version of this model is presented and the three-dimensional seam does not appear.