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Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 4754–4755

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COMMENT

Comment on "Optical conversion of conical intersection to avoided crossing" by Y. Arasaki and K. Takatsuka, *Phys. Chem. Chem. Phys.*, 2010, 12, 1239

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Received 28th July 2010, Accepted 8th December 2010
DOI: 10.1039/c0cp01358g

A recent paper in this journal proposed the conversion of conical intersections to avoided crossings by lowering the symmetry with an optical field. The article also claimed that the characters of nonadiabatic transitions caused by avoided crossings and conical intersections are qualitatively different. The present comment shows that this proposal and this claim result from an incorrect appreciation of the nature of conical intersections and avoided crossings. Conical intersections are moved, not removed, by almost all perturbations. Furthermore, there is no dichotomy between avoided crossing mechanisms and conical intersection mechanisms; as the parameters of the problem change and the typical locally avoided crossing involved in nonadiabatic dynamics becomes farther from the conical intersection, there is a gradual shift in the nature of the nonadiabatic transitions, with a continuum of possible behaviors, not just two.

A recent paper in this journal[1] proposed the conversion of conical intersections to avoided crossings by lowering the symmetry with an optical field. The article also claimed that the character of nonadiabatic transitions caused by avoided crossings and conical intersections are qualitatively different. This proposal and this claim result from an incorrect appreciation of the nature of conical intersections and avoided crossings. We will discuss this in the rest of this comment. As in ref. 1, we neglect spin–orbit coupling, so that all electronic wave functions and matrix elements can be taken as real. Apart from brief remarks, we confine ourselves to pointing out the error of ref. 1, and we do not attempt an exhaustive study of the behavior of conical intersections under perturbations.

A general polyatomic system with N atoms has $F = 3N - 6$ internal degrees of freedom, and conical intersections occur in $F - 2$ degrees of freedom.[2] Consider the NO_2 system of ref. 1; in this case a conical intersection can occur along a curve in a three-dimensional internal-coordinate space. As coordinates, we may choose (for example) the sum of the N–O distances, ξ, their difference, η, and the ONO angle, θ. Ref. 1 employed a two-state diabatic representation with matrix elements V_{ij}, and in the notation of ref. 1, a conical intersection will occur wherever the two criteria

$$V_{12} = 0 \tag{1}$$

and

$$\Delta \equiv V_{11} - V_{22} = 0 \tag{2}$$

are satisfied. Both V_{12} and Δ are continuous real functions of the three coordinates, so in general there will be regions where V_{12} is positive, regions where it is negative, and the borders (two-dimensional surfaces between those regions) where it is zero; along the border surfaces the first of the conical intersection criteria is satisfied. (In accordance with the universal practice of Born–Oppenheimer theory, we choose the signs of the wave functions so that they are continuous as functions of the nuclear coordinates and therefore undergo no abrupt and discontinuous sign changes.) The same considerations apply to Δ. A zero (border) surface for V_{12} may intersect with one for Δ along a curve, and along this curve there will be a conical intersection.

In general, these zero-surfaces must be found by calculation. But in systems like unperturbed NO_2, at least one surface where V_{12} equals zero can be found by symmetry because V_{12} vanishes identically on the plane $\eta = 0$ if the two states transform according to A_1 and B_1 or A_2 and B_2 under the C_{2v} symmetry that holds in this case. On one side of this plane, say $\eta > 0$, V_{12} will be positive, and on the other side it will be negative. There may, of course, be other zero-surfaces for V_{12}, but these must be found by calculation if they exist. Conical intersections will occur wherever a zero-surface for Δ intersects the plane $\eta = 0$.

Now what happens if we apply a perturbation, such as an external field? Clearly, the forms of the functions V_{12} and Δ will change, and V_{12} will no longer necessarily be zero

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wherever $\eta = 0$, but, apart from large and very special perturbations, both V_{12} and Δ will still have the property of having negative and positive regions, separated by borders where they are zero. Thus, there will still in general be conical intersections, with their locations simply shifted by small amounts by small perturbations, by larger amounts by larger ones, and removed only by very special large perturbations. The conclusion of ref. 1 that the conical intersection is replaced by a totally avoided crossing is thus false because the CI is shifted in location, not eliminated. An analog would be a chemical substitution that breaks symmetry; for example, NaH_2 has a conical intersection seam in C_{2v} geometries, whereas a system with similar valence bond structure, for example, Na + HCl, would be expected to have corresponding conical intersections, but at nonsymmetrical geometries. In this respect, there is not a major distinction between symmetry-allowed and symmetry-required conical intersections. Another example of a conical intersection being moved rather than removed by a perturbation is the case where a molecule is placed into solution, as in a recent example involving the photoactive yellow protein chromophore.[3]

(We also note that although—to make the argument as clear as possible—much of the present discussion is written for the case of a triatomic molecule, the general conclusion that conical intersections are moved, not removed, by perturbations is true for arbitrarily large polyatomic molecules. In NH_3, for example, where $F = 6$, there is C_{3v} symmetry in a 2-dimensional subspace, and in this subspace states transforming under the E representation will be degenerate. This subspace is thus a subspace of the 4-dimensional CI subspace for these states. A perturbation that removes the symmetry will complicate the task of locating the CI, but will not remove it. The situation is more complicated when spin–orbit coupling is included and the total electronic spin is half-odd-integer,[4] but it is beyond our scope to discuss that here because it is not relevant to the error in ref. 1.)

In general, due to the reduced dimensionality, a nuclear trajectory does not pass precisely through a conical intersection, but for trajectories passing near to the conical intersection, there will be a locally avoided crossing along the path, where we define a locally avoided crossing as a local minimum in the energy gap between two states as a function of distance along a path, in this case the path being the nuclear trajectory. Thus, even in the presence of conical intersections, most nonadiabatic transitions are dominated by passage through locally avoided crossings that sit, so to speak on the "shoulder" (lower cone) of the conical intersection.

What about the case of a totally avoided crossing, defined as a case where the energy gap, considered as a function in the entire nuclear configuration space, experiences a minimum but is never zero? This case hardly exists. In particular, it has been shown[5] that "when one encounters a local minimum along a path of the gap between two potential energy surfaces, almost always it is the shoulder of a conical intersection." It may be the case that the lowest-energy point on the seam of conical intersection is dynamically or even energetically inaccessible under the conditions of an experiment. In such a case, the locally avoided crossing may be some distance away from the conical intersection. But there is no dichotomy between avoided crossing mechanisms and conical intersection mechanisms; as the parameters of the problem change and the typical locally avoided crossing involved in the dynamics becomes farther from the conical intersection, there is a gradual shift in the nature of the nonadiabatic transitions, with a continuum of possible behaviors, not just two.

We conclude that, although we do not question the correctness of the calculations in ref. 1, the interpretation in terms of the disappearance of the conical intersection is wrong.

This material is based upon work supported by the National Science Foundation under grant no. CHE09-56776.

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