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Up to a Sign. The Insidious Effects of Energetically Inaccessible Conical Intersections on Unimolecular Reactions

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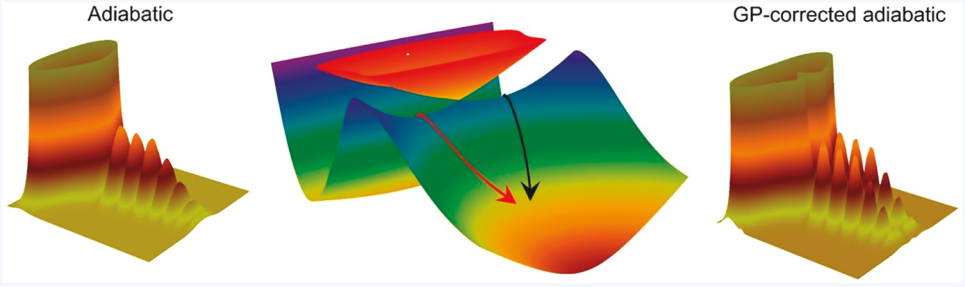

CONSPECTUS: It is now well established that conical intersections play an essential role in nonadiabatic radiationless decay where their double-cone topography causes them to act as efficient funnels channeling wave packets from the upper to the lower adiabatic state. Until recently, little attention was paid to the effect of conical intersections on dynamics on the lower state, particularly when the total energy involved is significantly below that of the conical intersection seam. This energetic deficiency is routinely used as a sufficient condition to exclude consideration of excited states in ground state dynamics. In this account, we show that, this energy criterion notwithstanding, energy inaccessible conical intersections can and do exert significant influence on lower state dynamics. The origin of this influence is the geometric phase, a signature property of conical intersections, which is the fact that the real-valued electronic wave function changes sign when transported along a loop containing a conical intersection, making the wave function double-valued. This geometric phase is permitted by an often neglected property of the real-valued adiabatic electronic wave function; namely, it is determined only *up to an overall sign*. Noting that in order to change sign a normalized, continuous function must go through zero, for loops of ever decreasing radii, demonstrating the need for an electronic degeneracy (intersection) to accompany the geometric phase. Since the total wave function must be single-valued a compensating geometry dependent phase needs to be included in the total electronic-nuclear wave function. This Account focuses on how this consequence of the geometric phase can modify nuclear dynamics energetically restricted to the lower state, including tunneling dynamics, in directly measurable ways, *including* significantly altering tunneling lifetimes, thus confounding the relation between measured lifetimes and barrier heights and widths, and/or completely changing product rotational distributions.

Some progress has been made in understanding the origin of this effect. It has emerged that for a system where the lower adiabatic potential energy surface exhibits a topography comprised of two saddle points separated by a high energy conical intersection, the effect of the geometric phase can be quite significant. In this case topologically distinct paths through the two adiabatic saddle points may lead to interference. This was pointed out by Mead and Truhlar almost 50 years ago and denoted the Molecular Aharonov-Bohm effect. Still, the difficulty in anticipating a significant geometric phase effect in tunneling dynamics due to energetically inaccessible conical intersections leads to the attribute *insidious* that appears in the title of this Account. Since any theory is only as relevant as the prevalence of the systems it describes, we include in this Account examples of real systems where these effects can be observed. The accuracy of the reviewed calculations is high since we use fully quantum mechanical dynamics and construct the geometric phase using an accurate diabatic state fit of high quality *ab initio* data, energies, energy gradients, and interstate couplings. It remains for future work to establish the prevalence of this phenomenon and its deleterious effects on the conventional wisdom discussed in this work.

INTRODUCTION: ADIABATIC STATES

A cornerstone of modern theoretical chemistry is the Born−Huang[1] approximation, which separates the electronic and nuclear motions based on their mass disparity. Since the total Schrödinger equation

$$[\hat{H}^{\text{total}}(\mathbf{r}, \mathbf{R}) - E_N^{\text{total}}]\Psi_N^{\text{total}}(\mathbf{r}, \mathbf{R}) = 0 \quad (1)$$

is rarely solvable for molecular systems, it is advantageous to expand the total wave function in terms of products of adiabatic (a) electronic and nuclear wave functions:

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$$\Psi_N^{\text{total}}(\mathbf{r}, \mathbf{R}) = \sum_{n=1}^{N^{\text{state}}} \Phi_n^{(a)}(\mathbf{r}; \mathbf{R})\Theta_{N,n}^{(a)}(\mathbf{R}) \tag{2}$$

Here, $\mathbf{r}$ and $\mathbf{R}$ denote the electronic and nuclear coordinates, respectively. $n \in [1, N^{\text{state}}]$ and N label electronic and ro-vibrational states, respectively. The adiabatic electronic wave functions are taken as the eigenfunctions of the electronic Hamiltonian:

$$[\hat{H}^e(\mathbf{r}; \mathbf{R}) - E_n^{(a)}(\mathbf{R})]\Phi_n^{(a)}(\mathbf{r}; \mathbf{R}) = 0 \tag{3}$$

in which the semicolon indicates that this equation is solved at fixed nuclear geometries. The eigenvalues form the adiabatic potential energy surfaces (PESs), which are $(3N^{\text{nuc}} - 6)$-dimensional functions of the nuclear coordinates where N^{nuc} is the number of atoms in the system.

While the Born−Oppenheimer Approximation (BOA), eq 2 with $N^{\text{state}} = 1$, works well near the equilibrium geometry of the ground electronic state, it is known to fail at or near electronic degeneracies. This was realized in early days of quantum mechanics by London.[2] The most commonly encountered degeneracy in polyatomic molecules is the conical intersection (CI).[3−6] This degeneracy, which is not a single isolated point but spans a $(3N^{\text{nuc}} - 8)$-dimensional subspace or seam, facilitates transitions between different electronic states, a process known to manifest in many important reactions, particularly when photoexcitation is involved.[7−10] A complete understanding of the nonadiabatic aspects of these processes has not been achieved and indeed nonadiabatic interactions in general remain a major frontier in physical chemistry.[11−17] In this Account we consider an often ignored class of nonadiabatic processes for which the dynamics takes place on what appears to be a single adiabatic state but for which nonadiabatic interactions play a role. These processes, referred to as nonadiabatic tunneling, are a type of tunneling for which traditional single-state adiabatic models of tunneling fail.

NUCLEAR DYNAMICS: BEYOND ADIABATIC APPROXIMATION

The standard single-state BOA[18] is obtained by inserting eq 2 with $N^{\text{state}} = 1$, into eq 1 and using eq 3 which gives

$$\left[\sum_I \frac{1}{2M_I}(-\nabla_I^2 + k_{I,I}^{n,n}) + E_n^{(a)}(\mathbf{R}) - E_N\right]\Theta_{N,n}^{(a)}(\mathbf{R}) = 0 \tag{4}$$

where

$$k_{I,I}^{n,n} = \langle \nabla_I \Phi_n^{(a)}(\mathbf{r}; \mathbf{R})|\cdot \nabla_I \Phi_n^{(a)}(\mathbf{r}; \mathbf{R})\rangle_{\mathbf{r}} \tag{5}$$

is the diagonal Born−Oppenheimer correction (DBOC), and is routinely neglected in the adiabatic approximation. In eq 4, $\hat{T} = -\sum_I \frac{1}{2M_I}\nabla_I^2$ is the nuclear kinetic energy operator with M_I the mass of the Ith atom.

Geometric Phase: Global Influence

For polyatomic molecules, it is convenient to take the nuclear wave functions $(\Theta_{N,n}^{(a)}(\mathbf{R}))$ to be single-valued functions of $\mathbf{R}$, leaving the single or double valuedness to be decided by the adiabatic electronic wave functions $(\Phi_n^{(a)}(\mathbf{r};\mathbf{R}))$. Since $\Phi_n^{(a)}(\mathbf{r};\mathbf{R})$ are real-valued, they are only determined *up to a sign*. Thus, when $\Phi_n^{(a)}$ is transported along a closed loop, both $\pm\Phi_n^{(a)}$ are possible outcomes. As early as 1958, Longuet-Higgins identified the sign change, $\Phi_n^{(a)} \rightarrow -\Phi_n^{(a)}$, along a closed loop encircling a CI in Jahn−Teller systems, giving rise to double-valued electronic wave functions.[19] For Jahn−Teller systems, the phase $(e^{i\pi} = -1)$ is a consequence of the symmetry-required CIs[3−6] found at the high symmetry geometries. (Interestingly, Teller proved the existence of symmetry-required CIs in these systems in 1937,[20] but it took 20 years for the sign issue to be discovered.) This result is not limited to Jahn−Teller systems, but is quite general, occurring for any system with a CI, symmetry required or accidental. Furthermore, the size and shape of the loop are irrelevant. What determines the phase at the end of the loop is the number of CIs contained in the loop: even numbers including 0, no sign change, odd numbers a sign change. The phase is a consequence of the singular nature of a CI and is often referred to as the geometric phase (GP),[5,21,22] a special case of the Berry's phase.[23] Because the total wave function must be single-valued (how else could one describe quantum interference), the double valuedness has to be corrected by introducing a geometry-dependent phase into the adiabatic electronic wave function.[24] Alternatively the use of a double-valued nuclear basis is possible in favorable high symmetry cases.

GEOMETRIC PHASE: BEYOND CONICAL INTERSECTIONS

The above discussion shows that eq 2 is only correct in the absence of CIs, as is the case in diatomic molecules. For polyatomic molecules, eq 2 must be replaced by

$$\Psi_N^{\text{total}}(\mathbf{r}, \mathbf{R}) = \sum_{n=1}^{N^{\text{state}}} \tilde{\Phi}_n^{(a)}(\mathbf{r}; \mathbf{R})\Theta_{N,n}^{(a)}(\mathbf{R})$$
$$\tilde{\Phi}_n^{(a)}(\mathbf{r}; \mathbf{R}) = e^{iA_n(\mathbf{R})}\Phi_n^{(a)}(\mathbf{r}; \mathbf{R}) \tag{6}$$

where the sole purpose of $e^{iA_n(\mathbf{R})}$ is to make $\tilde{\Phi}_n^{(a)}(\mathbf{r}; \mathbf{R})$ single-valued. Note the single-valued electronic wave function remains an eigenfunction of eq 3, but is now complex-valued.

Substituting eq 6 into eq 1 and using eq 3, we have the nuclear Schrödinger equation:

$$[\hat{T} + E_n^{(a)}(\mathbf{R}) - E_N^{\text{total}}]\Theta_{N,n}^{(a)}(\mathbf{R}) - \sum_{n'}\left\{\sum_I\left[\frac{\tilde{\mathbf{f}}_I^{n,n'}(\mathbf{R})\cdot\nabla_I}{M_I} + \frac{\tilde{g}_{I,I}^{n,n'}(\mathbf{R})}{2M_I}\right]\right\}\Theta_{N,n'}^{(a)}(\mathbf{R}) = 0 \tag{7}$$

The adiabatic states are coupled by the vector $(\tilde{\mathbf{f}})$ and scalar $(\tilde{g})$ couplings:

$$\tilde{\mathbf{f}}_I^{n,n'}(\mathbf{R}) = \langle \tilde{\Phi}_n^{(a)}(\mathbf{r}; \mathbf{R})|\nabla_I|\tilde{\Phi}_{n'}^{(a)}(\mathbf{r}; \mathbf{R})\rangle_{\mathbf{r}} \tag{8}$$

$$\tilde{g}_{I,I}^{n,n'}(\mathbf{R}) = \langle \tilde{\Phi}_n^{(a)}(\mathbf{r}; \mathbf{R})|\nabla_I^2|\tilde{\Phi}_{n'}^{(a)}(\mathbf{r}; \mathbf{R})\rangle_{\mathbf{r}} \tag{9}$$

The above adiabatic representation can be formally used to study nonadiabatic dynamics.

The single-state form of eq 7

$$\left\{\sum_I\left[\frac{1}{2M_I}(-i\nabla_I + \mathbf{A}_I^{(n)})^2 + k_{I,I}^{n,n}\right] + E_n^{(a)}(\mathbf{R}) - E_N\right\} \times\Theta_{N,n}^{(a)}(\mathbf{R}) = 0 \tag{10}$$

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describes adiabatic nuclear dynamics when the effect of energetically inaccessible CIs must be considered. Taking explicit account of the product form of $\tilde{\Phi}_n^{(a)}$ the complex phase of $\tilde{\mathbf{f}}_I^{n,n}$ gives rise to a vector potential (VP) $[\nabla_I A_n(\mathbf{R}) = \mathbf{A}_I^{(n)}(\mathbf{R})]$ while $\mathbf{f}_I^{n,n} = 0$. Equation 10 can be compared with eq 4, but it has some major difficulties. First, adiabatic PESs are not smooth at a CI seam; rather, there are cusps, which are very difficult to represent with an analytic function.[25] Furthermore, the derivative coupling which couples adiabatic PESs, and the DBOC which modifies PESs,[26] become singular at the CI seam, making numerical calculations very difficult.[27] Despite these complications, the adiabatic representation remains the conceptual foundation for describing nonadiabatic chemical transformations.

DIABATIC REPRESENTATION: DEFINING CONDITIONS

To avoid these singularities in the adiabatic representation, a diabatic representation is introduced.[28] Diabatic wave functions are defined as wave functions whose derivative couplings vanish. If the adiabatic electronic energies are to be reproduced, the diabatic wave functions must be obtained from the adiabatic wave functions by the adiabatic to diabatic (AtD) transformation[5]

$$\Phi_m^{(d)}(\mathbf{r};\mathbf{R}) = \sum_{n=1}^{N^{\text{state}}} \Phi_n^{(a)}(\mathbf{r};\mathbf{R})\Omega_{n,m}(\mathbf{R}) \tag{11}$$

Ω, an $N^{\text{state}} \times N^{\text{state}}$ unitary transformation, designed to eliminate the derivative coupling, that is

$$\langle \Phi_m^{(d)}(\mathbf{r};\mathbf{R})|\nabla|\Phi_{m'}^{(d)}(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}} = 0 \tag{12}$$

Substituting eq 11 into eq 12 yields

$$\begin{aligned}&\langle \Phi_m^{(d)}(\mathbf{r})|\nabla|\Phi_{m'}^{(d)}(\mathbf{r})\rangle_{\mathbf{r}}\\ &= \sum_{k,k'=1}^{N^{\text{state}}} \Omega_{m,k}^{\dagger}(\mathbf{R})[\mathbf{F}^{k,k'}(\mathbf{R})\Omega_{k',m'}(\mathbf{R}) + \delta_{k,k'}\nabla\Omega_{k',m'}(\mathbf{R})]\\ &= (\Omega^{\dagger}\mathbf{F}\Omega)_{m,m'} + (\Omega^{\dagger}\nabla\Omega)_{m'} = 0\end{aligned} \tag{13}$$

or

$$\nabla\Omega + \mathbf{F}\Omega = 0 \tag{14}$$

where

$$\mathbf{F}^{k,k'}(\mathbf{R}) = [\mathbf{f}_1^{k,k'}(\mathbf{R}), \mathbf{f}_2^{k,k'}(\mathbf{R}), \ldots] \qquad \nabla = [\nabla_1, \nabla_2, \ldots] \tag{15}$$

Using $\Theta^{(d)} = \Omega^{\dagger}\Theta^{(a)}$, the total wave function in the diabatic representation becomes

$$\Psi_N^{\text{total}}(\mathbf{r},\mathbf{R}) = \sum_m \Phi_m^{(d)}(\mathbf{r})\Theta_{N,m}^{(d)}(\mathbf{R}) \tag{16}$$

and the diabatic state nuclear Schrödinger equation becomes

$$[\hat{T} + \varepsilon_{m,m}^{e}(\mathbf{R}) - E_N^{\text{total}}]\Theta_{N,m}^{(d)}(\mathbf{R}) + \sum_{m'\neq m} \varepsilon_{m,m'}^{e}(\mathbf{R})\Theta_{N,m'}^{(d)}(\mathbf{R}) = 0 \tag{17}$$

Here $\varepsilon_{mm}^{e}(\mathbf{R})$ and $\varepsilon_{m,m'}^{e}(\mathbf{R})$ are the diagonal and off-diagonal elements of the diabatic potential energy matrix (PEM). They, unlike their adiabatic counterparts, are smooth functions of the nuclear coordinates easily represented by analytic functions. Since the diabatic functions are single-valued, the GP is absent (implicitly included) in the diabatic representation, provided all coupled adiabatic states have been included in $\Omega(\mathbf{R})$. The diabatic representation is ideally suited for quantum dynamics.[29]

DIABATIC REPRESENTATION: CURL CONDITION

Equation 14 is a key result as it places limitations on $\Omega(\mathbf{R})$. The elements of $\Omega(\mathbf{R})$ are functions of the internal coordinates. For this to be true, the mixed second partial derivatives of each $\Omega_{n,n'}(\mathbf{R})$ must be equal. Equation 14 relates this curl condition[30,31] to the properties of $\mathbf{F}$; $\mathbf{F}$, which satisfies the curl condition, are referred to as removable or curl free. For polyatomic molecules, the curl condition shows that the mixed second partial derivatives are equal, provided all electronic states are included in the AtD transformation, an impossible requirement for *ab initio* wave functions.[30,31] As a result, except for diatomic molecules, which have only one internal degree of freedom, all diabatization schemes are approximate, thus denoted as *quasi*-diabatic representations.[32] However, all electronic structure theories are based on the adiabatic representation, since diabatizations are neither straightforward to determine nor unique.

NUCLEAR DYNAMICS

The nuclear Schrödinger eqs 4 and 10 are central to this Account. The difference between eqs 4 and 10 is the VP, $\mathbf{A}_I^{(n)}$, which is key to understanding the effects of energetically inaccessible CIs. Here, we address the following fundamental question: *If the energy of a chemical reaction on a particular adiabatic state is well below the energy of a CI between this and a higher electronic state, can the dynamics of this reaction still be treated with the adiabatic model?* This question has been raised before by Mead and Truhlar in the context of the H + H_2 exchange reaction,[24] in which the ground electronic state forms a D_{3h} CI with an excited state at 2.78 eV. Studies of this system found that the GP effect canceled out at high collision energies,[33] but later work suggests a pronounced effect in cold collisions.[34] More recently, a combined experimental-theoretical study confirmed the GP effect in the differential cross section.[35]

As noted above, the GP induces the VP for the intersecting adiabatic states. The molecular analog of the Aharonov-Bohm effect,[36] the molecular Aharonov-Bohm (MAB) effect,[37] recognizes the fact that the acquired GP around a CI might allow the reactive "trajectories" to interfere. Below, the insidious but significant nature of the GP in unimolecular reactions is illustrated, particularly in the tunneling regime.

NONADIABATIC TUNNELING

Tunneling is a commonly encountered quantum effect in which quantum particles, such as electrons, penetrate classically forbidden regions. Atomic tunneling is often considered within the adiabatic approximation (i.e., eq 4)[38] and the transmission probability is largely determined by the height and width of the adiabatic tunneling barrier. As a result, it is generally possible to gain information about these barrier parameters by measuring the tunneling probability. The tunneling probability also depends on the mass of the tunneling particle, resulting in measurable isotope effects.

Let us now consider the chemical transformation of a molecule occurring via tunneling on an adiabatic state that

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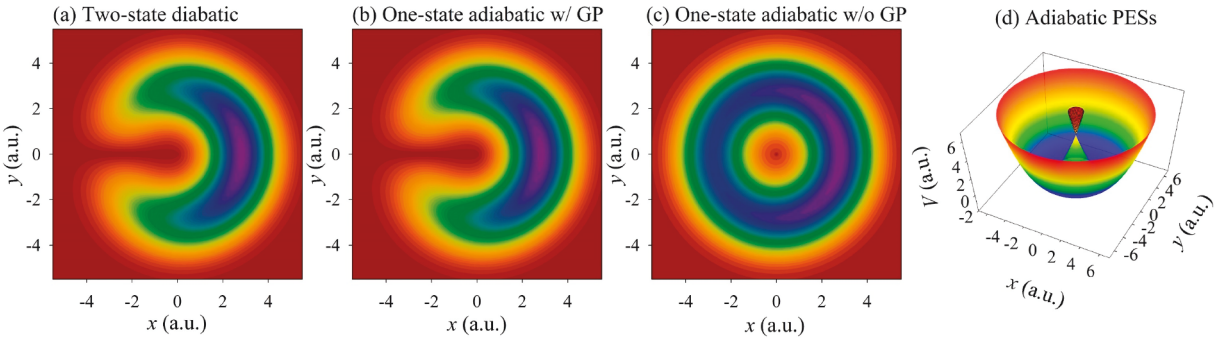

Figure 1. Moduli of the adiabatic wave functions ($|\Theta|$) of the lowest-lying vibronic state in a two-dimensional Jahn−Teller system for (a) the two-state diabatic model, (b) one-state adiabatic model with GP, and (c) one-state adiabatic model without GP. The adiabatic PESs are shown in (d). Reproduced with permission from ref 51. Copyright 2017 American Physical Society.

forms a CI with a higher state. If tunneling occurs at energies that are significantly below the minimum energy CI on the seam, it is a common practice to resort to the single-state adiabatic approximation, namely, BOA, completely ignoring the contribution of the higher state(s).[39−42] This treatment of tunneling ignores the GP, which can lead to qualitatively incorrect results, as discussed below.

Jahn−Teller Systems: Nodes Reveal Nonadiabatic Effects

In a bound Jahn−Teller system, it was recently shown that the presence of a CI at a high symmetry point greatly retards the tunneling through the pseudorotation barriers leading to significantly slower tunneling than that obtained with a BOA treatment.[43,44] In addition, the tunneling wave packet develops a unique nodal structure after passing through the CI, a signature of the MAB effect, suggestive of destructive interference between the two tunneling paths on opposite sides of the CI.[24,33,45−49] This is very different from adiabatic tunneling where no such node can emerge.[50] Our recent work further demonstrated that the BOA model (eq 4) for such a system leads to not only qualitatively incorrect wave functions (see Figure 1c) but also wrong energies for the vibronic levels, even when these states are significantly lower in energy than the CI.[51] Using the VP method,[24] the GP-corrected single-state adiabatic model recovers the correct eigen-energies and nodal structure of the wave functions (Figure 1b), very similar to the exact result (Figure 1a).[51] These results underscore the importance of a GP effect in adiabatic dynamics in the presence of a CI.

Dissociation: Constructive and Destructive Interferences

Similar phenomena exist in unimolecular dissociation where a CI exists near the reaction path. It is clearly seen in Figure 2a, where the adiabatic and diabatic PESs of a two-dimensional (2D) model system are plotted, that the lower adiabatic PES has two equivalent saddle points flanking a CI. To understand the impact of the GP and DBOC, four models were established:[52] Model I is a two-state diabatic model, which is considered exact; Model II is a single-state adiabatic model including GP and DBOC; Model III is a single-state adiabatic model with GP; and Model IV is a single-state adiabatic model without either GP or DBOC.

For the lowest vibronic resonance in Figure 2b (top panels), if the two tunneling paths converge at $y = 0$ after passing through the CI, they would carry exactly the same dynamical phase and no interference would result. However, because of $e^{i\pi} = -1$ from the GP for a closed path around the CI, the paths may interfere destructively, as alluded to for the bound Jahn−Teller system. A consequence of this MAB effect is a node in the dissociative wave function outside the CI ($x > 0$) at $y = 0$ where the destructive interference takes place,[24,43,53] as shown by the exact wave function (Model I) in the same figure. This is in sharp contrast to the adiabatic wave function (Model IV), which has no such node. In the same panel, it is shown that the nodal structure in the dissociative wave function can be recovered if the GP is included with the VP (Models II and III). Thus, the DBOC provides an effective potential barrier which retards tunneling, while the GP slows down tunneling via destructive interference.[52]

Further evidence of GP-induced interference effects in tunneling comes from vibrationally excited resonances. Our 2D calculations found that tunneling lifetimes of vibronic resonances with odd quanta in the y coordinate (the coupling mode) are shorter with the GP than those without.[52] This suggests that for these states the tunneling paths constructively interfere outside the CI, due to the opposite phases already in the initial wave functions. Indeed, the exact dissociative wave function (Model I) for $n_y = 1$ outside the CI possess no node at $y = 0$, as shown in Figure 2b (middle panels). Removing the GP, however, leads to reappearance of the node (Model IV). On the other hand, excitation in the x direction (the tuning mode) leads to no change in the nodal structure (bottom panels in Figure 2b for $n_x = 1$)

In such a case where nonadiabatic tunneling is operative, the tunneling lifetime is dependent on the strength of the nonadiabatic coupling in the off-diagonal element of the diabatic PEM, rather than the height and widths of the adiabatic barrier.[52] *Thus, in such cases, the tunneling lifetime cannot be used to extract barrier information.* We further note that GP could in special cases completely quench tunneling.[54,55]

Nonadiabatic Tunneling: Phenol

The photodissociation of phenol ($C_6H_5OH \rightarrow C_6H_5O+H$)[56,57] provides an experimentally verifiable example of the MAB effect and nonadiabatic tunneling. The system is prepared in its quasi-bound S_1 state leading to O−H bond cleavage through tunneling.[58] As shown in Figure 3, there are equivalent nonplanar saddle points along two adiabatic tunneling paths, resulting from a planar CI coupling the $S_1(^1\pi\pi^*)$ and $S_2(^1\pi\sigma^*)$ states in the Franck−Condon region.[59−61] The g and h vectors[12] of this CI are approximately aligned with the O−H dissociation coordinate (R) and the out-of-plane torsional angle of OH (ϕ), respectively. A reduced-dimensional quantum model for phenol photodissociation was proposed, which includes R, ϕ, and θ (the HOC bending angle).[62,63] While the lifetimes calculated using a four-state *ab initio* based diabatic PEM[61] were found to be in

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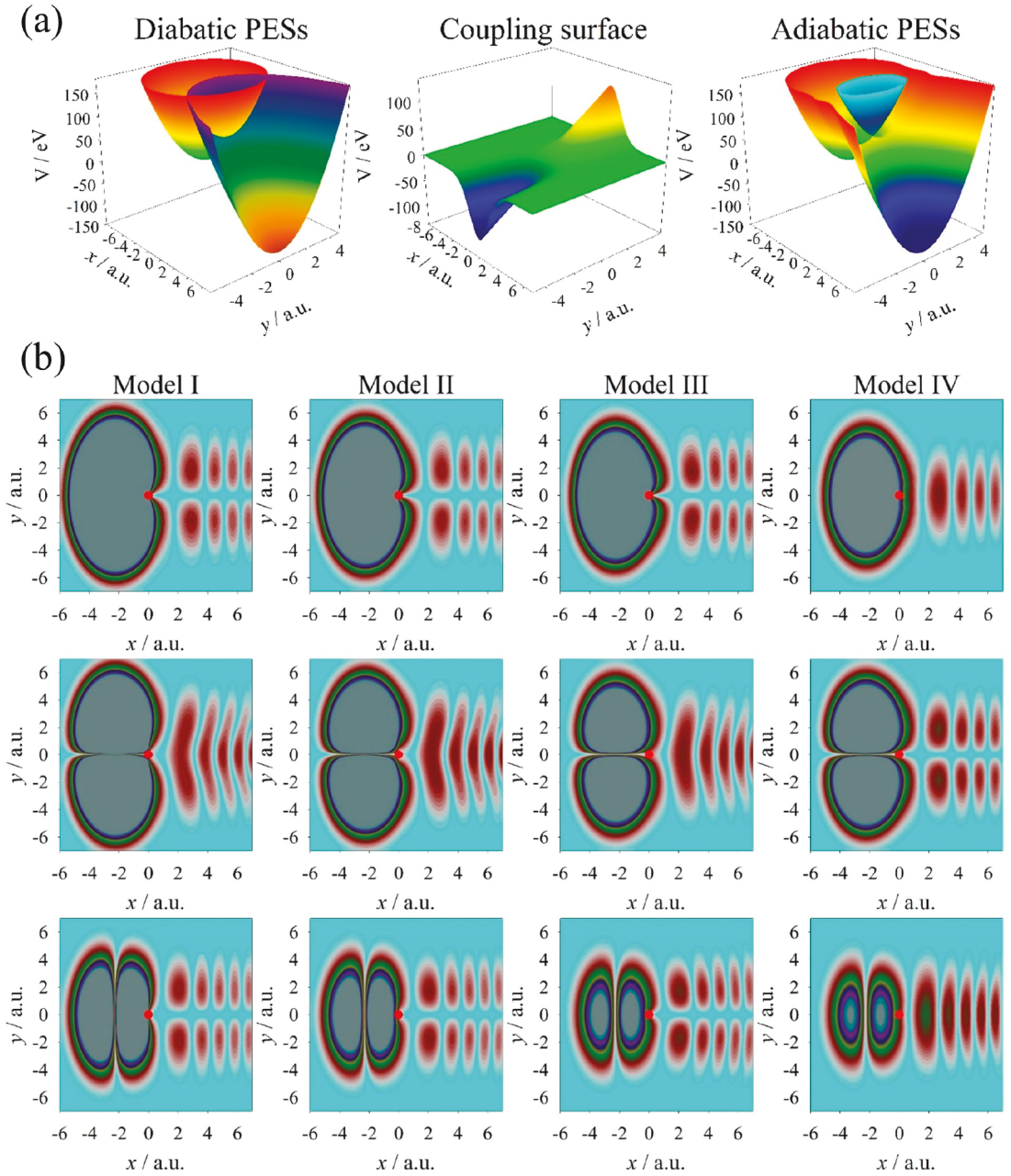

Figure 2. (a) Contour plots of the diabatic PESs, coupling surface, and adiabatic PESs for a two-dimensional dissociative system with a CI. (b) Moduli of the adiabatic dissociative wave functions ($|\Theta|$) for the $(n_x, n_y) = (0, 0)$ (upper panels), (0, 1) (middle panels), and (1, 0) (lower panels) states for Models I, II, III, and IV. Reproduced with permission from ref 52. Copyright 2017 American Chemical Society.

good accord with experimental data,[39,64] the adiabatic counterpart obtained with only the S_1 adiabatic PES is 100 times faster![62] This surprising overestimation of the tunneling lifetime in BOA is readily understood as the absence of GP induced destructive interference discussed above in the 2D case (Model IV), thus yielding a much shorter tunneling lifetime. The destructive interference is clearly illustrated by the node in the dissociative wave function outside the CI.[62,65,66]

Constructing the Geometric Phase

The conceptually appealing adiabatic single-state treatment requires the inclusion of the GP to make the electronic wave function single-valued. This can be done with a VP, which is relatively easy to define in a 2D space in which the CI is simply a point.[43,51] However, it is much more difficult to obtain an accurate VP in a multidimensional space. Since the *ab initio* determined derivative couplings are not removable, they cannot be used to obtain the VP. Instead, a removable approximation of the *ab initio* determined coupling is constructed and used to give the VP.[30,31] An additional complication is that the CI seam is in general multidimensional, not restricted to a few internal coordinates. This behavior of the CI seam presents a central difficulty in the description of multidimensional nonadiabatic (tunneling) dynamics with a GP-corrected single-state model.

A recent work proposed a new and general approach based on an *ab initio* determined diabatic representation consisting of only two electronic states, the state on which the tunneling occurs and the upper state with which the CI seam is formed.[67] In this case, we construct a two-adiabatic-state representation using the line integral of the derivative coupling to construct the

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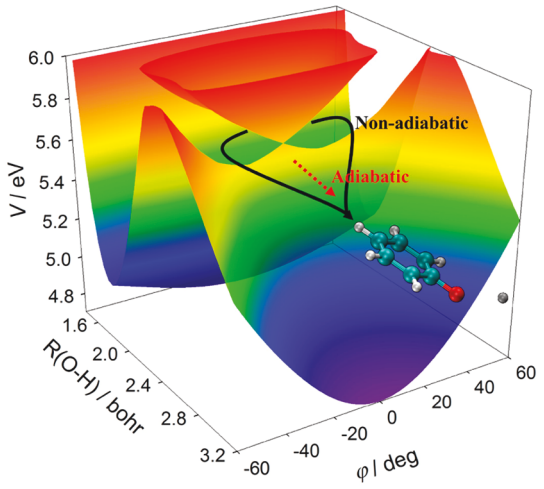

Figure 3. Schematic diagram for the paths in both adiabatic and nonadiabatic tunneling in the photodissociation of phenol via its S_1 state. Reproduced with permission from ref 29. Copyright 2016 Royal Society of Chemistry.

GP. In this case, by design, the derivative coupling is completely removable, so that its line integral is path independent in the simply connected domains that exclude the CI seam.[29,30] Then with the CIs included, the line integral of the derivative coupling can be used to construct the complex-valued geometry-dependent phase needed to completely eliminate the double-valued character of the real-valued adiabatic electronic wave function. As discussed following eq 10, this geometry-dependent phase gives rise to a VP which, when included in the adiabatic representation, accounts for the GP effect in a system with an arbitrary locus of the CI seam and an arbitrary number of internal coordinates. This approach enabled a three-dimensional (3D) treatment of the tunneling facilitated dissociation of the S_1 state of phenol, which is impacted by an accidental C_s symmetry-allowed CI seam (Figure 4). Since the space is 3D and not the simpler 2D case, the seam is a curve rather than a point. The nodal structure of the GP-corrected ground-state vibronic wave function is shown in Figure 4 to map out the CI seam (red line).[68] The dynamical mapping of the CI seam illustrated here in 3D is expected to be present in higher-dimensional problems, albeit with higher level of complexity. We emphasize here that our method of introducing an *ab initio* based VP is completely general and extendable arbitrary dimensions. However, the efficiency of the dynamics method needs improvement in handling the singularities at the CI.

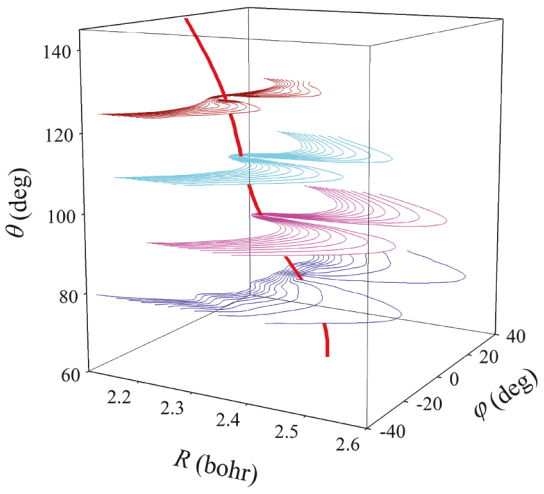

Figure 4. CI seam (red curve) mapped out from the nodal structure of the wave function of the lowest vibronic state in phenol photodissociation in three coordinates. The seam is identified by zeros in the wave function in the (R, φ) plane for distinct values of θ. Reproduced with permission from ref 68. Copyright 2017 American Institute of Physics.

Product State Distributions: Hydroxymethyl

Another example of the MAB/nonadiabatic tunneling effect involves the overtone-induced tunneling dissociation of the hydroxymethyl radical ($CH_2OH \rightarrow H_2CO+H$) on its ground electronic state.[69] The complication here is a CI between the D_0 and D_1 states in the dissociation path, as shown in Figure 5. In a previous theoretical simulation of the unimolecular reaction, only the D_0 PES was used,[40] and the GP effect and DBOC were ignored. We undertook a quantum dynamical study[70] of the unimolecular reaction using a reduced-dimensional model including the O−H (R) and C−O bonds, the C−O−H angle, and the H−C−O−H torsional angle (ϕ),[71] on the *ab initio* based diabatic PEM.[72,73] Interestingly, the overtone lifetimes immediately above the dissociation limit were found to be insensitive to the incorporation of the GP. A detailed analysis revealed that the tunneling paths through the equivalent saddle points on each side of the CI repel each other (see Figure 5), due to the repulsive topography of the PES along ϕ. As a result, their interference is quite weak. This case the GP has limited impact on the tunneling lifetime in a unimolecular dissociation reaction, attributable to an exit channel topography.

However, the GP still exerts an unmistakable influence on the dissociation dynamics. In Figure 5b, two resonance wave functions with and without the GP are displayed. The former has a clear nodal structure in $\phi = 0$ outside the CI ($R > 3.55$ bohr), which is absent in the latter, although the wave functions have relatively small amplitudes near $\phi = 0$.[70] This difference in the wave function symmetry leads to a different product state distribution.[66] Indeed, the rotational state distribution of the H_2CO product is shown to possess different parities with and without the GP. This predicted property can be verified, serving as a signature of the GP effect.[70]

SUMMARY

To summarize, CIs are known to cause nonadiabatic transitions, but their effects on adiabatic dynamics are often ignored. It is shown in this Account that the presence of a CI in the dissociation pathway of unimolecular reactions can have a significant impact on the tunneling dynamics through the GP effect induced by the CI. The GP introduces distinct topological phases for different tunneling paths around the CI in a single-state adiabatic treatment, thus enabling interference. This is a manifestation of *nonadiabatic tunneling*,[62] which refers to a tunneling process which occurs on a single adiabatic state connected to a higher state by an energetically inaccessible CI seam. Nonadiabatic tunneling is fundamentally different from adiabatic tunneling in that the excited state is tacitly involved, even if the minimum energy CI is much higher in energy. This involvement of the excited state is naturally included in a multistate diabatic model, as the coupling term changes the symmetry of the electronic wave functions along the dissociation path. Adiabatically, this tacit involvement of the excited electronic state can be included by a VP, which enables the

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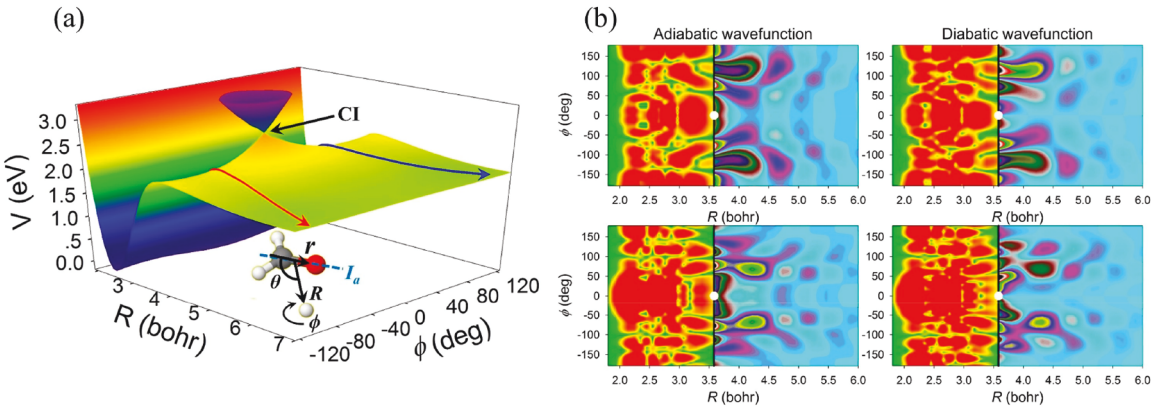

Figure 5. (a) Adiabatic PESs of the two lowest electronic states of CH_2OH as a function of the R and ϕ coordinates. (b) Moduli (left) and real parts (right) of cross sections of 4D wave functions on the ground-state PES as a function of (R, ϕ) for two predissociative resonances, obtained from the single-state adiabatic and two-state diabatic models. The CI position is marked by a white dot. Reproduced with permission from ref 70. Copyright 2018 American Chemical Society.

GP-induced interference on the lower adiabatic state. Such interference can be either destructive or constructive. It can be quite strong in some case, but weak in others. It can impact experimentally measurable properties such as tunneling lifetimes and product state distributions. A clear understanding of the MAB effect requires of determination of an accurate global VP and accurate quantum dynamics. The former can now be achieved with our new method outlined here.

Importantly, the results presented here raise questions concerning the validity of the BOA treatment of tunneling, which is the standard paradigm in discussing molecular spectroscopy and reaction dynamics, when a CI is present in the reaction path. For such systems, the explicit inclusion of the GP is required, even on the ground electronic state.

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Notes

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