Chemical Physics xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

# Investigation of geometric phase effects in photodissociation dynamics at a conical intersection

Foudhil Bouakline

*Max Born Institute, Max Born Strasse 2a, 12489 Berlin, Germany*

ARTICLE INFO

*Article history:*
Available online xxxx

*Keywords:*
Photodissociation
Conical intersection
Geometric phase
Topological unwinding of wavefunctions

ABSTRACT

We investigate the effect of the geometric phase (GP) on photodissociation dynamics at a two-dimensional symmetry-allowed conical intersection (CI). To disentangle the pure effect of the GP from other effects due to non-adiabatic couplings between the two coupled potential energy surfaces, we perform two different calculations, one adopting the diabatic representation which implicitly includes the GP, and another one using the adiabatic picture where GP effects are excluded. To interpret the impact of the GP on nuclear dynamics, we use a recent topological approach (Althorpe et al., 2008 [45]) to completely unwind the nuclear wavefunction from around the CI. This unwinding allows us to extract from the nuclear wavepacket two contributions of reaction paths that wind in different senses around the CI. The solely effect of the GP is to change the sign of the relative phase between their corresponding wavefunctions, and hence to convert any constructive (destructive) interference of the two components, in the asymptotic dissociative limit, into a destructive (constructive) one. This results in a change of the product-state vibrational distribution from only-even (-odd) quanta progression to only-odd (-even) quanta progression. Although our calculations are based on a reduced-dimensionality model Hamiltonian, our observations and conclusions should apply to realistic polyatomic molecules, and could be useful to interpret product-state vibrational distributions of photodissociation experiments.



## 1. Introduction

Conical intersections (CI) of electronic potential energy surfaces [1] are nowadays widely recognised to be ubiquitous in polyatomic molecules [2–4], and to play a major role in their spectroscopy, photodynamics and also chemical reactivity [4–7]. At a CI, the Born–Oppenheimer approximation (stipulating that electronic and nuclear motions are decoupled) breaks down [8–10]. Molecular systems which exhibit such topologies can easily hop between the two coupled electronic states through the funnel of the CI, giving rise to a rich variety of physico-chemical processes [11–18], such as electron transfer, isomerisation, photoinduced unimolecular decay, and radiationless relaxation of electronic excited states.

Another more subtle quantum effect resulting from the presence of conical intersections is the geometric phase (GP) [19,20], also known as the Longuet–Higgins phase, and most commonly as the Berry phase. It is simply the sign change acquired by the electronic wavefunction when the nuclei complete an odd number of loops around the CI. Because the total molecular wavefunction must be single-valued, the GP introduces a corresponding sign change in the boundary condition of the nuclear wavefunction [21–23], whenever the latter encircles the CI. This has important consequences on molecular spectra and also on molecular collisional processes. For instance, it is well-known that the GP shifts the spectrum of a bound molecular system by altering the pattern of nodes in the nuclear wavefunction [24–31]. Also, substantial geometric phase effects in molecular reactive scattering and photodissociation processes have been reported [32–41].

In order to understand the effect of the geometric phase on non-stationary nuclear wavefunctions, one may adopt a semiclassical picture in which a nuclear wavepacket, approaching the neighbourhood of a conical intersection, splits into two components encircling the CI on opposite sides, and eventually interfere in the asymptotic reactive or dissociative limits. For instance, Köppel and coworkers [42,43] demonstrated numerically that the GP leads to destructive self-interference of the two parts of the wavepacket as it exits the CI region. To further unravel the origin of this destructive interference, and to build a quantum analogue of the above semiclassical picture, Althorpe and coworkers [34,44,45] have recently developed a topological approach to completely unwind the nuclear wavefunction encircling the CI. This method uses simple topological arguments, similar to those

*E-mail address:* bouaklin@mbi-berlin.de

http://dx.doi.org/10.1016/j.chemphys.2014.02.010
0301-0104/

previously used in Feynman path integral treatments of the Aharonov–Bohm effect [46–49], to separate the nuclear wavefunction into two contributions, each of which contains all the Feynman paths that wind different numbers of times, and in different senses, around the CI. It is shown that the separation of the wavefunction into even- and odd-looping parts reveals the true effect of the geometric phase on the nuclear wavefunction: It solely changes the sign of the relative phase of these two components. Thus, the recombination and interference of these two parts govern the extent to which dynamical observables are affected by the GP.

This unwinding technique applies to the exact nuclear wavefunction, i.e., the paths that it extracts are true Feynman paths, not Newtonian trajectories. To extract the even- and odd-looping components, the only numerical work required is to add and subtract nuclear wavefunctions computed with and without GP boundary conditions. In addition, it has been recently shown that this topological interpretation applies, not only to situations where nuclear dynamics is restricted to the adiabatic electronic ground state, but also to the case where nuclei evolve on both coupled electronic states [45], and could access the conical intersection seam.

In this contribution, we aim to exploit this unwinding technique to investigate the effect of the Berry phase in photodissociation dynamics at a symmetry-allowed conical intersection. We use a two-dimensional model Hamiltonian of two coupled electronic states involving one reaction coordinate and one coupling mode. To explore the effect of the geometric phase on the photo-induced nuclear dynamics on the two coupled surfaces, and to disentangle its pure effect from other effects due to non-adiabatic couplings, we perform two sets of calculations, (i) one adopting the diabatic picture which implicitly includes the GP, and (ii) another one using the adiabatic representation where the GP is omitted. Nuclear wavefunctions computed in both representations are used to extract two components that wind in different senses around the CI. These two different reaction paths are then exploited to interpret the observed effects of the GP on the dynamics.

The paper is organised as follows. In Section 2, we summarise the basic ingredients of the diabatic and adiabatic representations, used to describe nuclear dynamics at a symmetry-allowed conical intersection, whose main features are given in Section 3. The model Hamiltonian used in our calculations is described in Section 4. In Section 5, we present our results, and discuss the influence of the GP on dynamical observables such as electronic populations, and most importantly its effect on the topology of the wavepacket in the dissociative limit, and on the subsequent product-state vibrational distributions. Finally, in Section 6, we use the topological unwinding technique to interpret the observed effects of the GP on the dynamics. Section 7 concludes the paper.

## 2. Quantum nuclear dynamics in the adiabatic and diabatic representations

We want to describe nuclear motion on two coupled electronic potential energy surfaces. To do so, two representations are invoked, the adiabatic and diabatic ones. Within the adiabatic picture, the nuclear Hamiltonian has the following form [50]

$$\mathbf{H}^{\mathrm{ad}} = \begin{pmatrix} T_{\mathrm{n}} + V_{-} & 0 \\ 0 & T_{\mathrm{n}} + V_{+} \end{pmatrix} + \begin{pmatrix} \Lambda_{11} & \Lambda_{12} \\ \Lambda_{21} & \Lambda_{22} \end{pmatrix} \tag{1}$$

where $T_{\mathrm{n}}$ represents the nuclear kinetic energy operator, and $V_{-}$ and $V_{+}$ are the potential energies of the ground and excited adiabatic electronic states, respectively. These states are coupled through the non-adiabatic matrix elements $\{\Lambda_{\mathrm{ij}}\}$, which are given in mass-scaled coordinates by

$$\Lambda_{\mathrm{ij}} = -\frac{\hbar^2}{2M}(2\mathbf{F}_{ij}\cdot\boldsymbol{\nabla} + G_{ij}) \tag{2}$$

where $\mathbf{F}_{\mathrm{ij}} = \langle\Phi_i|\boldsymbol{\nabla}|\Phi_j\rangle$ is the (vectorial) first derivative coupling matrix element in the adiabatic electronic basis $\{\Phi_{\mathrm{i}}\}$, and $G_{ij} = \langle\Phi_i|\nabla^2|\Phi_j\rangle$ is the (scalar) second derivative coupling matrix element. Numerical wavepacket propagation in the adiabatic picture is potentially difficult because the off-diagonal non-adiabatic couplings become singular at the CI seam. To overcome these numerical problems, one can convert to a (quasi-) diabatic representation of the wavefunction via a unitary transformation [50]

$$H^{\mathrm{d}} = \mathbf{S}\, H^{\mathrm{ad}}\, \mathbf{S}^{+} \tag{3}$$

where the transformation matrix is given by

$$\mathbf{S} = \begin{pmatrix} \cos(\Theta) & \sin(\Theta) \\ -\sin(\Theta) & \cos(\Theta) \end{pmatrix}. \tag{4}$$

The adiabatic–diabatic mixing angle $\Theta$, which is a function of the nuclear coordinates $\{\mathbf{Q}\}$, must be chosen to remove the off-diagonal non-adiabatic kinetic couplings. Although exact diabatic electronic states do not strictly exist [51], several diabatisation schemes [52] have proven to be very efficient to remove the divergent part of the off-diagonal couplings, and to ensure that the residual derivative couplings are vanishingly small. Using these diabatic construction procedures, kinetic derivative couplings are removed and transformed into smooth potential energy couplings, giving rise to the following form of the diabatic nuclear Hamiltonian

$$\mathbf{H}^{\mathrm{d}} = T_{\mathrm{n}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} U_1 & U_{12} \\ U_{21} & U_2 \end{pmatrix}. \tag{5}$$

The adiabatic and diabatic pictures are related through the mixing angle

$$\Theta(\mathbf{Q}) = \frac{1}{2}\arctan\frac{2U_{12}(\mathbf{Q})}{U_2(\mathbf{Q}) - U_1(\mathbf{Q})}. \tag{6}$$

This transformation angle allows to avoid the numerical calculation of the non-adiabatic kinetic couplings, and facilitates their evaluation analytically. After some simple algebra [50,52,53], we can show that

$$\begin{aligned} \mathbf{F} &= \boldsymbol{\nabla}\Theta(\mathbf{Q}) \\ G &= (\boldsymbol{\nabla}\cdot\mathbf{F}) + \mathbf{F}\cdot\mathbf{F}. \end{aligned} \tag{7}$$

Although the adiabatic and diabatic representations are linked by a unitary transformation, and hence, should give the same nuclear measured observables, a subtle difference emerges in the presence of a conical intersection. The geometric phase is implicitly taken into account only in the diabatic picture. In the adiabatic representation, to describe nuclear dynamics correctly, the GP has to be included explicitly on both coupled electronic states.

## 3. Symmetry-allowed conical intersections

Conical intersections are widespread in real polyatomic molecules [4]. Their occurrence requires two different conditions to be fulfilled, the diagonal elements of the diabatic potential matrix given in Eq. (5) must be equal, and the off-diagonal elements must vanish. This gives rise to a conical intersection seam of a dimension $(N - 2)$ in the nuclear coordinate space, where N is the number of the internal nuclear degrees of freedom. In general, there is no symmetry element that would determine the location of conical intersections in the nuclear coordinate space. However, there are some specific cases where symmetry plays an important role in the characterisation of CIs. Here, we consider the case of the so-called *symmetry-allowed conical intersections* [5,8]. They arise from the interaction of two nondegenerate electronic states with different spatial symmetries. For these states to interact, a nuclear distortion of the molecular system along a nonsymmetric nuclear mode is required.

Please cite this article in press as: F. Bouakline, Chem. Phys. (2014), http://dx.doi.org/10.1016/j.chemphys.2014.02.010