The role of geometric phase in the formation of electronic coherences at conical intersections

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The direct observation of non-adiabatic dynamics at conical intersections is a long-standing goal of molecular physics. Novel time-resolved spectroscopies have been proposed which are sensitive to electronic coherences induced by the passage of an excited state wavepacket through a region of conical intersection. Here we demonstrate that inclusion of the geometric phase effect, and its manifestations, is essential for the correct description of the transient electronic coherences that may or may not develop. For electronic states of different symmetry, electronic coherences are suppressed by the geometric phase. Conversely, for states of the same symmetry, appreciable electronic coherences are possible, but their magnitude depends on both the topography of and direction of approach to the conical intersection. These general results have consequences for all studies of electronic coherences at conical intersections.

The concept of seams of conical intersections (CIs) is central to our understanding of ultrafast electronic relaxation from molecular excited states. The points forming the seam correspond to degeneracies between adiabatic electronic states, providing the pathways by which internal conversion may occur on vibrational timescales.1

The existence of such ultrafast non-adiabatic pathways is of immense importance in many areas of photoinduced molecular dynamics, including vision, photosynthesis, the photostability of biomolecules, and light harvesting systems. There is thus global interest in developing experimental methods to directly observe populations and coherences induced by CI mediated molecular dynamics.

Ultrafast spectroscopic probes of dynamics at CIs can be broadly split into two categories. The first encompasses methods which are sensitive to electronic state population dynamics of a vibronic wavepacket as it transits the region of strong non-adiabatic coupling surrounding a CI seam. These include, but are not limited to, ultrafast pump-probe spectroscopies such as transient absorption or time-resolved photoelectron spectroscopy.1-6

The second category is comprised of (generally non-linear) spectroscopic methods which are sensitive to the transient electronic coherences induced as a wavepacket passes through a region encompassing a CI.7-11

For a coherence to exist between two electronic states, two conditions must be satisfied: (i) both electronic states must be appreciably populated; (ii) the nuclear components of the wavepacket on each adiabatic state must have appreciable overlap. Since the nonadiabatic coupling becomes large in the region around a CI, population is readily transferred between the electronic states, ensuring the first criterion is met. However, we show here that the geometric phase effect can lead to zero, or near-zero, overlaps of the nuclear components of the wavepacket on different electronic states. For example, the geometric phase effect is found to suppress the formation of coherences between electronic states of different symmetry. Conversely, for CIs between electronic states of the same symmetry, large coherences may form. However, the magnitude of the electronic coherences thus formed strongly depends on both the CI topography and the direction of approach of the wavepacket.

We begin with a brief exposition of the problem using a minimal model which captures all the fundamental physical effects involved. Consider the excitation of a molecule from its ground electronic state to an excited state manifold spanning by two adiabatic states $|\psi_1^{(a)}\rangle$ and $|\psi_2^{(a)}\rangle$. We consider the case where only $|\psi_2^{(a)}\rangle$ is initially populated. The non-stationary vibronic wavepacket produced in $|\psi_2^{(a)}\rangle$ may evolve towards a CI between the two states, leading to internal conversion and population transfer to $|\psi_1^{(a)}\rangle$. This process is more easily modeled by switching to a set of diabatic states, $|\psi_1^{(d)}\rangle$ and $|\psi_2^{(d)}\rangle$, related to the adiabatic states by a unitary transformation,

$$
\begin{bmatrix}
|\psi_1^{(a)}\rangle \\
|\psi_2^{(a)}\rangle 
\end{bmatrix} =
\begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta 
\end{bmatrix}
\begin{bmatrix}
|\psi_1^{(d)}\rangle \\
|\psi_2^{(d)}\rangle 
\end{bmatrix},
$$

where $\theta$ is the (geometry-dependent) adiabatic-to-diabatic transformation (ADT) angle.

In the diabatic representation, the Hamiltonian matrix reads

$$
H = \hat{T}_n \mathbf{1}_2 + \begin{bmatrix}
W_{11} & W_{21} \\
W_{12} & W_{22}
\end{bmatrix},
$$

where $\hat{T}_n$ is the nuclear kinetic energy operator and $W_{ij}$ are the elements of the diabatic potential matrix, the off-diagonal elements of which account for the non-adiabatic coupling between the two electronic states.
First, consider a system comprised of two electronic states of different symmetry. The simplest possible model correctly accounting for the underlying physics and symmetries of this problem is a two-mode linear vibronic coupling (LVC) Hamiltonian, $\hat{H}_{LVC}$, expressed in terms of a totally symmetric tuning mode $q_t$ and a coupling mode $q_c$:

$$\hat{H}_{LVC} = \left[ \hat{T}_n + \frac{1}{2} \left( \omega_t q_t^2 + \omega_c q_c^2 \right) \right] 1_2 + \left[ \kappa_1 q_t \lambda q_c \frac{b_1}{\kappa_2 q_c} \Delta + \kappa_2 q_c \right].$$ \hspace{1cm} (3)

This model describes a system of shifted, coupled harmonic oscillators with frequencies $\omega_t/\omega_c$ and a CI located at $Q_{C1} = (q_t = \Delta/(\kappa_1 - \kappa_2), q_c = 0)$. Note that the coupling mode in this case is non-totally symmetric, with a symmetry given by the direct product of the irreducible representations generated by the two electronic states.

The quantity of interest here is the magnitude of the coherence between the adiabatic electronic states as the excited state wavepacket passes through the CI. Let $\Psi(t)$ denote the total vibronic wavepacket, which can be expressed in the Born-Huang framework as

$$\Psi(t) = \sum_{j=1}^{2} |\psi_j^{(a)}\rangle \chi_j^{(a)}(q_t, q_c, t).$$ \hspace{1cm} (4)

where the $\chi_j^{(a)}$ are the adiabatic nuclear wavepackets.

The magnitude of the coherence between the electronic states is given by the absolute value of off-diagonal element of the reduced electronic density matrix in the adiabatic representation,

$$\rho_{12}^{(a)}(t) = \langle \Psi(t) | \psi_1^{(a)} \rangle \langle \psi_2^{(a)} | \Psi(t) \rangle = \langle \chi_1^{(a)}(t) | \chi_2^{(a)}(t) \rangle.$$ \hspace{1cm} (5)

As stated above, in order for $|\rho_{12}^{(a)}(t)|$ to be large in value, two conditions must be met: both electronic states must be populated and the nuclear wavepackets, $\chi_j^{(a)}$, on each adiabatic state must have appreciable overlap. The strong non-adiabatic coupling in the CI region ensures that the first condition is met. The second condition, however, is generally not satisfied when the electronic states are of different symmetry.

The reason for poor overlap between the two adiabatic nuclear wavepackets of concern is best seen by re-writing $\rho_{12}^{(a)}(t)$ as

$$\rho_{12}^{(a)}(t) = A_{12}(t) + B_{12}(t),$$ \hspace{1cm} (6)

$$2A_{12}(t) = \langle \chi_1^{(d)} | \sin 2\theta | \chi_1^{(d)} \rangle + \langle \chi_2^{(d)} | \sin 2\theta | \chi_2^{(d)} \rangle,$$ \hspace{1cm} (7)

$$2B_{12}(t) = \left\{ \langle \chi_1^{(d)} | \chi_2^{(d)} \rangle + \langle \chi_1^{(d)} | \cos 2\theta | \chi_2^{(d)} \rangle \right\} + h.c.$$ \hspace{1cm} (8)

where $\theta$ is the ADT angle, and the $\chi_j^{(d)}$ are the diabatic nuclear wavepackets. In the following, we will refer to $A_{12}$ as the “on-diagonal” contribution to $\rho_{12}^{(a)}$, and $B_{12}$ as the “off-diagonal” contribution.

We can show that both the $A_{12}$ and $B_{12}$ terms in Equation (7) vanish using the following simple symmetry arguments:

1. Because the two electronic states are of different symmetry, the coupling mode $q_c$ will be non-totally symmetric. This implies that $W_{11}$ and $W_{22}$ are even functions with respect to $q_c$, while $W_{12}$ is an odd function of $q_c$.

2. Given the even symmetry of $W_{22}$ with respect to $q_c$, and assuming vertical excitation from the ground state, $\chi_2^{(d)}$ will be an even function of $q_c$.

3. Given the odd symmetry of $W_{12}$ with respect to $q_c$ and the even symmetry of $\chi_2^{(d)}$, the nuclear wavepacket $\chi_2^{(d)}$ formed on the lower electronic state will have a node along the coupling mode $q_c$, and thus will be an odd function of this coordinate.

4. Using the relation

$$2\theta = \arctan \left( \frac{2W_{12}}{W_{22} - W_{11}} \right),$$ \hspace{1cm} (9)

it can be shown that the functions $\sin 2\theta(q_t, q_c)$ and $\cos 2\theta(q_t, q_c)$ are odd and even with respect to $q_c$, respectively (see the Supplementary Information for more details).

Given these symmetries, we see that the integrands in both Equations (7) and (8) are all overall odd with respect to $q_c$ and vanish in this two-mode LVC model. We conclude that electronic coherences are suppressed for CIs between states of different symmetry.

As detailed in the Supplementary Information, the symmetries of $\sin 2\theta(q_t, q_c)$ and $\cos 2\theta(q_t, q_c)$ are intimately linked to the geometric phase effect. Further, the geometric phase effect will exist if the leading term in the diabatic coupling is odd with respect to $q_c$. This symmetry is realized in the LVC model above and is responsible for the node in $\chi_2^{(d)}$. This is the reason why the geometric phase effect is present in the case of conical intersections, but is absent for glancing (e.g. Renner-Teller) intersections. Thus, the suppression of coherences between electronic states of different symmetry is best understood as simply a consequence of the geometric phase effect.
To demonstrate this, we note that by forcing the diabatic coupling to contain only even terms with respect to the coupling mode(s), the geometric phase effect may be “turned off”. This can be achieved by replacing $W_{12}$ in Equation 2 by its absolute value: $W_{12} \rightarrow |W_{12}|$. In the following, we denote the physically correct Hamiltonian as $H_{\text{wGP}}$ (i.e. with geometric phase), and the Hamiltonian with $W_{12}$ replaced by its absolute value by $H_{\text{noGP}}$ (i.e. no geometric phase). Importantly, using $H_{\text{noGP}}$ has no effect on the adiabatic potential energy surfaces. However, it allows us to clearly demonstrate the role of the geometric phase effect on the formation of electronic coherences. In the following, we perform wavepacket propagations using both $H_{\text{wGP}}$ and $H_{\text{noGP}}$ and track the resulting changes in the values of $|\rho_{12}^{(a)}(t)|$.

As a representative system, we choose the excited electronic states of the same symmetry. Here, the coupling mode $q_c$ will generate the totally symmetric irreducible representation of the point group of the molecule. Hence, there can exist non-zero gradients of diabatic potentials with respect to $q_c$, and the diabatic nuclear wavepackets $\chi_1^{(d)}$ will no longer necessarily be even or odd functions of it. Accordingly, neither the on- or off-diagonal contributions to $\rho_{12}^{(a)}$ necessarily vanish, and it is possible for appreciable electronic coherences to form.

The magnitude of the electronic coherence formed in this case depends on both the topology of the CI and the direction of approach of the wavepacket to the CI. To see this, consider the first-order expansion of the diabatic potentials about the CI point, and determine whether the CI is “sloped” or “peaked”\cite{15, 16}. In Equation 11, the diabatic and adiabatic representations are equal at the CI point $X_{CI}$, in terms of intersection-adapted coordinates $x$ and $y$\cite{15},

$$W^{(1)}(x, y) = (s_x x + s_y y) I_2 + \begin{bmatrix} -g x & h y \\ h y & g x \end{bmatrix},$$

where $g$ and $h$ are the norms of the gradient difference and non-adiabatic coupling vectors evaluated at the CI point, respectively. The terms $s_x/y$ are the gradients of the average energy with respect to $x$ and $y$ at the CI point, and determine whether the CI is “sloped” or “peaked”\cite{15, 16}. In Equation 11, the diabatic and adiabatic representations are equal at the CI point $X_{CI}$. In order to apply symmetry arguments analogous to the different state symmetry case above, we require that the linear component of the diabatic coupling introduces a node at the centre of $\chi_2^{(d)}$. This is achieved by transforming to a different, but entirely equivalent, diabatic representa-
tion in which the diabatic and adiabatic representations are equal at the centre of the initial wavepacket \( \Psi(t = 0) \). Note that this is possible because the ADT is only defined up to a constant unitary transformation. Let \( \theta_0 \) denote the ADT angle of the original diabatic representation evaluated at the centre of the initial wavepacket. Then, as detailed in the Supplementary Information, the first-order potential in the new diabatic representation takes the form

\[
W^{(1)}(x, y) = (s_x x + s_y y) 1_2 + \begin{bmatrix}
- \cos(2\theta_0)gx + \sin(2\theta_0)hy & \cos(2\theta_0)hx + \sin(2\theta_0)gx \\
\cos(2\theta_0)hy + \sin(2\theta_0)gx & \cos(2\theta_0)gx - \sin(2\theta_0)hy
\end{bmatrix}.
\]

To form an electronic coherence in this first-order vibronic coupling model, there must be both on- and off-diagonal elements which are non-vanishing with respect to either \( x \) or \( y \). The diabatic nuclear wavepackets \( \chi_{1/2}^{(d)} \) will then be neither even nor odd with respect to both nuclear degrees of freedom, allowing for non-zero values of both the on- and off-diagonal contributions to \( \rho_{12}^{(a)} \). Importantly, from Equation 12 we see that this criterion will be satisfied if either: (i) \( s_y \neq 0 \), and/or; (ii) \( \sin(2\theta_0) \neq 0 \). The parameter \( s_y \) determines the tilt of the CI axis along the non-adiabatic coupling direction, whereas \( \theta_0 \) is determined by the position of the initial wavepacket relative to the CI point. In a trajectory-based treatment of the nuclear dynamics, this initial position would be analogous to the “direction of approach” to the CI. In the limiting case of a peaked (i.e., non-tilted) CI and an initial wavepacket displaced from the CI purely along the gradient difference direction, the dominant first-order contributions to the electronic coherence will, again, vanish.

To illustrate the effects of CI topography on electronic coherences, we consider the case where the centre of the initial wavepacket is displaced from the CI point purely along the gradient difference direction. In this case, the magnitude of the electronic coherence will be determined by the tilt of the CI axis along the non-adiabatic coupling direction, and thus, by the parameter \( s_y \) in Equation 12. A two-mode, two-state LVC Hamiltonian was constructed to describe ultrafast, gradient-directed internal conversion through a CI (see the Supplementary Information for the parameters used). The parameter \( s_y \) was varied to yield tilt angles, \( \alpha_y \), of 0.5°, 3°, 7° and 10° along the \( y \) direction. The conical intersections for these tilt angles are shown in Figures 2b through 2f. For \( \alpha_y = 0.5° \), the CI is almost peaked along \( y \). Upon increasing \( \alpha_y \), the slope of the CI along \( y \) gradually increases. As illustrated in Figure 3, the magnitude of the electronic coherence is negligible for a nearly peaked CI (\( \alpha_y = 0.5° \)), and grows with increasing tilt angle along \( y \). Again, the adiabatic state population dynamics are found to be only very weakly affected by the tilt of the CI along \( y \). Finally, we show in Figure 3g the same electronic state populations and coherences, but with the geometric phase effect removed from the model Hamiltonian (via the use of \( H_{\text{geoGP}} \)). Strikingly, the removal of the geometric phase effect results - erroneously - in large magnitude electronic coherences for all tilt angles. This again serves to highlight the importance of correctly accounting for the geometric phase in any simulation of electronic coherences at CIs.

In summary, we have explored the factors affecting the formation of electronic coherences as a wavepacket passes through a CI. Specifically, we have shown that the explicit consideration of the geometric phase effect is essential for a qualitatively correct description of the coherences which may or may not form in the vicinity of a CI. In the case of two electronic states of different symmetry, geometric phase is responsible for the suppression of electronic coherences around a CI. For the unavoidable case of a CI between electronic states of the same symmetry, electronic coherences may in general form. However, their magnitude depends on both the topography of the CI and the direction of approach of the wavepacket to it. These results will help to identify molecular systems for the experimental study of electronic coherences in dynamics at CIs, an opportunity identified in a recent road-map on ultrafast X-ray science. We emphasize that a proper accounting of the geometric phase effect is required in any theoretical study of electronic coherences induced by nuclear motion near CIs. This recognition should result in the simulations required to guide experimental efforts to identify unique signatures of CI dynamics.

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FIG. 1. Dynamics at a conical intersection in pyrazine, showing the nuclear wavepacket evolution in the coupled $B_{3u}(n\pi^*)$ and $B_{2u}(\pi\pi^*)$ states. The magnitude in the $z$ direction in each plot shows the squared absolute values $|\chi_j^{(d)}|^2$ of the diabatic nuclear wavepackets. The phase angle $\zeta_j$ of the wavepackets is encoded in the color maps. (a) Upper diabatic state using $H_{wGP}$. (b) Upper diabatic state using $H_{noGP}$. (c) Lower diabatic state using $H_{wGP}$. (d) Lower diabatic state using $H_{noGP}$. In all cases, the phase angle is plotted along the coupling mode $q_c$ with all other nuclear degrees set to their time-dependent centroid values.

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FIG. 2. Quantum dynamics of pyrazine following vertical excitation to the optically bright $B_{2u}(\pi\pi^*)$ using $\hat{H}_{\text{wGP}}$ (solid lines) and $\hat{H}_{\text{noGP}}$ (dashed lines). (a) Adiabatic state populations. (b) Electronic coherences. It can clearly be seen that omission of the geometric phase leads, incorrectly, to large electronic coherences which vanish when geometric phase is properly included.

FIG. 3. Conical intersections, population and electronic coherence dynamics in a two-mode, two-state model system as a function of the CI tilt angle $\alpha_y$ along the non-adiabatic coupling direction $y$. In panels (a) to (d) we show adiabatic potential surfaces as a function of increasing tilt angle $\alpha_y$. (e) Populations (solid lines) and electronic coherences (dashed lines) computed calculated using the physically correct $\hat{H}_{\text{wGP}}$. (f) Populations and coherences computed using the physically incorrect $\hat{H}_{\text{noGP}}$. It can be seen that the omission of geometric phase leads to artificially larger electronic coherences for all tilt angles. In both cases, the population and coherence dynamics correspond to an initial wavepacket displaced from the CI point only along the gradient difference direction, thus isolating the effects due to CI topography alone.
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