

# Conical Intersections in Dynamics and Spectroscopy

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## Abstract:

Conical intersections (CIs) occur when adiabatic potential energy surfaces (PES) intersect. These points provide the ability for a system to undergo rapid diabatic relaxations from one energy surface to another. Consequently, they also fall outside of the Born-Oppenheimer regime. Conical intersections are important to understanding chemical dynamics, such as in the case relaxation from an excited to a ground state occurs. Rotation in configuration space around a CI point introduces a phase shift in the electronic wavefunction, known as the Berry phase. Advanced femtosecond optical spectroscopy has been able to show experimentally the role CIs play in chemical dynamics. Application uses the Maple Quantum Chemistry Toolbox.

## Introduction

The Born-Oppenheimer approximation is one of the most important simplifications to the many-body Schrodinger equation. By neglecting nuclear motion, the nuclear and electronic motion can be separated, in what is known as an adiabatic system. In this adiabatic regime, nuclear motion occurs incrementally such that the system remains an energy eigenfunction of the instantaneous Hamiltonian at all times. The Born-Oppenheimer approximation leads to the typical paradigm of electronic, rotational, and vibrational degrees of freedom, which can be calculated independently. The limitations of the Born-Oppenheimer regime occur when nuclear motion is coupled to electronic motion, in what is known as vibronic coupling. This diabatic regime commonly occurs in photochemistry or chemical reactions, where nuclear motion becomes significant enough for vibronic coupling to come into play. For every adiabatic state, a potential energy surface (PES) can be plotted. As shown in the theory section below, different excited states potential energy surfaces are often degenerate at a single point, which forms a cone-like shape where the two surfaces intersect. This is the conical intersection, the 0th dimensional space where degeneracy is possible. Conical intersections are key to understanding transitions between states, particularly in excited state dynamics such as that which occurs in photochemistry. For instance in fluorescence, a transition occurs from a singlet excited state  $S_1$  to a singlet ground state  $S_0$ , which may occur as a transition down the seam of a conical intersections.

Conical intersections introduce what is known as a Berry phase (more generally, the geometric phase) to the wavefunction, a measurable phase shift in the electronic wavefunction that is induced by cyclical processes. In an adiabatic system where the wavefunction is parametrized by the nuclear coordinates, motion through parameter space generates a phase factor. The sign of the nuclear wavefunction changes with the opposite of the electronic wavefunction in order to preserve the sign of the total wavefunction.

A closely related phenomenon to that of the conical intersection is that of Dirac cones. This occurs in the solid state, where valence and conduction bands meet at Dirac points, forming the same cone-like structure as conical intersections. In k-space (the space containing the crystal momentum  $\mathbf{k}$  in the plane wave basis), Dirac cones occur at the vertices of the Brillouin zone (the unit cell in k-space). Dirac cones produce similar phenomena to CIs such as Berry phase shifts, which contribute to phenomena such as the anomalous Hall effect and topological insulators.

# Theory/Methodology:

## Born-Oppenheimer Approximation:

The total Hamiltonian can be written as

$$H\psi = E\psi$$

Or in expanded form:

$$\left( \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} - \sum_{k=1}^M \frac{Z_k}{r_{ik}} \right) + \left( \sum_{k=1}^N \left( -\frac{\nabla_k^2}{2} + \sum_{l=1}^M \frac{Z_k Z_l}{r_{lk}} \right) + \sum_{i \neq j=1}^N \frac{1}{|r_i - r_j|} \right) \right) |\Psi_n\rangle = E_n |\Psi_n\rangle$$

The Born-Oppenheimer approximation assumes that the electronic and nuclear wavefunctions are separable

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_k\}, t) = \Psi_{ele}(\{\mathbf{r}_i\}; \{\mathbf{R}_k\}) \Psi_{nuc}(\{\mathbf{R}_k, t\})$$

And  $H = H_{ele} + H_{nuc}$

$$H_{ele} = \left( \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} - \sum_{k=1}^M \frac{Z_k}{r_{ik}} \right) + \sum_{i \neq j=1}^N \frac{1}{|r_i - r_j|} \right)$$

$$H_{nuc} = \sum_{k=1}^N \left( -\frac{\nabla_k^2}{2m_k} + \sum_{l=1}^M \frac{Z_k Z_l}{r_{lk}} \right)$$

Since the motion of the nuclei occurs on a much slower scale than the electronic motion, the kinetic energy term can be neglected.

$$H_{nuc} = \sum_{k=1}^N \sum_{l=1}^M \frac{Z_k Z_l}{r_{lk}}$$

The electronic wavefunction now only has parametric dependence on the nuclear positions  $\mathbf{R}_k$

## Potential Energy Surfaces

An important tool to visualize the energy of a molecule is to plot the energy as a function of nuclear coordinates. This is done under the Born-Oppenheimer approximation, where it is assumed the electrons instantly adapt to incrementally increasing nuclear coordinates. This adiabatic approximation yields potential energy surfaces, multi-dimensional functions of the nuclear coordinates.

## Avoided Crossing:

The breakdown of the Born-Oppenheimer approximation can be described perturbatively. A diabatic perturbation is applied to the system, which can be analyzed with degenerate perturbation theory.

$$H = H_0 + H'$$

$$H' = \begin{bmatrix} V_{1,1} & V_{1,2} \\ V_{2,1} & V_{2,2} \end{bmatrix}$$

$$H = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + \begin{bmatrix} V_{1,1} & V_{1,2} \\ V_{2,1} & V_{2,2} \end{bmatrix} = \begin{bmatrix} E_1 + V_{1,1} & V_{1,2} \\ V_{2,1} & E_2 + V_{2,2} \end{bmatrix}$$

Since  $H'$  is Hermitian,  $H_{2,1} = H_{1,2}$

$$H' = \begin{bmatrix} V_1 & V \\ V^* & V_2 \end{bmatrix}$$

$$H = \begin{bmatrix} E_1 + V_1 & V \\ V^* & E_2 + V_2 \end{bmatrix}$$

Solving for the eigenvalues now yields

$$E = \frac{1}{2} (E_1 + E_2 + V_1 + V_2) \pm \sqrt{(E_1 - E_2 + V_1 - V_2)^2 + 4 |V|^2}$$

For a crossing of states, the two solutions must be degenerate,

$E_- = E_+$  which requires that the square root term be zero, and thus that that

$$E_1 - E_2 + V_1 - V_2 = 0$$

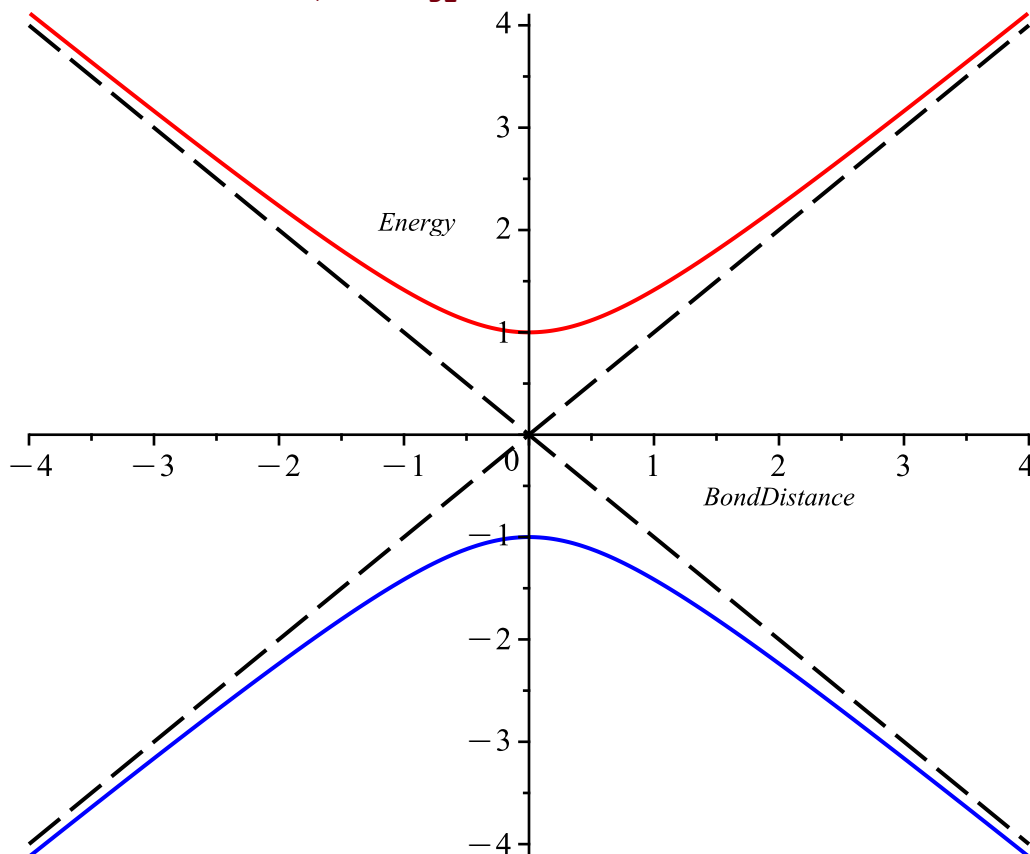
$$|V| = 0$$

The energy is a function of the molecular geometry, so the system of equation must be solved using the parameters corresponding to nuclear positions.

$$E_1(\{\mathbf{R}_k(t)\}) - E_2(\{\mathbf{R}_k(t)\}) + V_1(\{\mathbf{R}_k(t)\}) - V_2(\{\mathbf{R}_k(t)\}) = 0$$

$$|V(\{\mathbf{R}_k(t)\})| = 0$$

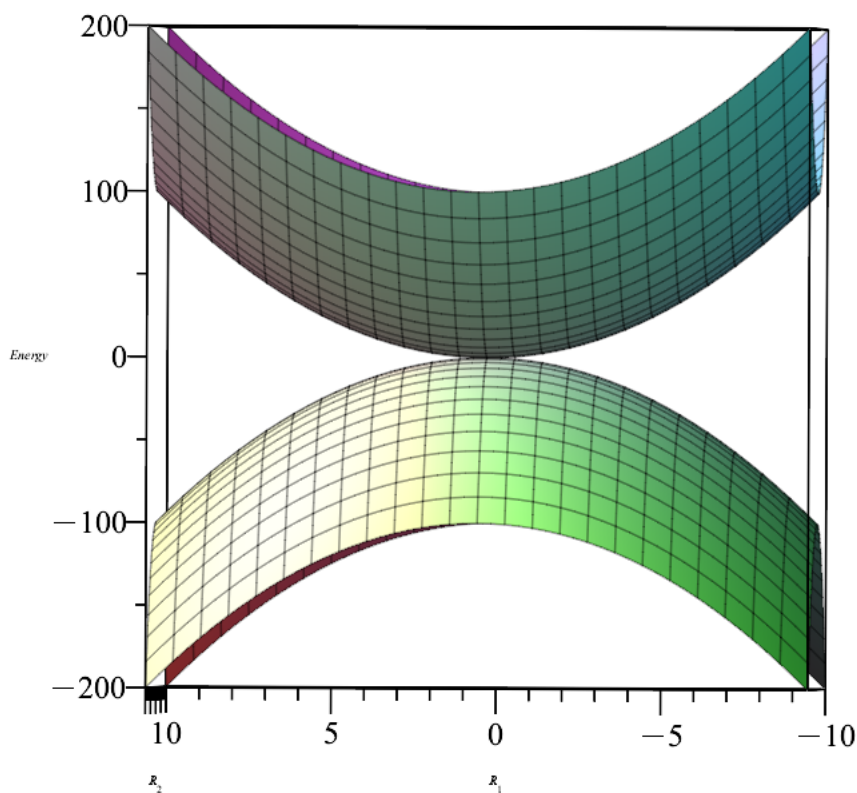
```
> plot([sqrt(x^2+1), -sqrt(x^2+1), x, -x], x = -4..4, color = [red,
blue, black, black], linestyle = [solid, solid, dash, dash],
labels = [BondDistance, Energy])
```



For a diatomic molecule, where only one nuclear coordinate exists, there is only one degree of freedom (the bond length) and this no solution to this system of equations exists. This results in what is known as an avoided crossing, where the potential energy surfaces of two states become very close, but do not actually cross. If a diabatic basis is used (see theory section) instead of an adiabatic basis, then the states do appear to cross, as indicated by the dashed black lines in the above figure. The idealized avoided crossing takes the form of a hyperbola (see figure 1). For polyatomic molecules, the multiple internuclear distances provide the degrees of freedom necessary for there exists a single solution to the equations. It is at this point at which the conical intersection occurs.

```
> plot3d([x^2 + y^2, -x^2 - y^2], x = -10..10, title = "Conical Intersection", labels = [R[1], R[2], Energy]);
```

Conical Intersection



## Adiabatic Theorem and Geometric (Berry) phase:

The Born-Oppenheimer approximation leads to the wavefunction as

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_k\}, t) = \Psi_{ele}(\{\mathbf{r}_i\}; \{\mathbf{R}_k\}) \Psi_{nuc}(\{\mathbf{R}_k\}, t)$$

The time-dependent Schrödinger equation is

$$H(\mathbf{R}(t)) \left| \Psi(\mathbf{R}(t)) \right\rangle = i\hbar \frac{d}{dt} \left( \left| \Psi(\mathbf{R}(t)) \right\rangle \right)$$

Writing as an ansatz:

$$\left| \Psi(\mathbf{R}(t)) \right\rangle = \sum_n c_n(t) \left| \varphi_n(t; \mathbf{R}) \right\rangle \left| \chi_n(\mathbf{r}; \mathbf{R}) \right\rangle = \sum_n c_n(t) \left| \psi_n(\mathbf{r}; \mathbf{R}(t)) \right\rangle$$

A simple example where the system depends on a singular nuclear coordinate will suffice to illustrate the adiabatic theorem. In the adiabatic regime, the system will be an eigenstate of the Hamiltonian at every time point, thus

$$H(\mathbf{R}) \left| \psi_n(\mathbf{r}; \mathbf{R}(t)) \right\rangle = E_n(\mathbf{R}(t)) \left| \psi_n(\mathbf{r}; \mathbf{R}(t)) \right\rangle$$

The system begins in the initial state

$$\left| \Psi(\mathbf{R}(0)) \right\rangle$$

Plugging into the TDSE and projecting the eigenbasis

$$\left\langle \psi_m(\mathbf{R}(t)) \left| i\hbar \frac{d}{dt} \left| \Psi(\mathbf{R}(t)) \right\rangle \right\rangle = \left\langle \psi_m(\mathbf{R}(t)) \left| H(\mathbf{R}(t)) \left| \Psi(\mathbf{R}(t)) \right\rangle \right\rangle$$

Using the product and chain rule to expand the time derivative

$$\dot{c}_m + \sum_n c_n(t) \dot{\mathbf{R}} \left\langle \psi_m(\mathbf{R}(t)) \left| \frac{\partial}{\partial \mathbf{R}} \left| \Psi(\mathbf{R}(t)) \right\rangle \right\rangle = -\frac{i}{\hbar} E_m(\mathbf{R}(t)) c_m(t)$$

The adiabatic approximation means that the terms in the summation  $m \neq n$  can be ignored

$$\dot{c}_m = - \left[ \dot{\mathbf{R}} \left\langle \psi_m(\mathbf{R}(t)) \left| \frac{\partial}{\partial \mathbf{R}} \left| \psi_m(\mathbf{R}(t)) \right\rangle \right\rangle - \frac{i}{\hbar} E_m(\mathbf{R}(t)) \right] c_m(t)$$

Integrating this gives

$$c_m(t) = \exp \left( -\frac{i}{\hbar} \int_0^t dt' E_m(\mathbf{R}(t')) \right) e^{i\gamma_m(t)}$$

Where

$$\gamma_m(t) = i \int_0^t dt' \dot{\mathbf{R}} \left\langle \psi_m(\mathbf{R}(t')) \left| \frac{\partial}{\partial \mathbf{R}} \left| \psi_m(\mathbf{R}(t')) \right\rangle \right\rangle$$

The total wavefunction can be written as

$$\left| \Psi(\mathbf{R}(t)) \right\rangle = e^{-\frac{i}{\hbar} \int_0^t dt' E_m(\mathbf{R}(t'))} e^{i\gamma_n(t)} \left| \psi_n(\mathbf{R}) \right\rangle$$

More generally, for a multi-dimensional problem the Berry phase is

$$\gamma_m(t) = i \int_0^t dt' \dot{\mathbf{R}} \cdot \left\langle \psi_m(\mathbf{R}(t')) \left| \nabla_{\mathbf{R}} \left| \psi_m(\mathbf{R}(t')) \right\rangle \right\rangle$$

Where the Berry connection is

$$A(\mathbf{R}) = i \langle \psi_m(\mathbf{R}) | \nabla_{\mathbf{R}} | \psi_m(\mathbf{R}) \rangle$$

Thus, the Berry phase can be written as a path integral independent of time

$$\gamma_n(C) = i \oint_C \langle \psi_n(\mathbf{R}) | \nabla_{\mathbf{R}} | \psi_n(\mathbf{R}) \rangle \cdot d\mathbf{R}$$

Or alternatively,

$$\gamma_n(C) = i \oint_C d\mathbf{S} \cdot \boldsymbol{\Omega}$$

Where  $\boldsymbol{\Omega}$  is the Berry curvature, a second rank tensor.

The Berry phase is Gauge invariant, in other words, there is a freedom to construct the phase factor by multiplying  $\psi_m$  by some factor  $e^{i\beta(\mathbf{R})}$

The Berry phase is observed as a change in the sign of the wavefunction as it circles the conical intersection. A rotation around the CI in parameter space results in a path-dependent Berry phase. The exact value of this phase depends on the number of CIs enclosed by the path. An odd number of CIs enclosed results in an odd multiple of  $\pi$ , and vice versa for even numbers of enclosed CIs. If no CIs are surrounded, then the Berry phase is zero. The Chern theorem postulates that

## Diabatic Representations:

Diabatic states are used to describe rapid processes where the adiabatic theorem does not hold. The coupling term in this case is the non-negligible nuclear kinetic energy term, which becomes relevant during rapid molecular motion. Diabatic states are found by diagonalizing the nuclear kinetic term in the Hamiltonian. This is achieved by a unitary transformation from the adiabatic basis to the diabatic:

$$|\psi_n^d(\mathbf{r}; \mathbf{R}(t))\rangle = U |\psi_n^a(\mathbf{r}; \mathbf{R}(t))\rangle$$

In the diabatic basis, avoided crossings that do not intersect because of symmetry are seen to intersect, as shown above.

> **with (QuantumChemistry) ;**

> `bond_distances := map(x → x/3 + 1.33, [fsolve(expand(ChebyshevT(8, x))]);`

A set of geometries is created for a dinitrogen molecule for a series of bond distances.

> `molecules := [seq([["N", 0, 0, 0], ["N", 0, 0, R]], R in bond_distances)];`

The energy for each specified geometry is calculated with DFT for both the ground state and a series of excited states.

> `energies := [seq(Energy(molecule, method = DensityFunctional, basis = "cc-pVDZ"), molecule in molecules)];`

`excited_energies := [seq(ExcitedStateEnergies(molecule, method = DensityFunctional, basis = "cc-pVDZ"), molecule in molecules)];`

(1)

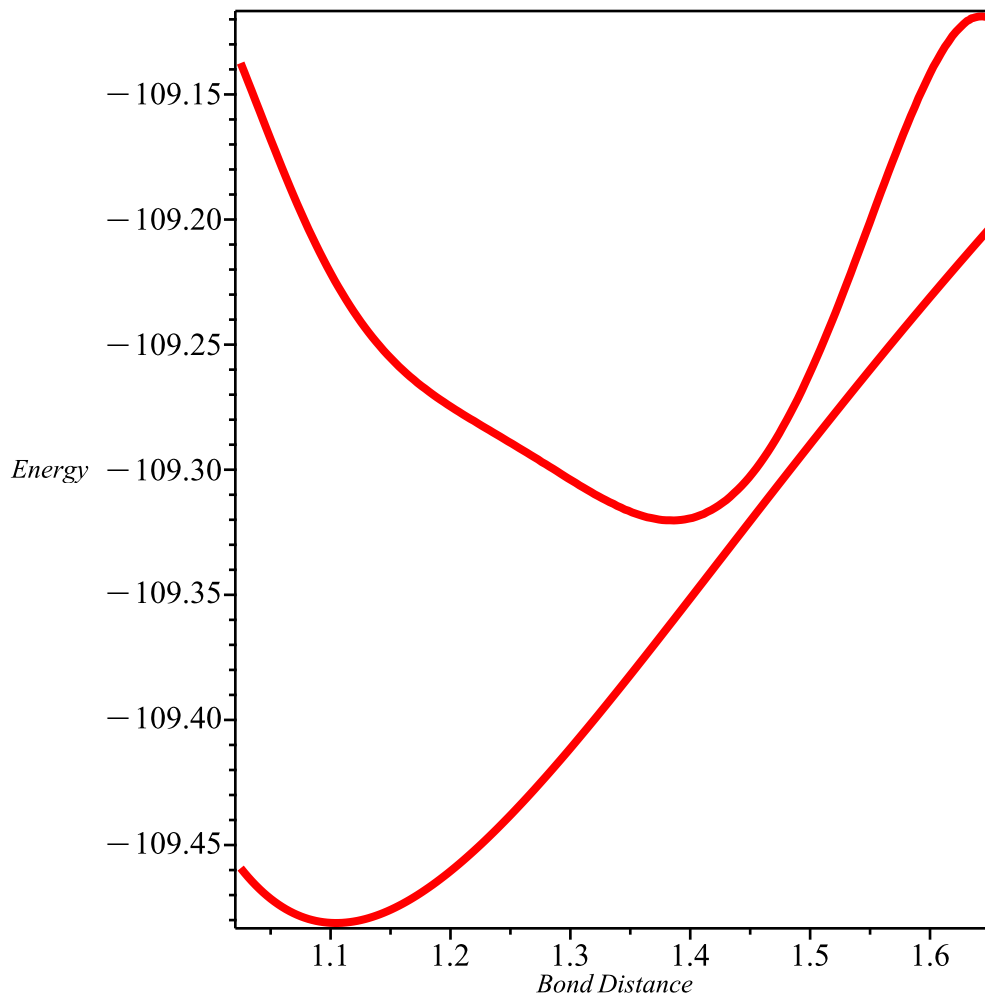
`excited_state1 := [-109.11371692, -109.17138558, -109.25262714, -109.29354222, -109.31986136, -109.2441791, -109.13516977, -109.12210858];`

`pes := interp(bond_distances, energies, R);`

`pes2 := interp(bond_distances, excited_state1, R);`

The potential energy surfaces are plotted for the ground state and the first excited state.

```
plot([pes(R), pes2(R)], R = 1.025 ..1.65, axes = boxed, labels = ['Bond Distance','Energy'], color = red, thickness = 3);
```



An avoided crossing-like feature can be seen where the ground state and first excited state potential energy surfaces meet. Since dinitrogen is a homonuclear diatomic molecule, this feature is an avoided crossing rather than a conical intersection.

## Applications/Results:

Conical intersections are of great interest in systems where transition states or photochemistry occurs. As mentioned in the introduction, conical intersections allow for rapid transitions from one energy state to the next. Typical molecular processes occur in the adiabatic regime, where the adiabatic theorem holds, requiring that the system evolve slowly so that the system is always an eigenfunction of the Hamiltonian. Around a CI, however, diabatic effects take hold. In a diabatic process, rapid changes in the system cause the eigenstates of the system to be in a form drastically different than the initial state. In order to observe conical intersections experimentally, femtosecond level time resolution is needed, as molecules rapidly transition from one excited state to another. Since the energy gap between states becomes small at this level, long wavelengths are required. The combination of short time resolution and low energies makes observation of conical intersection spectroscopically much more challenging. Significant advances in femtosecond resolution spectroscopy were required before spectroscopists were able to resolve CIs experimentally. The key experimental signature of a CI is a narrowing of an energy gap between two electronic states over time, followed by a subsequent increase in the gap again as the molecule crosses the CI. Though it was suspected that CIs played an important role in excited state dynamics, it would take some time before this was able to be verified in the lab. A key paper in this field was the observation of conical intersections in the light sensing protein rhodopsin by Polli *et al.*, which demonstrated experimentally that conical intersections could play an important role in excited state dynamics.

While diatomic molecules in free space have avoided crossings rather than conical intersections, conical intersections can be generated within diatomic molecules if an external electric field such as a laser pulse inside a cavity, is present, since the polaritonic coupling of the light and matter provides additional degrees of freedom. Studying such polaritonic effects on CIs has become a hot topic in recent literature. CIs have also been experimentally demonstrated in optical matter, artificial lattices created with laser light. One of the key hallmark characteristics of a system involving CIs is the presence of geometric or Berry phase effects. Dynamics of excited state wavepackets need consideration of geometric phase effects due to phase changes resulting in destructive or constructive interference. The effects of the Berry phase on dynamics are complicated and vary drastically from one system to another, but modeling the auto-correlation function of the excited state populations shows significant deviations from that expected without accounting for the geometric phase.

The physics around Dirac points is responsible for several unique phenomena in solids, including the anomalous Hall effect and the origin of topological insulators. In graphene, Dirac cones produce geometric phase effects that influence electron dispersion relations.

## Conclusion:

Conical intersections are key to understanding dynamical processes, in both chemical reactions and photochemical processes. Both computational and experimental tools for understanding chemical dynamics and spectroscopy require accurate representations of conical intersections. There remains much work to be done to accurately characterize CIs in both theory and spectroscopy.



## References:

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7. Ghahari, Fereshte *et al.* "An on/off Berry phase switch in circular graphene resonators". *Science* **356**, 845–849 (2017) <https://www.science.org/doi/10.1126/science.abm3770>