Conical Intersections, nonadiabatic couplings with applications to chemical physics

*Itamar Borges Jr.*

Dep. de Química

Instituto Militar de Engenharia
Introduction

- Computer development – computational investigation of “realistic” models of molecular systems
- Various possible applications
- Thermal reactions – state of art ab initio quantum chemistry provide a complete description of what happens at the molecular level during bond-breaking bond-forming processes (Transition structure and associated barrier with chemical accuracy ~1kcal/mol error and reactions path)
- Until beginning of 90’s – studies limited to thermal reactions, or in general occurring on a single potential surface
• Photochemical reactions where the reactants typically reside on a excited potential energy surface and products accumulates on the ground state could not easily studied.
• Reaction is expected to have two branches: one located on the excited state and the other in the ground state
• Main difficulty: correct definition and practical calculation of the “funnel” where the excited state reactant or intermediate is delivered to the ground state
A bit of history

• Neumann and Wigner (1929) – discussed the existence of conical intersections between PES in poliatomic molecules – N-W Theorem: “in general two parameters have to be independently varied in order to achieve eigenvalue degeneracy”.

• Jahn and Teller (1937) – polyatomic molecule in an orbitally degenerate electronic state is unstable with respect to linear displacement along some non-totally symmetric coordinates (i.e, it will distort the geometry). The Jahn-Teller geometry is a conical intersection between the two components of a degenerate state.

• Herzberg and Longuett-Higgins (1963) – a real-valued electronic wave function changes sign when the nuclear coordinates traverse a closed path encircling a conical intersection – geometric phase effect.

• Berry (1984) – every hamiltonian that depends on a parameter (for instance, the Born-Oppenheimer hamiltonian) presents geometric phase effect – topological effect in quantum mechanics – unexpected new effect
Basic Concepts

Born Oppenheimer (B.O.)
approximation to treat the motion of electrons separately from the motion of nuclei ($m_{electrons} << M_{nuclei}$)
(conceptual basis of chemistry)

A Potential Energy Surface (PES)
describes how the energy of a molecular system changes with small changes in its structure

Concepts like PES for molecular motion, equilibrium geometries, transition structures and reactions paths are derived from the B.O. Aprox.
Where the B.O. aprox. fails? In the vicinity of surface crossings

PES for a diatomic molecule – only one degree of freedom - the interatomic distance

For a molecule of N atoms, there are $3N - 6$ degrees of freedom (=internal coordinates); for a linear molecule there are $3N-5$

3 comes from degrees of translation, 3 from rotation (2 for linear molecules)
Minima and Saddle Points are stationary points, structures of chemical interest (min: different conformations or isomers), characterized by first and second derivatives. The first derivative is zero.

Expanding in the neighbourhood of a stationary point ($q_i$: internal coords.):

$$U = U(0) + \frac{1}{2} \sum_{ij} q_i q_j \left( \frac{\partial^2 U}{\partial q_i \partial q_j} \right)_0 + \ldots$$

$$H_{ij} = \frac{\partial^2 U}{\partial q_i \partial q_j}$$

Hessian matrix (force constant matrix)

Eigenvalues of $H_{ij}$:
- minimum: all eigenvalues $> 0$ (Hessian index zero)
- saddle point: one eigenvalue $< 0$ (Hessian index one)
- maximum: all eigenvalues $< 0$
The “Non-Crossing Rule” and Conical Intersections

- In diatomic molecules the PES of two states (e.g., the ground state and the first excited state) will only intersect if the states have a different (spatial or spin) symmetry.

- However, an analogous statement is not true of polyatomic systems: two PES of a polyatomic molecule can in principle intersect even if they belong to states of the same symmetry and spin multiplicity.

- (Teller, 1936) Consider $\varphi_1$ and $\varphi_2$ to form a complete orthonormal sets; Two solutions of the electronic Schrödinger equation can be written as (two electronic states):

$$\psi = c_1 \varphi_1 + c_2 \varphi_2$$

Then

$$H\psi = E\psi \implies (H - E)\psi = 0$$
\[
\begin{pmatrix}
H_{11} - E & H_{12} \\
H_{21} & H_{22} - E
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

Eigenvalues – energies – \( E_1 \) and \( E_2 \) are the solutions:

\[
E_i = \frac{1}{2} \left( (H_{11} + H_{22}) + \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right)
\]

where the matrix elements are:

\[
H_{11} = \langle \varphi_1 | H | \varphi_1 \rangle \\
H_{22} = \langle \varphi_2 | H | \varphi_2 \rangle \\
H_{12} = \langle \varphi_1 | H | \varphi_2 \rangle = H_{21} \quad \text{(because } \varphi_{1,2} \text{ are real)}
\]
In order to have two degenerate solutions (i.e. $E_1 = E_2$) it is necessary to satisfy two independent conditions:

\[
\begin{align*}
H_{11} &= H_{22} \\
H_{12} &= 0
\end{align*}
\]

• For a diatomic molecule there is only one variable coordinate – the interatomic distance – so THE NON-CROSSING RULE follows:

_for states of different spatial spin symmetry $H_{12}$ is always zero and we have to verify the only condition $H_{11}=H_{22}$: this is possible with a suitable value of a single variable coordinate (i.e. states of different symmetries can cross)._  

• Otherwise, if the two states have the same symmetry, they will not intersect; but in a system of three or more atoms, there are enough degrees of freedom for the rule to break down: the two conditions can be simultaneously satisfied by choosing suitable values for two independent variables, while the other $N-2 = (3N-6)-2$ degrees of freedom are free to be varied without exiting the crossing region.
Let’s denote the two independent variables \( x_1 \) and \( x_2 \) and take the origin at the point where \( H_{11} = H_{22} \) and \( H_{12}(=H_{21}) = 0 \). The secular eqs. then

\[
\begin{pmatrix}
W + h_1 x_1 - E & lx_2 \\
lx_2 & W + h_2 x_1 - E
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

or

\[
\begin{pmatrix}
W - (m+k) x_1 - E & lx_2 \\
lx_2 & W + (m-k) x_1 - E
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

where

\[
m = \frac{1}{2}(h_1 + h_2), \quad k = \frac{1}{2}(h_1 - h_2)
\]
The eigenvalues are

\[ E = W + mx_1 \pm \sqrt{k^2 x_1^2 + l^2 x_2^2} \]

This is the equation of a double cone with vertex at the origin. For this reason such crossing points are called CONICAL INTERSECTIONS.

Fig. Plotting of the two intersecting states against the two internal coordinates \(x_1\) and \(x_2\).
At the crossing \((H_{11} = H_{22})\) the energies of two real states become

\[
E_1 = \frac{1}{2} \left[ (H_{11} + H_{22}) - \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right] \Rightarrow E_1 = \frac{1}{2} [2H_{11} - 2H_{12}] = H_{11} - H_{12}
\]

\[
E_2 = \frac{1}{2} \left[ (H_{11} + H_{22}) + \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2} \right] \Rightarrow E_2 = H_{11} + H_{12}
\]
Energy gap between the two states:

\[ E_2 - E_1 = H_{12} \]

• Thus if \( H_{12} \) is not zero, the crossing will be avoided and the potential surfaces of the two real states will “diverge”, being one of the two energies lower and the other higher than the energy \( H_{11} \).
• Moreover, the value of the exchange term \( H_{12} \) determines how deep the avoided crossing minimum is (small values will generate deep minima, big values shallow minima).
• In general, \( H_{12} \) is zero (and the crossings will be real) when the two electronic states have a different (spatial or spin) symmetry, while it is usually assumed not zero for states of the same symmetry (which will generate avoided crossings).
Anyway, we have shown that this rule is true only for diatomic molecules: in a polyatomic system we can have real crossings for suitable values of a pair of independent coordinates \((x_1 \text{ and } x_2)\), which will simultaneously satisfy the two conditions.

In conclusion the following statement is true:

_for a polyatomic system two states (even with the same symmetry) will intersect along a \(n-2\) dimensional hyperline as the energy is plotted against the \(n\) internal nuclear coordinates_
It is convenient to rewrite the secular equation in order to establish physical meaning

\[ H(Q) = \overline{H}(Q) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + R(Q) \begin{pmatrix} \cos \alpha & \sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix} \]

where

\[ \overline{H}(Q) = \frac{1}{2}(H_{11} + H_{22}); \quad \Delta H = \frac{1}{2}(H_{11} - H_{22}) \]

\[ R(Q) = (\Delta H^2 + H_{12}^2)^{1/2} \]

\[ \alpha(Q) = \cos^{-1}(\Delta H / R) = \sin^{-1}(H_{12} / R) \]

\[ Q = (q_1, q_2, \ldots, q_{3N-6}) \quad \text{Internal coordinates} \]
• the diagonal elements $H_{11}$ and $H_{22}$ have as eigenfunctions the two adiabatic basis functions $\varphi_1$ and $\varphi_2$

• $\Delta H$ (energy separation): determines the strength of the interaction between the electronic states $\varphi_1$ and $\varphi_2$

• $H_{12}$ is the non-adiabatic, vibronic coupling or exchange element

The eigenfunctions and eigenvalues of $H(Q)$ are

\[ E_1 = \overline{H} - R, \quad E_2 = \overline{H} + R \]
\[ \psi_1 = \cos(\alpha / 2)\varphi_1 + \sin(\alpha / 2)\varphi_2 \]
\[ \psi_2 = -\sin(\alpha / 2)\varphi_1 + \cos(\alpha / 2)\varphi_2 \]

where $\psi_1$ and $\psi_2$ are often called diabatic states, since the transformation to them will cause the non-adiabatic, off-diagonal matrix elements $H_{12}$ and $H_{21}$ to vanish (or at least to vanish).
• If one completes a loop by varying the values of $Q$ around a conical intersection such that $\alpha \rightarrow \alpha + 2\pi$ then the electronic wave functions $\psi_1$ and $\psi_2$ change sign – manifestation of the so called BERRY or GEOMETRIC PHASE.

• BERRY PHASE (1984): Physical systems whose behavior is specified up to a phase by certain parameters. Under certain circumstances, the traversal of closed path by varying the parameters, at the end of which they have returned to their original values, can result in change of phase whose magnitude depends on the path. In the Born-Oppenheimer approximation the electronic hamiltonian depends parametricaly on the nuclear coordinates (Herzberg and Longuett-Higgins, 1963).

• The BERRY PHASE is a topological effect in quantum mechanics which have profound effects on the behavior of several physical systems.
Since the overall eigenfunction (total wave function) cannot change upon rotation by $2\pi$ (i.e., to make it single-values), one must either:

- Impose multivalued boundary conditions on the nuclear wave function (multivalued potential energy surfaces)
- make the electronic wave function complex single valued through the introduction of a vector potential (i.e. adiabatic coupling) into the Hamiltonian

The existence in the electronic wave function of the geometric phase has proved a powerful means of locating conical intersections along reactions paths.
The Physical Chemistry of Conical Intersections

• Relationship between surface crossing and photochemical reactivity? (be suspicious!)

• Let’s draw a parallel between the role of transition state in thermal reactivity and that of a conical intersection in photochemistry reactivity.
Thermal reaction: the transition state (TS) forms a bottleneck through which the reaction must pass on its way from reactants (R) to products (P). A transition state separates the reactant and product energy wells along the reaction path – (a).

An accessible conical intersection also forms (CI) also forms a bottleneck that separates the excited state branch of the reaction path from the ground state branch – (b).

Crucial difference between CI and TS: TS connects must connect the reactant energy well to a single product well via a single reaction path; an intersection connects the intersection to two or more products on the ground state via a branching of the excited reaction path into several ground state relaxation channels.
Theoretical investigations of surface crossings – new mathematical concepts

The double cone shape of the two intersecting potential energy surfaces can only be seen if the energies are plotted against two special internal geometric coordinates of the molecule – the coordinates $x_1$ and $x_2$:

$$x_1 = g^{1,2} = \frac{\partial (E_1 - E_2)}{\partial Q} \text{ gradient difference vector (tuning modes)}$$

$$x_2 = h^{1,2} = \langle C_1^* | \frac{\partial H}{\partial Q} | C_2^* \rangle \text{ interstate coupling vector (coupling modes)}$$

where $C_1^*$ and $C_2^*$ are the configuration interaction (CI) eigenvectors in a CI problem. The vector $x_2$ is parallel to the non-adiabatic coupling vector

$$f^{1,2} = \langle \psi_1 | \frac{\partial}{\partial Q} | \psi_2 \rangle$$
These coordinates form the “branching space”. As we move in this plane, away from the apex of the cone, the degeneracy is lifted (a), and ground state valleys must develop on the lower cone.

In contrast, if we move from the apex of the cone along any of the remaining $n-2$ internal co-ordinates (where $n$ is the number of degrees of freedom of the molecule), the degeneracy is not lifted. This $n-2$ dimensional space, called “intersection space”, is a hyperline consisting of an infinite number of conical intersection points.
Often the chemically relevant conical intersection point is located along a valley on the excited state potential energy surface. Figure below illustrates a two-dimensional model.

Surfaces plotted along the branching space \((x_1,x_2)\)
There are situations where there is no transition state connecting M* to the intersection point or where an excited state intermediate on the upper energy surface does not exist. In such cases, mechanistic information can be obtained by locating the lowest lying intersection point along the \( n-2 \) intersection space of the molecule.
Effect of conical intersections in molecular processes

• **Direct effects**
  - nonradiative decay from excited state
  - "non-adiabatic recrossing": nuclei motion occurs on two PES despite the process beginning and ending on the same PES

• **Indirect effects**
  - happens on the same adiabatic PES: geometric phase effect
Conical intersections were believed to be rare events:

- point group symmetry required: normal degeneracies (Jahn-Teller effect)
- group symmetry allowed: accidental degeneracies allowed by symmetry

Intersections between two surfaces of same symmetry (accidental degeneracy)

⇒UBIQUITOUS AND DIABOLICAL (the latter in the sense it cannot be foreseen)
Princípios básicos

- Hamiltonia não relativística:

\[ \mathcal{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{\nabla^2_{R_{\alpha}}}{M_{\alpha}} - \frac{\hbar^2}{2} \sum_{i} \frac{\nabla^2_{r_i}}{m_{e_i}} + V(r, R) = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{\nabla^2_{R_{\alpha}}}{M_{\alpha}} + \mathcal{H}_{el}(r; R) \]

com

\[ V(r, R) = V_{ee} + V_{en} + V_{nn} \]

Definimos as funções de onda eletrônicas (Born-Oppenheimer) \( \Phi_j (r; R) \) como \( (R \text{ fixo}) \):

\[ \mathcal{H}_{el}(r; R)\Phi_j (r; R) = \mathcal{E}_j (R)\Phi_j (r; R) \]

\( \mathcal{E}_j (R) \) é superfície de energia potencial Born-Oppenheimer ou adiabática correspondente ao estado \( j \).
\[ \Rightarrow \{ \Phi_j(r; R) \}, \text{ para qualquer } R \text{ fixo, constituem um conjunto completo. Expandindo a função de onda molecular exata nesta base,} \]

\[ \Psi(r; R) = \sum_i \Phi_j(r; R) \Omega_i(r) \]

- Substituindo na equação de Schrödinger \( \mathcal{H} \Psi(r; R) = E \Psi(r; R) \) e fazendo \( \nabla r \Phi_j^*(r; R) \)

\[ \downarrow \]

Conjunto de equações de Schrödinger acopladas descrevendo o movimento nuclear em cada superfície de energia potencial \( \mathcal{E}_j(R) \)

\[ -\frac{\hbar^2}{2} \sum_\alpha \frac{\nabla^2_{R_\alpha} \Omega_i(R) + \mathcal{E}_i(R) \Omega_i(R)}{M_\alpha} - E \Omega_i(R) = -\sum_\alpha \frac{\hbar^2}{2M_\alpha} \left( \sum_j g_{ij}(R) \Omega_j(R) + 2 \sum_j f_{ij} \cdot \nabla_{R_\alpha} \Omega_j(R) \right) \]

onde

\[ f_{ij} = \int \Phi_i^*(r; R) (\nabla_{R_\alpha} \Phi_j^*(r; R)) dr = \langle \Phi_i | \nabla_{R_\alpha} \Phi_j \rangle_r = \frac{\langle \Phi_i | \nabla_{R_\alpha} \mathcal{H}_{el} | \Phi_j \rangle_r}{E_i - E_k} \]

\[ g_{ij} = -\int \Phi_i^*(r; R) (\nabla^2_{R_\alpha} \Phi_j(r; R)) dr \]
Desprezando o lado direito da equação obtemos

$$\left[ -\frac{\hbar^2}{2} \sum_{\alpha} \frac{\nabla_{R\alpha}^2}{M_{\alpha}} + \mathcal{E}_i(R) - E \right] \Omega_i(R) = 0$$

obtemos a aproximação de Born-Oppenheimer. Isto equivale a truncar a expansão

$$\Psi(r; R) = \sum_i \Phi_j(r; R) \Omega_i(r) \approx \Phi_0(r; R) \Omega_0(r)$$

e despezar o acoplamento do estado fundamental com estados eletrônicos excitados ($f_{ij} = 0$ e $g_{ij} = 0$). “Válido” para dinâmica a baixas energias e estado fundamental não-degenerado.
Conical Intersections, nonadiabatic couplings with applications to chemical physics-
PART 2

Itamar Borges Jr.
Dep. de Química
Instituto Militar de Engenharia
• two weeks ago: 450 papers found from the keywords “conical intersections” in web of science

• Janh-Teller effect (over 6000 articles)
Columbus calculates the nonadiabatic couplings at the MR/CI level
Some examples of conical intersections
The $\text{H}_3$ conical intersection

- conical intersection at equilateral geometry (D$_{3h}$ point group)
- simplest polyatomic system
- Hypersurface for the simplest reaction (the exchange H + H$_2$)
• $H_3$ potential surfaces of the ground and first excited states as 3D surface plot.

• At equilateral triangular geometry ($D_{3h}$ symmetry), the ground state energy surface touches the surface of the first excited state and forms a conical intersection.
Figure 4

\[ E = 6n - 43 \text{ kcal mol}^{-1} \]

\[ a', b', c' \]

\[ \text{H}^2(S) + \text{H}_2(b^3\Sigma_u^+) \]

\[ 2^2A' \]

Relaxed plot for \( \text{H}_3 \)

\[ E = 6n - 109 \text{ kcal mol}^{-1} \]

\[ a, b, c \]

\[ \text{H}^2(S) + \text{H}_2(X^1\Sigma_u^+) \]
Tri-hydrogen and isotopic invariants – vibrational spectra

Differences between NGP (non-geometric phase effect) and GP vibrational spectra decreases along the sequence

\[ H_3 \sim D_3 > HD_2 > \mu H_2 > \mu HD > \mu DT \]

Geometric phase effects in the H+H$_2$ reaction

- prototype reaction: accurate calculations can be compared with experiment

- ground state surface connected to first excited state by a seam of conical intersections running through equilateral triangle geometries

- Experimental data: state to state integral and differential cross sections ranging from threshold up to 2.5 eV above the potential minimum

- Since the lowest point on the CI seam lies at E=2.7 eV, these experiments cannot access the CI seam and the first excited state

- However, paths that encircle the CI are accessible at these energies

- Question: Is the H+H$_2$ reaction dynamics on the ground electronic state affected influenced by the geometric phase (GP)?
Early works

- Mead (80’s): GP changes the relative phases of the inelastic and reactive contributions to the fully symmetrized cross sections.
- Kuppermann et al. (90’s): quantum reactive scattering calculations the GP using multivalued basis functions.
  \[\Rightarrow\] GP effect was found to change markedly the state to state rovibrational bringing them into better agreement with early experiments.
• Newer experiments have shown that product state distributions and state to state differential cross sections (DCSs) are in excellent agreement with calculations that omit GP

• Kendrick (2000): new quantum reactive scattering included GP contradict Kupperman et al.:

For individual values of the total angular momentum quantum number J, the state to state reaction probabilities showed small but noticeable effects which cancel rigourously, upon summing over J to give the integral and the differential cross sections

• Juanes-Marcos and Althorpe (2005): agreement with Kendrick using other methodology
Red: direct reaction path
Blue: looping reaction path

Why the effect of GP for scattering solutions of odd and even J cancels out at the energies considered?

Topological argument of Althorpe et al. (Science 2005)
There are two possible paths to H₂ + H products:

• for energies below de conical intersection (< 2.7 eV), most reaction paths pass just through one transition state that correspond to even or “direct” component

• A very small proportion of reactions paths can also pass through the two transition states, and these give rise to the odd or “loop” components

• These odd and even components can quantum-mechanically interfere (non-classical effect)
Conical intersections and geometric phase in the $2^3\text{A}^{\parallel}$ and $3^3\text{A}^{\parallel}$ of CH$_2$

- Avoided/conical intersections of these states near the equilibrium geometry of the ground $1^3\text{A}^{\parallel}$ ($1^3\text{B}_1$) state play a key role in non-adiabatic decomposition originating on the $3^3\text{A}^{\parallel}$ surface.

- The $2^3\text{A}^{\parallel}$ - $3^3\text{A}^{\parallel}$ conical intersection can in principle also lead to the geometric phase effect in the adiabatic process on the $2^3\text{A}^{\parallel}$ surface.

It is important to characterize the seam of conical intersections of the two PES and determine those motions that can lead to the geometrical phase effect.

• In the vicinity of the minimum energy crossing point $R_{\text{me}}$ nuclear configurations are most conveniently expressed of polar coordinates on the plane $g-h$

• Therefore it can be defined closed loops around the conical intersection (pseudo rotations)

• Next figure depicts selected geometries of the pseudo-rotation
Pseudo-rotation

\[ x = \rho \cos \theta \]
\[ y = \rho \sin \theta \]

\( R, \gamma \) are the polar coordinates for the line connecting the C to the center of the \( H_2 \) moiety.
C^I(R) for R corresponding to \( \rho = 0.1 \) and \( 0^0 \leq \theta \leq 360^0 \). 4a, 4b and 4c designate CI\( ^{4a} \), CI\( ^{4b} \) and CI\( ^{4c} \) denotes CSF corresponding to three different electron configurations.

- No change of sign.

- Change of sign! (at \( \theta = 180^0 \))
Derivative couplings for $f_\alpha$, $\alpha = r, R, \gamma$ and $\omega$ (overall molecular rotation about an axis perpendicular to the molecular plane).

**Note:**

- $\theta = 180^0$: where the sign changes, corresponds to a maximum in the energy separation between the two states and a minimum in the derivative couplings.

- $\theta = 90^0$ and $270^0$: largest values for the derivative couplings, for which the energy difference is minimal.

(For both cases remember the dependence of $f$ on the reciprocal of the energy difference).
Variation of the energies of the two states – at the origin, $\rho = 0$, is the conical intersection point $R_{\text{mex}}$. 

$E(\text{cal/mol})$ versus $\theta$ (deg) for different values of $\rho$. The graph shows the energy levels of the states $3\Sigma^+$ and $2\Pi^+$.
The $S_1/S_0$ Conical Intersection of Benzene

- In $S_1$ benzene there is a $\sim3000$ cm$^{-1}$ threshold for the disappearance of $S_1$ fluorescence.
- This observation is assigned to the opening of a very efficient, radiationless decay channel leading to the production of fulvene and benzvalene.
- *Ab initio* CAS-SCF and multi-reference MP2 computations [10] show that the topology of the first ($\pi$-$\pi^*$) excited state energy surface is consistent with that of Fig.
- Thus the observed energy threshold (which is reproduced) corresponds to the energy barrier which separate $S_1$ benzene from a $S_1/S_0$ conical intersection point.
• The optimized conical intersection structure for $S_1$ benzene is shown above. The structure contains a triangular arrangement of three carbon centres corresponding to a -(CH)$_3$- kink of the carbon skeleton.
• The electronic structure corresponds to three weakly interacting electrons in a triangular arrangement which are loosely coupled to an isolated radical centre.
• This type of conical intersection structure appears to be a general feature conjugated systems and has been documented in a series of polyene and polyene radicals.
• The electronic origin of this feature can be understood by comparison with H$_3$ where any equilateral triangle configuration corresponds to a point on the D$_1$/D$_0$ conical intersection in which the three H electrons have identical pairwise interactions.
Normal coordinate with the imaginary frequency at the transition structure

Transition Vector

The vectors \( g(x_1) \) and \( h(x_2) \) only have meaning together, i.e., just the plan spanned by \( (x_1, x_2) \)

Interstate
Non Adiabatic Coupling

\[
X_2 = \left\langle \phi_\alpha \frac{\partial H}{\partial Q} \phi_\beta \rightangle
\]

Gradient Difference

\[
X_1 = \frac{\partial (E_\alpha - E_\beta)}{\partial Q}
\]

Corresponds to the deformation which lift the degeneracy and that therefore causes a fast decrease in \( S_0 \) energy

By examining the molecular structure of the conical intersection, its electronic distribution and the directions indicated by the $x_1$ and $x_2$ vectors we can derive information on the photochemical reaction path (be careful).

• The kink feature suggest the formation of a cyclopropyl ring upon decay to the ground state. Indeed this structure corresponds with that of pre-fulvene which was previously proposed as the intermediate in fulvene photochemical production (see scheme).
• The same conclusion can be reached by looking at the shape of the non-adiabatic coupling and gradient difference vectors. These corresponds, by definition, to the deformation which lift the degeneracy and that therefore causes a fast decrease in $S_0$ energy. Thus, in turn they represent, loosely, the possible directions of relaxation along the ground state potential energy surface.
• There is little doubt that the gradient difference vector, which is almost parallel to the $S_1$ transition vector, suggest a relaxation towards the pre-fulvene diradical in the positive direction and a planar ground state benzene in the negative direction (ie. reversing the arrows).
• On the other hand the non-adiabatic coupling vector describes the simultaneous double bond re-construction which occurs upon relaxation.
• On the interaction of two conical intersections: the H₆ system

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A. J. C. Varandas, A. I. Voronin and I. Borges, Jr.

We report a study on the interaction of two H₃ systems, which are known to possess a conical intersection when infinitely separated from each other. The topology of the crossing seam is analysed for different geometrical arrangements of the two interacting partners.
rotational angle

(a)

$D_{3h}$

(b)

$D_{3d}$

(c)

$C_s$
Question: Does the coupling of the two interacting systems remove the original degeneracy? What happens to them?
Computational details:

- CAS/MR-CI//cc-pVTZ
Cut along the 2D surface for \( r = 1.5 \ a_0 \).

Insert indicates that the lowest energy state for \( r \leq 1.28 \ a_0 \) is the third non-degenerate state.

- Coincidence of the two lowest roots.

\[
\begin{align*}
D_{3h} & : E' \otimes E' = A_1 \oplus A_2 \oplus E' \\
D_{3d} & : E_g \otimes E_g = A_{1g} \oplus A_{2g} \oplus E_g
\end{align*}
\]

\( \Rightarrow \) \( H_3 \) ... \( H_3 \) interaction in arrangement (a) – two \( E' \) components of the group

-Locus of CI is a preserving manifold (i.e., degeneracy is preserved for each pair of \((r, R)\))
$\text{C}_s$ has only nondegenerate (1D) representations $\Rightarrow$ 3 lowest states become nondegenerate for all values of coordinate $R$

Interaction between the original CI destroy the crossing seam in the many dimensional space of the H$_6$ system.
Some final comments

• Conical intersections are **UBIQUITOUS AND DIABOLICAL**

• There is a plethora of chemistry phenomena, specially photochemical, that can be understood/explained through the present concepts

• At the same time, research on fundamental aspects of quantum mechanics in chemistry can be carried out

• Mead and Truhlar (2005): “conical intersections are much more likely than local minima of the electronic energy gap. Therefore, if one encounters a very small electronic energy gap along a path through configuration space, it is much more likely to be associated with a conical intersection than with an avoided intersection.” (**conical intersections are not rare.**)

• Columbus provides tools to study conical intersections and derivative couplings not available in other programs
Some bets