L5

Conical intersections

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Linear approximation around a crossing

Suppose a two-level molecule whose electronic Hamiltonian is H(**R**), where **R** are the nuclear coordinates.

Given a basis of unknown orthogonal functions ϕ_1 and ϕ_2, we want to solve the Schrödinger equation

$$(H_e - E)\psi_i = 0 \qquad \psi_i = c_{i1}\phi_1 + c_{i2}\phi_2 \quad i = 1,2$$

The energies are given by

$$\det\begin{bmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{bmatrix} = 0 \qquad H_{ij} = \langle \phi_i | H_e(\mathbf{R}) | \phi_j \rangle = H^*_{ji}$$

Prove it!

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

$$E_2 = \frac{1}{2}(H_{11} + H_{22}) + \frac{1}{2}\left[(H_{11} - H_{22})^2 + 4|H_{12}|^2\right]^{1/2}$$

In a more compact way:

$$E_{1,2} = \Sigma \pm \left[\Delta^2 + H_{12}^2\right]^{1/2}$$

where

$$\Sigma = \frac{1}{2}\left(H_{11} + H_{22}\right) \quad \text{and} \quad \Delta = \frac{1}{2}\left(H_{11} - H_{22}\right)$$

A degeneracy at $\mathbf{R}_x$ will happen if

$$\Delta\left(\mathbf{R}_X\right) = 0$$

$$H_{12}\left(\mathbf{R}_X\right) = 0$$

In general, two independent coordinates are necessary to tune these conditions.

In a more compact way:

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where

$$\Sigma = \frac{1}{2}\left(H_{11} + H_{22}\right) \quad \text{and} \quad \Delta = \frac{1}{2}\left(H_{11} - H_{22}\right)$$

Expansion in first order around $\mathbf{R}_x$ for Σ:

$$\Sigma = \frac{1}{2}\left(\nabla H_{11}(\mathbf{R}_X)\cdot \mathbf{R} + \nabla H_{22}(\mathbf{R}_X)\cdot \mathbf{R}\right)$$

$$= \frac{1}{2}\left(\mathbf{G}_1^X \cdot \mathbf{R} + \mathbf{G}_2^X \cdot \mathbf{R}\right) \qquad \mathbf{G}_i^X = \nabla H_{ii}(\mathbf{R}_X)$$

$$= \frac{1}{2}\mathbf{s}_{12}^X \cdot \mathbf{R}$$

In a more compact way:

$$E_{1,2} = \Sigma \pm \left[\Delta^2 + H_{12}^2\right]^{1/2}$$

where

$$\Sigma = \frac{1}{2}\left(H_{11} + H_{22}\right) \quad \text{and} \quad \Delta = \frac{1}{2}\left(H_{11} - H_{22}\right)$$

In first order around $\mathbf{R}_x$ each of these terms are:

$$\Sigma = \left(\mathbf{G}_1^X + \mathbf{G}_2^X\right)\cdot \mathbf{R} = \mathbf{s}_{12}^X \cdot \mathbf{R} \qquad \mathbf{G}_i^X = \nabla H_{ii}\left(\mathbf{R}_X\right)$$

$$\Delta = \left(\mathbf{G}_1^X - \mathbf{G}_2^X\right)\cdot \mathbf{R} = \mathbf{g}_{12}^X \cdot \mathbf{R}$$

$$H_{12} = \nabla H_{12}^X \cdot \mathbf{R} = \mathbf{f}_{12}^X \cdot \mathbf{R}$$

And the energies in a point $\mathbf{R}_X$ + $\mathbf{R}$ are in first order:

$$E_{1,2} \approx \mathbf{s}_{12}^X \cdot \mathbf{R} \pm \left[\left(\mathbf{g}_{12}^X \cdot \mathbf{R}\right)^2 + \left(\mathbf{f}_{12}^X \cdot \mathbf{R}\right)^2\right]^{1/2}$$

$$E_{1,2} \approx \mathbf{s}_{12}^{X} \cdot \mathbf{R} \pm \left[\left(\mathbf{g}_{12}^{X} \cdot \mathbf{R} \right)^2 + \left(\mathbf{f}_{12}^{X} \cdot \mathbf{R} \right)^2 \right]^{1/2}$$

Writting $\mathbf{g} = g\hat{\mathbf{x}}; \quad \mathbf{f} = f\hat{\mathbf{y}}; \quad \mathbf{s} = r\hat{\mathbf{x}} + s\hat{\mathbf{y}}$

then $\mathbf{g} \cdot \mathbf{R} = gR\cos\theta = gx$

$$\mathbf{f} \cdot \mathbf{R} = fR\sin\theta = fy$$

$$\mathbf{s} \cdot \mathbf{R} = s_x R\cos\theta + s_y R\sin\theta$$

$$E_{1,2} \approx s_x x + s_y y \pm \left[g^2 x^2 + f^2 y^2 \right]^{1/2}$$

$$E_{1,2} \approx \mathbf{s}_{12}^{X} \cdot \mathbf{R} \pm \left[\left(\mathbf{g}_{12}^{X} \cdot \mathbf{R} \right)^2 + \left(\mathbf{f}_{12}^{X} \cdot \mathbf{R} \right)^2 \right]^{1/2}$$

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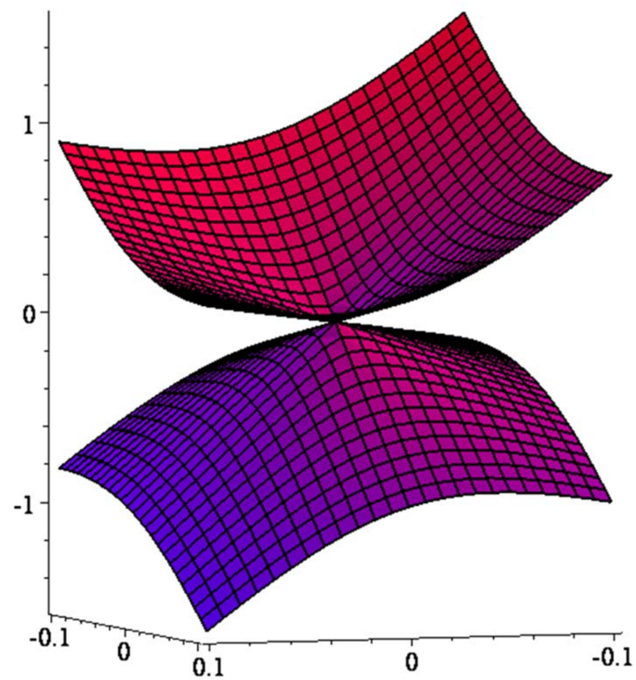


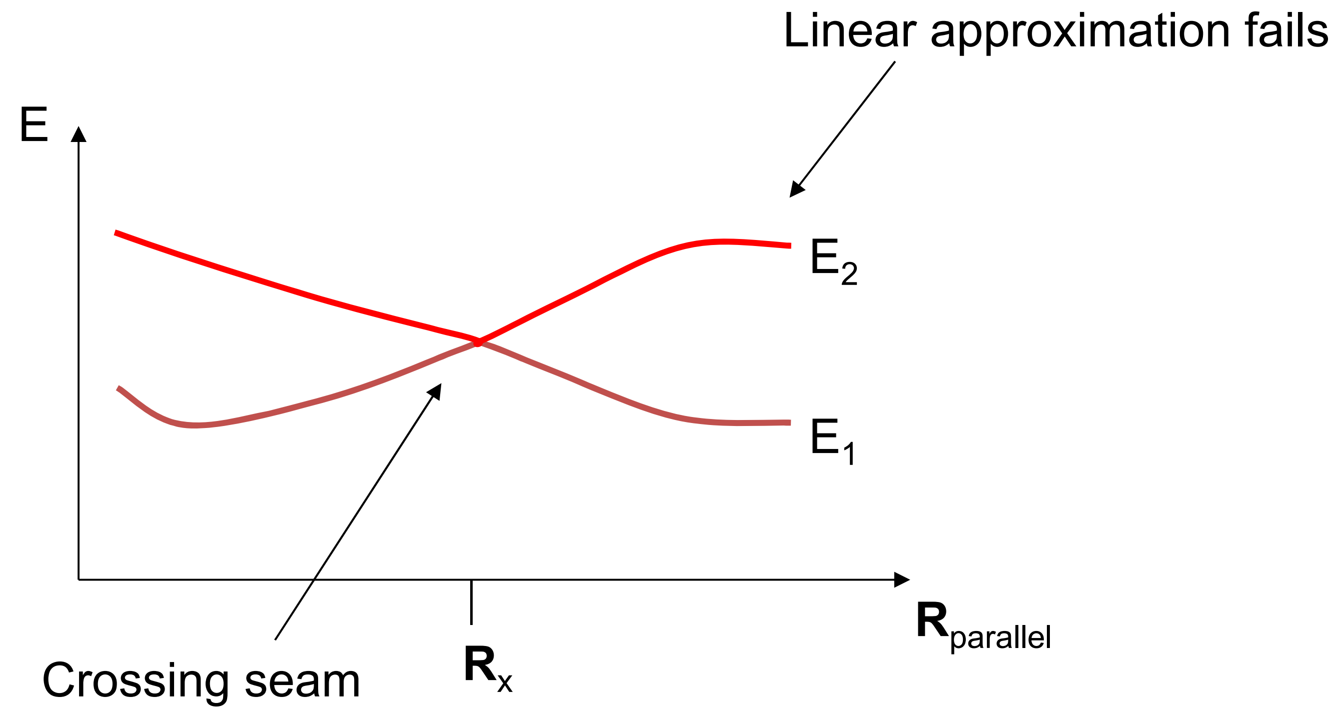
Atchity, Xantheas, and Ruedenberg, J. Chem. Phys. **95**, 1862 (1991)

The branching space

Parallel distortion

$$E_{1,2} \approx \mathbf{s}_{12}^{X} \cdot \mathbf{R} \pm \left[\left(\mathbf{g}_{12}^{X} \cdot \mathbf{R} \right)^2 + \left(\mathbf{f}_{12}^{X} \cdot \mathbf{R} \right)^2 \right]^{1/2}$$

What does happen if the molecule is distorted along a direction that is parallel to **g** or **f**?

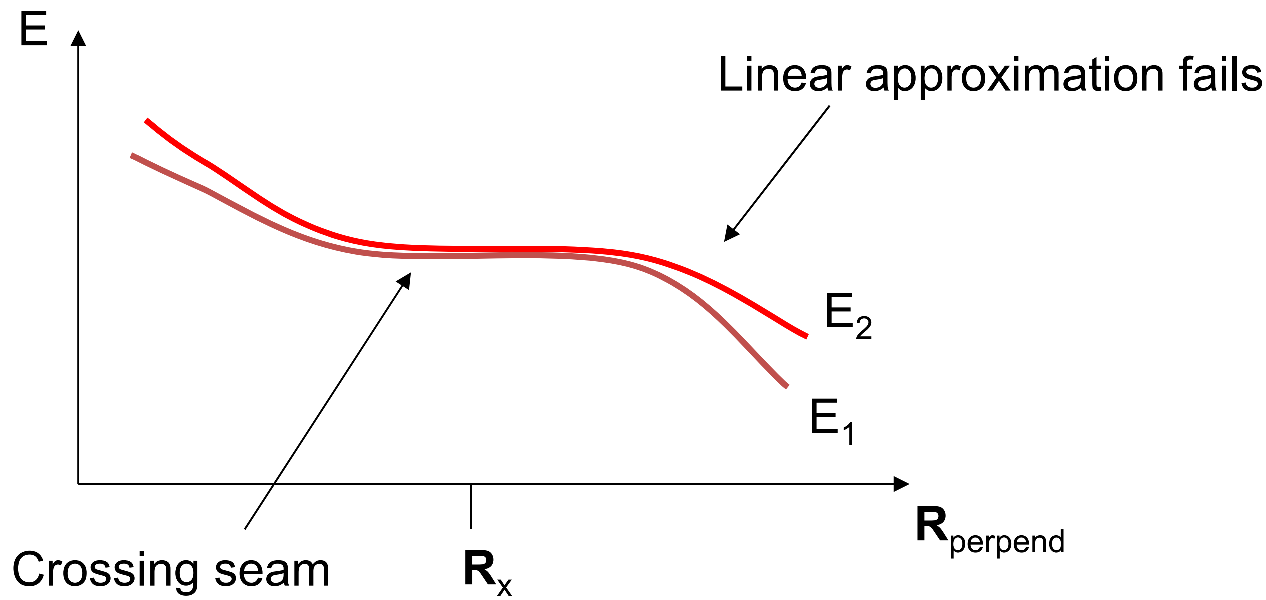


Perpendicular distortion

$$E_{1,2} \approx \mathbf{s}_{12}^{X} \cdot \mathbf{R} \pm \left[\left(\mathbf{g}_{12}^{X} \cdot \mathbf{R} \right)^2 + \left(\mathbf{f}_{12}^{X} \cdot \mathbf{R} \right)^2 \right]^{1/2}$$

What does happen if the molecule is distorted along a direction that is perpendicular to **g** and **f**?

$$E_{1,2} = \mathbf{s}_{12}^{X}$$



The branching space

• Starting at the conical intersection, geometrical displacement in the „branching space“ lifts the degeneracy linearly.

• The branching space is the plane defined by the vectors **g** and **f**.

• Geometrical displacements along the other 3*N*-8 internal coordinates keep the degeneracy (in first order). These coordinate space is called *seam* or *intersection* space.

Note that

$$\mathbf{f}_{12}^{X} \equiv \nabla H_{12}^{X} = -(E_1 - E_2)\mathbf{h}_{12}^{X}$$

$$\mathbf{h}_{12} \equiv \langle \psi_1 | \nabla \psi_2 \rangle$$ Nonadiabatic coupling vector

For this reason the branching space is also referred as **g-h** space.

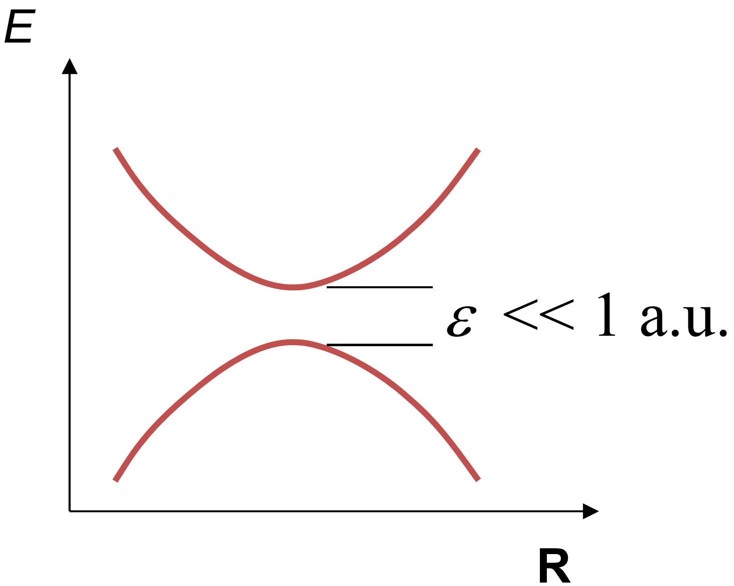
See the proof, e.g., in Hu at al. J. Chem. Phys. **127**, 064103 2007 (Eqs. 2 and 3)

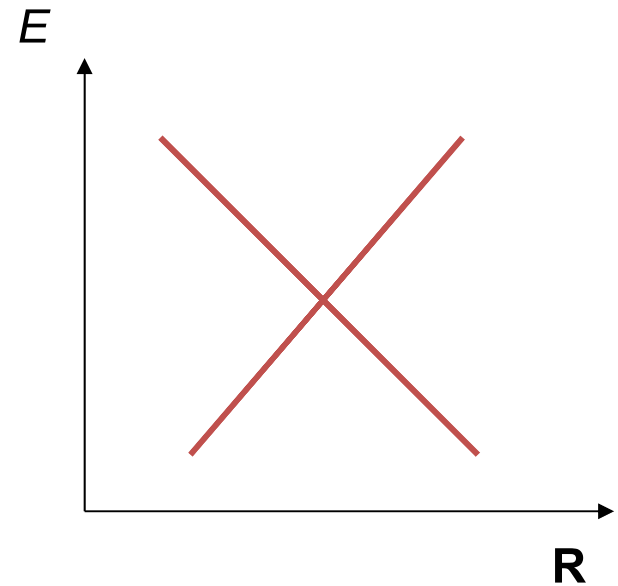
Characteristics of a conical intersection

Conical intersections are not rare

LIGHT AND MOLECULES

"When one encounters a local minimum (along a path) of the gap between two potential energy surfaces, almost always it is the shoulder of a conical intersection. Conical intersections are not rare; true avoided intersections are much less likely."



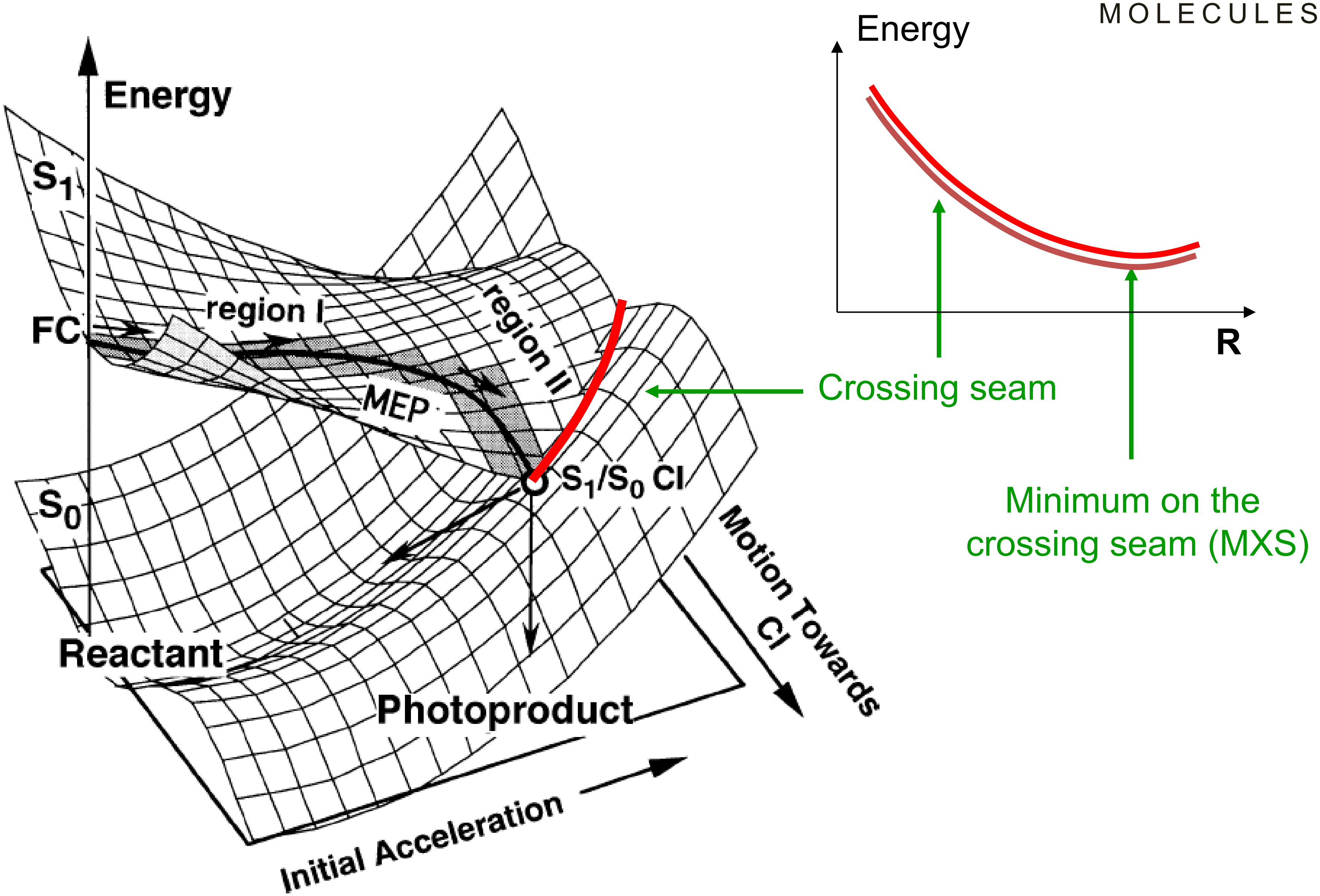


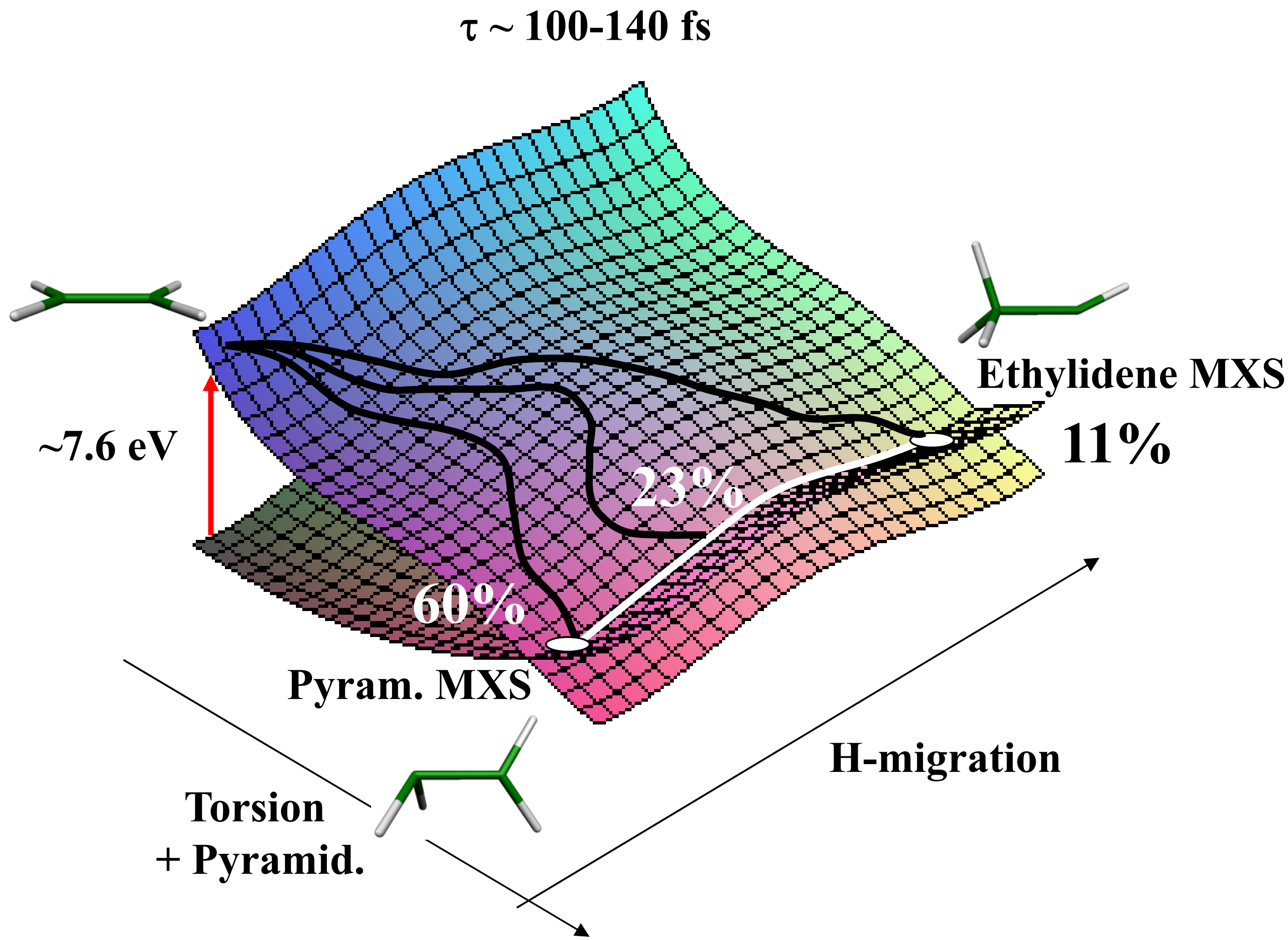
$$\frac{V_{tot}(min)}{V_{tot}(CI)} = \left(\rho^2 \varepsilon\right)^{(3N-4)/2} \sim 0$$

$\rho \sim O(1)$ is the density of zeros in the H_{el} matrix.

Truhlar and Mead, Phys. Rev. A **68**, 032501 (2003)

Conical intersections are connected




τ ~ 100-140 fs
~7.6 eV
Ethylidene MXS
11%
23%
60%
Pyram. MXS
H-migration
Torsion
+ Pyramid.

Conical intersections are distorted

$$E_{1,2} \approx \mathbf{s}_{12}^{X} \cdot \mathbf{R} \pm \left[\left(\mathbf{g}_{12}^{X} \cdot \mathbf{R} \right)^2 + \left(\mathbf{f}_{12}^{X} \cdot \mathbf{R} \right)^2 \right]^{1/2}$$

It can be rewritten as a general cone equation (Yarkony, JCP **114**, 2601 (2001)):

$$E_{1,2} \approx d_{gh} \left[\sigma_x x + \sigma_y y \pm \left(\frac{1}{2}\left(x^2 + y^2\right) + \frac{\Delta_{gh}}{2}\left(x^2 - y^2\right) \right)^{1/2} \right]$$

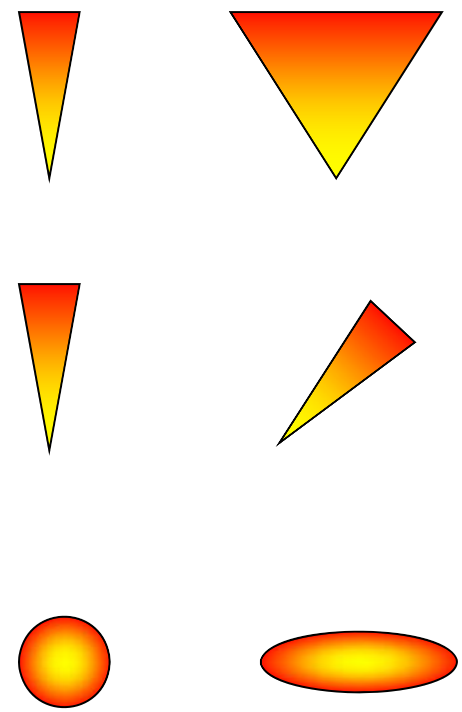
$$d_{gh} = \left(|\mathbf{g}|^2 + |\mathbf{h}|^2 \right)^{1/2}$$ pitch parameter

$$\sigma_x = \frac{\mathbf{s}}{d_{gh}} \cdot \frac{\mathbf{g}}{|\mathbf{g}|}$$

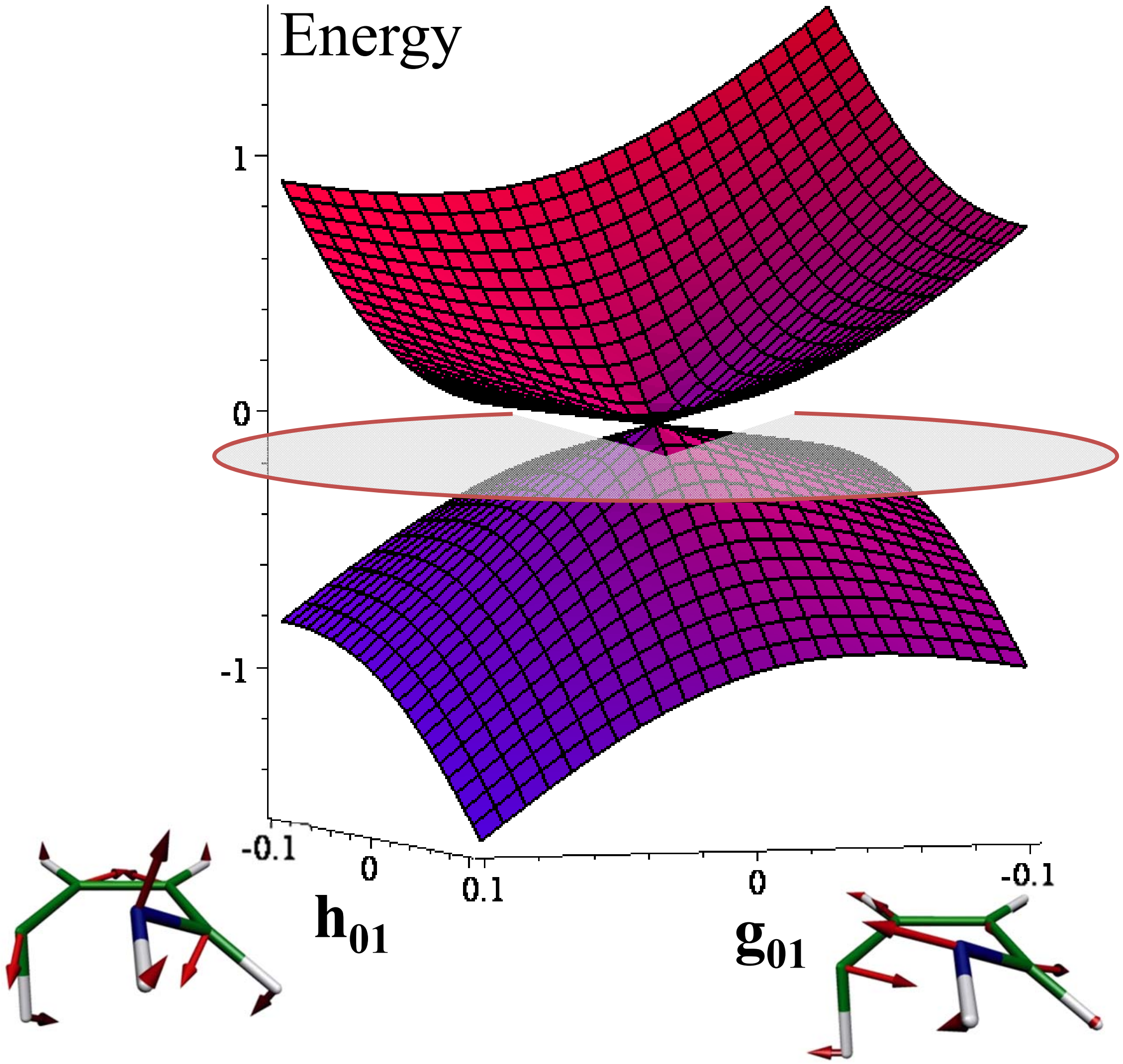
$$\sigma_y = \frac{\mathbf{s}}{d_{gh}} \cdot \frac{\mathbf{h}}{|\mathbf{h}|}$$

tilt parameters

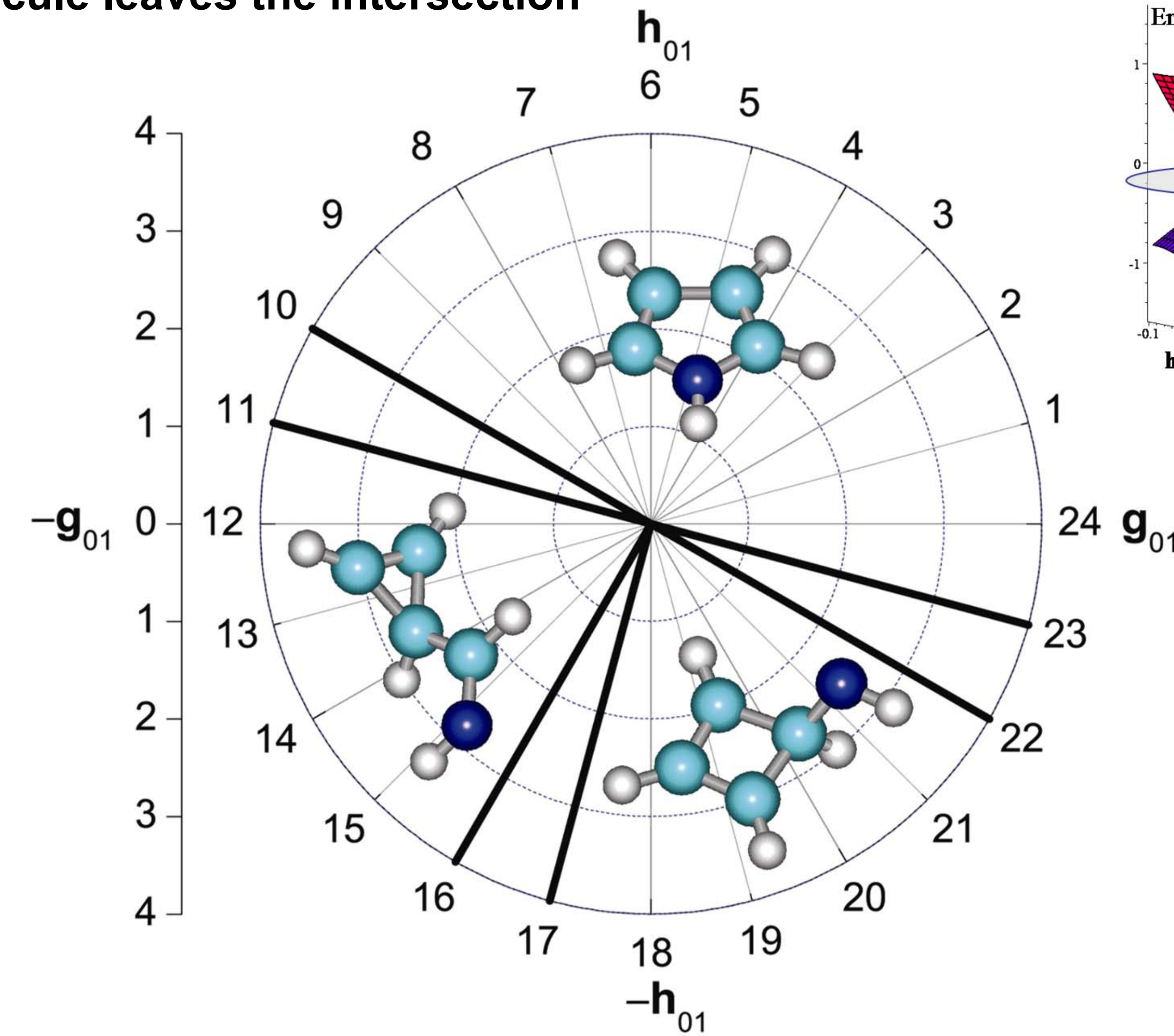
$$\Delta_{gh} = \frac{\left(|\mathbf{g}|^2 - |\mathbf{h}|^2 \right)}{d_{gh}^2}$$ asymmetry parameter

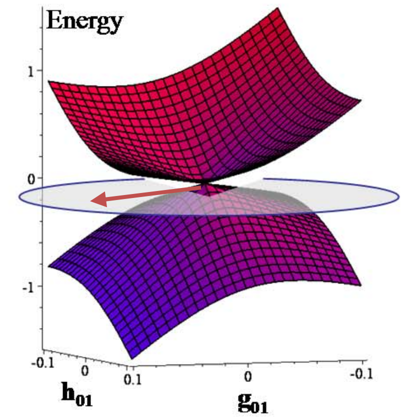


Example: pyrrole

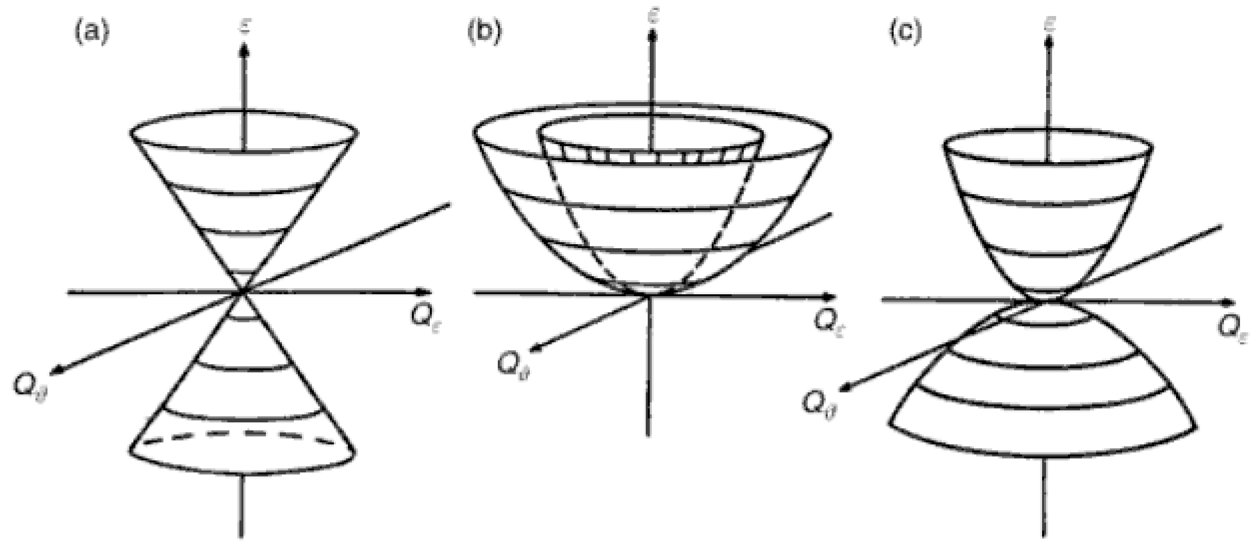


Photoproduct depends on the direction that the molecule leaves the intersection





Intersections don't need to be conical!



- Bersuker, The Jahn Teller effect, 2006

Finding conical intersections

Finding conical intersections

Conventional geometry optimization:

- Minimize: $f(\mathbf{R}) = E_J$

Conical intersection optimization:

- Minimize: $f(\mathbf{R}) = E_J$
- Subject to: $E_J - E_I = 0$

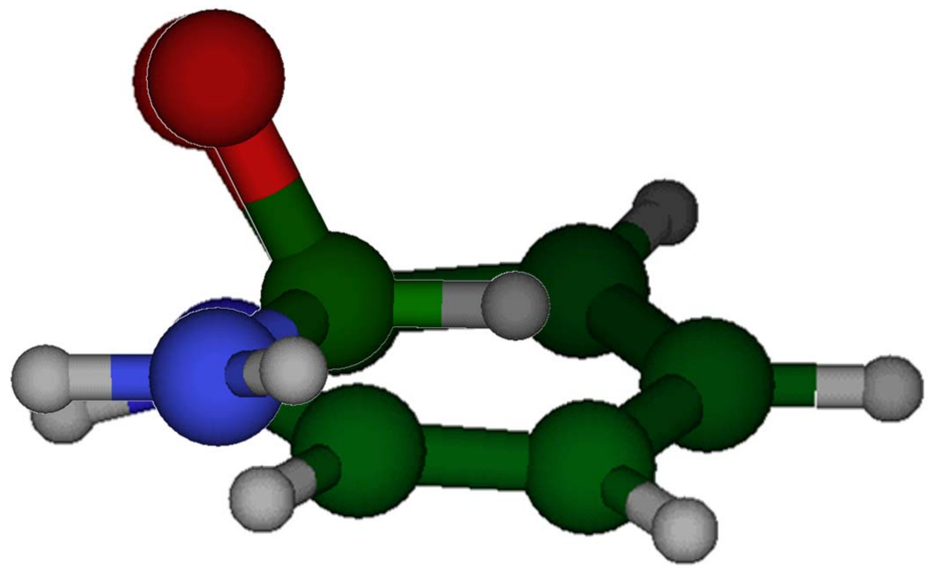
  $H_{IJ} = 0$

Three basic algorithms:

- Penalty function (Ciminelli, Granucci, and Persico, 2004; MOPAC)
- Gradient projection (Beapark, Robb, and Schlegel 1994; GAUSSIAN)
- Lagrange-Newton (Manaa and Yarkony, 1993; COLUMBUS)

- Keal et al., Theor. Chem. Acc. **118**, 837 (2007)

Where are the conical intersections?

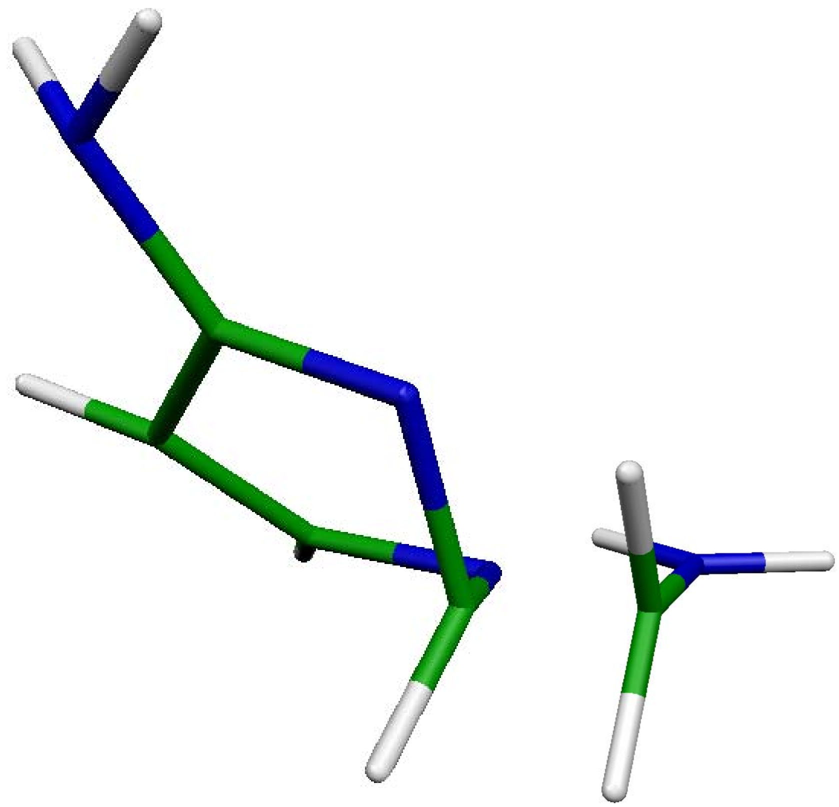


formamide pyridone

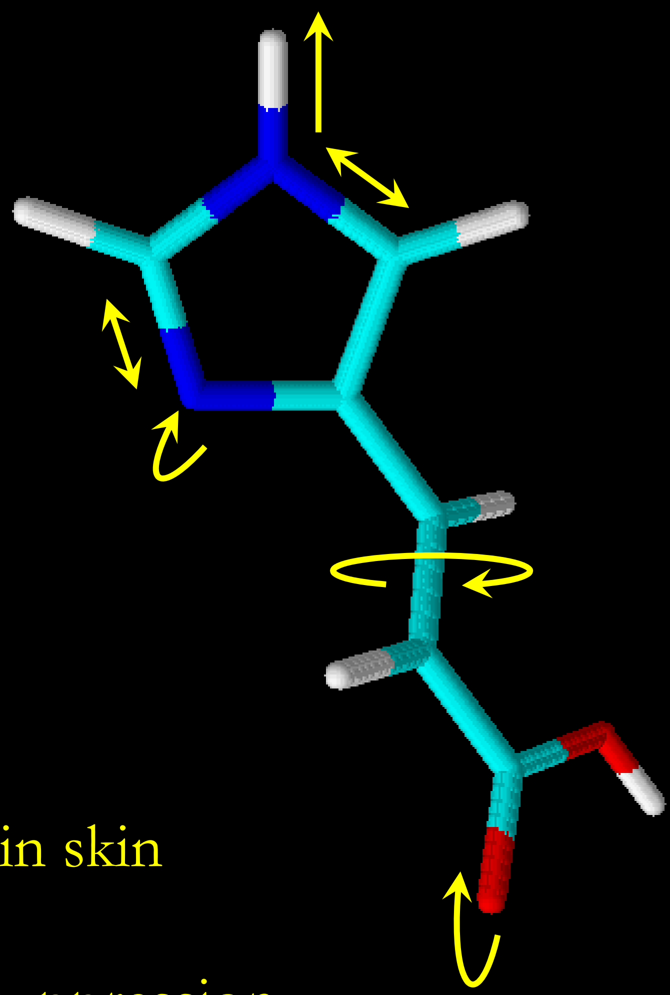
- Antol et al. JCP **127**, 234303 (2007)

Look for:

- Twist around double bonds
- Ring puckering
- Ring opening
- Bond stretching
- Proton transfer
- Pyramidalization



Urocanic acid



- Major UVB absorber in skin
- Photoaging
- UV-induced immunosuppression

Key points

- **Conical intersections surface crossing points allowing radiationless deactivation.**
- **There are two directions lifting the crossing linearly (branching space).**
- **There are 3N-8 directions along which the crossing remains (crossing seam).**
- **There are typical geometrical distortions that cause conical intersections.**