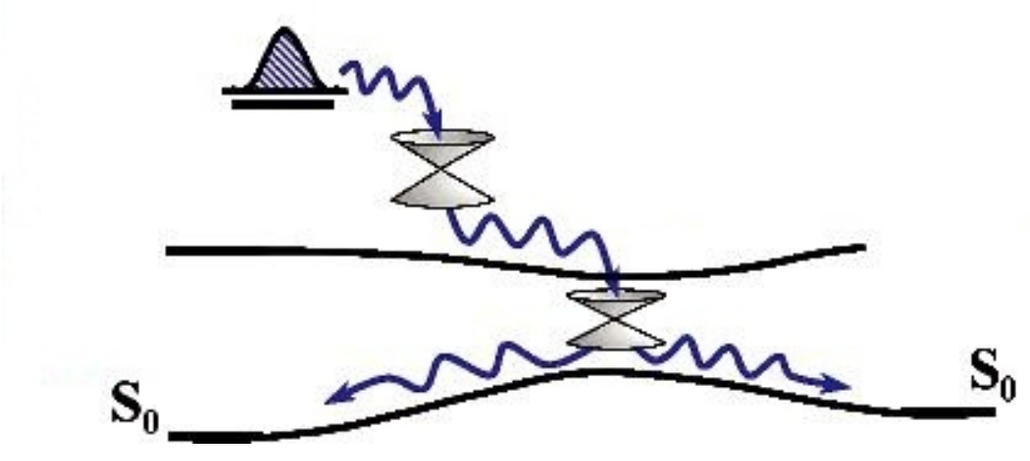
Theoretical Photochemistry WiSe 2017/18

Lecture 4



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http://www.theochem.uni-frankfurt.de/teaching/ $\longrightarrow$ Theoretical Photochemistry

Topics

1. Photophysical Processes
3. Wavepackets
5. The Franck-Condon picture of electronic transitions
6. What do we measure experimentally?
2. The Born-Oppenheimer approximation
4. Beyond Born-Oppenheimer – non-adiabatic transitions
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
9. Some electronic structure aspects
10. Dynamics: trajectories or wavefunctions?
11. Wavefunction propagation techniques

12. **Trajectory surface hopping techniques**
13. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
14. **Extended systems: Excitons, light-harvesting, etc.**
15. **Solvent/environmental effects**

Literature

1. P. W. Atkins and R. Friedman, Molecular Quantum Mechanics, 5th Edition, Oxford University Press (2011).

2. D. Tannor, Introduction to Quantum Mechanics: A Time-Dependent Perspective, University Science Books (2006).

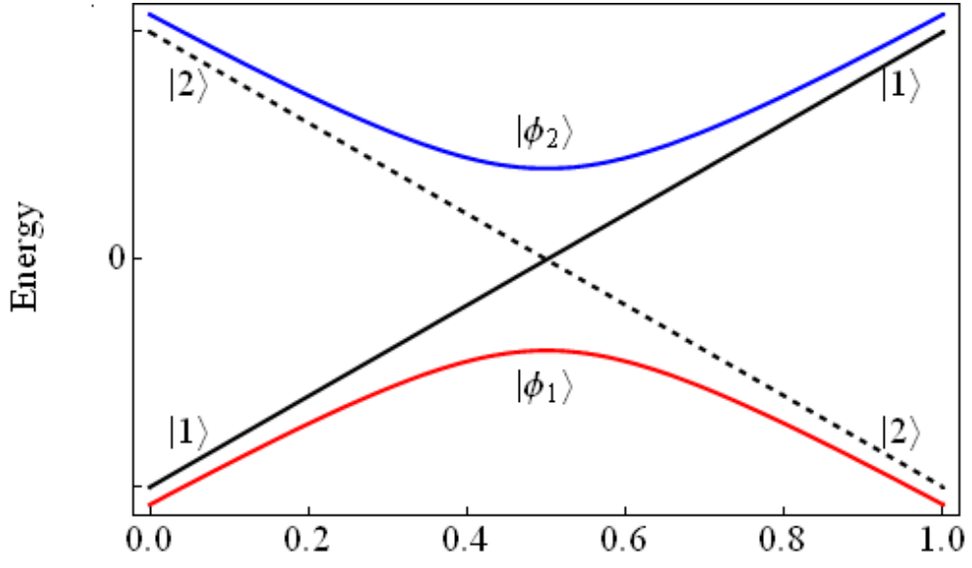
3. M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH-Wiley (1995).

4. I. N. Levine, Quantum Chemistry, 6th Edition, Pearson International Edition (2009).

5. F. Jensen, Introduction to Computational Chemistry, 2nd Edition, Wiley (2007).

6. C. J. Cramer, Essentials of Computational Chemistry – Theories and Models, 2nd Edition, Wiley (2004).

Curve Crossings – Basics



$$\boldsymbol{H}^{\rm dia} = \boldsymbol{T_N} + \begin{pmatrix} \boldsymbol{e_1(x)} & \boldsymbol{\delta} \\ \boldsymbol{\delta} & \boldsymbol{e_2(x)} \end{pmatrix} = \boldsymbol{T_N} + \begin{pmatrix} \boldsymbol{e + \kappa(x - x_0)} & \boldsymbol{\delta} \\ \boldsymbol{\delta} & \boldsymbol{e - \kappa(x - x_0)} \end{pmatrix}$$

$$\longrightarrow \quad \boldsymbol{\epsilon^{\rm ad}_{1/2}(x)} \;=\; \boldsymbol{\frac{1}{2}(e_1(x) + e_2(x)) \pm \frac{1}{2}[(e_2(x) - e_1(x))^2 + 4\delta^2]^{1/2}}$$

If $\boldsymbol{e_1 = e_2 = e_0} \quad \longrightarrow \quad \boldsymbol{\epsilon_{1/2} = e_0 \pm \delta}$

Non-Crossing Rule & Avoided Crossings

Adiabatic potential surfaces of the same symmetry cannot cross in 1D

Take a diabatic potential:

$$\hat{H} = \begin{pmatrix} \hat{T}_N + V_1(R) & V_{12}(R) \\ V_{12}(R) & \hat{T}_N + V_2(R) \end{pmatrix}$$

Conditions for a crossing:

(1) $V_1(R) - V_2(R)\Big|_{R=R_X} = 0$ **(2)** $V_{12}(R)\Big|_{R=R_X} = 0$

This is unlikely to happen in 1D, unless imposed by symmetry!

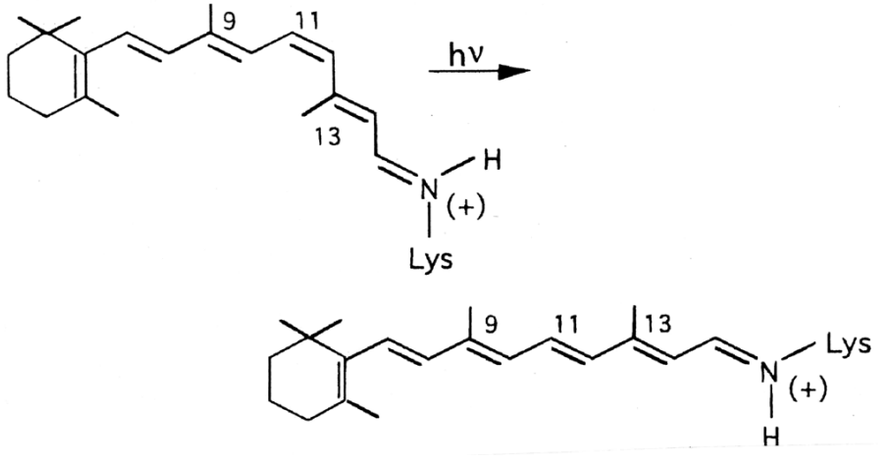
Non-Crossing Rule: More Detailed

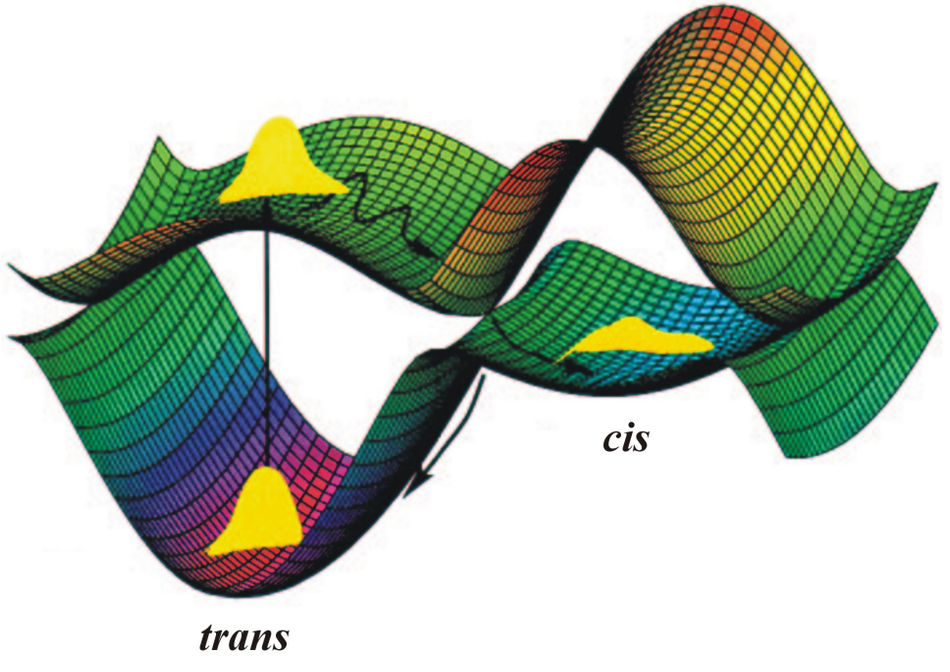
1929: Eugene P. Wigner and John von Neumann:

Intersections of potential surfaces of the same symmetry ("same-symmetry intersections") have dimension $N^{\mathrm{int}} - 2$ where N^{int} is the number of internal degrees of freedom.

Equivalently, two internal coordinates must be varied to find an intersection (if such an intersection exists at all).

Crossings in Two Dimensions: Conical Intersections

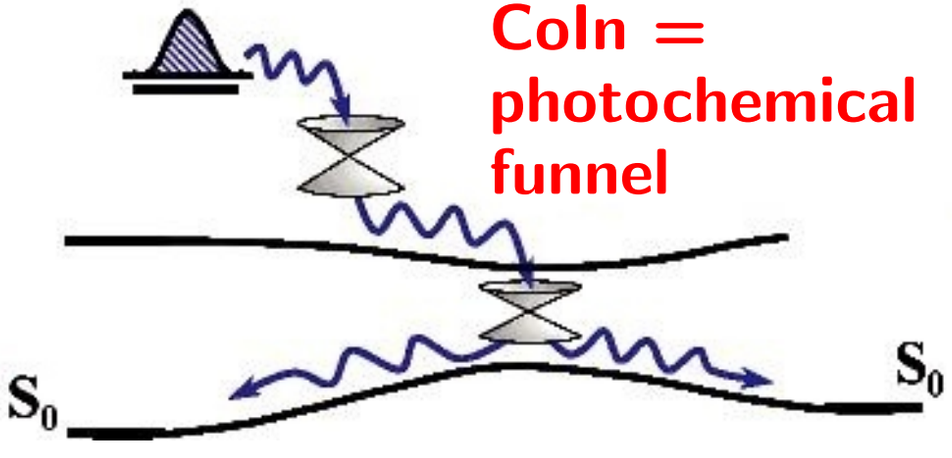




S. Hahn and G. Stock, J. Phys. Chem. B 104, 1146 (2000).

- primary process of vision
- relevant coordinates: twist + skeletal stretch + . . .
- excited-state decay in the protein: $\sim$ 200 fs / in solution phase: $\sim$ 5 ps

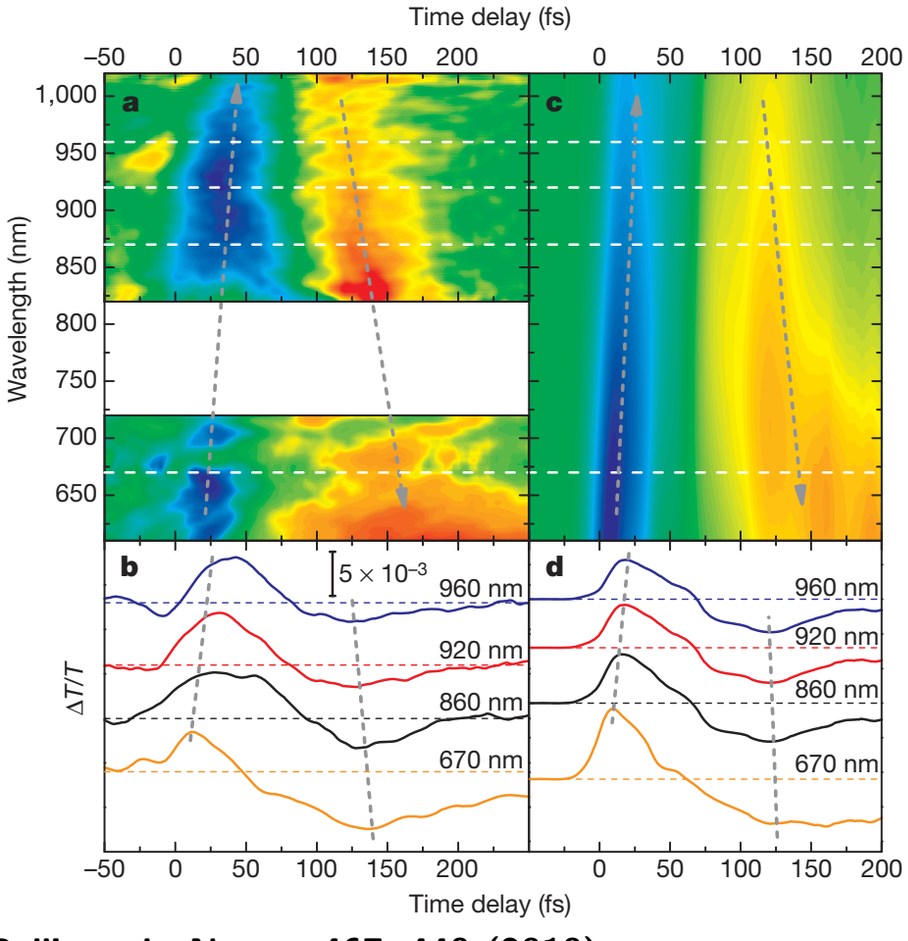
Conical intersections (CoIn's) as landmark topology



adapted from: Schultz et al., J. Am. Chem. Soc. 125, 8098 (2003)

- Conical intersection topologies are highly anharmonic
- Extreme breakdown of the Born-Oppenheimer approximation
- The electronic decay at a CoIn is ultrafast (femtosecond to picosecond scale)
- CoIn's are ubiquitous (Truhlar/Mead: "Principle of non-rareness of CoIn's")
- Polyatomic molecules; Jahn-Teller effect in solids

Retinal isomerisation, cont'd



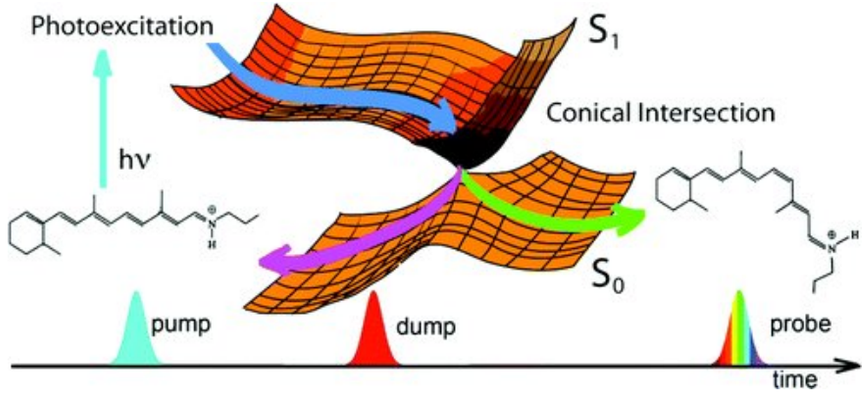


Figure 1 | Wave-packet dynamics through the rhodopsin conical intersection. **a**, **c**, Experimental (**a**) and simulated (**c**) differential transmission ($\Delta T/T$) map as a function of time delay and wavelength in the visible and NIR spectral regions. The white area in the experimental data around 750 nm corresponds to the 'blind region' of our set-up. Grey lines are guides to the eye, highlighting the temporal shifts of the stimulated emission (blue) and photoinduced absorption (red/orange) signals. **b**, **d**, Experimental (**b**) and simulated (**d**) $\Delta T/T$ dynamics at selected probe wavelengths.

Polli et al., Nature 467, 440 (2010)

CoIn's – diabatic picture

$$V_{\mathrm{CoIn}}(x_t, x_c) = V_0(x_t, x_c) + \begin{pmatrix} \kappa^{(1)}\,\Delta x_t & \lambda\,\Delta x_c \\ \lambda\,\Delta x_c & \kappa^{(2)}\,\Delta x_t \end{pmatrix}$$

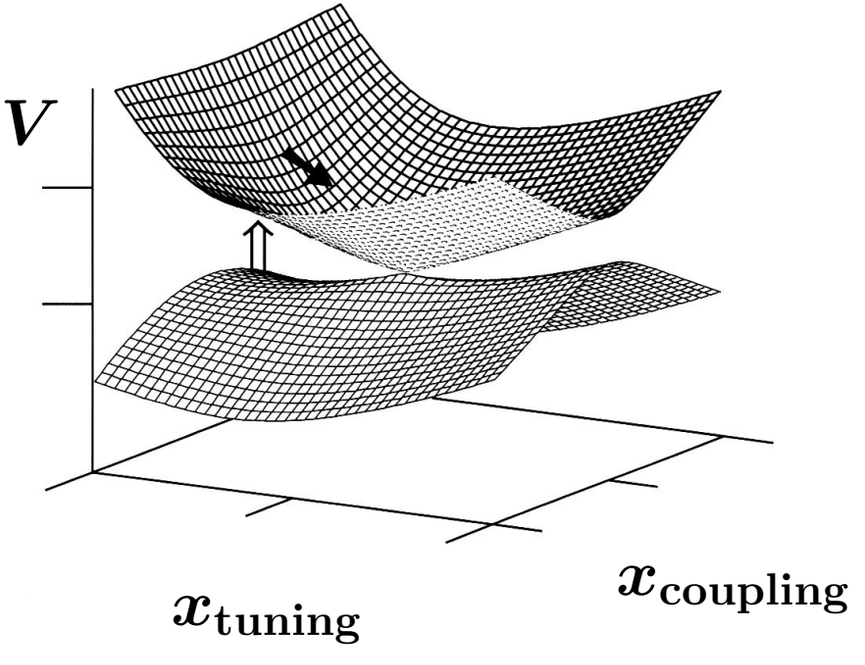
$\Delta x_t = x_t - x_t^0$ **tuning mode**

$\Delta x_c = x_c - x_c^0$ **coupling mode**

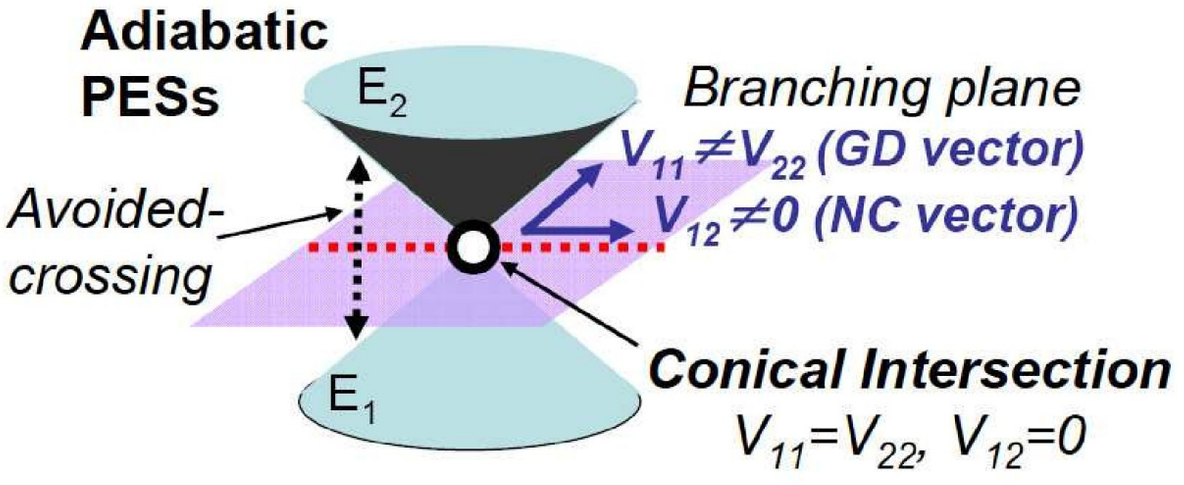
2 dimensions: CoIn point
3 dimensions: CoIn seam
N dimensions: (N-2) dimensional intersection space

(*) **here, diabatic linear vibronic coupling (LVC) form**

(*) **can be embedded in a correct representation of the overall potential via regularized diabatic states**



CoIn's – adiabatic picture



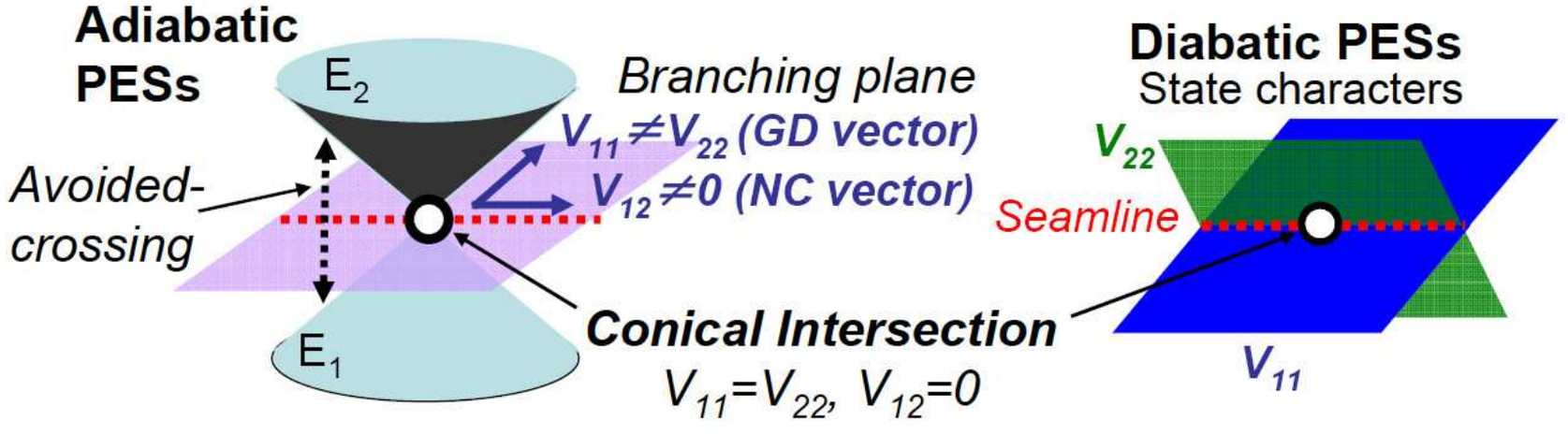
gradient difference vector: $g = 1/2(\langle \psi_1^{\mathrm{ad}} | \nabla \hat{H}_{\mathrm{el}} | \psi_1^{\mathrm{ad}} \rangle - \langle \psi_2^{\mathrm{ad}} | \nabla \hat{H}_{\mathrm{el}} | \psi_2^{\mathrm{ad}} \rangle)$

non-adiabatic coupling vector: $h = \langle \psi_1^{\mathrm{ad}} | \nabla \hat{H}_{\mathrm{el}} | \psi_2^{\mathrm{ad}} \rangle$

NB.: Connection to derivative couplings:

$$\langle \psi_1^{\mathrm{ad}} | \nabla | \psi_2^{\mathrm{ad}} \rangle = \frac{\langle \psi_1^{\mathrm{ad}} | \nabla \hat{H}_{\mathrm{el}} | \psi_2^{\mathrm{ad}} \rangle}{V_2(R) - V_1(R)} = \frac{h}{V_2(R) - V_1(R)}$$

CoIn's – adiabatic vs. diabatic



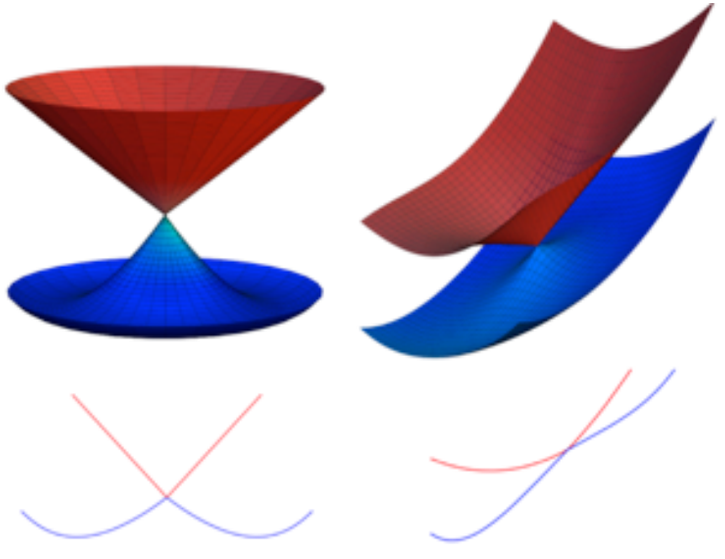
$$\boldsymbol{E}_{\text{adiabatic}} = \boldsymbol{U}^T \boldsymbol{V}_{\text{diabatic}} \boldsymbol{U} \; ; \quad \boldsymbol{V}_{\text{diabatic}} = \boldsymbol{V}_0 + \begin{pmatrix} \boldsymbol{V}_{11} & \boldsymbol{V}_{12} \\ \boldsymbol{V}_{12} & \boldsymbol{V}_{22} \end{pmatrix} = \boldsymbol{V}_0 + \begin{pmatrix} \sum_i \boldsymbol{\kappa}_i^{(1)} \boldsymbol{x}_i & \sum_i \boldsymbol{\lambda}_i \boldsymbol{x}_i \\ \sum_i \boldsymbol{\lambda}_i \boldsymbol{x}_i & \sum_i \boldsymbol{\kappa}_i^{(2)} \boldsymbol{x}_i \end{pmatrix}$$

- two intrinsic modes $(\boldsymbol{X}_-, \boldsymbol{X}_\Lambda)$ along which the degeneracy is lifted, where $\boldsymbol{X}_- = \sum_i (\boldsymbol{\kappa}_i^{(1)} - \boldsymbol{\kappa}_i^{(2)}) \boldsymbol{x}_i$ and $\boldsymbol{X}_\Lambda = \sum_i \boldsymbol{\lambda}_i \boldsymbol{x}_i$
- these are directly related to the adiabatic g and h vectors

Classification of conical intersections

by symmetry: "accidental symmetry-allowed intersections" vs. "accidental same-symmetry intersections"

by topology: "peaked" vs. "sloped"



Note that an ultrafast decay to the lower state is not always guaranteed!