Ovidiu Tirnovan | 17.12.2024

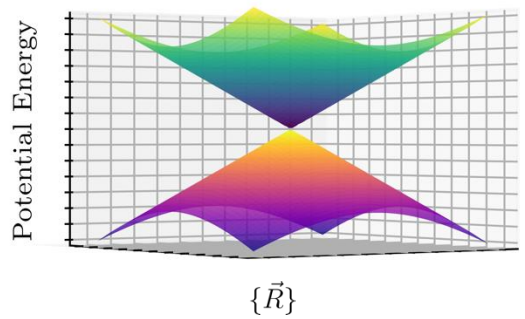
Minimum Energy Conical Intersections

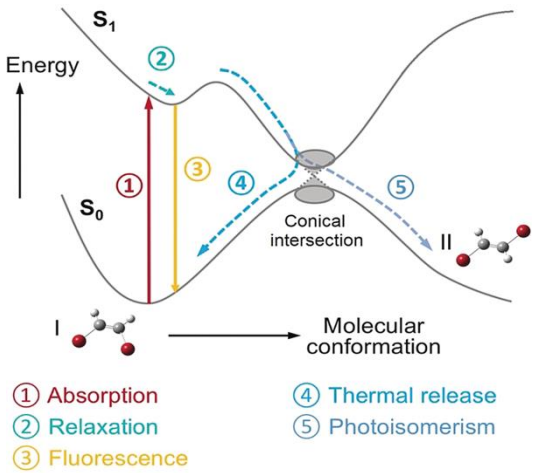
Overview of conical intersections

- CIs are points of degeneracy between two or more PES.
- The MECI is a local point in the CI seam which has the lowest energy.
- Intersections can be thought of as analogous to transition states in the ground state.
- There are multiple algorithms for finding the MECI, but the main two categories are with or without derivative coupling vectors.
- You generally compute CIs by simply minimising the gap between the two states you are interested in.
- To find the MECI you must also minimise the overall energy of the states, which increases the complexity of the problem.
- It's hard to know the lowest level of theory sufficient for the system you are studying: MS-CASPT2 [1], SF-TDDFT [2], SA-CASSCF [3], TDDFT(TDA) [4] and more.

"Diabolical conical intersections"

David R. Yarkony, *Rev. Mod. Phys.* **1996**, *68*, 985.





Photoexcitation and de-excitation mechanism [5].

[1] *J. Phys. Chem. B* **2008**, *112*, 405.
[2] *Chem. Phys. Lett.* **2019**, *737*, 100007 (image reprinted under CC BY-NC-ND 4.0 license, OA).
[3] *J. Chem. Theory Comput.* **2008**, *4*, 257.
[4] *Phys. Chem. Chem. Phys.* **2015**, *17*, 12065.
[5] Reprinted with permission from *Angew. Chem. Int. Ed.* **2020**, *59*, 3793. © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Simple method for finding the MECI [1]

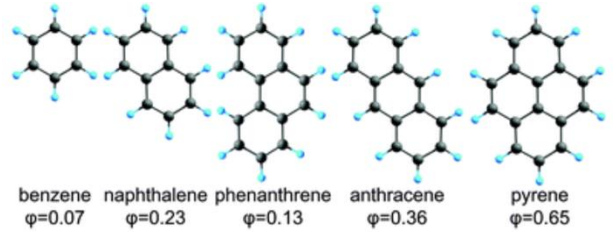
$$O_{IJ}(\vec{R};\sigma,\alpha) = \frac{E_I(\vec{R}) + E_J(\vec{R})}{2} + \sigma G_{IJ}\left(\Delta E_{IJ}(\vec{R});\alpha\right)$$ (Minimise this)

$$G_{IJ}(\Delta E_{IJ};\alpha) = \frac{\Delta E_{IJ}^2}{\Delta E_{IJ} + \alpha}$$

$$\left.\begin{aligned} O_{IJ}\left(\vec{R}_{\text{prior}};\sigma,\alpha\right) - O_{IJ}(\vec{R};\sigma,\alpha) &\leq tol_{\text{step}} \\ \frac{1}{\sigma}\frac{\mathrm{d}O_{IJ}(\vec{R};\sigma,\alpha)}{\mathrm{d}\vec{R}}\cdot\vec{u} &\leq tol_{\text{grad}} \\ \left|\frac{\mathrm{d}O_{IJ}(\vec{R};\sigma,\alpha)}{\mathrm{d}\vec{R}} - \left(\frac{\mathrm{d}O_{IJ}(\vec{R};\sigma,\alpha)}{\mathrm{d}\vec{R}}\cdot\vec{u}\right)\vec{u}\right| &\leq tol_{\text{grad}} \end{aligned}\right\}$$ (Convergence Criteria)

Machine learning enters the stage

- Penalty methods are computationally expensive, no research exists on the MECI of large molecules [2].
- Some methods exist for MECI computation *via* KRR but they haven't been applied to larger systems [6].
- MLIPs such as MACE output continuously differentiable functions, making the problem well-posed.
- Using them to train a model would severely reduce the computational cost.
- Can also use existing databases to reduce the computational cost of running DFT calculations.



[6] *J. Phys. Chem. Lett.* **2023**, *14*, 7780.