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Conical Intersections and Photochemical Mechanisms: Characterizing the Conical Intersection Hyperline using Gradients, Second Derivatives, and Dynamics.

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Conical intersections (CIs) are essential for the description of radiationless decay processes involved in photochemistry.[1-8] In two geometrical variables (ie the branching space spanned by the gradient difference vector and the inter-state coupling vector), a conical intersection appears as a funnel. However, we know that an intersection is in fact a hyperline, i.e., a (3N-8)-dimensional space, where (3N-6) is the number of vibrational degrees of freedom, and that the 'conical intersections' we optimize with gradient-driven algorithms are critical points in this (3N-8)-dimensional space. Now that on-the-fly dynamics is possible,[9-13] computations are beginning to explore the nature of the intersection hyperline away from its minimum. Such competitions show that these higher-energy regions of a conical intersection hyperline can be chemically significant. In addition, algorithms have been developed to map out (minimum energy path) segments of the hyperline explicitly.[14]

For a discussion of mechanistic photochemistry, one needs a minimum of three geometric variables to describe the non-adiabatic event: the reaction path, and the two vectors which span the branching space. When the reaction path is contained in the branching space, one has a "sand in the funnel model". However, as we shall show, there are many chemical problems where it the reaction path lies almost "parallel" to the seam of the conical intersection. In this type of problem, dynamics is essential.

The quantum chemistry tools that we have available for the study of non-adiabatic processes include gradient driven methods that can be used to optimise a critical point on a conical intersection. Many questions on photochemical reactivity can be answered by optimising such conical intersections and by following minimum energy pathways on excited-state. In this approach, it becomes useful to determine whether or not an optimised conical intersection is a minimum on the conical intersection hyperline (or perhaps a transition state or higher order maximum). To this end, we will discuss a second order approach to the characterisation of conical intersections.

Our method[15] uses the projected Hessians of the degenerate states, after elimination of the two branching space coordinates, and is equivalent to a frequency calculation on a single Born-Oppenheimer potential energy surface. Based on projected Hessians, we have developed an equation for the energy as a function of a set of curvilinear coordinates where the degeneracy is preserved to second-order (i.e., the conical intersection hyperline). The curvature of the potential energy surface in these coordinates is the curvature of the conical intersection hyperline itself, and thus determines whether one has a minimum or saddle-point on the hyperline. The equation used to classify optimized conical intersection points depends in a simple way on the first- and second-order degeneracy splittings calculated at these points. As an example, for fulvene we can show that the two optimized conical intersection points of C_{2v} symmetry are saddle-points on the intersection hyperline. Accordingly, there are further intersection points of lower energy, including one of C_2 which is the global minimum in the intersection space.

When the sand in the funnel model is not appropriate because the reaction path does not lie in the branching space, then only dynamics can provide mechanistic information. Accordingly, the second thread in our development will be a review of the information on the topology of the conical intersection hyperline that has emerged from our dynamics computations. As an example we shall discuss the dynamics of the photoactivation[16] of the photoactive yellow protein PYP. Our objective is to obtain an understanding of why photon absorption triggers a trans-to-cis isomerization of the chromophore in the protein.

In vacuo, there is a transition-state and minimum where the chromophore is partly twisted, and a minimum with a half twist. The coordinates that lift the degeneracy are the skeletal deformations. The main point is that the conical intersection in the protein and in the gas-phase are significantly different. Dynamics in the gas-phase involves substantial additional motion to reach the seam at the half twist geometry.

In the gas phase dynamics, using the same initial conditions as in the protein simulations, the system never makes it over the first partial twist torsion barrier. In contrast, in the protein, the excited state is specifically stabilized by the charge distribution of the protein. Thus in the protein one observes a decrease of the S_1-S_0 energy gap in the region of the twisted intermediate (from 80 kJ mol^{-1} in *vacuo* to less than 1 kJ mol^{-1} in the protein), accompanied by a displacement of the crossing seam closer to the global minimum. One also sees a decrease of the energy barrier separating the early *planar* S_1 minimum and the *twisted* S_1 minimum. In total 14 dynamics simulations are discussed in ref 16. In the protein, the lifetime of the excited state ranged from 129 to 2293 fs. The ratio of the number of successful isomerizations to the number of excited-state trajectories is ca. 0.3, close to the experimental quantum yield of 0.35[7]. Statistically, the number of trajectories is small but nevertheless yields a consistent mechanistic picture.

The PYP example is a dramatic example of a situation the reactivity is changed when you add the electric field of the protein. Nature has been very careful to position one charged residue in exactly the right place.

[1] Atchity, G. J.; Xantheas, S. S.; Ruedenberg, K. *J. Chem. Phys.* **1991**, *95*, 1862.
[2] Klessinger, M.; Michel, J. *Excited States and Photochemistry of Organic Molecules*; VCH: New York, 1995.
[3] Yarkony, D. R. *Rev. Mod. Phys.* **1996**, *68*, 985.
[4] Yarkony, D. R. *Acc. Chem. Res.* **1998**, *31*, 511.
[5] Yarkony, D. R. *J. Phys. Chem. A* **2001**, *105*, 6277.
[6] Bernardi, F.; Olivucci, M.; Robb, M. A. *Chem. Soc. Rev.* **1996**, *25*, 321.
[7] Robb, M. A.; Garavelli, M.; Olivucci, M.; Bernardi, F. A Computational Strategy for Organic Photochemistry. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2000; Vol. 15; pp 87–146.
[8] Olivucci, M.; Migani, A. In *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*; Domcke, W., Yarkony, D., Köppel, H., Eds.; World Scientific, 2004; Vol. 15.
[9] Sanchez-Galvez, A.; Hunt, P. A.; Robb, M. A.; Olivucci, M.; Vreven, T.; Schlegel, H. B. *J. Am. Chem. Soc.* **2000**, *122*, 2911.
[10] Ben-Nun, M.; Quenneville, J.; Martinez, T. J. *J. Phys. Chem. A* **2000**, *104*, 5161.
[11] Boggio-Pasqua, M.; Ravaglia, M.; Bearpark, M. J.; Garavelli, M.; Robb, M. A. *J. Phys. Chem. A* **2003**, *107*, 11139.
[12] Ko, C.; Levine, B.; Toniolo, A.; Manohar, L.; Olsen, S.; Werner, H.-J.; Martinez, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12710.
[13] Weingart, O.; Migani, A.; Olivucci, M.; Robb, M. A.; Buss, V.; Hunt, P. *J. Phys. Chem. A* **2004**, *108*, 4685.
[14] Migani, A.; Robb, M. A.; Olivucci, M. *J. Am. Chem. Soc.* **2003**, *125*, 2804.
[15] Paterson, M. J.; Bearpark, M. J.; Robb, M. A.; Blancafort, L. (submitted).
[16] Groenhof, G.; Bouxin-Cademartory, M.; Hess, B.; de Visser, S. P.; Berendsen, H.; Olivucci, M.; Mark, A. E.; Robb, M.A. *J. Amer. Chem. Soc.* **2004** *126* , 4228-4233.