COST P9-STSM 02572 Visit Report

Adenine, cytosine, guanine and thymine are the four nucleic acids, which encode the genetic information of all living creatures in the deoxyribonucleic acid (DNA). Recently, these DNA bases have been extensively studied both experimentally and theoretically (for a recent review *see* Ref.1). As new experimental data are collected, several theoretical studies have been carried out to interpret them. For example, spectroscopic results have shown that DNA bases absorb strongly in the range of 200-300 nm. However, the quantum yields of their photoproducts are very low. In addition, experiments have demonstrated that the lifetimes of the excited states for these molecules are only a few hundred femtoseconds long. Accordingly, computational studies have shown that very efficient channels of radiationless deactivation are indeed energetically accessible. Studies on cytosine,[2-4] 5-fluoro cytosine,[5] and adenine,[6] have shown that conical intersections geometries are involved in these radiationless decays from the excited states. Conical intersections have a key role in the ultrafast decays, as they provide direct access from the excited state to the ground state.

Over the years, several algorithms to locate conical intersection structures have been proposed (*see* for instance Ref. 7). All of these methodologies have the common scope to locate the conical intersection structure with the lowest energy. This is mainly due to the belief that the lowest-energy point in the intersection space is the structure at which the surface hop takes place. That is, the conical intersection geometry involved in the radiationless decay has been thought to be the lowest in energy. However, recent studies have showed that decay may take also place at a higher energy points along the intersection space (*see* for example Ref. 8). Particularly, in systems of biological interest would appear that structures along the crossing seam away from the minimum might play a key role in the decay processes. Thus, a complete mapping of finite segments of the intersection seam may reveal unexpected connections between the connectivity of points along the crossing hyperline and the photoproducts of a given photochemical reaction. Furthermore, such analysis may also uncover possible relationships between the topological features of the crossing seam and the photostability of molecular systems.

In this spirit, we have recently developed a new methodology to describe conical intersections at the second order. This extended description allows one to compute the curvature of the crossing seam energy, such that saddle points could be distinguished from minimum points within the intersection space[9]. In the applicant's previous visit a new and more efficient conical intersection algorithm was implemented exploiting the insights gained by this second-order characterization of the intersection seam[10]. During this further STMS visit, the applicant has instead implemented an algorithm to compute the minimum energy path within the intersection space. Such coordinate, or path, is capable to connect two conical intersection minima through a saddle point along the crossing hyperline. Thus, a uniquely definition of the crossing seam can be obtained and possible connections amongst structures belonging to the same crossing seam found.

The methodology here described is partly based on the algorithm proposed by Gonzales *et al.*[11] and on the algorithm implemented by the applicant in his previous SMST visit[10]. However, we opted for reporting here only a qualitatively description of the implemented algorithm, rather than its detailed mathematical derivation. Thus, we begin recalling that a conical intersection is a point at which two potential energy surfaces become degenerate. When the two potential energy surfaces are plotted with respect to two well-defined coordinates, *e.g.* the gradient difference and the non-adiabatic interstate coupling vector (*see* for example Ref. 12), the classical double cone profile arises. The plane spanned by these two vectors is the first-order approximation of the branching space[13], that is, the subspace where the degeneracy is lifted. However, a conical intersection point is not an isolated point, but rather belongs to a (*3N-8*)-dimensional subspace, where N is the number of atoms. That is, the intersection space[13]. As extensively discussed elsewhere, the intersection seam is not generally linear, but curved (*see* for example Ref. 14 and references therein). Thus, it is intuitive to expect that any rectilinear displacement taken away form a degeneracy point will make the two potential energy surfaces to split apart. In the algorithm implemented during the applicant's SMST visit, projector matrices are used to obtain the intersection space energy gradient and Hessian. Then, using a Raphson-Newton method an intersection space displacement is computed. As described for the conical intersection optimization algorithm[10], a further step is added to the intersection space displacement, such that the degeneracy can also be achieved. Our methodology enables one to compute an intrinsic reaction coordinate equivalent to that described by Gonzales *et al.*[11], but confined exclusively to the first-order intersection space.

Recently we have extensively investigated the crossing seam between the S_0/S_1 ($1^1A_g/2^1A_g$) electronic states of butadiene[14]. Thus, we decided to use such crossing seam to demonstrate the potentialities and applicability of the implemented algorithm. As we will discuss below, the results obtained are decisively encouraging so that we will shortly begin to investigate more complex systems, such as DNA bases.

The algorithm has been implemented in a development version of Gaussian[15] and all the calculations were carried out at state-average complete-active-space-self-consistent-field (SA-CASSCF) level of theory. An active space constituting of four π electrons and four π orbitals and a STO-3G basis set were used throughout this study. We emphasize that a geometry was considered converged when the gradient perpendicular to the intersection-space coordinate and the displacement were below a certain threshold. This threshold was set to 0.0018 a.u. for the displacement; and to 0.00045 a.u. for the gradient.

In our recent investigation of the butadiene crossing seam, we have found a region where several conical intersection saddle point structures were located[14]. With saddle points we mean structures belonging to the intersection space, and therefore at which two electronic states are degenerate, but also characterized by one or more negative curvatures.

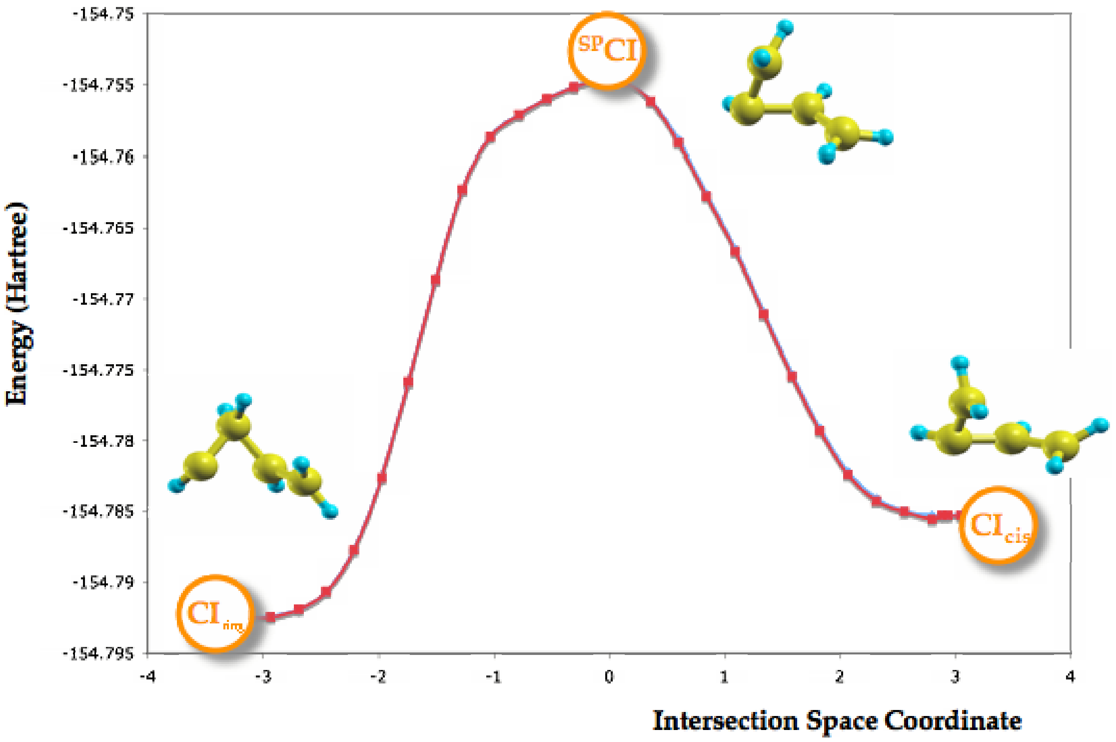

Figure 1 – Minimum energy path connecting three conical intersections, which belong to the S_0/S_1 butadiene crossing seam.

In our previous study, we also used a nomenclature that could help one to realize possible connections amongst different structures. For example, the **^{SP}CI$_{cis/ring}$** indicated a saddle point (^{SP}) conical intersection (CI) connecting the

$\mathbf{CI_{cis}}$ to the $\mathbf{CI_{ring}}$. The latter structures had both been characterized as minima along the crossing seam. In that study, however, we could only suspect that the three geometries were actually connected, as a connecting path could not be computed.

In Figure 1, we report the results obtained using the newly implemented algorithm to compute the intersection minimum energy path connecting the $\mathbf{CI_{cis}}$, $\mathbf{^{SP}CI_{cis/ring}}$ and $\mathbf{CI_{ring}}$. Starting from the $\mathbf{^{SP}CI_{cis/ring}}$ structure, a step has been taken in the direction of the eigenvector corresponding to the imaginary seam frequency. The energy profile along the computed coordinate is reported in Figure 1. The degeneracy between the two crossing states is always maintained below 0.1 kcal mol^{-1}. Thus, the implemented algorithm seems to maintain satisfactorily well the degeneracy between the two states. In addition, it should also be noticed that the energy profile along the computed coordinate shows no discontinuities. Therefore, this study allows us to confirm our initial proposal that the three structures are connected along the same crossing seam. In addition, from Figure 1, it is apparent that the implemented algorithm is capable to compute a uniquely defined portion of intersection space connecting the three different conical intersection geometries.

Another example of a minimum energy path calculation is reported in Figure 2. In this case the path connecting $\mathbf{CI_{cis}}$, $\mathbf{CI_{trans}}$ and $\mathbf{^{SP}CI_{cis/trans}}$ have been studied.

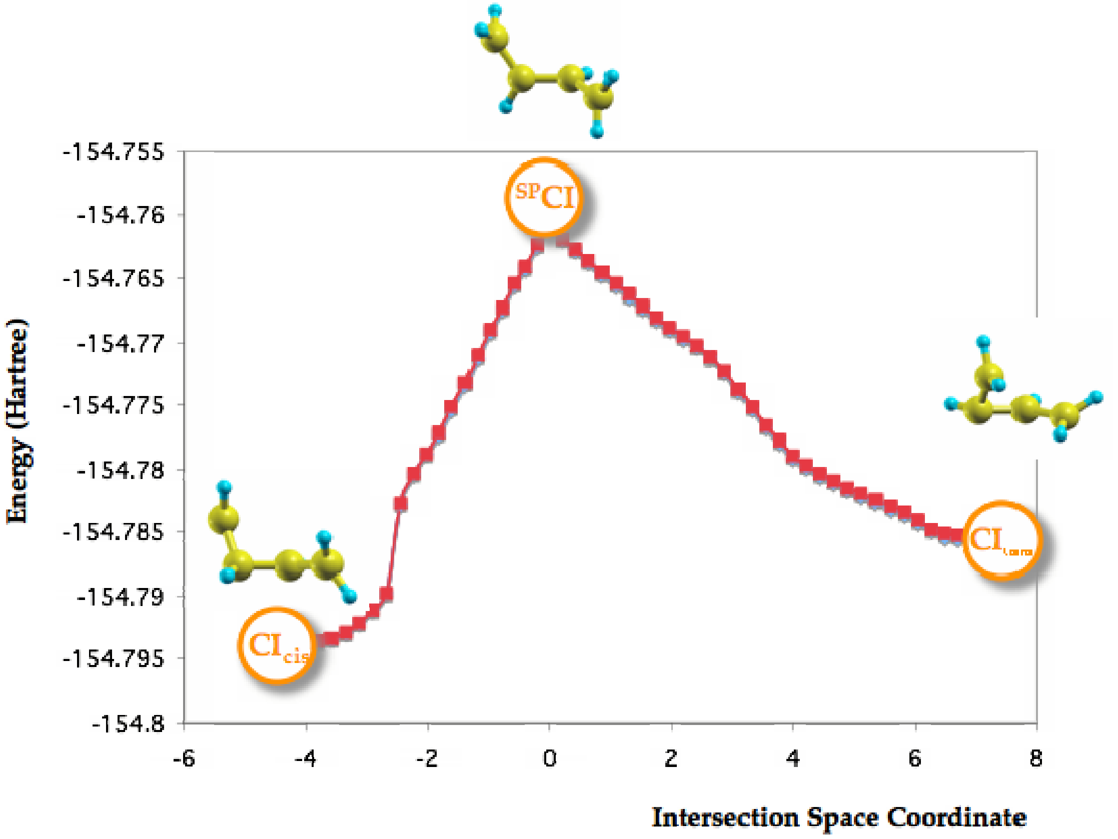

Figure 2 – Portion of the crossing seam connecting three distinct conical intersection geometries. The intersection space coordinate and the corresponding energy profile has been computed with the implemented algorithm here described.

Although also in this case the degeneracy is well retained, the energy profile obtained for this coordinate is not as smooth as the previous one. However, similar profiles have been previously reported by other workers[8], who studied cis-trans isomerizations.

To summarize, we have shown the preliminary results obtained with the algorithm implemented during the applicant's SMTS visit. Such algorithm was tested on a well-studied S_0/S_1 butadiene crossing seam and the results are consistent with the data reported in literature (*see* Ref. 9 and references therein). The possibility of linking different conical intersections and mapping out finite regions of intersection space has several implications. One can understand, for instance, whether all crossing seam structures are energetically accessible and belonging to the same crossing seam. Furthermore, the energetic accessibility can be used to establish the possible role in the radionless decay.

In the two visits of the applicant, a more efficient conical intersection algorithm to optimize conical intersection geometries and a new algorithm capable to trace out regions of the crossing seam have been developed. The potentialities of the two algorithms have been demonstrated in the investigations of two well-known crossing seams. These preliminary tests have produced encouraging results, which would suggest that the two algorithms can be successfully used to study more complex and bigger systems, e.g. DNA nucleobases.

We conclude mentioning that the results of the research carried out by the applicant during his SMST visit and partly reported here are part of a manuscript in preparation.

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