STMS Visit Report

In the recent years, the photophysics of DNA nucleobases has attracted the attention of many workers. The availability of spectroscopic results at femtosecond resolution has stimulated several theoretical studies, of which aim was to interpret such data and eventually to understand the photophysics of these important building blocks of life[1]. Studies on cytosine,[2-4] 5-fluoro cytosine,[5] and adenine,[6] have shown that conical intersections geometries are involved in the decay from the excited states of these molecular systems. In these studies mechanisms involving fast decays from excited states through conical intersections were proposed to rationalize the ultra-short fluorescence lifetimes of DNA nucleobases. Conical intersections have a key role in the ultrafast decays, as they provide direct access from the excited state to the ground state.

The study of the photochemistry and photophysics of a given molecular system is often carried out at the CASSCF level of theory, which allows for a balanced treatment of the ground and excited states. However, at this level of theory to carry out an optimization of conical intersection geometries for large systems, such as a DNA nucleobase, may become expensive or even prohibitive. Thus, in order to study molecular system of biological interest, efficient algorithms become mandatory. The purpose of the STMS visit has been to improve the algorithm currently available in the Gaussian package.

The conical intersection algorithm currently implemented in Gaussian package was designed by Bearpark et al.[8]. In this algorithm the Hessian, necessary to carry out a standard optimization based on the Newton-Raphson method, is an approximated Hessian. The update of this matrix is carried out by means of a gradient obtained as linear combination of the gradient difference vector and the excited-state gradient projected onto the intersection space. An ill-conditioned

Hessian seems to be the major cause of the algorithm failures. Thus, a more accurate definition of the intersection space gradient as well as of the intersection-space Hessian could improve drastically the algorithm.

Recently we have presented elsewhere a second–order description of conical intersections[9-12]. In these studies, the intersection-space Hessian was defined and analytically computed. Thus, our proposal for the applicant's SMTS visit was to exploit the insight gained from the analysis of the conical intersection at the second order to the optimization related issues in order to define a more efficient algorithm to optimize conical intersection geometries.

During the STMS visit of the candidate a new algorithm for conical intersection has been implemented in a development version of Gaussian[7]. The implemented algorithm is partly based on the theoretical work previously proposed by Anglada et al.[13] In that work, a "reduced Hessian" was proposed to compute the Newton-Raphson step in the intersection-space. Such matrix corresponds exactly to the intersection-space Hessian that we have recently proposed[8-11].

As we will show below, the algorithm proposed by Anglada et al. is capable to provide an accurate description of the potential energy topology of the crossing seam. However, such methodology considers the branching space only at the first order, through the so-called parabolic approximation[10]. Thus, the algorithm proposed in that study is fairly slow in approaching the crossing seam. We have then decided to implement a hybrid algorithm. In the first part of the optimization, *i.e.* when the seam is to be approached, the Bearpark algorithm[7] is used. Subsequently, when a point close to the crossing seam is found the Anglada-Bofill algorithm[13] is adopted to carry out the intersection space optimization. The hybrid algorithm proposed here can be thought of as an application of the penalty function method with non-constant penalty

parameters[14]. In the first part of the optimization, when the Bearpark algorithm is used, the gradient and the Hessian used are the gradient and Hessian of an *augmented Lagrangian*[14] with penalty factor set to 2. Once we are in the region of the crossing seam (the energy difference is smaller than a certain threshold) such penalty parameter is then set to zero. Consequently, the gradient and the Hessian of the new Lagrangian function equal the gradient and the Hessian proposed by Anglada et al.

The hybrid method proposed uses the two algorithms in different regions of the potential energy surface. However, from a strictly theoretical point the two algorithms should perform equally well along the intersection seam. There is therefore no apparent reason to implement the Anglada algorithm in addition to the Bearpark algorithm already present. Nevertheless, in practice the Hessian computed with the composite gradient used in the Bearpark algorithm fails to give the correct curvature of the intersection seam. Therefore the step taken within the intersection-space is often too large and the degeneracy is lost.

We finally mention that the hybrid conical intersection optimization algorithm was implemented such that the optimization is entirely carried out in redundant coordinates, as suggested by Peng et al.[15]. Preliminary tests show the promising potentialities of this hybrid algorithm, as we will now discuss.

The implemented algorithm has been tested on the S_0/S_1 crossing seam of benzene. The same seam had been used as benchmark for the algorithm currently implemented in the commercial version of Gaussian, i.e. the Bearpark algorithm[7]. In that study as well as in the one proposed here, the calculations were carried out at the CASSCF level of theory, with a six electron and six orbitals active-space and a STO-3G basis set. In this study, a conical intersection geometry is considered converged when the largest component of the

intersection-space gradient is smaller than 0.00045 a.u. and the RMS of the same vector does not exceed 0.00030 a.u.. In addition to the gradient, also the maximum component of the Newton-Raphson displacement is checked.

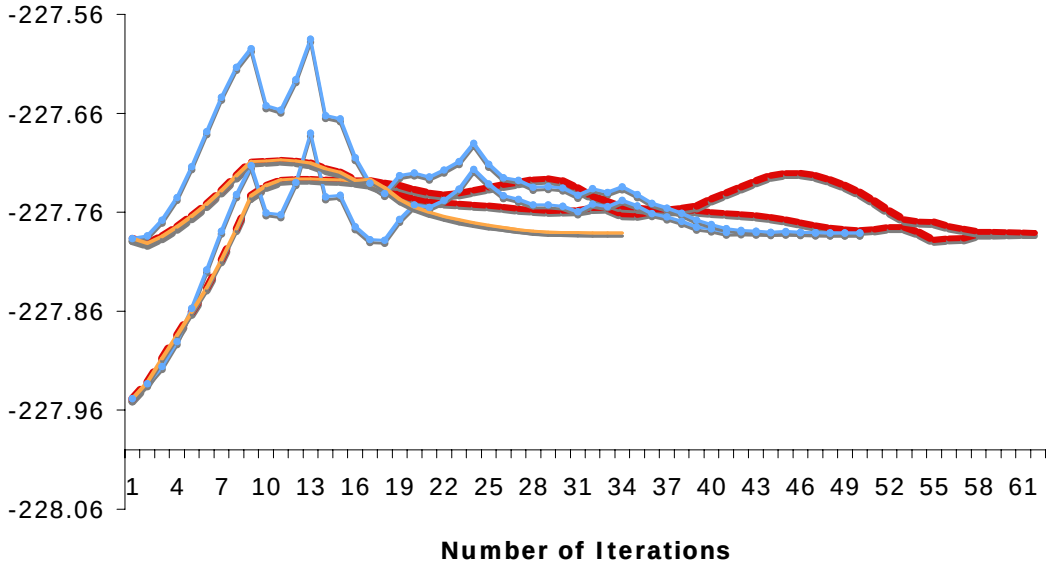

Figure 1 – Global convergence of an optimization of the S_0/S_1 conical intersection of benzene. The results obtained with the Anglada-Bofill algorithm (line and filled circles), with the Bearpark angorithm (dotted line) and the proposed hybrid algorithm (bold line) are reported.

A geometry is considered converged when the largest component of such a displacement is smaller than 0.0018 a.u. with RMS 0.0012 a.u.. In the application reported here, the hybrid algorithm used the Bearpark gradient and Hessian in the regions where the energy difference between the two states was bigger than 5 milliHartrees.

In Figure 1, the global convergence of the benzene S_0/S_1 conical intersection optimization computed with the Bearpark, the Anglada-Bofill and the hybrid algorithm is reported. The three conical intersection optimizations were started from a benzene structure obtained by distorting slightly the minimum structure (Figure 2a) on the S_1 potential energy surface[16]. All the three algorithms located the same conical intersection geometry (Figure 2b). Nevertheless the number of

steps required by the algorithms to converge is considerably different. The hybrid algorithm is the fastest algorithm to converge (Figure 1) and is also capable to better retain the degeneracy between the two crossing states.

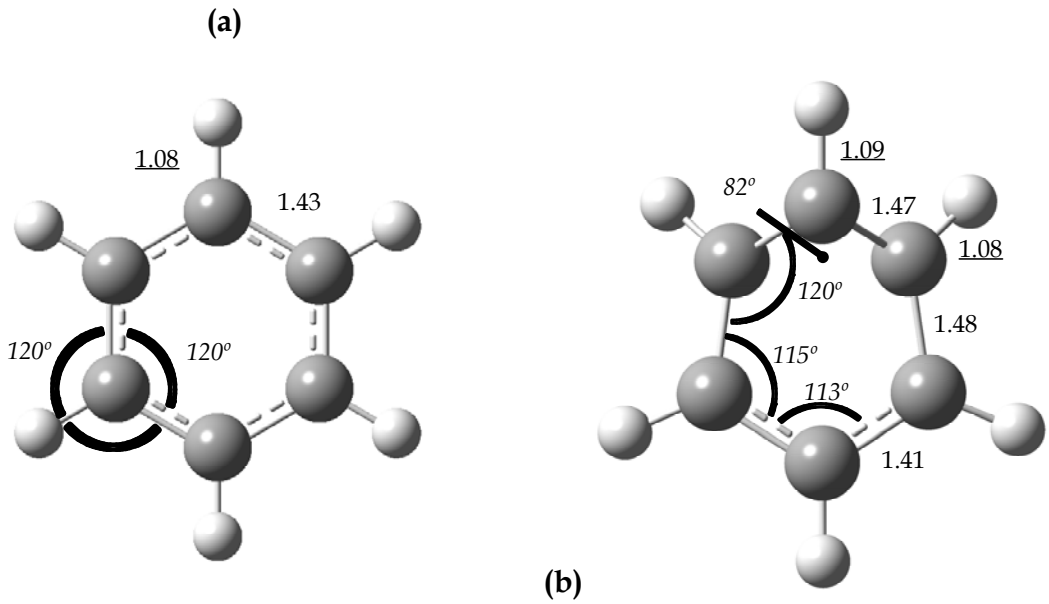

Figure 2 – Starting benzene geometry **(a)** and optimized S_0/S_1 conical intersection geometry **(b)**. All the angles (*italic*) are reported in degrees, while the C-H (underlined) and C-C bonds are reported in Angstrom.

To emphasize this last point, in Figure 3, the difference of the energies of the S_0 and S_1 states of benzene is shown. The hybrid algorithm keeps diminishing constantly the energy gap between the two states as the optimization proceeds. In addition, the proposed algorithm shows fewer oscillations of the energy difference values. This result is consistent with having a more accurate intersection-space Hessian.

In summary, from this preliminary test the hybrid algorithm shows a faster convergence to an optimized conical intersection, presumably, due to a better estimation of the approximated Hessian. These results are encouraging and suggest that the use of the implemented algorithm may be involved successfully

in the optimization of conical intersection geometries for large systems, such as DNA nucleobases. In a further visit, the applicants will begin the investigation of the intersection seam of some DNA bases using the implemented algorithm.

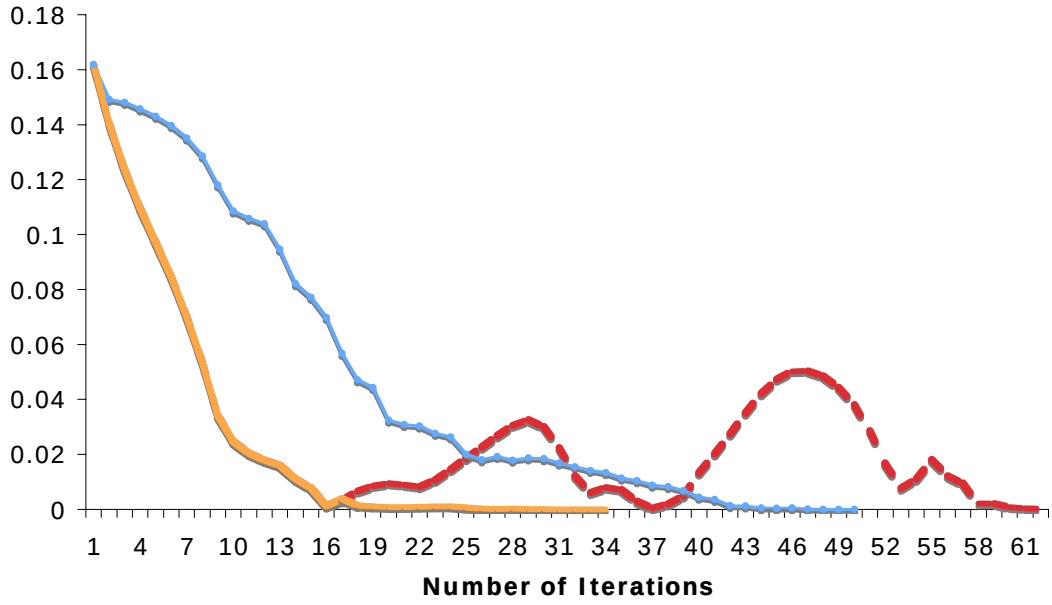

Figure 3 – Energy Difference between S_0 and S_1 states in benzene during the conical intersection optimization. The results obtained with the Anglada-Bofill algorithm (line and filled circles), with the Bearpark angorithm (dotted line) and the proposed hybrid algorithm (bold line) are reported.

In addition, further tests will be run, in order to test the validity of the method in circumstances where the crossing states have different spin symmetries and give rise to, for instance, singlet-triplet crossings.

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.

• References

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