CONICAL INTERSECTION OPTIMIZATION ALGORITHMS BASED ON THE INTERSECTION SPACE HESSIAN.

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Conical intersections are crucial for the understanding of photochemical reactions, and their location is one of the main steps in computational photochemistry studies. This is usually carried out by optimizing the geometry in an (N-2)-dimensional subspace of the potential energy surface, applying an energy degeneracy constrain.

One of the most commonly used algorithms is the one of Bearpark and coworkers,[1] which uses a hybrid gradient composed of the gradient projected to the subspace, and a penalty term to reach the degeneracy. Recently a new algorithm was proposed based on the intersection space Hessian,[2] which improves the optimization in the subspace of intersection.

Here we carry out a comparison of the convergence of both algorithms for 13 test cases, paying special attention to different update schemes for the intersection space Hessian. We also present a new algorithm that aims to improve the approach to the intersection seam by using two separate Hessians, the intersection space Hessian and one based on the energy difference.

[1] Bearpark, M. J. ; Robb, M. A.: Schlegel, H. B. *Chem. Phys. Lett.*, 223, 269 (1994)
[2] F. Sicilia, Ll. Blancafort, M. J. Bearpark, M. A. Robb, *J. Chem. Theory Comput*., 4, 257-266 (2008)