An Algorithm to Locate Optimal Bond Breaking Points on a Potential Energy Surface for Applications in Mechanochemistry and Catalysis

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Mechanochemistry is an emerging research field that focuses on the promotion of chemical reactions by means of mechanical forces.[1] It is well established that that the force-induced structural changes of minima and saddle points can be described by a Newton Trajectory (NT) on the original or stress-free potential energy surface (PES).[2] Given a reactive molecular system and a well-fitting pulling direction, there is a sufficiently large value of the force for which the minimum configuration of the reactant and the saddle point configuration of a transition state collapse at one point on the corresponding NT. This point is called barrier breakdown point or bond breaking point (BBP).[3] The Hessian matrix at the BBP has a zero eigenvalue and the corresponding gradient indicates which force (both in magnitude and direction) should be applied to the system to mechanically induce the reaction in a barrierless process. Within the manifold of BBPs, there exist optimal BBPs [3] which indicate what is the optimal pulling direction and what is the minimal magnitude of the force to be applied for a given mechanochemical transformation. At the optimal BBPs, the gradient coincides with the eigenvector of the Hessian matrix with null eigenvalue. Since these special points are very important in the context of mechanochemistry and catalysis, it is crucial to develop efficient algorithms for their location. Here, we shall present a Gauss-Newton algorithm that is based on the minimization of a positively defined function (the so called σ-function). The behavior and efficiency of the new algorithm will be shown for 2D test functions and for a real chemical example.

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