AN ALGORITHM TO LOCATE OPTIMAL BOND BREAKING POINTS ON POTENTIAL ENERGY SURFACES FOR MECHANOCHEMICAL REACTIONS

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Introduction

Mechanochemistry is an emergent research field that focuses on the promotion of chemical reactions by means of mechanical forces.[1] Single-molecule force spectroscopy techniques, sonochemical techniques and molecular force probes have enabled the application of tensile forces to molecular systems. From a conceptual point of view, the phenomenon of mechanical activation can be understood on the basis of the fact that the potential energy surface (PES) of a given reactive system changes when this system is subjected to tensile stress. As a result of these force-induced changes of the PES, the barriers between the reactant and the product change. If we consider the case in which a constant stretching is applied to a molecular system, the resulting modified PES (which can be called force-transformed PES[2]) or force-modified PES[3]) is obtained via

\[ \nabla V(x) = \frac{\partial V(x)}{\partial x} = s(x) \quad \text{Eq (1)} \]

The movement of the stationary points on the original or stress-free PES can be described by a Newton Trajectory (NT).[4]

An algorithm to locate optimal BBPs

The algorithm herein proposed[4] is based on the rational function optimization technique, where \( \psi \) and \( \Delta \) are obtained by the solution of the following eigenvalue equation:

\[ \begin{bmatrix} 0 & s^{(\psi)} \Delta^{(\psi)} \\ \Delta^{(\psi)} & 1 \end{bmatrix} = \psi \begin{bmatrix} 1 & \Delta^{(\psi)} \\
0 & 1 \end{bmatrix} \quad \text{Eq (9)} \]

taking the eigenvector of the lowest eigenvalue. The matrix \( \psi \) is updated following the Broyden formula. The algorithm flow is illustrated in the following steps:

Step 1. Set \( \psi \) and \( \Delta \), and calculate the \( \psi \) matrix with

\[ \psi = \frac{\partial U(x)}{\partial x} \quad \text{Eq (5)} \]

where \( \psi \) is the i-th component of the unit matrix. Calculate \( \Delta \).

Step 2. Set \( \psi = \psi + 1 \) and form the following vector and matrix:

\[ \psi^{(\psi)} = \psi^{(\psi)} \quad \text{Eq (6)} \]

Step 3. Form the following matrix and diagonalize:

\[ \begin{bmatrix} 0 & \psi^{(\psi)} \\ \psi^{(\psi)} & 1 \end{bmatrix} = \psi^{(\psi)} \begin{bmatrix} 1 & \Delta^{(\psi)} \\
0 & 1 \end{bmatrix} \quad \text{Eq (7)} \]

Step 4. Let \( \Delta \) be the eigenvector of the smallest eigenvalue of the matrix \( \psi \). Set \( \psi^{(\psi)} = \psi^{(\psi)} \), where \( \psi^{(\psi)} \) is the first component of the \( \psi \) vector. Set \( \psi^{(\psi)} = \psi^{(\psi)} \), where \( \psi^{(\psi)} \) is formed by the last \( \psi \) components of the \( \psi \) vector.

Step 5. Perform a line search to determine \( \psi^{(\psi)} \) that minimizes \( s \) and \( \psi^{(\psi)} \).

The line search is stopped when

\[ \text{max} = \text{max} + \Delta \psi^{(\psi)} \quad \text{Eq (8)} \]

Step 6. If \( \text{max} \leq \epsilon \), exit else go to Step 7.

Step 7. Compute the vectors \( \psi^{(\psi)} \) and \( \psi^{(\psi)} \) and the matrix \( \psi^{(\psi)} \)

\[ \begin{bmatrix} \psi^{(\psi)} & \psi^{(\psi)} \Delta^{(\psi)} \\
\psi^{(\psi)} & 1 \end{bmatrix} = \psi^{(\psi)} \begin{bmatrix} 1 & \Delta^{(\psi)} \\
0 & 1 \end{bmatrix} \quad \text{Eq (9)} \]

The algorithm only needs the parameters \( \psi^{(\psi)}, \psi^{(\psi)} \), and the maximum number of iterations.

Performance of the algorithm

Two dimensional examples. The Rosenbrock and Müller-Brown surfaces

The algorithm is able to efficiently locate optimal BBPs in the case of well-known 2D test functions

A chemical example: the 1,2-sigmatropic H-shift rearrangement of cyclopentadiene

The algorithm also works efficiently when located optimal BBPs of a multidimensional PES associated with a real chemical transformation. We have chosen the 1,2-sigmatropic H-shift rearrangement of cyclopentadiene as a model system.

In order to locate the optimal BBP associated with the reactant valley of this reaction, the algorithm was interfaced with the TURBOMOLE code. The electronic structure calculations were done at the B3LYP/TZVP level. Starting from the IRC-BBP, the minimization of the \( \psi \) function converged in 19 steps.

Conclusions

We have presented an algorithm based on the Gauss–Newton method to locate optimal bond-breaking points on the PES of a molecular system. Given the relevance of the bond-breaking point concept, we hope that our algorithm will assist in the design of more efficient ways of harnessing mechanical forces in the activation of chemical reactions.

References