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

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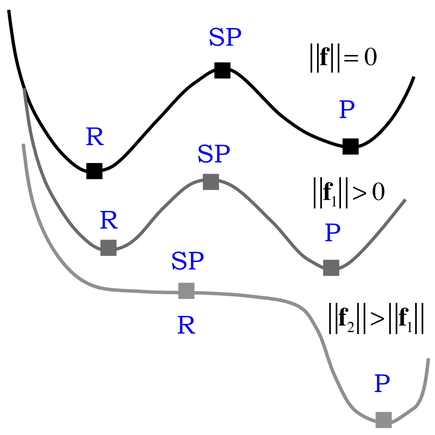
Introduction

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 minimums and the saddle points 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[2a] or force-modified PES[2b]) is obtained via

$$V_f(\mathbf{x}) = V(\mathbf{x}) - \mathbf{f}^T \cdot (\mathbf{x} - \mathbf{x}_0) \qquad \text{Eq (1)}$$



The movement of the stationary points on the original or stress-free PES can be described by a Newton Trajectory (NT).[3]

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**).[4] 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 of a given PES, there is an ***optimal BBP***, which satisfies the following equation:

$$\mathbf{H}(\mathbf{x})\mathbf{g}(\mathbf{x}) = 0 \qquad \text{Eq (2)}$$

which means that at an optimal BBP, the gradient is an eigenvector of the Hessian matrix with null eigenvalue. The location of ***optimal BBPs*** is extremely important in the context of mechanochemistry because these points reveal which is the most efficient way to trigger a reaction by means of a mechanical force.

The σ function for locating optimal BBPs

Locating optimal BBPs is equivalent to finding the zero of the σ function, which is defined as[5]:

$$\sigma(\mathbf{x}) = \frac{\mathbf{g}^T(\mathbf{x})\mathbf{H}^2(\mathbf{x})\mathbf{g}(\mathbf{x})}{\mathbf{g}^T(\mathbf{x})\mathbf{g}(\mathbf{x})} = \mathbf{s}^T(\mathbf{x})\mathbf{s}(\mathbf{x}) \qquad \text{Eq (3)}$$

where $\mathbf{s}(\mathbf{x}) = \mathbf{H}(\mathbf{x})\mathbf{g}(\mathbf{x})\left|\left|\mathbf{g}(\mathbf{x})\right|\right|^{-1}$ Eq (4)

The σ function is a sum of squares of nonlinear functions. To find its zero falls into the class of the so-called nonlinear least squares problems.

The zeros of the σ function can be found using the *Gauss-Newton* method. For such a task, one needs the expression of the first derivative of the function and an approximate expression for the second derivative:

$$\nabla_{\mathbf{x}}\sigma(\mathbf{x}) = 2\mathbf{J}(\mathbf{x})\mathbf{s}(\mathbf{x}) \qquad \text{Eq (5)} \qquad \nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T\sigma(\mathbf{x}) \approx 2\mathbf{J}(\mathbf{x})\mathbf{J}^T(\mathbf{x}) \qquad \text{Eq (6)}$$

where **J**(**x**) is the Jacobi matrix: $\mathbf{J}(\mathbf{x}) = \left[\nabla_{\mathbf{x}}\mathbf{s}^T(\mathbf{x})\right]$ Eq (7)

Since the Gauss-Newton method can fail or converge slowly, we use the restricted step algorithm to improve its performance. In the *i*th-iteration, the *modified Gauss-Newton* is:

$$\begin{cases} [\mathbf{J}^{(i)}\mathbf{J}^{(i)T} - \nu^{(i)}\mathbf{I}]\Delta\mathbf{x}^{(i)} = -\mathbf{J}^{(i)}\mathbf{s}^{(i)}, \quad \nu^{(i)} \le 0 \\ \mathbf{x}^{(i+1)} = \mathbf{x}^{(i)} + \alpha^{(i)}\Delta\mathbf{x}^{(i)}, \end{cases} \qquad \text{Eq (8)}$$

where $\mathbf{J}^{(i)} = \mathbf{J}(\mathbf{x}^{(i)})$, $\mathbf{s}^{(i)} = \mathbf{s}(\mathbf{x}^{(i)})$ and $\alpha^{(i)}$ is a parameter

An algorithm to locate optimal BBPs

The algorithm herein proposed[5] is based on the rational function optimization technique, where $\nu^{(i)}$ and $\Delta\mathbf{x}^{(i)}$ are obtained by the solution of the following eigenvalue equation:

$$\begin{pmatrix} 0 & \mathbf{s}^{(i)T}\mathbf{J}^{(i)T} \\ \mathbf{J}^{(i)}\mathbf{s}^{(i)} & \mathbf{J}^{(i)}\mathbf{J}^{(i)T} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta\mathbf{x}^{(i)} \end{pmatrix} = \nu^{(i)} \begin{pmatrix} 1 \\ \Delta\mathbf{x}^{(i)} \end{pmatrix} \qquad \text{Eq (9)}$$

taking the eigenvector of the lowest eigenvalue. The matrix $\mathbf{J}^{(i)}$ is updated following the Broyden formula. The algorithm flow is illustrated in the following steps:

Step 1. Set *i*=0 and set $\mathbf{x}^{(1)}$. Calculate the $\mathbf{J}^{(1)}$ matrix with

$$J_{ij}^{(1)} = \frac{\partial s_j(\mathbf{x}^{(1)})}{\partial x_i} \approx \frac{s_j(\mathbf{x}^{(1)} + h\mathbf{e}_i) - s_j(\mathbf{x}^{(1)} - h\mathbf{e}_i)}{2h}$$

where the $\mathbf{e}_i$ vector is the *i*-th column of the unit matrix. Calculate $\sigma(\mathbf{x}^{(1)}) = \sigma^{(1)}$

Step 2. Set *i*=*i*+1 and form the following vector and matrix:

$\mathbf{q}^{(i)} = \mathbf{J}^{(i)}\mathbf{s}^{(i)}$ $\quad \mathbf{J}^{(i)}\mathbf{J}^{(i)T}$

Step 3. Form the following matrix and diagonalize it:

$$\begin{pmatrix} 0 & \mathbf{q}^{(i)T} \\ \mathbf{q}^{(i)} & \mathbf{J}^{(i)}\mathbf{J}^{(i)T} \end{pmatrix}$$

Step 4. Let $\mathbf{t}(i)$ be the eigenvector of the smallest eigenvalue of the matrix of Step 3. Set $\mathbf{t}'^{(i)} = \mathbf{t}^{(i)}/\mathbf{t}_1^{(i)}$, where $\mathbf{t}_1^{(i)}$ is the first component of the $\mathbf{t}^{(i)}$ vector. Set $\Delta\mathbf{x}^{(i)} = \mathbf{t}_N'^{(i)}$, where $\mathbf{t}_N'^{(i)}$ is the vector formed by the last *N* components of the $\mathbf{t}'^{(i)}$ vector.

Step 5. Perform a line search to determine $\alpha_{opt}^{(i)}$ that minimizes $\sigma(\mathbf{x}^{(i+1)}) = \sigma(\mathbf{x}^{(i)} + \alpha_{opt}^{(i)}\Delta\mathbf{x}^{(i)}) = \mathbf{s}^{(i+1)T}\mathbf{s}^{(i+1)}$

The line search is stopped when $\left|\mathbf{s}^{(i+1)T}\Delta\mathbf{x}^{(i)}\right| \le \varepsilon_l$

Step 6. If $\max_{1\le j\le N}\left|s_j^{(i+1)}\right| \le \varepsilon$ ➡ exit

else ➡ go to Step 7

Step 7. Compute the vectors $\mathbf{y}^{(i)}$ and $\mathbf{v}^{(i)}$ and the matrix $\mathbf{J}^{(i+1)}$

$$\mathbf{y}^{(i)} = \mathbf{s}^{(i+1)} - \mathbf{s}^{(i)}, \ \mathbf{v}^{(i)} = \mathbf{y}^{(i)} - \mathbf{J}^{(i)T}\Delta\mathbf{x}^{(i)}\alpha_{opt}^{(i)},$$

$$\mathbf{J}^{(i+1)} = \mathbf{J}^{(i)} + \frac{\Delta\mathbf{x}^{(i)}\mathbf{v}^{(i)T}}{\Delta\mathbf{x}^{(i)T}\Delta\mathbf{x}^{(i)}\alpha_{opt}^{(i)}}$$

Step 8. If *i*+1 > maximal number of iterations ➡ exit

else ➡ go to Step 2

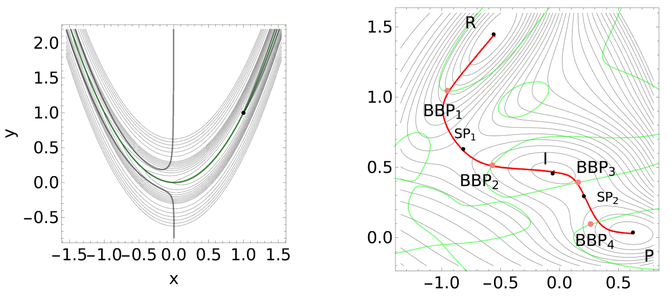
The algorithm only needs the parameters *h*, ε, ε_l, and the maximum number of iterations.

A good start point for the above algorithm is the point with the highest norm of the gradient along the IRC.

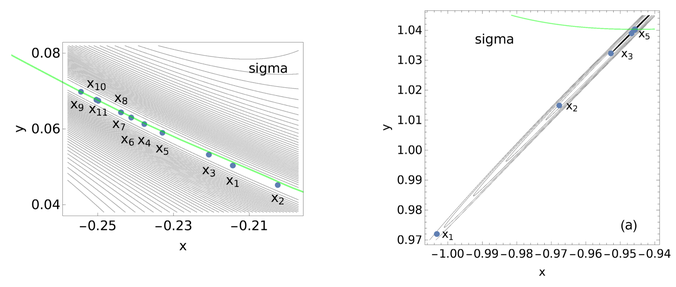
Performance of the algorithm

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



Contours of the Rosenbrock (*left*) and Müller-Brown (*right*) functions

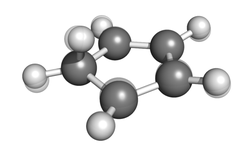


Behavior of the algorithm to locate the optimal BBP on the Rosenbrock (*left*) and Müller-Brown (*right*) functions.

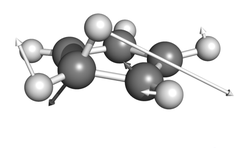
A chemical example: the 1,2-sigmatropic H-shift rearrangement of cyclopentadiene

The algorithm also works efficiently when locating 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 σ function converged in 19 steps.



Optimal BBP for the sigmatropic reaction



The arrows correspond to the components of the gradient at the optimal BBP

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

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