

Simple Models for Mechanochemistry

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The talk starts with an explanation of the key idea of mechanochemistry.¹

The simplest model of mechanochemistry is fulfilled by Newton trajectories (NT).²

On an NT, at every point the gradient of the potential energy surface (PES) points into the same direction.

A further definitions of NTs is reviewed.

We apply NTs to the simplest Models of Mechanochemistry:³

NTs describe the movement of stationary points on an effective PES under an external force.

It can be a mechanical pulling or an electrostatic force of an enzyme.

Refs: ¹W.Quapp, J.M.Bofill, J.Phys.Chem.B 120 (2016) 2644; Theor.Chem.Acc. 135 (2016) 113;

J.Computat.Chem. 37 (2016) 2467-2478; J.Phys.Chem.A 121 (2017) 2820-2838;

J.M.Bofill, J.Ribas-Ariño, S.P.Garcia, W.Quapp: J.Chem.Phys. 147, Iss.15 (2017) 152710

²W.Quapp, M.Hirsch, O.Imig, D.Heidrich, J.Computat.Chem. 19 (1998) 1087;

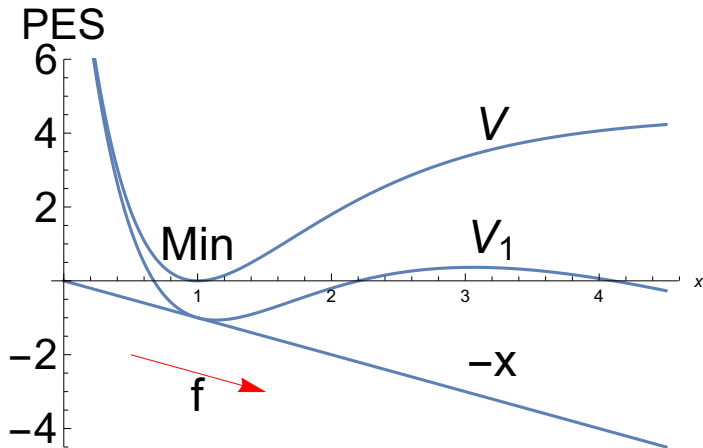
W.Quapp, M.Hirsch, D.Heidrich, Theor.Chem.Acc. 100 (1998) 285

³W.Quapp, J.M.Bofill, J.Ribas Ariño, Int.J.Quan.Chem.(2018) e25775, in press: "Simple Models..."

Example 1

One-dimensional example of the mechanochemical model:

$$V_f(x) = V(x) - f \cdot x$$

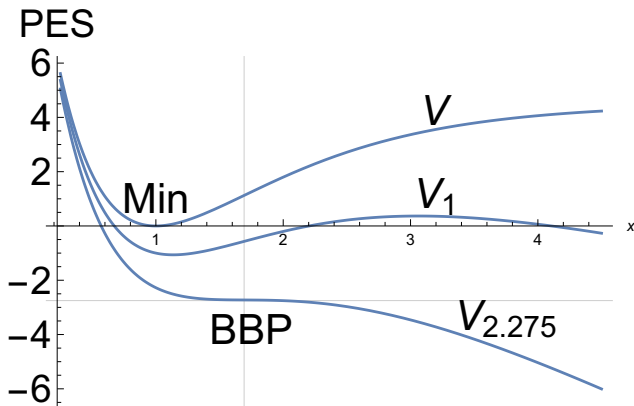


Morse potential over the x -axis: the upper curve.

Below is the effective potential curve V_1 with force $f = 1$.

Example 2

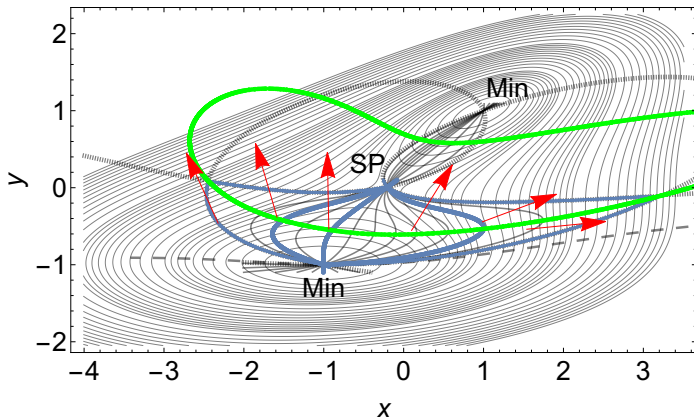
Again the one-dimensional case.



Morse potential: the upper curve. Below are two effective potential curves for increasing forces. The minimum moves to increasing x -values, where the SP moves to decreasing values. The lowest potential is the final case: minimum and SP coalesce to a shoulder. The former barrier is broken. The point is named barrier breckdown point (BBP).

Example 3

Let be two minimums connected by regular NTs over an SP.

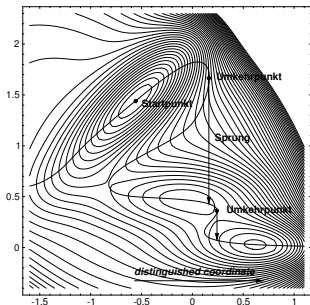


Pulling into a defined direction uses a respective curve for the movement of minimum and SP named Newton trajectory. The red arrows point into the constant gradient direction of the corresponding NT.

The green curve depicts the BBPs on the corresponding NT.

Definition of Newton Trajectory

- ▶ W. Quapp M. Hirsch O. Imig D. Heidrich, J Comput Chem **19** 1998, 1087-1100, "Searching for Saddle Points of Potential Energy Surfaces by Following a Reduced Gradient"
- ▶ W. Quapp M. Hirsch D. Heidrich, Theor Chem Acc **100** (1998) No 5/6, 285-299 "Following the streambed reaction on potential-energy surfaces: a new robust method"



- ▶ Chose a Search Direction \mathbf{r} .
- ▶ Build the Projector Matrix $\mathbf{P}_r = \mathbf{I} - \mathbf{r} \mathbf{r}^T$ where \mathbf{r} is a unit vector.
- ▶ Search the Curve $\mathbf{P}_r \mathbf{g} = 0$. It is the **Newton Trajectory**.

Mechanochemistry in N dimensions

Apply a pulling force \mathbf{f} to the PES:

the generally accepted model consists in a first order perturbation on the PES of the unperturbed molecular system due to a catalytic or pulling force by

$$V_f(\mathbf{x}) = V(\mathbf{x}) - \mathbf{f}^T \cdot (\mathbf{x} - \mathbf{x}_o)$$

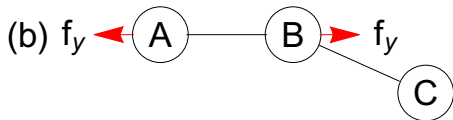
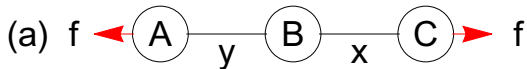
V_f is named the effective PES. The disarrangement of the stationary points of the new effective PES is described by NTs: The stationary points are given by the zero of the derivation

$$\nabla_{\mathbf{x}} V_f(\mathbf{x}) = \mathbf{0} = \mathbf{g} - \mathbf{f}$$

\mathbf{g} is the gradient of the PES. One searches a point where the gradient of the original PES has to be equal to the force, \mathbf{f} . If \mathbf{f} points always into the same direction then the solution is an NT.

Example

Reaction Pathways in a Triatom



A schematic triatomic molecule, ABC, connected by Morse potentials.

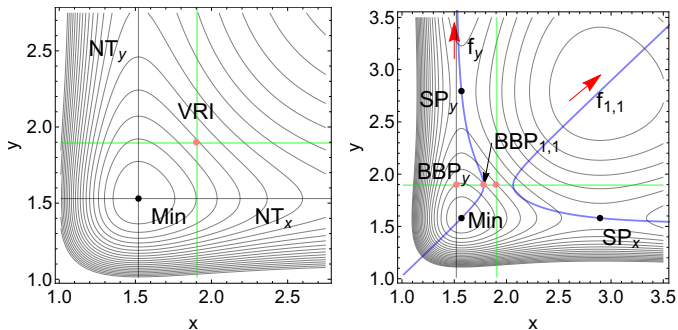
(a) Top line: the arrow \mathbf{f} is the pulling force for an end-to-end action with direction $\mathbf{l}=(1,1)$.

(b) \mathbf{f}_y is a pulling along only one bond with $\mathbf{l}_y=(0,1)$.

If in case (a) atom B is fixed then one can use with $\mathbf{f}=F(l_1, l_2)$ any direction of the (x, y) -plane.

PES:

A nearly symmetric, 2D-Morse potential.

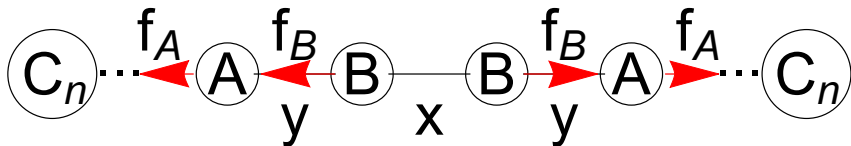


Left: Lines of BBPs are green. VRI: valley-ridge inflection point. Two straight NTs (gray) form the minimum energy pathways along the valleys. Note: the bond in x-direction is stronger.

Right: The effective potential under a force $\mathbf{f}_{1,1} = F(1,1)^T$. The blue curve is the NT to this direction which crosses the green lines at $\text{BBP}_{1,1}$. On the NT all stationary points move. It is the curve of FDSPs.

A Polymer

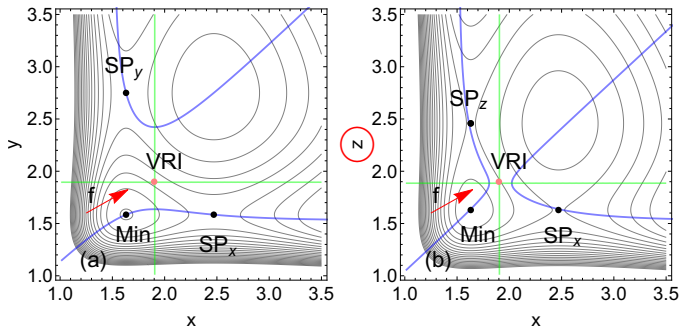
We treat a linear polymer chain in solution under the force of an ultrasound. The center of the chain may be the molecular part -ABBA- with similar Morse relations for $(x; y)$ like in the former Figures.



The arrows f_A and f_B are the pulling forces originating in a sonication experiment with a different magnitude. Experiments result in the fact that usually f_B acting on x is larger than f_A acting on y .

PES of the Polymer:

Again the 2D-Morse potential.

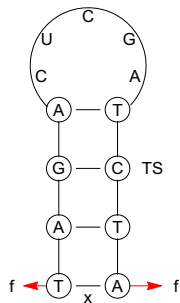


Left: Effective PES projection of the chain. NT (blue) to direction F (16,9), the red arrow. The amount is near the former Figure, however the force points in a different direction. It changes the dissociation path into the x-direction 'below' the VRI. **Right:** Effective PES of a new surface with a quite weaker bond in the former y-direction (now z) but the same drag force like in (a). Now the NT from the minimum turns 'back' into z-direction.

Conclusion: PES and the direction of the force decide the MEP.

Example

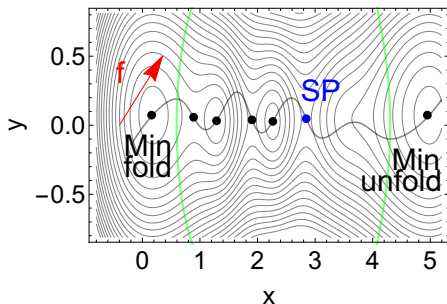
Reaction Pathway in a Hairpin



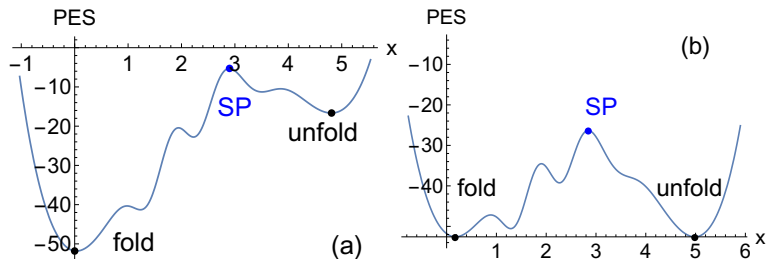
Left: A schematic 4-base pair hairpin.

Right:

We assume a one-dimensional MEP for the opening, and a scew force f . The blue SP may be the highest.



Hairpin

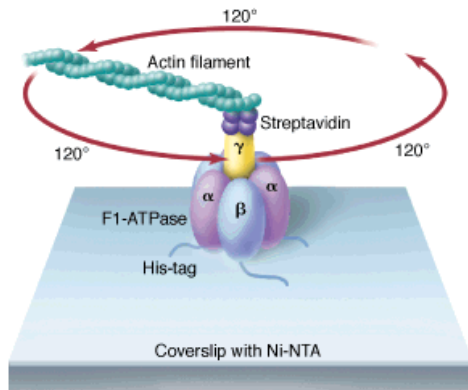


1D section of the PES of the 4-base pair.

Left: Profile on the original PES. The funnel-like shape of the curve is punctuated with small barriers and flat intermediate minima.

Right: Profile on the effective PES to the given force. This force is so strong that an equilibrium happens.

Molecular Motors



Noji, H.. *Science* **282**, 1844 (1998)

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Can one understand the uni-directional mechanical rotation of the motor from point of view of the free energy surface of the molecule?

Model of a Molecular Motor (WQ, J.Math.Chem.56 (2018) 1339-47)

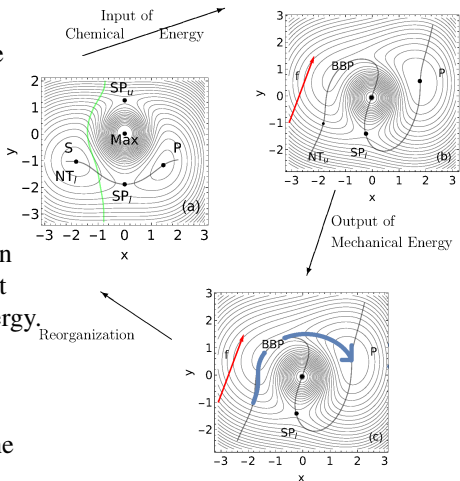
Scheme of a natural molecular motor cycle. We assume two competing ways between S and P. Thus two dimensions are the minimum for an understanding.

(a) The ground state may be at S. A line of BBPs between S and the SPs is thin and green.

(b) An enzyme (red arrow) can enforce the transformation over an upper way to an effective surface up to a BBP.

(c) Relaxation induces the reaction $S \rightarrow P$ over the upper pathway. It may be a source of mechanical energy. It is the bold, blue curve.

Then a back-reaction leads to the startpoint, S, in panel (a). It is depicted by another NT_I in the valley $P \rightarrow S$.



Summary: How to find a curve of the Force Displaced Stationary Points?

- ▶ Describe the FDSPs by Newton Trajectories: it is **tractable** – in many practical cases.
- ▶ Different directions of the external force can change the order of different reaction pathways.
- ▶ On the curve of FDSPs move the minimums and the SPs of the PES. SPs can decrease in energy, or also go uphill.
- ▶ A TS stabilization with an enzyme means that the SP moves downhill, but the substrate minimum moves uphill. Both move together and collapse at the barrier breakdown point (BBP).
- ▶ Find the BBP along a Newton Trajectory: it is **tractable**.

Thank You for Your interest !

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