Patterns of Moving Saddle Points in Catalysis and 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.

Definitions of NTs and different calculation methods are reviewed.

We apply NTs to Mechanochemistry and Catalysis:

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.

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

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

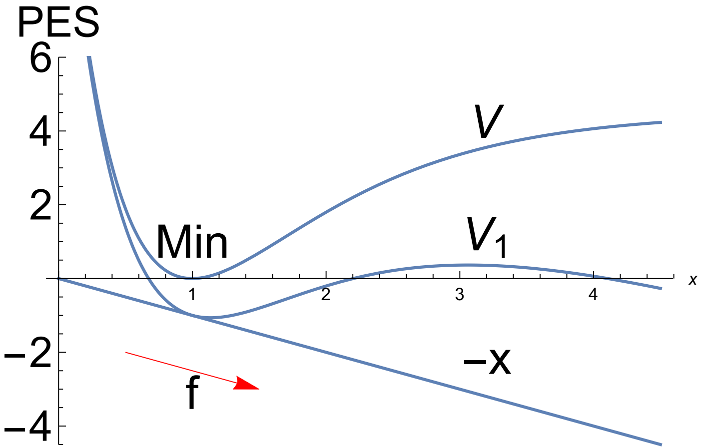
W.Quapp, J.M.Bofill, J.Ribas-Ariño, J.Chem.Phys. 147, 152710 (2017)

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

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

Example 1

One-dimensional example of the mechanochemical model:
$V_f(x) = V(x) - f \cdot x$



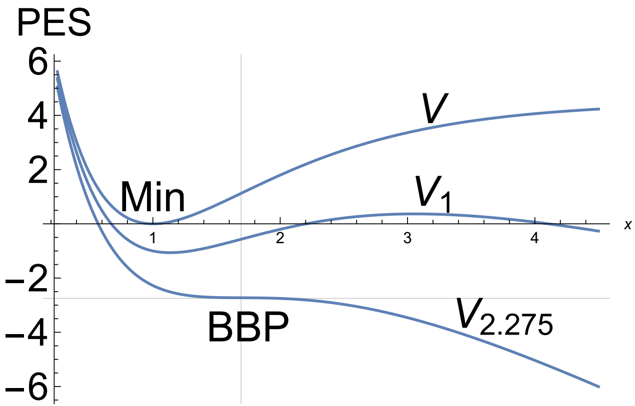
Morse potential over the x-axis: the upper curve.
Below is the effective potential curve V_1 with force $f = 1$.

Text Exam 1

First we treat the one-dimensional case. We assume a Morse potential curve. The minimum is at $x = 1$.
If we apply the potential $f \cdot x$, we get after a differentiation the constant force, f.
So we say we apply to V the constant force, f.
– Here with value $f = 1$.
(The slope of the straight line.)
The result is the curve V_1.
Note: the minimum moves to the right hand side,
but the SP has moved to the left hand side.
If we increase the force further, we get the next slight.

Example 2

Again the one-dimensional case.



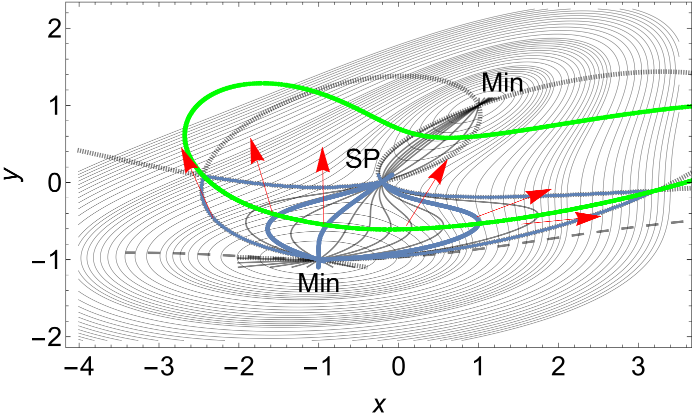
Morse potential: the upper curve. Below are two effective potential curves for increasing forces. The minimum moves to increasing x-values, where the SP moves to decreasing values. The lowest potential is the final case: minimum and SP coalesce to a shoulder. The former barrier is broken.

Text Exam 2

The text is on the slight.

Example 3

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



The red arrows point into the constant gradient direction of the corresponding NT.

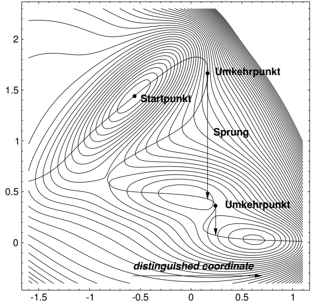
The green curve depicts the BBPs on the corresponding NTs.

Text Exam 3

What happens in two dimensions?
Now, the force, f, can point around. But it should be a constant direction. (The red arrows.)
To one curve, to one and the same direction, we obtain a movement of minimum and SP together, along the depicted curve.
The final BBP is marked by the green line.
The curves are mathematical known structures with name Newton trajectory (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 **r**.
- Build the Projector Matrix $\mathbf{P}_r = \mathbf{I} - \mathbf{r}\,\mathbf{r}^T$ where **r** is a unit vector.
- Search the Curve $\mathbf{P}_r\, \mathbf{g} = 0$. It is the Newton Trajectory.

Text Definition NTs

The definition of NTs was given (in Theoretical Chemistry) by Quapp et al. in 1998.
The Figure is the well known Müller-Brown potential.
The old distinguished coordinate, here in x-direction, does not jump if we follow the NT which is the same curve in the valleys.

Mechanochemistry and Catalysis

Apply a pulling force **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

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

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

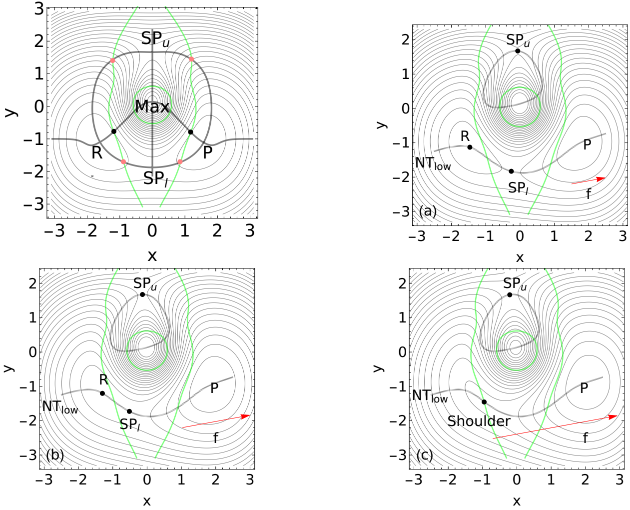
$$\nabla_{\mathbf{x}} V_f(\mathbf{x}) = \mathbf{0} = \mathbf{g} - \mathbf{f}$$

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, **f**. If **f** points always into the same direction then the solution is an NT.

Text Theory

The text is on the slight.

Example 4 Development of effective PESs



Left above F=0.0, original PES with GE and optimal BBPs (red points).
(a)-(c): Effective PESs for **f**=F **l** with pull direction **l**=$(0.98,0.18)^T$ and
(a) F=1.4, (b) F=2.8, and (c) F=4.25 force (red arrow) along the same NT.
The R_{eff}, $SP_{l,eff}$ and $SP_{u,eff}$ are marked by black points.

Text Exam 4

Now we come to an interesting two-dimensional example with
2 minimums, R and P, and with 2 TSs, a low SP_{low} below, and a quite higher SP_{up} at the top.
In panel (a) we have a NT from R to P where we have applied a force, f to the left surface.
We may observe that the minimum R and the lower SP_l move together.
You can also observe that the product, P, bowl becomes deeper.

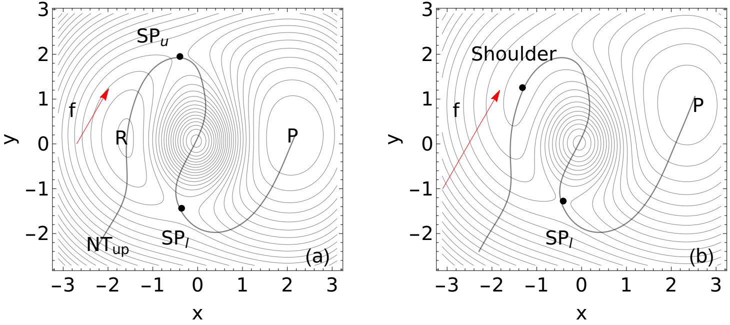
In panel (b) the process is shown for a stronger force – the red arrow.

(c) The final BBP is arrived, the reaction from R to P is enforced by such a large force, f, into the given direction of the NT.
Only the one minimum, P, has overlifed.

If f is turned around to $-f$, we may imagine that the effective PESs also turn around. At least, we enforce than
a backreaction from P to R.

Example 5

Turning off the reaction pathway from lower SP to upper SP



NT$_{up}$ is for a pulling over SP$_{up}$. The pull direction is **I**=$(0.51,0.86)^T$.
This pulling moves R and SP$_{up}$ together, but it moves also Max and SP$_{low}$ together. Thus, the hight of SP$_{up}$ decreases, but of SP$_{low}$ increases.
(a) F=8.33 makes an equal height of the two SPs, however panel
(b) with F=13 leads to the collapse of R and SP$_{up}$ in a shoulder, a BBP.

The red arrows are the forces.

Text Exam 5

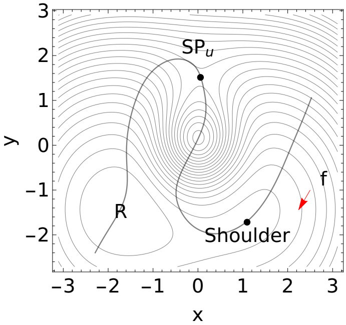
Now, on the same surface, we turn our interest to the upper SP_u.
There are also NTs which connect the reactant, R, with this TS, SP_u.
In panel (a) is a force into this direction applied. We may observe that now R and SP_u move together, on the given NT.
Contrary, we have to constate that the former lower SP_l moves uphill to the summit of the surface.
The panel (a) is the case of the strongness of the force, f, where the two SPs have get a nearly equal height.

In panel (b) is the force further strongly increased.
We get at least a shoulder from min R and SP_u which have disappeared.
Of course, now the reaction R to P has also finished, however, it goes over the other pathway, of the former upper SP.
The "MEP" of the reaction goes along the upper valley.

Different directions of the external force can enforce different reaction pathways.

Example 6

Now turn the direction:
it turns the reaction pathway back from SP_{up} to SP_l



HYSTERESIS!

Use the same NT like in the former case, but return the direction to the opposite. The pulling moves P and SP_{low} together, and now it moves also Max and SP_{up} together. The small amount of F=-3 enforces already the backreaction. It leads to the collapse of P and SP_{low} in a shoulder.
The pull direction is $\mathbf{l}$=-(0.51,0.86)^T.

Text Exam 6

If we turn again back the direction of the former force, f, to $-f$, on the same surface, and along the same NT like in the former example 5, then we get a movement of product P and SP_l together, here to the final shoulder.
Thus, we get a qualitative hysteresis of recation pathways. R to P goes with (large) f, but P to R goes on with (already small) $-f$ along different, alternating reaction pathways.

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

- Describe the FDSPs by Newton Trajectories:
  it is tractable – in many practical cases.
- On the curve of FDSPs move the minimums and the SPs of the PES. SPs can move downhill, or also 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 BBP.
- Find the BBP along a Newton Trajectory: it is tractable.
- Different directions of the external force can change the order of different reaction pathways .
- For alternate reaction pathways emerges a qualitative hysteresis.

Thank You for Your interest !

Some References to Newton Trajectories

WQ, M.Hirsch, O.Imig, D.Heidrich: J.Comput.Chem.19 (1998) 1087
WQ, M.Hirsch, D.Heidrich: Theor.Chem.Acc.100 (1998) 285
M.Hirsch, WQ, D.Heidrich: Phys.Chem.Chem.Phys.1 (1999) 5291
WQ, M.Hirsch, D.Heidrich: Theor.Chem.Acc.105 (2000) 145
WQ, V.Melnikov: Phys.Chem.Chem.Phys.3 (2001) 2735
WQ: J.Comput.Chem.22 (2001) 537
J.M.Anglada,E.Besalu,J.M.Bofill,R.Crehuet: J.Comp.Chem.22 (2001) 387
J.M.Bofill, J.M.Anglada: Theor.Chem.Acc.105 (2001) 463
R.Crehuet, J.M.Bofill, J.M.Anglada: Theor.Chem.Acc.107 (2002) 130
M.Hirsch, WQ: J.Math.Chem.36 (2004) 307
M.Hirsch, WQ: Chem.Phys.Lett.395 (2004) 150
WQ: J.Comput.Chem.25 (2004) 1277
M.Hirsch, WQ: J.Mol.Struct.THEOCHEM 683 (2004) 1
WQ: J.Mol.Struct.695-696 (2004) 95
WQ: J.Chem.Phys.122 (2005) 174106
WQ: J.Comput.Chem.28 (2007) 1834
WQ, E.Kraka, D.Cremer: J.Phys.Chem.A 111 (2007) 11287
H.Joo, E.Kraka, WQ, D.Cremer: Mol.Phys.105 (2007) 2697
WQ: J.Theor.Comput.Chem.8 (2009) 101
J.M.Bofill: J.Chem.Phys.130 (2009) 176102
WQ, B.Schmidt: Theor.Chem.Acc. 128, Iss 1 (2011) 47-61
J.M.Bofill, WQ: J. Chem. Phys. 134 (2011) 074101
WQ, J.M.Bofill, J. Aguilar-Mogas: Theor. Chem. Acc. 129 (2011) 803
WQ, J.M.Bofill: J. Math. Chem. 50, Iss 5 (2012) 2061
WQ, J.M.Bofill, M.Caballero: Chem. Phys. Lett. 541 (2012) 122
B.Schmidt, WQ: Theor. Chem. Acc. 132 (2012) 1305
WQ, J.M.Bofill: Int.J.Quant.Chem. 115 (2015) 1635
J.M.Bofill: J. Chem. Phys. 143 (2015) 247101
WQ: J. Math. Chem 54 (2015) 137
WQ, J.M.Bofill: J.Phys.Chem.B 120 (2016) 2644
WQ, J.M.Bofill: Theor.Chem.Acc. 135 (2016) 113
WQ, J.M.Bofill: J.Comput.Chem. 37 (2016) 2467
WQ, J.M.Bofill, J.Ribas-Ariño: J.Phys.Chem.A 121 (2017) 2820
WQ, J.M.Bofill, J.Ribas-Ariño: J.Chem.Phys. 147, (2017) 152710