Patterns of Moving Saddle Points in Catalysis and Mechanochemistry

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The description of a chemical process under mechanical stress or catalytic enhencement is performed by the generation of an effective potential energy surface (PES). Changes for minima and saddle points by the stress are described by Newton trajectories (NTs) on the original PES [1, 2]. Families of NTs define pulling corridors. If there are different exit saddles then there can exist saddles of index two, at least, in between. Then the case that a full pulling corridor crosses a saddle of index two, is the normal case. It leads to an intrinsic hysteresis of such pullings for the forward or the backward reaction, see Figure 1. Assuming such relations we can explain strange results in the literature, as well as the existence of roundabout corridors which can switch between different saddle points by a reversion of the direction. The findings concern the mechanochemistry of molecular systems under a mechanical load as well as the electrostatic force and can be extended to catalytic and enzymatic accelerated reactions. The ansatz includes both kinds of forces in a natural way without an extra modification.

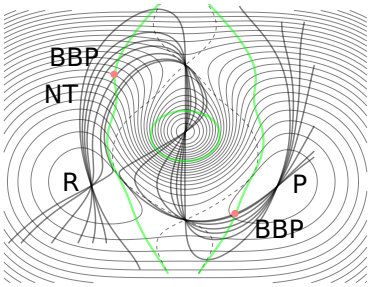

Figure 1: Bold NTs are good directions for a pulling force for successful pulling scenarios. An asymmetric chemical corridor by Newton trajectories (NT) from left to right minimum (R–>P).The red points are the optimal barrier breakdown points (BBP).

[1] W.Quapp, J.M.Bofill, *Theor. Chem. Acc.*, **135**, 113 (2016).

[2] W.Quapp, J.M.Bofill and J.Ribas-Ariño *J. Phys. Chem. A*, **121**, 2820 (2017)