Controlling Chemical Reactivity with Optimally Oriented Electric Fields: A Generalisation of the Newton Trajectory Method

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The application of oriented external electric fields (OEEF) to accelerate chemical reactions is of interest to understand enzymatic processes and catalysis in which an activated process becomes essentially barrierless. Recently, a recent landmark single–molecule experiment by Aragonès et al.[1] has shown that OEEFs created by a bias voltage between an electrode and an scanning tunnelling microscopy tip can catalyze a Diels–Alder reaction. Inspired by this work, we have developed a new model to calculate the optimal OEEF of the least intensity to induce a barrierless chemical reaction path [2]. In this model, which is an example of optimal control of a chemical process, a suitable ansatz is provided by defining an effective potential energy surface (PES) that considers the unperturbed or original PES of the molecular reactive system and the action of a constant OEEF on the overall dipole moment of system. Based on a generalization of the Newton Trajectories (NT) method previously developed by some of us [3], we show that the optimal OEEF can be determined upon locating a special point of the potential energy surface (PES), the so–called optimal bond–breaking–point (optimal BBP) [2]. Two different algorithms are proposed and applied to a 2–dimensional model (Fig. 2), to an SN_2 reaction and the 1,3–dipolar retrocycloaddition of isoxazole to fulminic acid plus acetylene reaction (Huysgen mechanism). It is concluded that the knowledge of the orientation of optimal OEEF provides a practical way to reduce the effective barrier of a given chemical process. Finally, in contrast to previous models that focus on the TS of the reaction [4], the oBBP structure represents the essential point in the PES to understand the effect of the OEEF applied to the molecular system. This model has potential utility to understand the basic mechanisms of enzymatic catalysis.

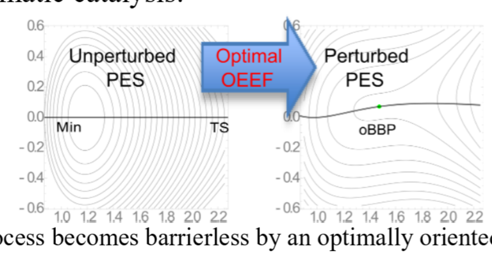

Figure 1. An activated 2D process becomes barrierless by an optimally oriented external electric field (OEEF)

References

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