Topological classification of chemical reactions: a new tool to understand and manipulate chemical reactivity

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New theoretical frameworks are needed to tackle the challenges of modern material design. For example, green chemistry efforts require new types of reactions and design strategies that move away from the conventional synthetic strategies employed by organic chemists. To address this challenge, we employ advanced theoretical methods to uncover the influence of previously overlooked features of the potential energy surface (PES) on the outcomes of chemical reactions. For example, higher-order saddle points and bifurcations can strongly influence the selectivity between competing pathways in chemical reactions. Here we show that these features are pivotal in determining the outcomes of electrocyclization reactions. We highlight the importance of multi-reference correlations and geometric instabilities that give rise to these features on the PES. Our findings provide strong evidence that these features necessitate moving beyond a conventional one-dimensional reaction path picture in this class of reactions. In a complementary approach, we use recent breakthroughs in the field of topological condensed matter physics to understand higher-dimensional features of the PES. In particular, the influence of conical intersections and avoided crossings away from the reaction path on reaction dynamics has been unexplored. Using both ab-initio as well as model calculations we provide evidence that a topological analysis can capture and classify the influence of the aforementioned features on the reaction dynamics.