IN-3

CHEMICAL REACTIVITY

F. Matthias Bickelhaupt

Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, The Netherlands
Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, The Netherlands
f.m.bickelhaupt@vu.nl

The aim of this talk is to convey a way of understanding the factors that determine bonding and reactivity in the framework of quantitative Kohn-Sham molecular orbital theory. Herein, a central role is reserved for how chemical bonding in transition states works and how it decides the course of chemical reactions. To this end, I will first discuss the activation strain model (ASM) which creates a causal relationship between, on one hand, reactivity trends and, on the other hand, electronic and structural properties of reactants as well as the nature of the chemical transformation (see Figure 1). The ASM covers not only the interaction between reactants but also the energy needed to distort them as they proceed along the reaction coordinate. A typical activation strain diagram (ASD) can be found in the illustration, showing the strain associated with distortion of reactants as well as the interaction between the ever more distorted reactants for a metal-mediated bond-activation reaction. Examples of ASM applications in this talk may, depending on the available time, comprise examples from homogeneous catalysis (bond activation), organic chemistry (S_N2, E2 and pericyclic reactions, including dual activation of aromatic Diels-Alder additions) as well as biochemistry (models for DNA replication).

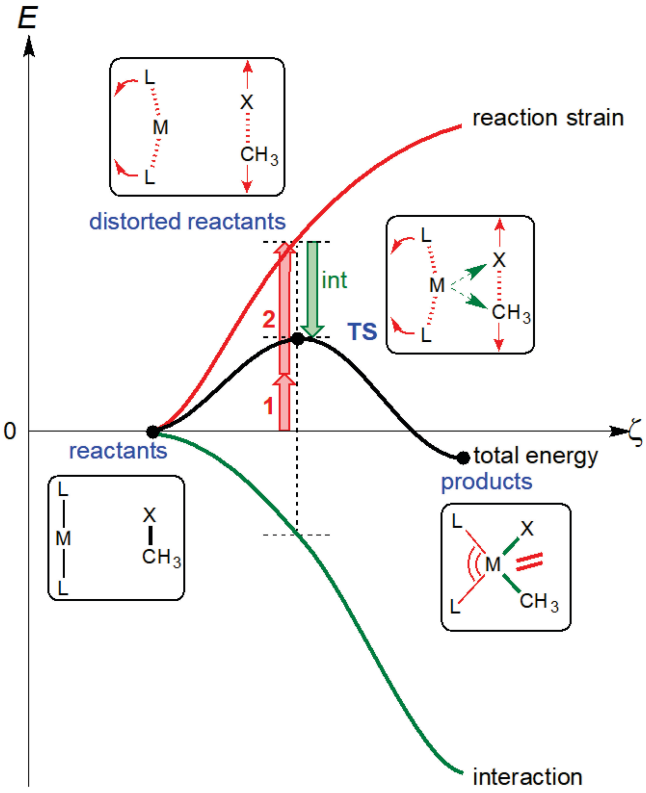

Figure 1. Schematic activation strain diagram (ASD) for bond activation via oxidative addition.