Influence of a Mechanical Force, Pressure and External Electric and Magnetic Fields on Chemical Concepts from Density Functional Theory

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Density Functional Theory is a well-suited theory for the introduction of chemical concepts, also known as reactivity indices. These are mostly introduced as response functions of the energy E of the system with respect to either the number of electrons N, the external potential $v(\mathbf{r})$ or both. This has afforded the non-empirical calculation of these reactivity indices, the rationalization and proof of several chemical principles and applications in many fields of chemistry. This DFT based chemical concepts framework is often called "Conceptual DFT".

In this lecture, efforts to incorporate new external variables in the Conceptual DFT framework are discussed motivated by the ever-increasing portfolio of experimental reaction conditions in the endeavour of experimentalists to synthesize new molecules with unprecedented properties.

In a first part, an external mechanical force is included which allows for the quantification of the global as well as local reactivity of molecules that are subjected to an external force, central in the field of mechanochemistry. First, applications to a series of diatomic molecules are discussed. Next, the effect of applied bending forces in 2-butyne fragments were investigated as a model for strained cyclic alkynes, an important class of molecules for in vitro applicable click-reactions. The local softness of the triple bond with an applied external force revealed interesting changes in its chemical reactivity in line with the reactivity observed in strain promoted alkyne-azide couplings.

Next, the effect of pressure on several atomic properties from conceptual DFT is described. In a final part, the influence of an external electric and magnetic field on DFT based reactivity descriptors is discussed.