Séminaire :

“Qualitative and quantitative tools for predicting the products and mechanisms of chemical reactions”

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Jeudi 11 décembre 2008, 11h00
Salle RAPHAEL 1 – site d’Ivry-sur-Seine

Given a set of reagents in a specific reaction environment, does a reaction occur and, if so, what are the products and what is the mechanism? This talk will feature two techniques for predicting chemical reagents’ reactivity. At a qualitative level, recent advances in conceptual density-functional theory (DFT) will be discussed. Unlike most other conceptual tools for elucidating the reactivity of a molecule, the reactivity predictors from conceptual DFT lie within the framework of a formally exact quantitative theory (DFT). A particularly useful approach to conceptual DFT is what may be termed the “perturbative” perspective on chemical reactivity, wherein the reactivity of a reagent is described by measuring its response to a small number of different “model perturbations,” which are chosen to simulate different types of reagents (hard acids, soft bases, etc.). The perturbative perspective provides a unifying framework for disparate DFT-based reactivity indices. Here, I’ll discuss applications of the perturbative perspective to situations where naïve frontier molecular orbital theory fails.

At a quantitative level, I will discuss recent work on finding reaction coordinates on multi-dimensional potential energy surfaces. Most existing methods for determining reaction coordinates require prior knowledge of the reactants, products, and—for multi-step reactions—reaction intermediates. (In addition, knowledge of the transition state structures is frequently helpful, and sometimes required.) The approach I’ll describe is based on the “fast-marching” algorithm commonly used for front-propagation problems, and is distinguished from most conventional methods because it only requires knowledge of the reactants. Reactive intermediates, transitions states, and products are output from, rather than input to, the computational method. Consequently, the fast marching method provides a rigorous mathematical approach to predicting not only the products, but also the mechanism, of a chemical reaction.