

Better Ways to Get Excited States and Reaction Barriers From DFT

*Troy Van Voorhis
Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Ave.
Cambridge, MA 02139*

Density functional theory (DFT) is the *de facto* standard for simulating the electronic ground state near equilibrium. At the same time, standard functionals have some well-advertised problems in dealing with electronic excited states and molecules that are near the transition state region. In this talk we show that, in many cases, the problem isn't as much that DFT gives the wrong answer as that electronic structure theorists insist on asking the wrong questions. Using chemical intuition, one can often choose initial and final states lead to accurate predictions (via cancellation of errors) even in cases where DFT nominally fails. For example, applying constraints to the charge density leads to reliable electron transfer energies; Δ SCF calculations give accurate results for valence and Rydberg excitations; localized charge states provide a basis for improving reaction barrier heights; configuration interaction based on a DFT active space gives a qualitatively correct description of conical intersections between ground and excited states. Time permitting, we will discuss how these developments could be leveraged to improve existing functionals.