

Physikalisches Kolloquium

Thursday, 08.05.14, 17:00, HS 100
 Reception with coffee & cookies 16:45



Prof. Alec M. Wodtke, Georg-August-Universität Göttingen

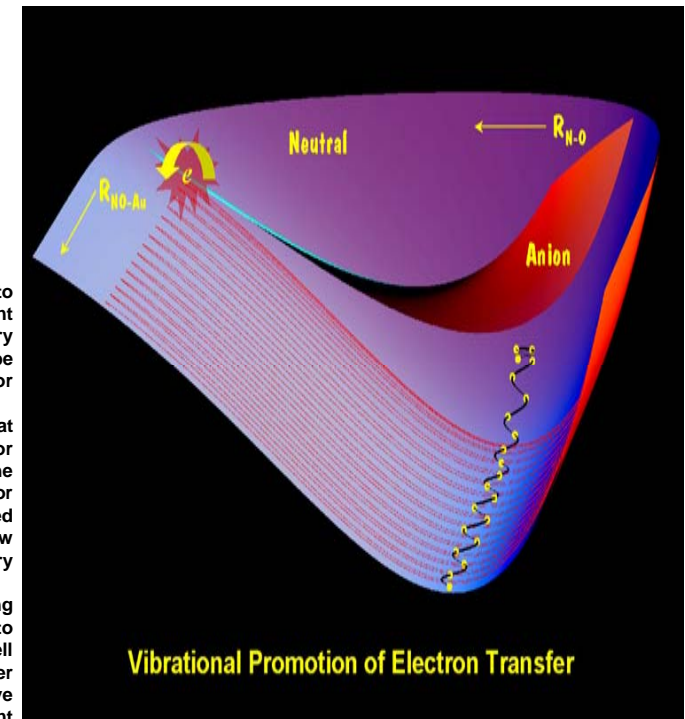
*Testing the assumptions underlying computational chemistry:
 Breakdown of the Born-Oppenheimer approximation*

Abstract

At least since the age of alchemy, people have been fascinated by chemical bonding and reactivity. Today, our most fundamental challenge is to develop predictive theories of chemistry rigorously grounded in the laws of physics. In 1929, Dirac identified the problem famously in a comment about the importance of quantum mechanics: “The underlying physical laws necessary for the mathematical theory of... ..the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble”. Despite electrifying advances in computational power, Dirac is still right. The theory of chemistry requires approximate methods for practical computations.

Perhaps the most important approximation for chemistry was introduced by Born and Oppenheimer. Recognizing the importance of the fact that light electrons move much faster than heavy nuclei, the Born-Oppenheimer approximation (BOA) solves the quantum equations of the electrons for stationary nuclei. Repeating this for many nuclear arrangements resembling reactants, products, the transition-state and structures in between, the electronically adiabatic potential energy surface (PES) emerges – the atomic scale forces that drive the reaction. This approach works perfectly for many simple gas phase reactions; however, highly efficient electronic structure methods like density functional theory (DFT) have now moved computations to much more complex problems. Due to its fundamental relevance to heterogeneous catalysis, reactivity on metal surfaces is now an important research area for computational chemistry, one having great impact. The growing importance of computational surface chemistry motivates us to design rigorous tests of the underlying assumptions that form the basis of this field.

In this lecture, I will present experimental results from our group that reveal the limits of the Born-Oppenheimer approximation in describing molecular and atomic interactions at metal surfaces. There is accumulating evidence that coupling of large amplitude molecular vibration to metallic-electron degrees-of-freedom can be strong and is associated with electron transfer reactions between the surface and the molecule as well as the high kinetic energies associated with bond compression/formation. This implies theoretical approaches relying on the Born-Oppenheimer approximation may not accurately reflect the nature of transition-state traversal in reactions at metal surfaces. Developing a predictive understanding of surface chemistry beyond the Born-Oppenheimer approximation represents one of the most important challenges to current research in chemical physics.



All of you interested in physics are cordially invited!

Contact: Prof. Dr. T. Baumert, More Information: uni-kassel.de/go/physikalisches_kolloquium