Combined ab initio complete-active-space and on-top-pair-density-mediated density-functional approach for efficient calculation of potential energy surfaces of excited molecular states

A true working horse of the rapidly expanding world of smart technologies is a tiny, charged elementary paticle-wave centaur, the electron. Huge swarms of electrons are at work when we switch on our smartphones and laptops. Catching energy in rooftop solar panels, electrons bring the warmth of our Sun to our homes.

Surely, we cannot ride these tiny horses, since we cannot even see them. But we can direct and govern them, using a light signal as our whip to send electrons to their working, excited states. And to predict the results of this action, one has to calculate the concerted dance of excited electrons in atoms and molecules with special types of quantum mechanics, the theory of microscopic world. Such a calculation remains a challenge for powers of modern super-computers and brains of theorists, since various theoretical methods exhibit their strong and weak sides in solving the problem of electronic excited states.

In this project, we propose a novel method to calculate excited electronic states for different arrangements of nuclei in molecules. With a careful design, a new method combines the strong sides of best existing methods, using multi-scale modeling and simulation approach applied to a world of electron configurations. Specifically, a few most important configurations describing chemical bonds in molecules are treated with a comprehensive non-empirical method of complete active space (CAS), which includes all (or nearly all) modes of the concerted "dance of electrons". The important collective effect of other electron configurations is calculated with density functional theory (DFT), which simplifies the complicated electronic dance to a solo dance of an individual electron moving under the averaged force of other electrons. The goal of the project is to design, implement and test the most efficient CAS+DFT combinations able to account for all important electron interactions, while avoiding their double counting.

The proposed combined CAS+DFT method will enable theorists to calculate the collections of electronic excitations in molecules, electronic potential energy surfaces (PESs) relatively accurately and in a reasonable time using modern cluster- and super-computers. This will give a theoretical tool to simulate and predict the optimal ways to govern the behavior of electrons in future information and energy nano-technology devices.