Ab initio modeling of organic and biomolecule - oxide surfaces: qualitative difference between small and big and the good and the bad of density functional tight binding

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Abstract
Interfaces of organic molecules with oxides are important for a wide range of applications, from photoelectrochemical cells to biocompatible implants. Ab initio modeling at the DFT (density functional theory) level is typically done for systems where quantum effects are key to functionality and where system size permits (such as small dyes – oxide interfaces with $10^{1-2}$ atoms), while force field based modeling has dominated the modeling of biomolecular systems. It is desirable to model bioinorganic interfaces with ab initio accuracy. Density functional tight binding (DFTB) has emerged as a promising route to such modeling of systems with $10^{3-4}$ atoms.

I will present comparative DFT-DFTB studies of small and large molecules' interaction with titania. I will show that with existing parameterizations DFTB may fail to reproduce the correct band structure of the interface and therefore adsorption energies and geometries. Specifically, I will analyse a complex of 2-anthroic acid with TiO$_2$ which results in interfacial charge transfer bands and application in direct injection type dye-sensitized solar cells.

On the other hand and counter-intuitively, I will show that for big molecules such as biomolecules, DFTB not only enables routine ab initio modeling due to its cpu cost advantage, but can be preferred also for accuracy. Hybrid functionals remain and will likely remain for some time prohibitively costly for modeling of bioinorganic interfaces; the only viable option is GGA. I will show that there is a qualitative difference between a small and a big molecule adsorption on a semiconductor, in that the HOMO of a big molecule can enter the conduction band leading to a qualitatively wrong picture with DFT. This effect has been under-appreciated due to the frequent use of abridged models of biomolecular adsorption. DFTB, which can effectively reproduce the band gap, avoids this problem and can provide qualitatively or quantitatively correct interfacial band structure and adsorption properties.

The speaker
Sergei Manzhos obtained a PhD in chemistry from Queen's University, Canada, in 2005 supervised by Hans-Peter Loock. He was Postdoctoral Fellow at the University of Montreal with Tucker Carrington in 2005-2008. In 2008-2012, he was Project Assistant Professor at the University of Tokyo, Japan, at the Department of Chemical System Engineering and Research Center for Advanced Science and Technology. Since 2012, he has been Assistant Professor at the Department of Mechanical Engineering at the National University of Singapore. Dr. Manzhos's research is focused on computational modeling of materials, primarily for post-lithium electrochemical batteries and for photoelectrochemical cells. He is also active in method development for quantum dynamics and orbital-free density functional theory. Web: https://sites.google.com/site/sergeimanzhos/