Computational Energy Materials Science: recent developments and applications

Dr. Gilberto Teobaldi, University of Liverpool

Implementation of a more sustainable energy economy relies on development of improved, industrially viable photocatalytic, photovoltaics, electrochemical energy conversion and storage devices. Atomic-scale understanding of the different materials and interfaces constituting such devices is crucial for the development of novel solutions. This, in turn, requires the possibility of accessing the atomic-scale parameters governing the thermodynamics and kinetics of atom, charge, energy transfer processes at the device interfaces. Along these lines, I will present an overview of recent results on:

(i) Scanning tunnelling microscopy contrast mechanisms for TiO_2 [1]. Controlled dual mode Scanning Tunnelling Microscopy (STM) experiments and first-principle simulations show that the tunnelling conditions can significantly alter the positive-bias topographic contrast of geometrically corrugated titania surfaces such as rutile TiO_2(011)-2x1. The mechanisms of contrast formation are elucidated in terms of the subtle balance between the surface geometry and the different vacuum decay lengths of the topmost Ti(*3d*) and O(*2p*) states probed by the STM-tip apex.

(ii) Density Functional Theory (DFT) investigation of the geometry and electronic structure of aluminosilicate and aluminogermanate nanotubes [2]. DFT simulations elucidate the previously reported polarisation of the nanotube walls as originating from a balance between compositional and geometrical factors. The peculiar electronic structure of the systems, leading to localisation of the low-energy conduction band and high-energy valence band edges on different sides of the tube cavity, is presented and discussed in terms of possible photo-catalytic applications.

(iii) Linear-scaling constrained Density Functional Theory in ONETEP [3a]. Very encouraging results have recently appeared regarding the potential of constrained Density Functional Theory (cDFT) for the study of charge (energy) transfer and chemical reactivity [3b]. Here we present the implementation of cDFT in the ONETEP program [3a]. The linear-scaling nature of the cDFT implementation opens up for cDFT simulation of systems up to a few thousands of atoms on academically available hardware. This should make the method useful for the study of extended interfaces present in photocatalysts, solar cells, fuel cells, and batteries.

[1] a) T. Woolcot et al., submitted; b) X. Torrelles et al., *Phys. Rev. Lett.* **101**, 185501 (2008).

[2] G. teobaldi et al., J. Phys.: Condens. Matter 21, 195301 (2009).

[3] a) www.onetep.org; b) B. Kaduk *et al.*, *Chem. Rev.*, **112**, 321 (2012).