O 102: New Methods: Theory

Time: Thursday 17:45–18:30 Location: WIL C107

O 102.1 Thu 17:45 WIL C107

A generalized 'dipole correction' for charged surfaces in the repeated slab approach — •Christoph Freysoldt, Arpit Mishra, and Jörg Neugebauer — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

The charging of surfaces plays an important role in electrochemistry, electronic sensors, field evaporation in atom probe tomography, and many other situations. *Ab initio* calculations are hampered by the problem that appropriate electrostatic boundary conditions must be taken into account. We will demonstrate that the commonly used dipole correction for neutral asymmetric slabs, that takes care of differences in the work function on either side of the slab, can be generalized to charged surfaces. This allows for simulations of strong electric fields where linear-response-based extrapolation schemes may not be appropriate. We show how flat-band or band-bending conditions can be realized, and discuss how to meaningfully define a potential reference level for total energies. Last, we will highlight the importance of *mechanical* boundary conditions for charged slab calculations.

O 102.2 Thu 18:00 WIL C107

Revised Chen's derivative rule for STM calculations — Gábor Mándi[1] and •Krisztián Palotás[1,2] — [1]Budapest University of Technology and Economics, Budapest, Hungary — [2]Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia

Chen's derivative rule for electron tunneling [1] is revised [2] for the purpose of computationally efficient calculations of scanning tunneling microscopy (STM). New features include (i) the weighting of tunneling matrix elements of different tip-orbital characters by an arbitrary energy-independent choice or based on first-principles data, (ii) arbitrary tip geometrical orientations, and (iii) the possibility of quantitative analysis of tip-orbital interference contributions. The model is applied to two functionalized surfaces where quantum interference effects play an important role in the STM imaging and the Tersoff-Hamann model fails to describe the correct STM contrast under certain conditions: N-doped graphene [3] and a magnetic Mn_2H complex on the Ag(111) surface [4]. For both studied surfaces, the importance of interference between s and p_z tip orbitals is highlighted that cause a significant contrast change in the STM images [2].

[1] C. J. Chen, Phys. Rev. B 42, 8841 (1990)
[2] G. Mándi, K. Palotás, Phys. Rev. B 91, 165406 (2015)
[3] M. Telychko et al., ACS Nano 8, 7318 (2014)
[4] T. Sachse et al., New J. Phys. 16, 063021 (2014)

O 102.3 Thu 18:15 WIL C107

Modeling Tip enhanced Raman spectrum influenced by an external electric field — •Otto Hauler, Kai Braun, Dai Zhang, and Alfred J. Meixner — Institut für Physikalische und Theoretische Chemie, Auf der Morgenstelle 18, 72076 Tübingen

Within the last years Scanning Tunneling Microscopy (STM) gets more and more attraction in Tip enhanced Raman Spectroscopy (TERS). Various groups showed strongly increased optical resolution by using STM as feedback mechanism to keep the tip in close proximity to the surface. Despite the increased sensitivity a STM also allows for direct manipulation of the molecules in the gap via the bias voltage. In this contribution we present a theoretical model to calculate TERS-spectra of molecules in an external DC electric field. An increasing bias voltage leads to significant changes of certain Raman bands, while others are only weakly affected. We will discuss the influence of the bias voltage on TERS of a self-assembling monolayer and propose a quantum chemical model to improve the understanding of the underlying phenomenon. In details we will discuss the influence of different parameters, e.g. the molecular orientation on the metal surface, the illumination geometry, and the electric field strength due to the bias voltage, on the Raman spectrum. Furthermore we will compare the theoretical results with experimentally obtained spectra.