PhD School in Physical and Nanosciences

PhD Student: Marta Rosa

PhD in Physics□ and Nanosciences □

Study Plan for the First or Second Year

Attended internal Courses
- Non Equilibrium Green Functions (C. Jacoboni)
- Advanced Solid State Physics (M. Rontani)
- Meccanica Statistica Classica e Sistemi Disordinati (C. Giardinà)
- Molecular biophysics of proteins and RNA:basic principles and single molecule studies (C. Cecconi)

Attended Seminars
I attended numerous seminars, including:

- **VALERIA LOSASSO**
  Computational studies on the protein alpha-synuclein: from disease-linked mutations to ligand binding
  13/12/2011
- **VALENTINA TOZZINI**
  Minimalist models for bio-molecules: open problems and perspectives
  07/12/2011
- **SUSANA TOMÁSIO**
  Modelling of the interactions between peptides and graphitic surfaces
  07/07/2011
- **ARRIGO CALZOLARI**
  Zooming in an excitonic solar cell: an ab initio investigation of the optically active site
  28/04/2011
- **ANGEL RUBIO**
  Photo-induced dynamical processes in nanostructures, biomolecules and oxides
  27/04/2011
- **OLIVER CARRILLO**
  Three stories. Or how to avoid tedious simulations of proteins

11/01/2011

External courses and schools

I have so far followed the following courses/schools:
- Corso di Introduzione alla programmazione Message-Passin (MPI) , CINECA, Bologna (2days)
- Corso di Introduzione alla programmazione OpenMP presso centro di calcolo CINECA, Bologna (1day)
- Corso di introduzione al Linguaggio C per la programmazione scientifica, CINECA, Bologna (2 days)

Tentative Title of your PhD and Name of the Responsible

Docking simulations of DNA on inorganic substrates

Report on the research activity of the first or second year

The aim of my PhD work is to investigate the DNA-surface interaction with docking simulations, which are a powerful tool already used to predict orientations and structures of proteins. To do so we conceived a multi-level computational scheme to sample different length- and time-scales at different levels.
First we want to parametrize a force field for DNA-surface interaction based on density functional theory (DFT) results of DNA bases on surfaces. Then we will carry out classical molecular dynamics (MD) simulations with the developed force field of entire DNA molecules on substrates. Finally we will be able to perform docking simulations based on scoring functions derived from the MD trajectories/energetics.

The first step is the understanding and description of the interaction between the DNA bases and the substrate. This was the objective of my first PhD year. In particular, a Au(111) surface was chosen as the substrate.
I devoted particular attention to the inclusion of van der Waals interactions in the DFT calculations, by exploiting the recent implementation of the vdw-DF functional [Langreth et al. Phys Rev. B, 82 (2010)] in quantum-espresso (www.quantum-espresso.org). Tests of this method were performed on the C6H6 dimer and C6H6 adsorbed on the Au(111) surface: the results of such tests indicate that the vdW-DF functional is suitable to describe the electronic structure of benzene-like molecules on Au(111). The vdw-DF approach inherently implies the choice of the revPBE exchange correlation functional, that minimizes the error in the exchange part due to fictitious contribution in the van der Waals regime. Nevertheless, recently different functional have been tested in conjunction with vdW-DF, to check if some inaccuracies could be corrected, such as errors in treating hydrogen bonded systems and the overestimation of lattice parameters for most of the solids. For this reason we tested the efficiency of both PBE and revPBE for the two test systems, expecting a better description of the Au surface with PBE. Our results are very similar for the two functionals, with a better agreement of PBE with results obtained at a higher level of theory and with experimental data.Finally, as the two functionals give the same results for the kind of systems we are interested in, we decided to use PBE, both because of a better description of solids and because of the possibility of comparing results with past calculations performed with DFT PBE.

Gas-phase molecules: We performed the structural optimization of Cytosine and Guanine both with and without vdW interaction and then we compared bond lengths and planar angles with literature results obtained at a higher level of theory[13]. Deviations from literature values are similar for the two methods, under 4,5% for bond lengths and under 0,5% for planar angles, while differences between the two DFT methods are below 0.5%.

Minor deviations between DFT and vdW-DF are observed for the gas-phase molecules in the density of states and molecular orbitals. A recurrent effect of vdW-DF calculations is that empty levels get closer in energy. For Cytosine energy levels for different orbitals show only little shift in energy and this does not affect the final charactes of MOs. For Guanine an already known problem appears: the empty orbitals are very close in energy and vith the contribution of vdW-DF they switch position. Comparing our results to those of DFT calculations with an atomic basis set we find that the inaccuracy was already present in DFT calculations: LUMO, LUMO+1 and LUMO+2 energy values are influenced by molecule structure, choice of the basis set and type of calculation. Virtual orbitals inversion is an already known problem for systems with close energy levels[15], and our analysis shows that the introduction of vdW interaction does not bring to unexpected effects.

The inversion of virtual orbitals can create problems in well describing the interaction between the molecule and the system if there is a charge transfer between surface and molecule. But from previous studies we do not expect charge transfer between the surface and the DNA bases.

Cytosine adsorbed on Au(111). We performed structural optimization of Cytosine/Au(111) with different orientations of the molecule relative to the surface and different adsorption sites: with oxygen on bridge, center and top adsorption sites, starting from a distance of 3.5 A between the molecule and the surface, with the molecule flat on the surface.

For the molecule adsorbed "flat" at the bridge position we performed both DFT and vdW-DF calculations, to find the equilibrium distance and the adsorption energy.Comparing our results also with literature[1,2] the difference in formation energy is sensitive, as in the vdW calculation is three times higher than without vdW [Fig 1].
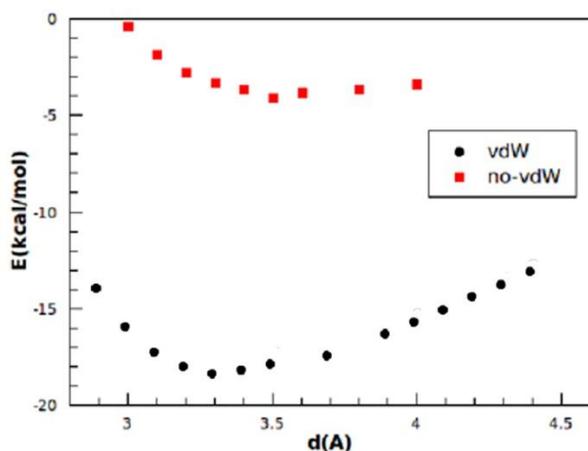

Figure 1. Adsorption energy versus cytosine-Au vertical distance for flat Cytosine starting configuration on Au(111) in bridge position. We relaxed the molecule with and without vdW, then we take the two final configurations and performed SCF calculations, varying the distance between the surface and the molecule to find the right equilibrium distance. Black circles are for calculations with vdW interaction, red squares for standard DFT calculations.

Since experimental adsorption energies for high coverage are around 35 kcal/mol, our results indicate that half of the energy is due to the interaction between the molecules and the surface (rather than to lateral interactions in the molecular layer). Our results show that the different adsorption sites are quite equivalent, as the formation energy difference is less than 1kcal/mol. This outcome is in line with the evidence of a large mobility of cytosine at low coverage, experimentally measured and indicated by std DFT calculations. The main difference between std DFT and vdw calculations is in the torsion angles and

in the planarity of the molecule. DFT results show that the relaxed configuration remains flat on the surface, even if results on monolayer, both theoretical and experimental, show molecules tilted respect to gold. Our vdW-DF calculations show, instead, that the relaxed molecule is tilted on the surface irrespectively of the adsorption site, starting from a 4 degrees inclination to a maximum inclination of 14 degrees for the top adsorption site.

Comparing the density of states of isolated and adsorbed cytosine it is possible to notice only minor perturbations in the electronic structure upon adsorption, without charge transfer between the molecule and the surface. From the charge density plots we can see different hybridized orbitals, with charge both on the molecule and on the surface, showing that there is a weak electronic coupling beyond pure physisorption. Nevertheless, no bonding orbitals are found. We performed similar calculations for Cytosine vertical above the surface and for Guanine flat and vertical on the surface.

Results are very similar to the ones obtained for flat Cytosine: molecule structure, density of state and molecular orbitals are very similar to the one of the gas-phase molecules and the molecule and the surface hybridize, but there is no formation of bonding orbitals between the two.

Future work will be dedicated to DFT calculations for Adenine and Thymine, to MD calculations and finally to docking simulations.

Publications

10% reflectance on TMAH textured a-Si/c-Si heterojunction solar cells,
M.Rosa, M.Allegrezza, M.Canino, C. Summonte, A. Desalvo
Solar Energy Materials and Solar Cells 95, 11, (2011) 2987-2993.

Heterojunction solar cells on multi-crystalline silicon,
Mario Tucci, S. De Iuliis, L. Serenelli, L. Pirozzi, C. Summonte, M. Canino, F. Zignani, E. Centurioni, M. Rosa, G. de Cesare, D. Caputo
Physica Status Solidi 8, 3, 928-931 (2011)

Optimizing the rear side of heterojunction solar cells on n-type CZ substrates, M. Canino, M. Rosa, M. Allegrezza, C. Summonte, F. Zignani, *24th EPVSEC, Hamburg, Sept 21-25 2009*

Optical properties of Silicon nanodots in SiC matrix *C. Summonte1, A. Desalvo, M. Canino, M. Allegrezza, M. Rosa, M. Ferri, E. Centurioni, A. Terrasi, S. Mirabella*
25th EPVSEC, Valencia, Sept 6-10 2010

Multi-ctystalline Silicon based heterojunction solar cells*M. Tucci, S. De Iuliis, L. Serenelli, M. Izzi, C. Summonte, M. Canino, M. Allegrezza, M. Rosa, G. de Cesare, D. Caputo, G. Boncompagni,*
25th EPVSEC, Valencia, Sept 6-10 2010

Participation to national and international conferences (poster, oral, invited)

- *5th Time-Dependent Density functional Theory: Prospects and Applications*, Benasque, Spain (3 Jan 2012 - 17 Jan 2012)
- *2nd Training School on G-Quadruplexes*, Spa, Belgium (11 Sept 2011 – 15 Sept 2011)

- *Summer School on Atomistic Simulation Techniques for Material Science, Nanotechnology and Biophysics*, SISSA, Trieste, Italy (11 July 2011 - 29 July 2011)