

**FA4-MS28-T01**

**Accurate ab initio calculation of the cohesive energies of molecular crystals.** Lorenzo Maschio<sup>a</sup>, Denis Usvyat<sup>b</sup>. <sup>a</sup>*Università di Torino, Italy.* <sup>b</sup>*Universität Regensburg, Germany.*  
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Molecular crystals certainly represent a tough challenge for the standard tools of modern solid state quantum chemistry. The main difficulties in trying to obtain a correct description of weakly-bound systems are due to the essential role that dispersive forces play, when covalent and ionic binding is absent, since the long-range forces cannot be correctly described neither by standard Density Functional Theory (DFT) nor Hartree-Fock (HF) approaches. Great efforts in the scientific community to tackle this problem are witnessed by the increasing number of works on this topic in recent literature and different approaches have been proposed.

Post-HF ab initio correlation methods, which are available for molecular calculations since a few years now, have been shown to be able to describe the interaction between molecules in a correct and reliable way. Thanks to the adoption of local methods the relative cost of the calculation is not prohibitive. Despite the potential interest the availability of such methods for crystalline systems is still rather scarce.

In this talk results will be presented concerning the periodic Local Møller Plesset second order perturbation theory (LMP2) method applied to the study of molecular crystals. All calculations are performed using the well known CRYSTAL code and the new CRYSCOR code, the first publicly available program to implement local correlation methods for crystalline systems, which are both developed in our research groups.

Different aspects of the electronic structure simulation of molecular crystals will be covered, including evaluation of cohesive energies and relative stability of different structures as well as properties like Compton profiles and bulk moduli. Results concerning Ice, Carbon dioxide, Urotropine, Urea and Formic acid crystals will be presented and discussed among others.

In addition, the local method allows us to analyze the correlation contribution to the cohesive energy by separating the intramolecular and intermolecular contribution,[4] allowing for an interesting insight on the role of weak interactions in the studied systems. In this respect, crystalline Formic acid is analyzed in more detail.

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**Crystal structure prediction of molecular compounds with d-DFT.** Jacco van de Streek, Marcus A. Neumann. *Avant-garde Materials Simulation, Freiburg, Germany.*  
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The talk will focus on the crystal structure prediction of molecular compounds with dispersion-corrected Density Functional Theory (d-DFT) calculations<sup>1</sup>. d-DFT was successfully used to predict all four crystal structures of the 2007 Crystal Structure Prediction Blind Test correctly<sup>2</sup>. This success has meanwhile been extended to larger molecules, to more flexible molecules and to molecular salts. The calculations are carried out with the computer software *GRACE* (<http://www.avmatsim.eu>), which uses the computer software *VASP*<sup>3-5</sup> for single-point uncorrected DFT calculations. An outline of the crystal structure prediction procedure will be given. Results on Efavirenz, Pyridine, Benzamide, Pyridinium Chloride and several Crystal Structure Prediction Blind Test compounds will be presented. Preliminary results for the 2010 Crystal Structure Prediction Blind Test will be included where possible.

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**FA4-MS28-T03**

**Temperature and Pressure in Computational Crystallography: A Case Study of Ice.** Detlef W. M. Hofmann, Marco Cogoni, Liudmila N. Kuleshova, Bruno D'Aguanno *CRS4, Pula, Italy.*  
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A notorious problem of computational crystallography are temperature and pressure. The importance of these factors in crystallography becomes obvious by the widespread polymorphism. Here we present molecular dynamic simulations as an alternative to effective potentials with intrinsic temperature and pressure effects. An excellent test case is ice, since it is very well investigated and 15 different crystal structures are known. Proton transfer, diffusion, and proton order/disorder in the ice crystals are studied.

In the last blind test it was shown that effective potentials can be used to predict correctly crystal structures at standard conditions. These requires potentials corrected for the entropy at standard conditions. Earlier we obtain such potentials by data mining on the Cambridge structure data base [1, 2]. Another very successful approach was the dispersion-corrected density functional theory introduced by M. A. Neumann, F. J. J. Leusen, and J. Kendrick.

Another possibility is molecular dynamics. Molecular dynamics gives, in addition to structural properties, access to thermodynamical properties as the entropy, diffusion, proton exchange rates, and conductivity. This method became accessible by the extended computer power available nowadays. For our simulations we used a cluster of 1600 nodes with a total performance of 36 TeraFLOPS.

We performed MD simulations at different conditions for all known structures of ice. As force field we used the reactive force field [3], which allows for proton exchange by bond breaking/formation. The reactive force field was recently derived from neutron scattering by recursive fitting. The simulations reproduce well the melting and boiling point. On the figure five snapshots of our video of the melting are shown.