CPP 14: Biological Systems

Time: Tuesday 10:00–12:30 — Location: H47

CPP 14.1 Tue 10:00 H47

DFT studies for structure, energetics, dynamics and electronics of glycine, alanine, and cysteine — •ROBERT MAUL[1], KARSTEN HANNEWALD[2], FRANK ORTMANN[2], MARTIN PREUSS[2], and FRIEDHELM BECHSTEDT[2] — [1]Institut fuer Nanotechnologie, Forschungszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen — [2]Institut fuer Festkoerpertheorie und -optik, Friedrich-Schiller-Universitaet, Max-Wien-Platz 1,07743 Jena, Germany

The gas-phase geometries of the most stable conformers of glycine, alanine, and cysteine were optimized using a plane-wave density functional theory implementation in the VASP code. Different approximations for the exchange-correlation functional like LDA, GGA-PW91, and the hybrid functional PBE0 allow for an estimation of the non-local contribution of the functional to several geometry parameters and relative energies. Furthermore we calculated dipole moments and infrared spectra of the three most stable conformers of glycine, alanine and cysteine in good agreement with experimental results. In addition the calculated ionisation- and two particle excitation energies deviate only by 3% from the experimental values. Therefore it can be concluded that DFT-GGA performs comparably well with respect to accuracy and the speed of calculation, which permits the investigation of more complicated systems.

CPP 14.2 Tue 10:15 H47

Dissipative single- and two-electron transfer via bridges — •SABINE TORNOW[1], F. ANDERS[2], and R. BULLA[1] — [1]Theoretical Physics III,Center for Electronic Correlations and Magnetism,University of Augsburg — [2]Institute of theoretical Physics,University of Bremen

Electron transfer (ET) reactions are common in chemical, physical and biological systems and are often performed via bridges. Dependent on the energy of the bridge and coupling to the environment the process can be an incoherent sequential ET or a coherent superexchange mediated ET. With the help of the time dependent Numerical Renormalization Group we investigate the coherent and incoherent dynamics in the nuclear tunnelling regime. Furthermore, we discuss the multi-electron dynamics when we include two excess electrons into the system at low as well as large temperatures.

CPP 14.3 Tue 10:30 H47

How finite (Ala)$_n$ polypeptides are stabilized by H bond cooperativity: A numeric atom-centered orbital based first-principles study — •VOLKER BLUM, JOEL IRETA, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin

An infinite alpha-helical polypeptide (Ala)$_\infty$ is clearly stable over a fully extended conformation. This stabilization is brought about by hydrogen bonds. In finite polypeptide chains, the strength of these crucial bonds depends on the length and environment of the helix, so that, e.g., a short α-helical polypeptide segment (Ala)$_4$ is actually *less* stable than a fully extended conformation. We here use all-electron density functional calculations in the PBE generalized gradient approximation by a recently developed, computationally efficient numeric atom-centered orbital based code[1] to investigate this H-bond *cooperativity* that is *intrinsic* to Alanine-based polypeptides (Ala)$_n$ (n=1-20,∞). We compare finite and infinite prototypical helical conformations (α, π, 3_{10}) on equal footing, with both neutral and ionic termination for finite (Ala)$_n$ peptides. Moderately sized NAO basis sets allow to capture E_{hb} with meV accuracy, revealing a jump in E_{hb} (cooperativity) when two H-bonds first appear in line, followed by slower and more continuous increase of E_{hb} towards $n \to \infty$. [1] V. Blum, R. Gehrke, P. Havu, V. Havu, X. Ren, M. Scheffler, *The FHI Ab Initio Molecular Simulations (aims) Project*, Fritz-Haber-Institut, Berlin (2006).

15 min. break

CPP 14.4 Tue 11:00 H47

Single molecule fluorescence at microstructured nanopatterns — •ALEX G F DE BEER[1], MARCO SCHWIEDER[1,2], EVA BOCK[1,2], GUENTER MAJER[1], and JOACHIM P SPATZ[1,2] — [1]Max-Planck Institute for Metals Research, Dept. of New Materials and Biosystems, Heisenbergstrasse 3, D-70569 Stuttgart, Germany — [2]University of Heidelberg, Dept. of Biophysical Chemistry, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany

Nanopatterns created using self assembly of block copolymer micelles can be used as a negative resist for electron beam lithography. This allows the preparation of surfaces consisting of patches of gold nanodots [1].

We use TIRF single molecule microscopy to study thiol-modified Alexa 488 labelled streptavidin molecules attached to single gold dots. The stoichiometry of attachment is of interest, along with electrodynamic interactions between the dye molecules and the gold dots. The size of the streptavidin molecule (roughly 6 nm) is small enough so that it fully lies within the interaction range of a gold particle (about 16 nm) [2]. We show a clear influence of the nanopattern on the properties of the dye, with an increased photobleaching resistance and decreased dye intensity. Using this decreased fluorescence intensity and accompanying increased photostability, it is possible to generate a photobleaching contrast between bound and unbound molecules, thus allowing to selectively image bound molecules only.

[1] R. Glass et al., Advanced Functional Materials 13, 569-575 (2003)
[2] E. Dulkeith et al., Nano Lett. 5(4), 585-589 (2005)

CPP 14.5 Tue 11:15 H47

Mineral phase distribution in biological composite material of a crustacean model organism — •SABINE HILD[1], OTHMAR MARTI[2], and ANDREAS ZIEGLER[1] — [1]Central Facility for Electron Microscopy; University of Ulm, Albert-Einstein-Allee 11, 89069 Ulm — [2]Experimental Physics; University of Ulm, Albert-Einstein-Allee 11, 89069 Ulm

Mineralized biological composites have attracted increasing interest because of their outstanding mechanical properties that are well adapted to their function. The mineralized exoskeleton (cuticle) of crustaceans is an excellent model in this field. To learn more about the properties, function and formation of biomaterials, we studied the spatial distribution of minerals, elements, and organic compounds within the cuticle of the terrestrial isopod Porcellio scaber on the sub-micrometer scale using confocal mciro-Raman microscopy, REM and SFM. In cross-sections of the cuticle we found calcite and amorphous calcium carbonate (ACC) as the main biominerals. For the first time, we show that minerals are arranged in distinct layers. Calcite is restricted to the outer area of the cuticle, whereas ACC is localized in the middle having only little overlap with the calcite layer. Since the cuticle is subjected to periodic molting it is periodically decalcified and shed. A new larger cuticle, synthesized before shedding, is mineralized after every molt. These processes cause spatial and temporal variations of the mineral distribution. We show that the protective outer calcite layer is shed away during each molt, while ACC is recycled to quickly re-establish the protective calcite layer in the new cuticle.

CPP 14.6 Tue 11:30 H47

Hydration of Oligo(ethylene glycol) Self-Assembled Monolayers: An in situ PMIRRAS study — •MAXIMILIAN SKODA[1,2], ROBERT JACOBS[3], and FRANK SCHREIBER[2] — [1]Physical and Theoretical Chemistry Laboratory, Oxford University, UK — [2]Angewandte Physik, Universität Tübingen, Germany — [3]Chemistry Research Laboratory, Oxford University, UK

The interaction with water of protein-resistant monolayers (SAMs), self-assembled from (triethylene glycol) terminated thiol $HS(CH_2)_{11}(OCH_2CH_2)_3$-OMe solutions, was studied using in and ex situ polarization-modulated Fourier transform infrared spectroscopy. In particular, shifts in the position of the characteristic C-O-C stretching vibration were observed after the monolayers had been exposed to water. The shift in frequency increased when the SAM was observed in direct contact with a thin layer of water. It was found that the magnitude of the shift also depended on the surface coverage of the SAM. These findings suggest a rather strong interaction of oligo(ethylene glycol) SAMs with water and indicate the penetration of water into the upper region of the monolayer. Since the complexity of this system requires careful consideration of experimental parameters, some theoretical aspects of the signal generation will be discussed.

CPP 14.7 Tue 11:45 H47

Mechanical Properties of Polypeptide by using Atom Force Microscopy — •Kaitian Li, Jens Hentschel, Hans Börner, and Andreas Fery — Max-Planck-Institut für Kolloid und Grenzflächen, Am Mühlenberg 14424 Potsdam

Helical, tube- or tape-like structures formed by peptide self aggregation are a common motive found in biological systems. In this work, we explore the mechanical properties of such tubular aggregates formed from well defined synthetic block-copolymers, which consist of a peptide block which triggers self aggregation and conventional polymeric blocks. The amino acid sequence of the peptide encodes a high tendency to adopt an antiparallel β-sheet motif, and thus programs the formation of tapelike microstructures. The helical superstructures undergo defined entanglement to form superhelices. A twisted two-dimensional core-shell tape is proposed as a structure model, in which the peptide segments form an antiparallel β-sheet with a polymer shell. [1] Here, we discovered that the resulting helical superstructures, when deposited on a substrate, are 2.9 nm high, 10 nm wide, and up to 2.3 μm long. We also try to measure their mechanical properties, which we directly measured through indentation type experiments using atomic force microscopy. We find that these structures which on the silicon substrate are deucedly soft and flexible. They could easily be deformed even by soft cantilever (K~0.05). From the averaged point we can have a correspondingly Young*s modulus as calculated by finite element analysis. We also plan test their bending elasticity by using a novel AFM based approach.

CPP 14.8   Tue 12:00   H47

Looping charged elastic rods — •Andrey Cherstvy and Ralf Everaers — Max-Planck-Institut für Physik Komplexer Systeme, Nöthnitzer Straße 38, D-01187 Dresden, Germany

Finding optimal shape of a charged elastic rod under external torque and forces, as a minimum of rod elastic [1] and electrostatic (el) energy, is a complicated problem [2]. We calculate el energy of DNA loops and planar untwisted DNA rings [3]. We sum Debye-Hueckel el potentials between charges on bent/looped rod. Equilibrium loop shape [4] is unchanged by el interactions and loops have no self-contacts. DNA charges are modeled as straight or helical arrays. For large loops the excess el energy of DNA bending is well described by OSF theory of rod el persistence length. For small loops (eg. DNA wrapped around histones or DNA bent by lac-repressor [2]) the OSF assumptions are violated and el energies obtained are larger. For large rings the actual el excess energy is larger than OSF prediction due to a final penalty of approaching two DNA ends into a contact upon cyclization. For small circles, as there are not so many charges to sum over, the OSF underestimates el energy, especially at low salt. Our results are relevant to description of tight DNA looping in DNA-proteins complexes [2,5] and to cyclization of short DNAs [6] as a function of added salt.

[1] A.E.H. Love, Dover, NY (1944). [2] D. Swigon, et al., PNAS 103 9879 (2006). [3] A.G. Cherstvy and R. Everaers, in preparation. [4] J. Coyne, IEEE J. Ocean. Ing., 15 72 (1990). [5] A.G. Cherstvy at al., JPCB, 109 2962 (2005). [6] L. Czapla, et al., J. Chem. Th. Comput. 2 685 (2006) and refs. therein.

CPP 14.9   Tue 12:15   H47

Non-affine rubber elasticity for stiff polymer networks — •Claus Heussinger and Erwin Frey — Arnold-Sommerfeld-Center, Ludwig-Maximilians Universität, München

The elastic response of cross-linked stiff polymer networks is usually interpreted in terms of affine stretching models, adopted from the theory of rubber-elasticity valid for flexible polymer gels. Unlike flexible polymers, however, stiff polymers have a highly anisotropic elastic response, where the low-energy elastic excitations are actually of bending nature. As a consequence, similar to springs connected in series, one would expect the softer bending mode to dominate the elastic energy rather than the stiff stretching mode. We propose a theory that, unlike recent affine models, properly accounts for the soft bending response of stiff polymers. It allows calculating the macroscopic elastic moduli starting from a microscopic characterization of the (non-affine) deformation field. The calculated scaling properties for the shear modulus are in excellent agreement with the results of recent simulations obtained in simple two-dimensional model networks, and can also be applied to rationalize bulk rheological data in reconstituted actin networks.