

CPP 29 Computational Techniques

Time: Friday 10:30–11:45

Room: ZEU 160

CPP 29.1 Fri 10:30 ZEU 160

First-principles calculation of noncovalent interactions - Diffusion Monte Carlo applied to hydrogen bonding and aromatic stacking — ●M. FUCHS¹, C. FILIPPI², J. IRETA¹, and M. SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin — ²Universiteit Leiden (NL)

Van der Waals (dispersion) forces are important in many molecular phenomena, such as self-assembly of molecular crystals and peptide folding. Calculating this nonlocal correlation effect requires accurate electronic structure methods. Usual density-functional theory (DFT) with generalized gradient functionals fails unless empirical corrections are added that still need extensive validation. Quantum chemical approaches like MP2 or coupled cluster (CCSD(T)) are accurate, yet their unfavorable computational scaling limits them to rather small systems. Diffusion Monte Carlo (DMC) can provide accurate molecular total energies and remains feasible also for larger systems. Hence DMC promises to be useful for benchmarking simpler but more approximate approaches. Here we apply the fixed-node DMC method to (bio-)molecular model systems where dispersion forces are significant. Our DMC binding energies for (dimethyl-) formamide dimers and adenine-thymine DNA base pairs fully agree with data from CCSD(T), in particular for stacked DNA base pairs where MP2 is insufficient. In addition we consider benzene dimers in the stacked, slipped parallel, and T-shaped structures. Resolving their relative energies requires carefully optimized DMC trial wavefunctions. We discuss the role of the determinantal part and the correlation factor, optimizing them simultaneously using a fluctuation potential approach.

CPP 29.2 Fri 10:45 ZEU 160

Modeling multi-body effects in ionic solutions with a concentration dependent dielectric permittivity — ●BERK HESS¹, CHRISTIAN HOLM^{2,1}, and NICO VAN DER VEGT¹ — ¹Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany — ²Frankfurt Institute for Advanced Study (FIAS), J.W. Goethe Universität, Max-von-Laue Strasse 1, D-60438 Frankfurt/Main, Germany

We report a new strategy to parameterize effective ion-ion potentials for large-scale implicit solvent simulations of charge systems. The effective potential includes a pair term, derived from explicit solvent simulation of a single ion pair, and a Coulomb term that by means of a concentration dependent dielectric permittivity takes into account all multi-body effects. We show that, for aqueous NaCl as an example system, this approach allows to accurately predict the solution osmotic properties up to concentrations of 2.8 molar salt. Replacing the pair term with a Weeks-Chandler-Andersen potential leads to equally good predictions, which indicates that ion-specific hydration effects featuring in the effective potential need not be included. The use of a concentration dependent dielectric permittivity opens new ways to study systems with inhomogeneous charges distributions.

CPP 29.3 Fri 11:00 ZEU 160

Some computational techniques for first-principles simulations on condensed matter systems — ●ALBERTO CASTRO¹, M. A. L. MARQUES², HEIKO APPEL¹, ANGEL RUBIO^{3,1}, and E. K. U. GROSS¹ — ¹Institut für Theoretische Physik, Arnimallee 14, Fachbereich Physik, 14195 Berlin (Germany). — ²Laboratoire de Minéralogie-Cristallographie de Paris (France). — ³Donostia International Physics Center and Departamento de Física de Materiales, Facultad de Ciencias Químicas, 20018 San Sebastián (Spain).

The real-space techniques for computational simulations in the condensed matter realm are usually praised for, at least, two strong advantages: On the first hand, the intrinsically local character of the "basis set" should permit, in principle, to allow for large scale parallelization by dividing the space in domains. This locality is also the basis for the use of techniques aiming at the linear-scaling of the computational effort. On the second hand, the real space mesh on which the magnitudes are represented may be locally adapted to the needs of each region – one feature difficult to translate to the more traditional plane wave representation. We will present our approach to these two time-saving computational techniques: (i) One possible route to implement curvilinear coordinates, able to adapt the local resolution to the needs of each region in space; (ii) A multiple-way parallelization scheme that may di-

vide the work among a given number of processors, splitting the tasks either in k-points, in Kohn-Sham states (assuming a density functional formulation of the condensed matter problem), in regions in real-space, or in a combination of all of them.

CPP 29.4 Fri 11:15 ZEU 160

Monte Carlo algorithms for electrostatic interactions in dielectric media — ●IGOR PASICHNYK¹, RALF EVERAERS¹, and ANTHONY MAGGS² — ¹Max Planck Institute for the Physics of Complex Systems, Noethnitzer Str. 38, D-01187 Dresden, Germany — ²Laboratoire de Physico-Chimie Théorique, UMR CNRS-ESPCI 7083, 10 rue Vauquelin, F-75231 Paris Cedex 05, France

Due to the magnitude and long-range nature of Coulomb forces, the accurate representation of electrostatic interactions in classical computer simulations is a difficult task and an area of on-going research.

Maggs and collaborators [1] have suggested rewriting the problem of a Coulomb system in a local lattice framework which admits also the effective treatment of nonhomogeneous dielectric medium.

The quenched version of the algorithm is applied for the construction of field lines and equipotential surfaces. The algorithm correctly reproduces fluctuations in the electrostatic field that correspond to the zero-frequency component of the van der Waals interaction. Fluctuations in the field produces inhomogeneous polarization, which in turn generates an induced charge density. This charge density interacts electrostatically and produces thermally dependent force between dielectrics. It is shown that these fluctuations lead to a Casimir-like attraction in the triple-slab dielectric system.

[1] A.C. Maggs and V. Rossetto, Phys. Rev. Lett., 88,196402, 2002

CPP 29.5 Fri 11:30 ZEU 160

Investigation of the condensation kinetics of methanol by molecular dynamics simulation — ●BJÖRN FISCHER and THOMAS KRASKA — Physical Chemistry, University Cologne, Luxemburger Str. 116, D-50939 Köln, Germany

The nucleation kinetics and the liquid cluster growth in the condensation process of supersaturated methanol vapour in a carrier gas is investigated. Methanol is chosen as an associating substance and also as the smallest member of the series of the 1-alkanols. For the modelling of the thermophysical properties of methanol several molecular models of differing complexity exist [1,2]. The suitability of these models for the direct simulation of the nucleation process has not been investigated yet.

The simulations performed here start with an equilibrated stable vapour state. The supersaturation is induced by a temperature jump to a state point in the metastable region of the phase diagram. Shortly after the jump clusters are formed by homogeneous nucleation which continue to grow by surface growth or coalescence.

The simulation results are analysed with respect to the nucleation rates at different state conditions and supersaturation and compared with experimental data. Furthermore, the cluster size distribution and the temperature development of the simulated systems are studied.

[1] M. E. van Leeuwen, B. Smit, J. Phys. Chem. 99, 1831 (1995)

[2] W. D. Cornell et al., J. Am. Chem. Soc. 117, 5179 (1995)