

27th May 2015 – 2:00 p.m.
 CFEL-bldg. 99, seminar room I EG. 076

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Local reduced-density-matrix-functional theory: Incorporating static correlation effects in Kohn-Sham equations

Despite of the great advances in density-functional based schemes for calculating structural and dynamical properties in the last decade, we still lack an exchange-correlation functional which can simultaneously describe equilibrium properties and the breaking and formation of bonds. At the same time, schemes based on either many-body perturbation theory or reduced density matrix functional theory (RDMFT) suffer from their high computational cost. Here, we present a novel idea that builds on the knowledge acquired in RDMFT to construct a density-functional scheme which accurately incorporates

static correlation effects. Within this scheme the natural orbitals, i.e. the eigenfunctions of the one-body density matrix, are constrained to be solutions of a single-particle Schrödinger equation with a local effective potential. This provides a natural way to connect an energy eigenvalue spectrum to the natural orbitals. This energy spectrum is found to reproduce the ionization potentials of different atoms and molecules very well. In addition, the dissociation limit of diatomic molecules is well described without the need to break any spin symmetry, i.e. this attractive feature of RDMFT is preserved. Due to the additional constraint the natural orbitals are only approximately determined which leads to differences between the unconstrained and the approximate natural orbitals with the latter being similar to the Kohn-Sham orbitals from a local density approximation. This suggests that a mixed density/density-matrix scheme can be developed which takes the best from both theories: the low computational cost and accurate description of equilibrium geometries from density functional theory and the accurate description of static correlation from reduced density-matrix functional theory.

