fast and accurate DFT calculations with QUICKSTEP

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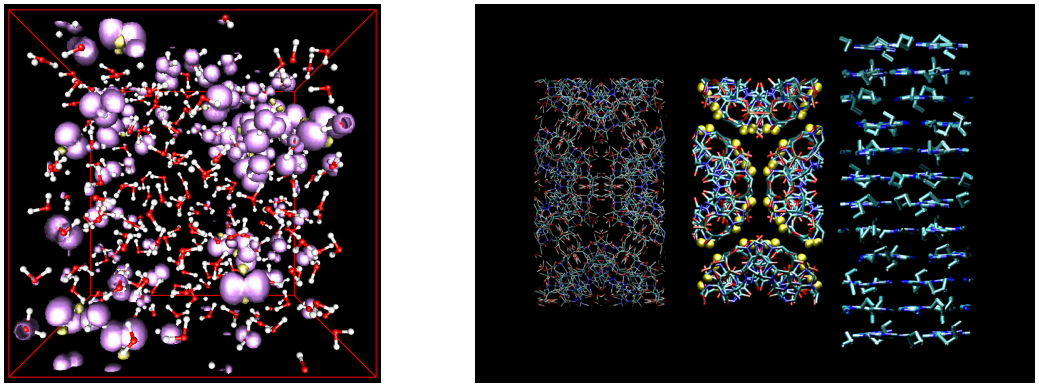
We present the implementation of the hybrid Gaussian and plane wave (GPW) DFT scheme[1] in the QUICKSTEP/CP2K program. In the GPW scheme, wavefunctions are represented using Gaussians, whereas plane waves are used as an auxiliary basis for the density. The compactness and the localized character of the Gaussians basis are exploited, leading to a low memory cost and a fast linear algebra part (e.g. wavefunction orthogonalisation). Simple screening and the use of FFTs to compute the Hartree potential lead to a linear scaling algorithm for the computation of the Kohn-Sham matrix. The efficiency of the code, related to the early onset of linear scaling, will be illustrated. Comparing with CPMD results for liquid water, it will be shown that high accuracy can be maintained throughout. Preliminary results on the onset of an Anderson-like localization, the nature of the hole, and of the excess electron in liquid water will be presented



Left: Spin density illustrates the extent of the hole in liquid water just after ionization. Right: Three views of the DNA crystal used in the benchmark computations.

In QUICKSTEP, the wavefunction optimization can be performed using a novel orbital transformation method[2]. As a direct minimization technique this method is guaranteed to converge and is thus very suitable for electronically 'difficult' systems such as radicals away from their equilibrium geometry. The method scales, for large systems, as $O(N^2M)$ with a small prefactor ($M = \#$ basis functions, $N = \#$ molecular orbitals). As a result, accurate basis sets can be used at a small additional cost. The method has been used to compute the electronic structure of a DNA crystal containing 2x12 base pairs, solvent and counter ions (2388 atoms) using a TZV(2d,2p) basis (38688 basis functions) in just 5h on 32 CPUs of an SP4. We conclude that the electronic structure of systems of this size can now be studied routinely with high accuracy.

[1] A hybrid Gaussian and plane wave density functional scheme
Lippert G, Hutter J, Parrinello M: *mol. phys.* 92 (3): 477-487 1997

[2] An efficient orbital transformation method for electronic structure calculations
VandeVondele J, Hutter J: *j. chem. phys.* 118 (10) : 4365-4369 2003