Going beyond DMRG using Matrix Product States

Sandeep Sharma

Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

A few years after the invention of the Density Matrix Renormalization Group (DMRG) algorithm, it was realized that DMRG is variationaly minimizing the energy of a highly flexible class of wave functions called the Matrix Product States (MPS). I will give a brief overview of MPS and will show that basic linear algebra operations can be performed very easily with these states. Having demonstrated this, I will describe a formulation of multi-reference perturbation theory that obtains a rigorous upper bound to the second order energy by minimizing the Hylleraas functional in the space of matrix product states. The algorithm has several advantages including: flexibility with respect to the choice of zeroth order Hamiltonian, no requirement to compute high body density matrices, and an embarrassingly parallel algorithm. With this algorithm we will first test the convergence of various perturbation theories. The same code will also be used to formulate a multi-reference linearized coupled cluster theory (MR-LCC) that reduces to the usual LCC theory in the single reference case. Using several benchmark calculations we will show that the theory reproduces FCI results with errors of around a few mH with energy differences being even more accurate. This MR-LCC theory will be used to study the dissociation of the Cr2 dimer.

In the second half of the talk I will present the first ever quantum calculation of the electronic levels of [2Fe2S] and [4Fe4S] clusters free from any model assumptions. Our results highlight that the widely used Heisenberg double exchange model used to study these clusters underestimates the number of states by one to two orders of magnitude, which can conclusively be traced to the absence of Fe $d \rightarrow d$ excitations, thought to be important in these clusters. Furthermore, the electronic energy levels of even the same spin are dense on the scale of vibrational fluctuations and this provides a natural explanation for the ubiquity of these clusters in bio-catalysis.