

Correlated electron calculations with Hartree-Fock scaling*

Roberto Car, Princeton University, USA

Due to its simplicity and numerical efficiency, density functional theory (DFT) is the most popular approach for calculating the electronic structure of large molecules and materials. Nevertheless, the accuracy of DFT is not always satisfactory and the search for improved approximations that avoid self-interaction and capture strong electron correlations faces severe difficulties. In this talk I will present an alternative approach in which the one- and two-particle density matrices needed to compute the ground-state energy, are explicit functionals of the natural spin orbital states and their joint occupation probabilities. The scheme is parameter-free and not affected by self-interaction error. In its simplest formulation, restricted to the seniority zero sector of the many-particle Hilbert space, it has the same scaling of Hartree-Fock theory. Yet, it describes strong correlations as demonstrated by the calculated dissociation energy curves of diatomic molecules and linear chains of hydrogen atoms. Improved approximations with a higher polynomial cost but not restricted to seniority zero will be discussed.

(*) Work in collaboration with Ralph Gebauer (ICTP, Trieste, Italy) and Morrel H. Cohen (Rutgers and Princeton University)