Approximation free approach to dual-scale problems : Calculating the electronic structure of molecules using multigrid techniques

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Since the dawn of quantum mechanical calculations for materials, describing the electronic structure in the vicinity of the atom has been a major difficulty. In density functional theory (DFT), this problem is commonly avoided either by using atomic pseudo potentials, or by spanning the electronic wavevectors in an atomic basis set. This approximation of the core introduces errors. These errors are often below those related to the choice of approximate exchange-correlation functional. However, in light of recent developments for new types of functionals, the effect of these core related errors has to be reevaluated. This brings about a need to perform all-electron calculations that do not involve any approximation of the core.

In this work, I have developed a fully numerical all-electron solver that is meant to provide bench mark computations for such functionals. High order real-space discretization, along with advanced multigrid techniques, were implemented in order to achieve high accuracy and efficiency. The Kohn-Sham equations of DFT are solved on a set of locally refined Cartesian grids that are adaptable to any type of geometry. The components of the non-linear equations are iterated together in a single, highly efficient multigrid cycle. Numerical results from calculations of diatomic molecules, H_2O and CO_2 are presented. The results were obtained by the solver using a local density exchange-correlation functional, and are in agreement with literature values (where such exist) up to 10^{-5} Hatree.