Efficient HF exchange evaluation through Fourier convolution in Cartesian grid for orbital-dependent density functionals

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ABSTRACT

We present a purely numerical approach in a Cartesian grid, for efficient computation of the Hartree-Fock (HF) exchange contribution in the HF and density functional theory models. This takes inspiration from a recently developed algorithm by Liu *et al.*, in 2017, where the rate-determining step is the accurate evaluation of electrostatic potential. This introduces the Fourier convolution theorem in conjunction with a range-separated Coulomb interaction kernel. The latter is efficiently mapped into a real grid through a simple optimization procedure, giving rise to a constraint in the range-separated parameter. The overall process offers logarithmic scaling with respect to the molecular size. It is then extended toward global hybrid functionals such as B3LYP, PBE0, and BHLYP within pseudopotential Kohn-Sham theory, through an LCAO-MO ansatz in a Cartesian grid, developed earlier in our laboratory. For the sake of comparison, a parallel semi-numerical approach has also been worked out that exploits the familiar Obara-Saika recursion algorithm without any additional techniques. An excellent agreement between these two routes is demonstrated through total energy and orbital energy in a series of atoms and molecules (including 10 π-electron molecules), employing an LANL2DZ-type basis function. A critical analysis of these two algorithms reveals that the proposed numerical scheme could lead to very attractive and competitive scaling. The success of our approach also enables us for further development of optimally tuned range-separated hybrid and hyper functionals.