

Efficient hybrid density functional calculations in real-space numerical grid methods

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Abstract:

Density functional theory (DFT) has been an essential tool for electronic structure calculations in various fields. In particular, its hybrid method including the Hartree–Fock (HF) exchange term remarkably improves the reliability of DFT for chemical applications and computational material design. However, the conventional hybrid DFT is inefficient for numerical grid-based methods as well as plane-wave-based ones. There are two different types of exchange–correlation potential that can be derived from hybrid functionals. In conventional approaches, the HF exchange operator is adopted as a part of Kohn–Sham (KS) potential. On the other hand, the optimized effective potential (OEP) method provides another way to incorporate the exact exchange in a mean field picture by constructing a local potential from the non-local HF exchange energy. Thus, one may construct a local version of HF that is equivalent to the exchange-only OEP KS-DFT. It has been known that the exchange-only OEP KS theory gives similar occupied orbitals to HF, while its virtual orbitals are different from those of HF.[1,2,3] Therefore, it is expected that an OEP-hybrid method will give similar results for ground state properties with those of the HF hybrid, but different properties for excited state properties.

Here, we show that such a local multiplicative potential can be derived from existing global hybrid functionals using the OEP method.[4,5] We investigate its accuracy for molecules. Furthermore, we find that the new approach enormously accelerates computational speed of grid-based methods compared to the conventional one, which is desirable for large-scale calculations.

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