

## Periodic Hartree-Fock and hybrid functionals in FHI-aims: Implementation and application to defects in doped MgO

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Density functional theory (DFT) with standard local and semilocal exchange-correlation (XC) functionals has repeatedly demonstrated the value of finding right tradeoff between accuracy and computational cost. At the same time, numerous applications of standard DFT have clearly shown its limitations. In particular, there are practically important cases when the self-interaction error (SIE) cannot be canceled by taking appropriate energy differences. The by now well understood examples include electronic structure and bonding in ionic materials, and electron transfer. Somewhat less documented examples include effects of SIE on geometric structure.

A consistent and well-defined way to remedy SIE at least partially is to add a fraction of Hartree-Fock (HF) exchange to the Kohn-Sham equations. This hybrid DFT approach has been proven to systematically correct SIE and its consequences in some systems. However, the results of these calculations may depend on the fraction of HF exchange. While viewed by some as a conceptual failure of hybrid DFT, this dependence is interpreted by others as a tool of exploring and making the hybrid approach more flexible.

Applications of hybrid DFT to materials are still relatively limited compared to molecules, although fast-growing. The reason is the non-locality of HF exchange and the computational cost associated with it. Due to its conceptual simplicity, the hybrid Kohn-Sham scheme can be easily implemented by extending existing standard DFT codes. However, making such an implementation efficient is a non-trivial task. We here describe an implementation of periodic HF exchange (bare and screened) using numeric atom-centered basis functions within the FHI-aims [1] all-electron code. The implementation is based on a localized “resolution of identity” strategy for the Coulomb operator, combined with efficient integral and density matrix screening operations (in real space) that allow to treat periodic systems up to (currently)  $O(100)$  atoms at essentially converged basis set accuracy, and seamlessly in parallel (memory and CPU time, tested up to hundreds of CPUs). We demonstrate the performance of our approach by applying the HSE family of density functionals to defects in MgO.

[1] V. Blum et al., *Comp. Phys. Comm.* 180, 2175 (2009)