Abstract

The properties of solids are described successfully within density-functional theory. However, the exact exchange-correlation functional is unknown and the commonly used local-density (LDA) and generalized gradient approximation (GGA) fail to predict the band gaps and structural properties of a number of oxide materials. This error is attributed to the self-interaction in LDA and GGA, which is partly corrected in hybrid functionals. Hybrid functionals contain a certain fraction of non-local Hartree-Fock exchange and give excellent agreement with experimental results for oxide materials. We present our implementation of the PBE0 and HSE06 functionals within the all-electron full-potential linearized augmented plane wave method realized in the FLEUR (www.flapw.de) code.[2] We highlight the excellent performance of these functionals for oxide materials, especially for systems in which LDA and GGA predict incorrect properties.

HSE Non-Local Part

For the HSE functional the Coulomb potential in (1) is replaced with an attenuated one

\[ V_{\text{coul}}(r) = \left( \frac{1}{r} - \frac{1}{r^4} \right) \]

While the Fourier transforms of either \( V_{\text{coul}} \) or \( V_{\text{ xc}} \) converge quickly, their difference does. The Fourier coefficients of the “rest” potential fall off exponentially (1/|k| ≈ 20).

This allows to evaluate the matrix elements efficiently by a sum over G vectors

\[ \langle k | G_i | q \rangle = \sum_j \langle k | G_j | q \rangle \Phi_i(q) \Phi_j(q) \]

The most expensive part of the self-consistency is the calculation of the non-local potential \( G_i | G_j \). However, the most change to the total potential during self-consistency origins from the local potential. Thus, an efficient implementation keeps the non-local potential fixed until the total potential is converged. Only then a new non-local potential is calculated.

Complex Mixed Basis

In a generalized Kohn-Sham non-local exchange-only potential is given by

\[ E_{\text{XC}}(\mathbf{k}) = \sum_{\alpha \beta} \int d^3r \left( V_{\text{ xc}}(r) \right) \chi_{\alpha}^* \chi_{\beta} \]

Mixed Basis Convergence

We investigated two rare earth compounds, namely EuO and GdN. These materials are ferromagnetic with an ordering temperature around 60 K. Upon passing the Curie temperature the resistance drops by several orders of magnitude.

Hybrid Functionals

In PBE hybrid functional[3] non-local Hartree-Fock (HF) exchange is represented by radial numerical functions and spherical harmonics, whereas in the IR a plane wave representation is used.

\[ V_{\text{coul}}(r) = \frac{1}{r} \sum_{\alpha \beta} \int d^3r \left( V_{\text{ xc}}(r) \right) \Phi_i(q) \Phi_j(q) \]

Functional using a nested SCF

The HSE functional using a nested SCF calculation is included. The electron density is calculated within the local SCF procedure, and thus unoccupied.

References