Selected Topics

1. Hybrid DFT/wavefunction methods
2. Strong correlation from first-principles

Applying hybrid functional and many body methods to rare earth: a study of Cerium clusters

***Marco Casadei (1); Xinguo Ren (1); Patrick Rinke (1); Angel Rubio (1) (2); Matthias Scheffler (1)**

1. Fritz-Haber-Institut der MPG (TH) - Berlin-Dahlem, Germany; 2. UPV/EHV, San Sebastian (Fisica Materiales) , Spain

Corresponding Author: Marco Casadei (casadei@fhi-berlin.mpg.de)

The presence of localized, partially occupied *f*-electron states is responsible for many of the peculiar physical properties of rare-earth materials. Of particular interest is the α-γ phase transition in Ce metal, which poses a considerable challenge to first-principles approaches. The current consensus is that local/semilocal approximations (LDA/GGA) to density functional theory (DFT) tend to delocalize the *f*-electrons too much, and thus fail to describe the γ-phase, whose *f*-electrons are believed to be more localized. It has been shown that dynamical mean field theory (DMFT) - traditionally the method of choice for strongly correlated systems - describes the α-γ phase transition, but the underlying mechanism responsible for the transition is still under debate [1].

We approach this problem from two different angles: for Ce cluster of increasing size (cut from Ce bulk), we investigate (a) electronic structure theories of increased complexity (DFT and many-body approximations) as a function of the lattice constant (b). The lowest order approximation we chose is the PBE0 hybrid functional. By incorporating a fraction of exact exchange, PBE0 reduces the self-interaction error, which is the main reason for the failure of LDA/GGA in this case, considerably. We contrast PBE0 with the screened hybrid functional HSE and then go beyond pure exchange approximations by combining the exact-exchange energy with a correlation energy in the random phase approximation (RPA).

For the Ce dimer we find that PBE0 gives a binding energy in excellent agreement with experiments [2]. The dimer and all other clusters we have investigated exhibit a multi-solution behavior for the three approaches, which is absent in LDA/GGA. The different solutions are found to be stable at different lattice constants, exhibiting multiple minima in the binding energy curve reminiscent of the volume collapse in the α-γ phase transition. The solutions can be discriminated by their electronic structure, most notably by the proximity of *f*-electron states to the Fermi level. The implications of this behavior for the α-γ phase transition in Ce bulk will be discussed.

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