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 $\alpha$-$\gamma$ 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 $\gamma$-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 $\alpha$-$\gamma$ 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 $\alpha$-$\gamma$ 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 $\alpha$-$\gamma$ phase transition in Ce bulk will be discussed.
