

Density Functional Theory and *f*-electron systems: relativity and exchange-correlation functionals.

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Density Functional Theory (DFT) based calculations constitute an increasingly important part of materials investigations in chemistry and physics. The wide use is a testament to the efficiency of DFT calculations to give sufficiently accurate information for large classes of systems. However, for materials containing heavier elements, specifically elements with *f*-electrons, the accuracy goes down, and information extracted from DFT calculations become less useful. The two main sources for accuracy limitations of DFT calculations for materials containing heavier elements are relativistic effects and inaccurate exchange-correlation (XC) functionals.

I will briefly review the approximations to the full relativistic treatment that are usually made in calculations and discuss possible influences on the results.

The traditional route for dealing with inaccurate XC functionals has for a long time been to circumvent the problem and use/develop theories outside of the pure DFT framework. Those theories are either computationally more expensive (for example, hybrids or quantum chemistry methods), or introduce tunable parameters (for example, LDA+U). We are following an alternative route aiming at developing a new generation of computationally fast density based DFT XC functionals with improved ability to treat also systems containing heavier elements. This would allow as successful use of DFT calculations in investigations of *f*-electron systems as is now possible for systems containing elements from the earlier parts of the periodic table. I will describe our philosophy of functional development: the sub-system functionals scheme [1,2].

The fundamental principle of the sub-system functional scheme is to describe the physics in a real material by mapping onto model systems that exhibit the characteristic physics in each separate part of the real system. The local density approximation (LDA) functional can be seen as a sub-system functional: in all parts of the real material the assumption is that the needed physics is well described by the uniform electron gas model system. It is well known that this assumption is less valid in certain cases but it holds for surprisingly large classes of materials. The Armiento-Mattsson 2005 (AM05) [3,4] functional takes this a step further by distinguishing between two separate types of regions in a real material, one type that is assumed to be well described by the uniform electron gas, and the other type of region assumed to be well described by a single surface model system. AM05 improves the description of normal solid-state systems [5,6]; in particular it cures the over-binding problem of LDA. However, AM05 is not expected to cure the problems arising in heavier materials. Improvement of AM05 is possible by fine-tuning the details in the construction. But a new major step in accuracy improvement is only expected if new physics is integrated into a functional via an additional model system. I will discuss what type of physics would be needed and what model systems could be used for this next step beyond AM05.

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