

Referee report on Ph.D. Thesis of Maxim Tchaplanka:

Electronic structure and magnetic properties of materials with strong electron-electron correlations

The objective of this thesis is to study materials with strong electron correlations by numerical methods based on extended ab initio methods. Essentially, two extensions of the standard density functional within the local-density approximation via an improved impurity solver are used in this thesis: exact diagonalization and the static Hubbard interaction. The materials studied were cobalt impurity attached to metals and magnetic anisotropy of iron-hafnium alloys.

The thesis is divided into four chapters. The first two contain a compendium of theoretical methods and the latter two present numerical calculations of selected materials. The four chapters are complemented with a summarizing Conclusion, Bibliography, List of Figures, List of Tables, List Publications of the candidate related to the thesis, List of Abbreviations and three short attachments with specific details of the used techniques and concepts. The layout of the thesis and the formal form of the presentation are adequate, the scientific language appropriate with only few typos and misprints. The same cannot be, however, said about the scientific content and the selection of the theoretical topics and the way they were discussed in the thesis. I will first comment on this generally.

Theoretical concepts:

This part aims to elucidate and detail the basic principles on which the ab initio calculations with impurity solvers are based. I find this part of the thesis unnecessarily too general and simultaneously rather superficial to be used as a learning tool for a reader unfamiliar with the method. Instead of using unspecified generic models, basis vectors, and various methods I would more appreciate, what would also be more appropriate, if only the used multi-orbital models were selected and their matrix elements explained. As well as if only the theoretical methods were presented that were later used in the application part. I have general questions related to this part:

1. Which DFT basis, discussed in Chapter 1, and which explicit form of the exchange and correlation functionals were used in the following numerical calculations?
2. Which explicit form of Hamiltonian \widehat{H}^{DFT} was used in the thesis?

Application to real materials:

The application part of the thesis consists of two disconnected chapters and it is unclear what was the reason to use both. I see neither physical nor mathematical connection. Physically different properties are studied and mathematically different approaches and numerical programs were used. I would find more appropriate to select a single method, e. g., DFT+ED, and to apply it to more materials with correlated impurities. General questions to the application part are:

1. What is the connected link between Chapters 3 and 4?
2. I assume that both DFT+ED and LSDA+U are open-access program packages. What was the own contribution of the candidate in their application. Has he extended or modified either of them or newly coded parts of them?

Apart from these general comments to the concept of the theoretical and application parts I further have more technical concerns and questions. They are related to insufficiently explained concepts or to inaccurate formulations.

Chapter 1:

1. What is $|\psi\rangle$ in Eq. (1.8)? Is it a Slater determinant or the exact ground state vector? Is the expression for $E_x[\rho]$ correct?
2. How is $n_{\gamma\gamma'} = \langle c_{\gamma}^{\dagger} c_{\gamma'} \rangle$ defined? What do the angular brackets stand for?
3. How are radii $r_{<}$ and $r_{>}$ in Sec. 1.3.2 defined?

Chapter 2:

1. How does the spin-orbit coupling, Eq. (2.32), enter the AIM Hamiltonian?
2. Can number N_{exc} be expressed via N_{tot} , N_{imp} , N_b , $N_{\underline{b}}$?

Chapter 3:

1. *Kondo effect in Sec. 3.1.* Equation (3.1) is correct when the spins are assumed quantum. While Eq.(3.2) holds only for a classical $s - d$ model. The Kondo effect is completely missed there, since non-commutativity of the spin operators, needed for the Kondo effect, is absent.
2. *Kondo effect in Sec. 3.2.3.* What is the indication of the Kondo effect in a static theory without quantum fluctuations? Is it merely a peak in DOS near the Fermi energy?
3. Did the DFT+ED method deliver new data not calculated by the QMC simulations of Ref. [57]? What is the advantage of the former over the latter approach?
4. Could it be decided which fitting in DFT+ED was optimal to reproduce the experimental results?

Chapter 4:

1. Was the aim of this chapter to test the method LSDA+U for the uranium-based compounds or to obtain new, not yet available data? How does the method compare to other approaches, e. g., LDA+DMFT?

The thesis as a whole represents a fair amount of work. It demonstrates a considerable effort of its author to present numerous quantitative results and test numerical methods beyond the standard density functional theory for the materials with correlated electrons. The thesis is, however, not free of dissonances and deficiencies. They are mostly related to a superficial and incoherent presentation of the theoretical part. I was not persuaded that the candidate sufficiently understood the applied theoretical methods and the range of their reliability.

I rate the thesis as acceptable for the Ph.D. degree that could be awarded to the candidate after he has responded to the raised questions and concerns, and clarified his original contribution to the methods and the results of the thesis and the supporting publications.

Praha, October 17, 2023

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