Abstract of the PhD thesis
“Electronic structure and magnetic properties of the materials with strong electron-electron correlation”

Agnieszka Lidia Kozub

Charles University supervisor:
Ing. Alexander B. Shick, CSc., DSc.

Gdańsk University of Technology co-supervisor:
dr hab. inż. Tomasz Klimczuk, prof. nadzw. PG.

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The objectives of the thesis is to study and understand the physical phenomena occurring in strongly correlated materials. The theoretical description of physical properties of solids, such as their electronic structure or magnetism, is a complex and fascinating many-body problem. One of the phenomena that in many cases should be taken into account is the electron-electron correlation. It occurs because the motion of electrons in solid is influenced by pairwise repulsion with the other electrons.

In the thesis, we summarize the material-specific theories of strongly correlated systems and apply them to several materials. The used methods combines first-principles electronic structure calculations based on density functional theory (DFT), with the many-body theories. We describe and apply the correlated band theory methods: the local density approximation plus Coulomb U (LDA+U), and the density functional theory plus exact diagonalization of single impurity Anderson model (DFT+ED).

The first two chapters of the thesis are dedicated to the computational methods and the next two to its applications in the investigated examples. The text is organized as follows:

- In Chapter 1 we present the basic approaches used in the electronic structure calculations. The chapter starts with the introduction of the
effective action functional formalism, a general framework within which various theories of interacting systems can be formulated. We derive DFT in this framework and shortly introduce dynamical mean field theory (DMFT), a commonly used approach to the strongly correlated systems. Afterwards, we derive the DFT method in the standard way, starting from the Hohenberg–Kohn theorems. We introduce its spin-polarized version, local spin density approximation (LSDA), where the total energy is an explicit functional of the charge and spin-magnetization densities. We derived the Kohn–Sham equations, and for the relativistic calculations the Kohn–Sham–Dirac equations. Finally, we shortly present the DFT++ scheme, a combination of DFT and the Hubbard model, which forms a general framework for computing the properties of materials with correlated electrons. It starts by building a material-specific Hubbard model on the top of the DFT band structure, which is then solved by means of the DMFT method.

- Chapter 2 describes the theoretical methods used in the thesis for the electronic-structure calculations of strongly correlated systems. First, the electronic correlations are incorporated into the system in a static way, by adding a Hartree–Fock-like expression for the Coulomb repulsion on the top of local density approximation (LDA) band structure. Afterwards, to go beyond the static approximation and to incorporate the dynamical effect, we turn towards the LDA+ED scheme. In that method, the multi-orbital single impurity Anderson model is parametrized to match LDA results, next the model is solved using the exact diagonalization (band-Lanczos) method. Finally, we present a practical scheme for calculations achieving the self-consistency over the charge density.

- In Chapter 3 we discuss the electronic structure of impurity atoms with partially filled $d$ or $f$ shells. The electron correlations in these systems were studied with the use of LDA+ED method. For a cobalt atom located in the bulk copper, the calculations yield nonmagnetic ground state, where the local moment at the Co atom is screened by the bath of conduction electrons. The computed spectra are in a good agreement with those obtained using the quantum Monte Carlo method by Surer et al. from Ref. [1].

The combined effect of electron correlations and spin-orbital coupling was illustrated on samarium and neodymium atoms adsorbed on graphene. The LDA+U method predicts both these adatoms to carry a local magnetic moment (spin as well as orbital). This is expected for Nd but not
for Sm which has a non-magnetic \( f^6 \) \((J = 0)\) ground state configuration as a free atom, and the weak bonding to graphene is not expected to substantially change this ground state. The more accurate method employing the Anderson impurity model cures this problem and yields the anticipated non-magnetic ground state with \( n_f = 6 \) and \( J = 0 \) for the Sm adatom. The Nd adatom remains magnetic with \( n_f = 3.7 \) and \( J = 4.2 \).

- In Chapter 4 we present the study of three Np-based compounds: NpPt\(_2\)In\(_7\), Np\(_2\)Ni\(_{17}\) and NpBC. After the short introduction to the properties of Np and Np-based materials, we summarize the experimental results obtained for the three compounds. The theoretical study of the materials was performed with the spin-polarized LSDA method, and its correlated version LDA+U, in the full-potential linearized augmented plane waves (FLAPW) basis (including scalar-relativistic terms and spin-orbit coupling). For all three compounds we analyze the spin, orbital and total magnetic moments, and the total density of states (DOS), as well as its projections for selected orbitals and spins. Finally, for NpPt\(_2\)In\(_7\) and NpBC we perform the total energy analysis between different magnetic moment arrangements on the Np atoms.

The first compound, NpPt\(_2\)In\(_7\), is an isostructural analogue of a known Ce-based superconductor CePt\(_2\)In\(_7\) and Pu-based paramagnet PuPt\(_2\)In\(_7\). The experimental results show that NpPt\(_2\)In\(_7\) is an antiferromagnet with Néel temperature \( T_N = 23 \) K. The electronic structure calculations performed in the LDA+U scheme are consistent with the experiment. The ground-state characterized by the lowest total energy is antiferromagnetically ordered. DOS analysis indicates fairly localized character of Np \( f \)-states.

The second studied compound is Np\(_2\)Ni\(_{17}\). Here, the experimental measurements reveal a long-range magnetic ordering below the transition temperature \( T_N = 17.5 \) K. It is found that Np atoms occupying one of the two inequivalent crystallographic sites do not take part in the transition. Theoretical calculations performed in the LDA+U scheme correctly predict the presence of two magnetically inequivalent Np sites, one of them is carrying a much larger total magnetic moment \( \mu_{\text{tot1}} = 2.46 \mu_B \) than the other \( \mu_{\text{tot2}} = 0.17 \mu_B \).

The third studied compound is NpBC. In this case, the experimental study reveal ferromagnetic ordering of the magnetic moments on Np atoms, with the Curie temperature below \( T_C = 61 \) K. The total energy calculations with LDA+U support formation of the ferromagnetic
ground state for this compound.

References