

Project title: Correlated materials from first principles: solving the nexus of Charge, Orbital, and Spin (CoCOS)

Project number: J50/2018

Executive Summary

This project aims at providing theory insights into correlated materials at the cutting edge of the experimental research. To this end, we apply state-of-the-art numerical tools that merge conventional band-structure techniques and advanced many-body methods, such as the combination of density functional theory and the dynamical mean-field theory (DFT+DMFT) as well as the dynamical vertex approximation (DGA).

The method development part of this venture included the implementation of DFT+DMFT functionality into the DFT code FPLO, and DGA calculations. For the latter, the case in point was the kagome Hubbard model; we found that major changes in the magnetic correlations occur already in the metallic phase and not in the vicinity of the metal-to-insulator transition. We also discovered the necessity of performing DGA calculations self-consistently and using a compact basis representation instead of the commonly used Matsubara representation.

In the application part of the project, we considered different classes of correlated materials. In collaboration with our cooperation partner Karsten Held (TU Wien), we made a pioneering DFT+DMFT and DGA study of the recently discovered superconducting nickelates; this work has been published and enjoys attention from the community. Among materials featuring an interplay between electronic correlations and spin-orbit coupling, we considered a triangular lattice cobaltate, for which we identified a distinct hierarchy of energy scales and estimated the magnetic exchange interactions. In our studies of van-der-Waals antiferromagnets NiPS_3 and FePS_3 , we elucidated the predominantly singlet character of the sharp optical excitation in the former, and showed how the large dichroism is rooted in the electronic structure of the latter. As a replacement of the initially planned comparative study of (111) pnictides, we explored a novel methodology based on machine learning, and applied it for prediction of transfer integrals in Cu^{2+} containing materials.

The main obstacle of scientific origin is the discovered necessity of performing self-consistent DGA calculations and using a compact basis representation instead of the commonly used Matsubara representation. In the quest for an efficient basis, we explored the possibility of combining the advantages of two recent methodological developments.

Our work resulted in 17 peer-reviewed publications, including 5 in high-impact ($\text{IF} > 7$) journals, 1 defended and 2 submitted PhD theses. We were successfully applied for extramural funding, including a D-A-CH project and a project with the CRC 1143 (both DFG). Despite the challenges due to the COVID-19 pandemic, we established an international junior group with more than 30% female researchers.

Most material-specific studies were performed jointly with the experimental groups at the IFW and TU Dresden. In addition to the successful collaboration with the cooperation partner, we established several international collaborations with colleagues from theory and experiment.

The field of correlated materials is very vibrant, and new materials are being synthesized and studied by numerous groups worldwide. The connections between nontrivial band topology and electronic correlations is particularly promising, and we expect rapid development of computational methods that can treat both on equal footing. Further work on optimization of the basis may facilitate highthroughput DFT+DMFT calculations and eventually allow for applying machine learning for solving problems that are not amenable to other techniques.

1. Achievement of objectives and milestones

The overarching idea of the project was to provide insights into correlated materials at the cutting edge of the experimental research. The physics of such materials is shaped by the interplay of charge, orbital, and spin degrees of freedom, and its understanding requires the usage of sophisticated numerical methods. Accordingly, our research program comprised two packages for method development (WP1–2) and four packages for real-material calculations (WP3–6).

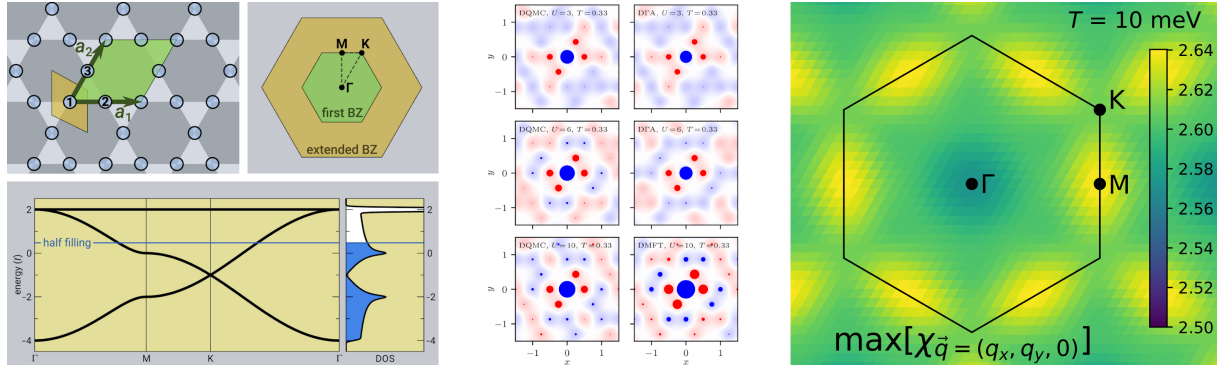


Fig. 1: Highlights from WP1 and WP2. Left: non-interacting part of the kagome Hubbard model (KHM). Unit cell of a kagome lattice in real (top left) and reciprocal (top right) space, and the band structure with the corresponding density of states (bottom). Middle: spin correlations of the KHM calculated using DMFT, DFA, and DQMC. Right: leading eigenvalue in the momentum-dependent (bubble) magnetic susceptibility calculated for an effective two-orbital model of the flat-band metal Ni_3In .

In WP1, we implemented the DFT+DMFT functionality into a merger of the in-house DFT code, FPLO, with the CT-HYB Anderson impurity solver w2dynamics. Such a combination allows us to perform finite-temperature DFT+DMFT calculations for real materials. The interface is written in Python and allows for a user-controlled construction of a Hamiltonian in the Wannier basis from a converged scalar-relativistic FPLO calculation. Here, we profit from the local-orbital basis of FPLO and directly use the projective technique instead of the more demanding minimization procedure. The Hamiltonian is supplemented with the interaction part and supplied to the solver. This interface provides the basic functionality and hence the main objective of WP1 is met.

In WP2, we focused on the dynamical vertex approximation DFA. Before applying it in the real-material context, we considered a model case, the kagome Hubbard model (Fig. 1, left). Geometrical frustration makes this 2D model particularly challenging, and even in the much more studied Heisenberg limit, the ground state is still under debate. Here, we addressed the respective Hubbard model at half-filling focusing on the moderately correlated regime. Typical for a Hubbard model, we found a phase transition between metallic and insulating phases. But it came as a surprise that this phase transition has little impact on magnetism: major changes in the magnetic correlations instead occur already within the metallic phase (Fig. 1, middle). In addition to this exciting scientific result, our work elucidated the importance of self-consistency in the DFA loop, which was hitherto unknown and therefore not considered in the original proposal. We also encountered the necessity of a compact basis representation instead of the commonly used Matsubara representation. This problem is common for diagrammatic approaches, and ways to mitigate it are actively sought-after. Presently, two most promising directions are the intermediate representation (IR) combined with sparse sampling, and discrete Lehmann representation (DLR), introduced, respectively, in 2020 and 2022. Here, we explored the idea of combining the advantages of IR and DLR and using a specially constructed basis with an analytical dependency on the imaginary time. This work goes much beyond the scope of original proposal, and is currently being finalized. Also in WP2, we developed the machinery to calculate momentum dependent susceptibilities; this was used to explain the suppression of magnetic ordering in the kagome-lattice material Ni_3In , featuring flat-band physics (Fig. 1, right).

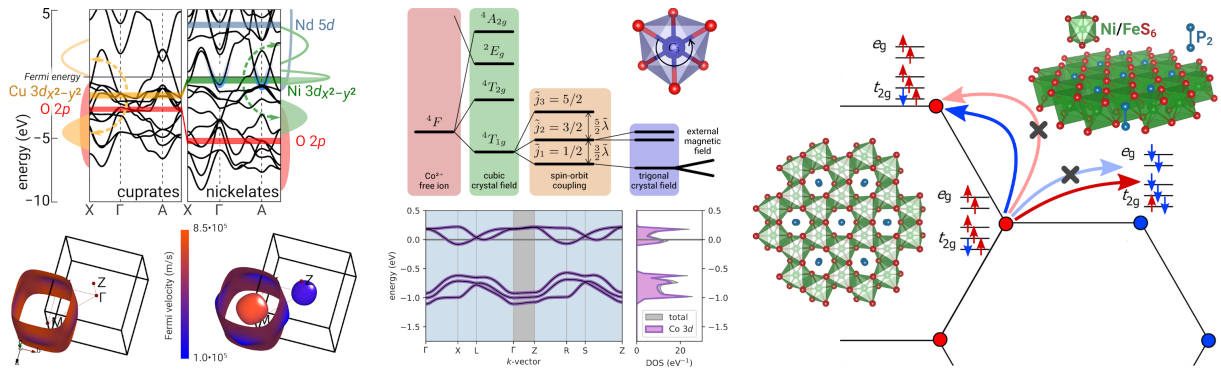


Fig. 2: Highlights from WP3-5. Left: electronic structure of superconducting nickelates in comparison with that of cuprates (top). Fermi surface plots reveal two additional pockets in nickelates (bottom). Middle: hierarchy of energy scales in effective $J = 1/2$ cobaltates (top). Band structure and the density of states of the triangular-lattice cobaltate $\text{Na}_2\text{BaCo}(\text{PO}_4)_2$ (bottom). Right: explanation of the strongly anisotropic optical response in the van-der-Waals honeycomb-lattice antiferromagnet FePS_3 .

The main objective of WP3 was to apply state-of-the-art methods such as DFT+DMFT and D Γ A to most interesting and at the same time less studied nickelate materials. At the time of preparation of this proposal, most promising systems were trilayer nickelates. The discovery of superconducting nickelates by the group of Harold Hwang in 2019 overturned the situation. Together with the cooperation partner at TU Wien, we decided to switch to the respective infinite-layer nickelates. Our central finding is the relevance of a simple physical picture – an effective one-band Hubbard model supplemented with an electron reservoir – for the doping range optimal for superconductivity. This is markedly different from another class of superconductors – cuprates, where the oxygen orbitals lie much closer in energy and play a crucial role in superconductivity (Fig. 2, left). This picture is corroborated by DFT+DMFT calculations, and D Γ A yields the critical temperature T_c in a good agreement with the experiment. This work resulted in two joint publications, one of which has been already collected more than 130 citations, and a popular review in Physik Journal of the DPG, fully meeting the goal of WP3.

WP4 was focusing on the interplay of electronic correlations with the spin-orbit coupling. As candidate materials, we picked two double-perovskite materials, Ba_2YRuO_6 and Ba_2YOso_6 , that were actively studied in the second half of 2010's. Yet, after 2019 there was nearly no experimental activity on these compounds. Instead, cobaltates – another class of materials in which the spin-orbit coupling is crucial – came to the forefront as a promising playground for quantum spin liquids. The magnetism of cobaltates is shaped by multiplet effects, and since both electronic correlations and the spin-orbit coupling are equally important, cobaltates can not be adequately described by standard band-structure methods. In collaboration with colleagues from the University of Marseille, we came up with a computationally cheap procedure capable of providing a realistic description of local processes in cobaltates. By applying this methodology to the recently synthesized (2019) triangular-lattice cobaltate $\text{Na}_2\text{BaCo}(\text{PO}_4)_2$, we identified a distinct hierarchy of energy scales stabilizing the effective $J = 1/2$ state (Fig. 2, middle). Furthermore, we studied magnetic exchange interactions and suggested the irrelevance of magnetic exchanges beyond nearest-neighbors and the importance of the Kitaev nearest-neighbor exchange. Subsequent studies confirmed the former, while showed no evidence for the latter. We published our results together with experimental colleagues from the IFW Dresden.

WP5 was devised as to study two-dimensional van-der-Waals compounds with a honeycomb lattice. We planned to focus on $\alpha\text{-RuCl}_3$, which was then actively studied by experimental groups of the IFW Dresden. However, already in the early stages of this project, the focus of the in-house experimental research largely shifted to another class of honeycomb van-der-Waals materials: transition-metal phosphosulfides MPS_3 . Two particularly exciting materials are NiPS_3 , featuring a sharp optical excitation confined to the magnetic zigzag state, and FePS_3 ,

showing giant optical linear dichroism. Similar to α - RuCl_3 , both materials exhibit the zigzag antiferromagnetic state, albeit at a much higher temperature, and therefore are more promising for potential applications. We studied the electronic structure and optical response of both materials. Our calculations elucidated that the sharp optical excitation in NiPS_3 has a predominantly singlet character. For FePS_3 , we demonstrated that the dichroism is directly related to electronic correlations that accompany the virtual transfer of minority electrons (Fig. 2, right).

Finally, for WP6 we initially planned a comparative study of (111) pnictides. This work was discontinued in the early stages, because a comparative analysis very similar to our planned program, has been published in the meantime (PRB 104, 125130 [2021]). As a replacement, we devised a new project, which a methodology that is now rising in computational condensed matter physics – machine learning (ML). The idea is to employ ML for prediction of transfer integrals that constitute the electronic structure of a material. We considered all Cu^{2+} containing materials with dozens of distinct structure types and hundreds of compounds, including parent compounds of high-temperature superconductors. We found that an artificial neural network, using descriptors that encode the spatial configuration and the chemical composition of the local crystalline environment, can predict the transfer integrals with reasonable accuracy. We wrapped the trained model into a web application that can be used for new cuprate materials.

2. Activities and obstacles

Our activities are essentially twofold: method development and real material calculations. As both pertain to particular goals of respective work packages (WP1 and WP2 for method development, WP3-6 for calculations), the previous section already provides an overview of our activities, including the activities done in collaboration with the project partner.

In the method development part, we implemented the DFT+DMFT framework, yet faced technical problems with the charge-self-consistency and support for full-relativistic calculations, the respective modules were not finished. In the DfA part, two main obstacles were the discovered necessity of performing self-consistent DfA calculations and the inappropriateness of the standard basis set for real-material problems. To overcome the latter, we explored the possibility of combining two recently developed techniques of basis construction. The ultimate solution has not been yet found, but the research is ongoing and a breakthrough may happen soon.

On the application side, our guiding principle was to target materials in the focus of the present-day experimental research. Some of these were unknown when the project has been devised. Naturally, we had to adjust our research program to the rapidly changing situation. In WP3-5, we achieved this without major changes of the research program. In WP6, a work similar to our planned research has been published by other group. We used this opportunity to explore new methodologies that we will continue to employ in future research.

As arguably any 5-year venture that started in 2019, our project did not remain unaffected by the COVID-19 pandemic. The second PhD and the postdoc joined the group half-a-year later than originally planned. In-presence participation at conferences, workshops and seminars was strongly affected by lockdowns and travel restrictions.

3. Results and successes

Our work resulted in 17 peer-reviewed publications, including 5 in high-impact journals (Nat. Phys., Phys. Rev. Lett., Mater. Today Phys., and two in npj Quantum Mater.) and 11 publications in Phys. Rev. B. The work on WP1 and WP2 resulted in a substantial contribution to one defended dissertation (TU Wien, 2021). Material-specific work resulted in two dissertations submitted to TU Dresden in 2024; both defenses are foreseen in the coming months.

We were active in acquisition of third-party funds. Together with the experimental colleague Ryan Morrow, we devised a project on machine learning for double perovskites and secured

funding from the internal IFW Excellence program. Following our successful collaboration on nickelate superconductors (WP3) with Karsten Held (TU Wien), we wrote an international D-A-CH project, where I am the project leader from the German (DFG) side. In 2023, I became one of the project leaders within the collaborative research center (SFB 1143) funded by the DFG.

4. Equal opportunities, career development & internationalisation

The researchers paid from the project were a integral part of a larger junior research group at the Institute for Theoretical Solid State Physics. Therefore, it is more appropriate to consider the entire group as regards to equal opportunities. In these 5 years, the cumulative number of group members is thirteen (with Austrian, Chinese, Estonian, Indian, Italian, German, Russian, and Ukrainian nationals), women make up 31% thereof. The group leader has been promoted to a permanent position at the IFW Dresden. Two former PhD students who worked on the project, switched to industry and are currently employed by companies in Vienna and Dresden.

5. Structures and collaboration

Collaboration with the group of Karsten Held (TU Wien) was very fruitful and led to 5 joint publications. Most material-specific studies were performed in close collaboration with the experimental groups at the IFW and TU Dresden. Beyond the planned program, we established fruitful collaborations with Roland Hayn (Marseille) and Tanusri Saha-Dasgupta (Kolkata).

6. Quality assurance

We took diverse measures to ensure high quality of our research. The generated data were stored in a central data repository supplied with a backup system. We strived to use uniform computational procedures and workflows. Quality of publications is assured by peer-review procedures of respective journals. Additionally, we make our works available for the general public by placing preprints on the arXiv preprint server.

7. Additional resources

Our activities are co-financed by IFW in accord with the original plan. Funds intended for publication fees were re-allocated, because respective fees were centrally covered by DEAL-Agreement. This agreement was not available at the time the proposal was prepared.

8. Outlook

The field of correlated materials remains vibrant, hence new materials and even new material classes like vanadium-based AV_3Sb_5 and RV_6Sn_6 , get in the spotlight. In many of them electronic correlations intertwine with nontrivial band topology, and further development of computational methods capable of treating both on equal footing is foreseen. Nickelates studied in WP3 remain vibrant, as evidenced by the recent discovery of high-temperature superconductivity in bulk $La_3Ni_2O_7$ at high pressures. Even seemingly well-studied materials can harbor surprises: we recently evidenced the rise of altermagnets – a long-overlooked class of collinear magnets with spin splitting, yet zero net magnetization. Unusual transport properties of these materials hold promise for functional applications, and we expect a flurry of studies in the coming years.

The combination high-throughput calculations with ML can give rise to trained models that are capable of unearthing material trends, and eventually eliminating the need of detailed calculations within the trial-and-error paradigm. Application of ML-based methods to correlated materials is highly desirable. However, it crucially depends on further development of more efficient schemes to replace the standard Matsubara basis, and one day enabling high-throughput DFT+DMFT calculations.