A solid theory for solid battery materials

Calculation of self-consistent DFT+U+V Hubbard parameters and their application for electrochemical purposes

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In Short

- Many cathode materials contain transition metal elements, causing traditional Density Functional Theory (DFT) to struggle due to the self-interaction error

- On-site and inter-site Hubbard corrections to DFT can mitigate this deficiency, but the numerical value of the parameters strongly impacts the correctness of calculations

- Here, we compute Hubbard parameters from first principles using a Density Functional Perturbation Theory (DFPT) approach that has been presented recently [1]

- As a model system, we investigate a handful of members from the promising Prussian Blue Analogue (PBA) family and compare calculated properties such as cathode potentials with results from experimental and other computational studies

Figure 1: *The structure of copper hexacyanoferrate, a member of the Prussian Blue Analogue family. Here, half of the zeolitic sites are occupied by potassium cations. This example shows only one of many possible combinations of transition metal cations and intercalation species.*

On the quest for novel efficient, safe and inexpensive battery materials, a reliable yet affordable computational technique with the ability to predict and understand electrochemical properties from first principles is indispensable. Various members from the diverse family of Prussian Blue Analogues (PBAs, see Fig. 1), for example, have shown to be attractive candidates for grid energy storage solutions, but the theoretical understanding of mechanisms such as cation diffusion in these materials is still very limited.

At least partly, this lack of theoretical studies is owing to an inherent deficiency of Density Functional Theory (DFT), the traditional "workhorse" for routine calculations in chemistry. In spite of being a powerful and often sufficiently accurate method, DFT's failure to capture the electronic structure of strongly correlated materials prevents it from being used to compute PBAs. Hybrid exchange-correlation functionals represent a common attempt to restore the correct physical behavior of strongly correlated systems in DFT. Nevertheless, adding plenty of computational complexity, these functionals are not ideal for the simulation of defective or non-stoichiometric compounds, which are commonly encountered among
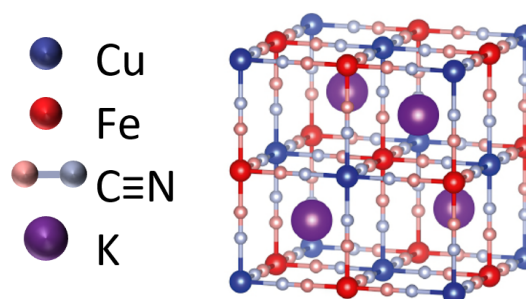
solid battery materials. Fortunately, with on-site and inter-site Hubbard corrections to DFT (DFT+U[2] and DFT+U+V [3], respectively), computationally less demanding alternatives to hybrid-DFT exist. However, achieving quantitative accuracy with these corrections requires a consistent and physically justified method from which the Hubbard parameters can be derived.

In this project, we want to test if correct (ground state) electronic, magnetic and crystallographic structures of Prussian Blue Analogues (PBAs) can be obtained from DFT+U+V when a self-consistent ab-initio approach is employed to compute the Hubbard parameters. Tackling specific electrochemical questions, we also want investigate whether the same procedure additionally delivers reliable energetics of pristine and defective systems. Once the applicability of the method is verified, reasonable estimations of battery potentials and other energy related properties can be made.

In detail, we obtain reliable *U* and *V* parameters from a Density Functional Perturbation Theory (DFPT) approach that yields performance and stability improvements over previous methods, e.g., linear response theory [1]. Once a set of Hubbard parameters is available, we apply it to perform geometry optimizations before we compute the parameters again, until convergence is reached (c.f., Fig. 2). Initially, we intend to carry out this procedure with the pristine unit cells of a handful of PBAs; however, at later stages we will also study the impact of hexacyanometallate vacancies as these occur frequently in PBAs.

With regard to potential applications of this study, reliable ab-initio cathode potentials for differently

composed PBAs could help to optimize the energy density of PBA-based batteries without compromising their chemical stability.
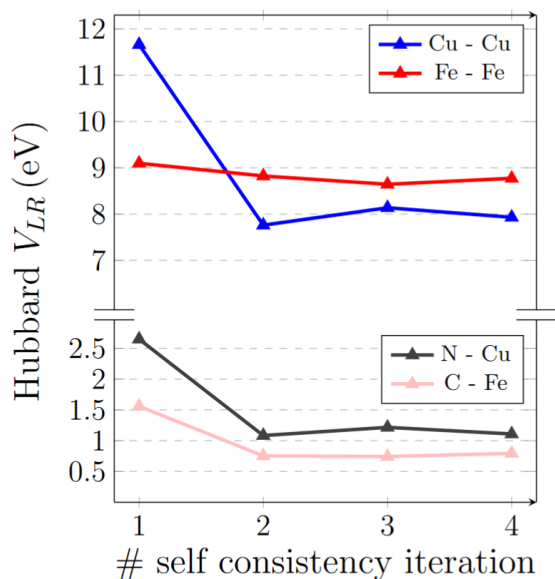

Figure 2: *Self-consistency of selected Hubbard V parameters in KCu[Fe(CN)$_6$].*

More Information

[1] I. Timrov, N. Marzari and M. Cococcioni; *Phys. Rev. B* **98**, 085127 (2018). doi: 10.1103/PhysRevB.98.085127

[2] V.I. Anisimov et al.; *Phys. Rev. B* **48**, 16929 (1993). doi:10.1103/PhysRevB.48.16929

[3] V. L. Campo Jr. and M. Cococcioni; *J. Phys.: Condens. Matter* **22**, 055602 (2010). doi: 10.1088/0953-8984/22/5/055602

Project Partners

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