Accurate electronic properties and intercalation voltages of Li-ion cathode materials from extended Hubbard functionals



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1. Objectives

- **Motivation:** The design of novel cathode materials for Li-ion batteries requires accurate first-principles predictions of their properties.
- **Problem:** Density-functional theory (DFT) with standard (semi-)local functionals (e.g. PBEsol) fails due to strong self-interaction errors for partially filled d shells of transitionmetal (TM) elements.
- **Solution:** DFT with extended Hubbard functionals (PBEsol+U+V) correctly predicts the digital change in oxidation states of the TM ions for mixed-valence phases occurring at intermediate Li concentrations, leading to voltages in remarkable agreement with experiments.

4. Results

Projected density of states (PDOS): PBEsol+U+V and HSE06 provide very similar PDOS at different concentrations x of Li, while PBEsol wrongly predicts the metallic nature of the olivines at intermediate concentrations x (see Fig. 3) [6].



Oxidation state: PBEsol fails to account for the digital changes in the atomic occupations of Mn and Fe atoms, while PBEsol+U+V correctly predicts such changes with even higher accuracy than HSE06 (see Fig. 4) [6].

Method: PBEsol+U+V requires onsite U and intersite V Hubbard parameters that are computed self-consistently using density-functional perturbation theory (DFPT).

2. DFT with extended Hubbard functionals

The simplified rotationally-invariant formulation:

The DFT total energy is augmented by a corrective Hubbard term [1]

$$E_{\rm TOT} = E_{\rm DFT} + E_{\rm Hub}$$

where

$$E_{\text{Hub}} = \frac{1}{2} \sum_{I} \sum_{\sigma m_1 m_2} U^{I} (\delta_{m_1 m_2} - n_{m_1 m_2}^{II\sigma}) n_{m_2 m_1}^{II\sigma} - \frac{1}{2} \sum_{I} \sum_{J(J \neq I)} \sum_{\sigma m_1 m_2} V^{IJ} n_{m_1 m_2}^{IJ\sigma} n_{m_2 m_1}^{JI\sigma} ,$$

where I and J are atomic site indices, m_1 and m_2 are the magnetic quantum numbers, and σ is the spin index. The generalized occupation matrix is defined as

$$n_{m_1m_2}^{IJ\sigma} = \sum_i \langle \psi_{i\sigma} | \varphi_{m_2}^J \rangle \langle \varphi_{m_1}^I | \psi_{i\sigma} \rangle$$



Fig. 3: Projected density of states.



Voltages: PBEsol greatly underestimates the intercalation voltages, while HSE06 and PBEsol+U overestimate them. DPBEsol+U+V gives the most accurate voltages that are in a remarkable agreement with experiments (see Figs. 5 and 6) [6,7].





where $\psi_{i\sigma}$ are the Kohn-Sham wave functions, and $\varphi^I_{m_1}$ and $\varphi^J_{m_2}$ are the localized atomic orbitals which characterize the Hubbard manifold (orthogonalized using the Löwdin method).

Linear-response/DFPT calculation of Hubbard parameters:



Hubbard interactions are computed as a second derivative of the total energy with respect to the occupation of the Hubbard manifold [2]:

 $\frac{d^2 E_{\rm DFT}}{dn^2} - \frac{d^2 E_{\rm DFT}^0}{dn^2} \equiv \left(-\chi^{-1}\right) - \left(-(\chi^0)^{-1}\right).$

U and V are defined as diagonal and off-diagonal matrix elements, respectively:

 $U^{I} = \left((\chi^{0})^{-1} - \chi^{-1} \right)_{II}, \quad V^{IJ} = \left((\chi^{0})^{-1} - \chi^{-1} \right)_{IJ}$

where χ_{IJ} and χ_{IJ}^0 are the interacting and non-interacting response matrices, respectively.

The response matrices χ^0 and χ are efficiently computed using DFPT [3,4].

The HP code [5] is part of QUANTUM ESPRESSO, it is based on DFPT, and it was used to compute U and V.

3. Materials

Fig. 5: Voltages for olivine cathodes.

Fig. 6: Voltages for spinel cathodes.

5. Conclusions

- \blacktriangleright PBEsol+U+V is an accurate and powerful tool for modeling cathode materials for Li-ion batteries.
- \triangleright PBEsol+U+V correctly predicts a digital change in the atomic occupations of TM ions in the mixed-valence phases of cathode materials.
- \blacktriangleright Voltages computed using PBEsol+U+V are more accurate than those computed using PBEsol+U and even HSE06, and are in remarkable agreement with experiments.
- \blacktriangleright PBEsol+U+V is computationally much cheaper than HSE06 but it gives the electronic structure that is similar to the HSE06 one.

7. References

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Fig. 2: Crystal structure of (a) antiferromagnetic phospho-olivine $LiMn_{1/2}Fe_{1/2}PO_4$ and spinel cathodes (b) antiferromagnetic LiMn₂O₄ and (c) ferrimagnetic LiMn_{1.5}Ni_{0.5}O₄.

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