

## Application of DFT+U with Magnetic Exchange Method to the Analysis of Redox and Magnetic Properties of Cathode Materials of Li- and Na-ion Batteries

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### Introduction

The first principles modelling of electrochemical properties of Li- and Na-ion batteries has proven to be quite instrumental for further advancements in battery technology. A challenging aspect of such modelling is the need for accurate description of electronic structure and energetics of transition metal compounds, which are commonly used as cathode materials of Li- and Na-ion batteries. Indeed, application of a widely used DFT+U approach [1] heavily depends on adequate U parameters, capable to provide accurate description of energetics, electronic structure and magnetic properties of materials that contain transition metal ions. In this contribution we present the linear response method, where U parameters of DFT+U scheme are evaluated computationally, relying on a definition of U as a double derivative of a total energy over localized electron density [2,3]. The U parameters are calculated iteratively, ensuring agreement of the U value, obtained by linear response method with the value of U, used in DFT+U calculations [3]. Moreover, we further extend DFT+U framework by adding a magnetic exchange term, which accounts for interactions between the electrons of the opposite spins. Our calculations show that inclusion of magnetic exchange is necessary for evaluation of redox and magnetic properties of sulphate based cathodes in a good agreement with experiment.

### Theoretical framework

We have employed a rotationally invariant form of Hubbard term [1]:

$$E_U = \frac{U}{2} \sum_{I\sigma} Tr[n^{I\sigma} (1 - n^{I\sigma})]$$

where  $n^{I\sigma}$  is a density matrix of  $I^{th}$  ion and  $\sigma$  is a spin state of respective projectors.

U parameters are evaluated using linear response approach [2,3] as

$$U = (\chi_0^{-1} - \chi^{-1})_{II}$$

where  $\chi_0^{-1}$  and  $\chi^{-1}$  are the inverted matrices of non-interactive and polarized linear response functions, explicitly defined in [2,3].  $U$  in the above expression is equal to the diagonal element of the difference of the inverted linear response matrices.

The magnetic exchange contribution is further added to the Hubbard term as:

$$E_U = \frac{U}{2} \sum_{I\sigma} Tr[n^{I\sigma} (1 - n^{I\sigma})] + \frac{J}{2} \sum_I Tr[m^I (m^I - 1)]$$

where  $m$  is a magnetic moment and  $J$  is a magnetic exchange parameter. We have found that for sulphates, magnetic exchange contribution is necessary to bring both redox potentials and magnetic moments of Fe to a reasonable agreement with experiment.

## Results

We have calculated average redox potentials of seven well characterized cathode materials, using established expression [4]

$$\phi = -\frac{E(\text{LiMO}_2) - E(\text{MO}_2) - E(\text{Li})}{e}$$

where  $\phi$  is a redox potential,  $E(\text{LiMO}_2)$  and  $E(\text{MO}_2)$  are enthalpies of formula units of intercalated and deintercalated compounds,  $E(\text{Li})$  is an enthalpy of a Li atom in Li bulk and  $e$  is the charge of an electron.

The evaluated DFT and DFT+U redox potentials of seven well characterized materials are presented in Fig. 1. A clear improvement of calculated values is observed when DFT+U is employed as compared to the local DFT. On the other hand, for sulfate materials (Fig. 2) DFT+U calculations provide quite overestimated values of redox potentials. Moreover, we find that both DFT and DFT+U calculations provide magnetic moments of Fe of intercalated structure that are by about  $0.4 \mu_B$  higher than those found experimentally [5]. As a remedy, we show that when magnetic exchange contribution is included, both redox potentials (Fig. 2) and magnetic moment of Fe can be brought to a much better agreement with experiment.

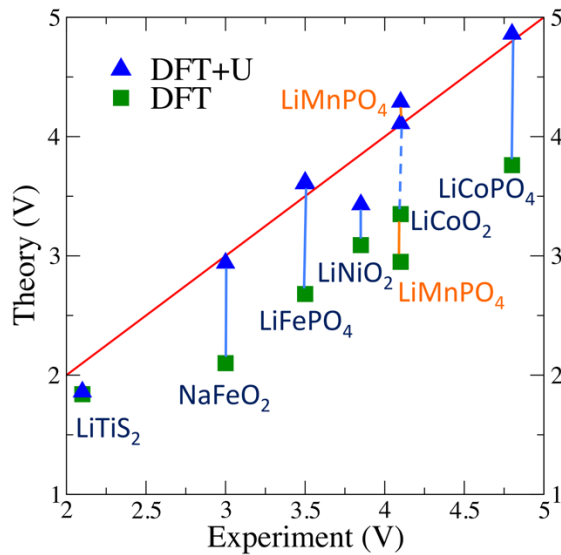


Fig.1 Comparison of DFT and DFT+U evaluated redox potentials with respective experimental values.

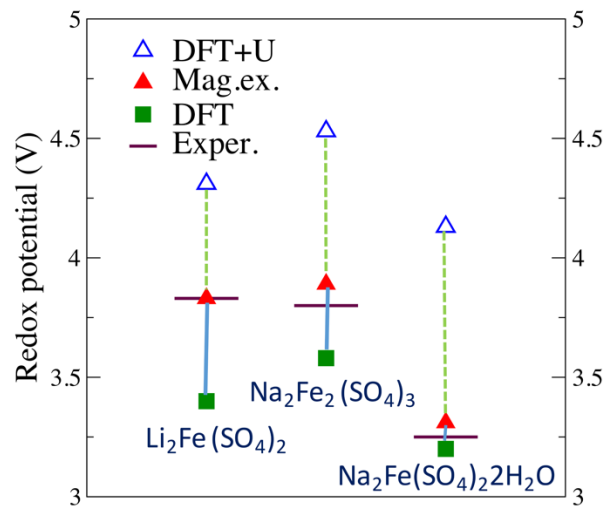


Fig.2 Redox potentials for sulfate materials. Addition of magnetic exchange contribution results in a reasonable agreement with experiment.

## References

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