

## Ab initio Calculations of Electrochemical Properties of Cathode Materials for Li- and Na-ion Batteries

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### Introduction.

Development of Li- and Na-ion batteries requires an ability to accurately model electrochemical properties such as battery operating voltage. From computation viewpoint the task of accurate calculation of operating voltage is translated into the task of precise evaluation of materials total energy differences. The local DFT calculations (e.g. LDA and GGA) are capable to provide reasonably accurate total energy differences for systems such as intermetallic alloys [1]. However, for semiconducting or insulating compounds, particularly those that include *d*- or *f*-electrons, local DFT calculations often predict a rather delocalized charge distributions of these *d*- and *f*-states and henceforth inadequate energetics (e.g. oxide formation enthalpies [1]). Possible solution of this deficiency of local DFT functions might be a recourse to non-local hybrid functions, which however are also featured by a much higher computational cost as compared to local DFT. On the other hand, Hubbard corrected DFT+U method [2] offers a reasonable compromise between accuracy and computational cost, with many successful reports on significant improvement of electronic structure and energetics description as compared to conventional local DFT [1]. As the accuracy of DFT+U calculations fully depends on *U* parameters, the development of a technique, which allows evaluation of adequate *U* values without reliance on empirical fitting is highly warranted.

### Theoretical framework

**Hubbard correction.** We have employed a rotationally invariant form of Hubbard term [2]:

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

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

**U evaluation: linear response [3].** The projector operator on *d*-states is defined as:

$$V = \alpha \sum_{\sigma} \sum_{i=-2}^2 |d_i^{\sigma}\rangle \langle d_i^{\sigma}| \quad (2)$$

Where  $\alpha$  is a chosen weight coefficient. By adding a projector to DFT Hamiltonian the new densities can be evaluated. *U* parameter can then be calculated as the difference between response functions for self-consistent and non-self-consistent (i.e. no Hamiltonian update upon calculations) cases, defined as:

$$U = (\chi_0^{-1} - \chi^{-1})_{ii} \quad (3)$$

where  $\chi_{ij} = \frac{dn_d^j}{d\alpha_i}$  and  $\chi_{0ij} = \frac{dn_{0d}^j}{d\alpha_i}$ . The projector operator can be added to local DFT as well as

DFT+U functionals. Within this work we have shown that *U* parameter, evaluated as in equ. (3) can be the same as in equ. (1). Such self-consistency has been applied for evaluation of *U* parameters using VASP code.

## Results

Redox potential can be evaluated as the energy difference between intercalated ( $\text{LiMO}_2$ ) and deintercalated ( $\text{MO}_2$ ) cathode minus the energy of a charge carrier ion (e.g. Li):

$$E_{\text{redox}} = -\frac{[G(\text{LiMO}_2) - G(\text{MO}_2) - G(\text{Li})]}{e^-} \quad (4)$$

The evaluated DFT and DFT+U redox potentials are presented on Fig. 1, allowing comparison with experimental measurements. For  $\text{LiFePO}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiMnPO}_4$  we find a reasonable agreement with experimental values. Special case is  $\text{LiNiO}_2$ . Here DFT+U provides an improved value of redox potential, however still substantially lower than experimentally derived. This discrepancy can be explained by hybridization of  $d$ -states of Ni with  $p$ -states of nearby oxygen ions, as attested by PDOS for Ni and O (Fig. 2) [4]. For more accurate treatment of hybridized  $p$ - and  $d$ -states, further extension of theoretical framework (e.g. DFT+U+V) should be applied [5].

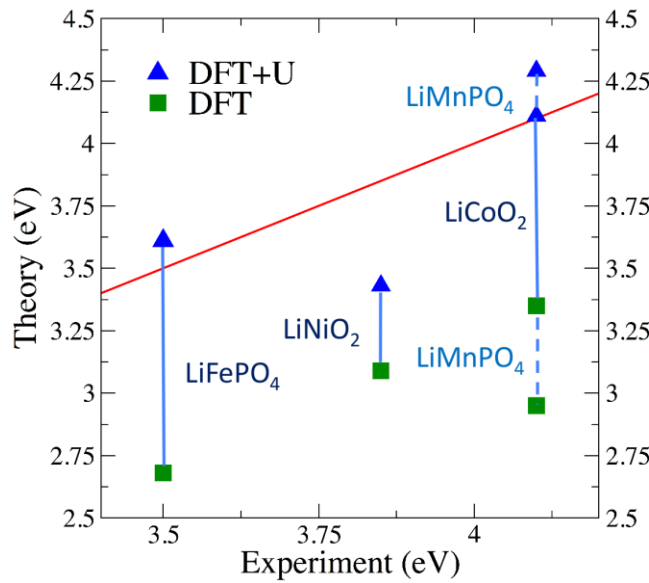


Fig.1 Comparison of DFT and DFT+U evaluated redox potentials with respective experimental values.

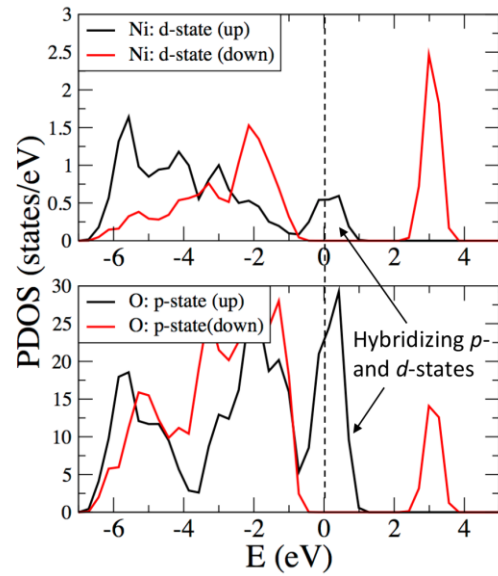


Fig.2 The PDOS of  $d$ -states of Ni and  $p$ -states of O of  $\text{LiNiO}_2$ . Hybridized states near Fermi level (broken line) are highlighted.

Overall we find that coupled linear response/DFT+U approach is suitable for modeling of novel cathode materials, which are usually featured by the lack of available experimental data, or even materials not yet synthesized to date.

## References

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