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First principles Computations on Li-Intercalation Compounds and Applications to Layered Materials and Phosphates

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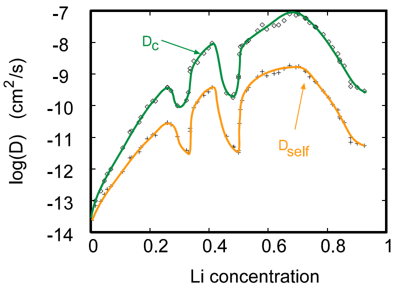
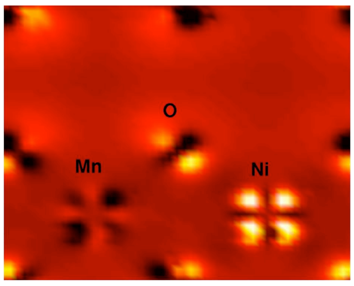
Predicting macroscopic engineering properties with computational quantum mechanics is usually a difficult task as it requires a detailed knowledge of the microscopic phenomena that are relevant for the macroscopic property of interest. For lithium-intercalation oxides, used in rechargeable Li batteries, many of these important microscopic features are known and can be directly related to quantities computable with quantum mechanics. I will review how basic information such as intercalation voltage [1], phase stability[2, 3], Li diffusion[4], and electronic behavior[5] of the cathode oxides can be extracted from quantum mechanics. I will then show how these approaches can be applied to study Li(Li,Ni,Mn)O_2 and $LiFePO_4$, which are both of considerable interest to the battery industry.

Density Functional Theory (DFT) is the most widely used framework in which to perform computational quantum mechanics. Both the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA) are applicable to lithium-transition metal oxides, though the GGA often gives a better representation of strongly magnetic systems, such as the Mn-oxides[6]. LDA and GGA make significant errors in intercalation potentials in Li insertion oxides. In phosphates this error is even larger due to the stronger localization of the transition metal *d* orbitals. Phase stability in $LiFePO_4$ is completely misrepresented in LDA or GGA. I will demonstrate how newer methods such as **DFT+U** can correct almost all of the LDA/GGA error and give very accurate predictions of **electrochemical potentials** in Li intercalation systems. This will further improve our ability to predict the behavior of novel materials.

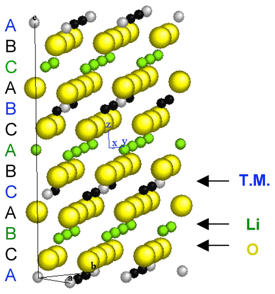


Properties, such as **diffusion**, or phase stability, can not be directly extracted from quantum mechanical calculations and require the construction of property models which use the zero temperature energy calculations as input. In the case of phase stability, a highly accurate approach can be formulated with lattice-like models which account for the contribution of configurational entropy to the free energy. Once the details of the Li configuration as function of composition and temperature are known, diffusion can be studied with kinetic lattice models. (see figure above).

Using first principles computations we have studied the behavior of $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$electrode materials. For the end member $Li(Ni_{0.5}Mn_{0.5})O_2$, the figure below shows the charge density change when Li is removed from the material, clearly illustrating that only the Ni^{2+}/Ni^{4+} redox couple is active.



We have also identified the stable, but unusual ordering of cations in the transition metal layer of **$Li(Ni_{0.5}Mn_{0.5})O_2$** and find that the presence of Li in the transition metal layers is not only essential for the particular structure formed, but also determines the electrochemical bahvior of this material. Li in the transition metal layer is electrochemical active and creates vacancies in the transition metal layer.



Structure of $Li(Ni_{1/2}Mn_{1/2})O_2$

I will also discuss the electronic structure of **$LiFePO_4$** and its relation to conductivity. Recently developed methods in our group can be used to predict electron mobility in these materials and may shed light on the controversial discussion surrounding the electron transport in these materials and whether it can be affected by cation doping.

Acknowledgement

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