Theoretical spectroscopy to investigate degradation in NMC cathodes

First principles investigation of the electronic structure of NMC-111

Aditya Varshney, Hrishit Banerjee, Clare Grey, Andrew Morris

Introduction and Motivation

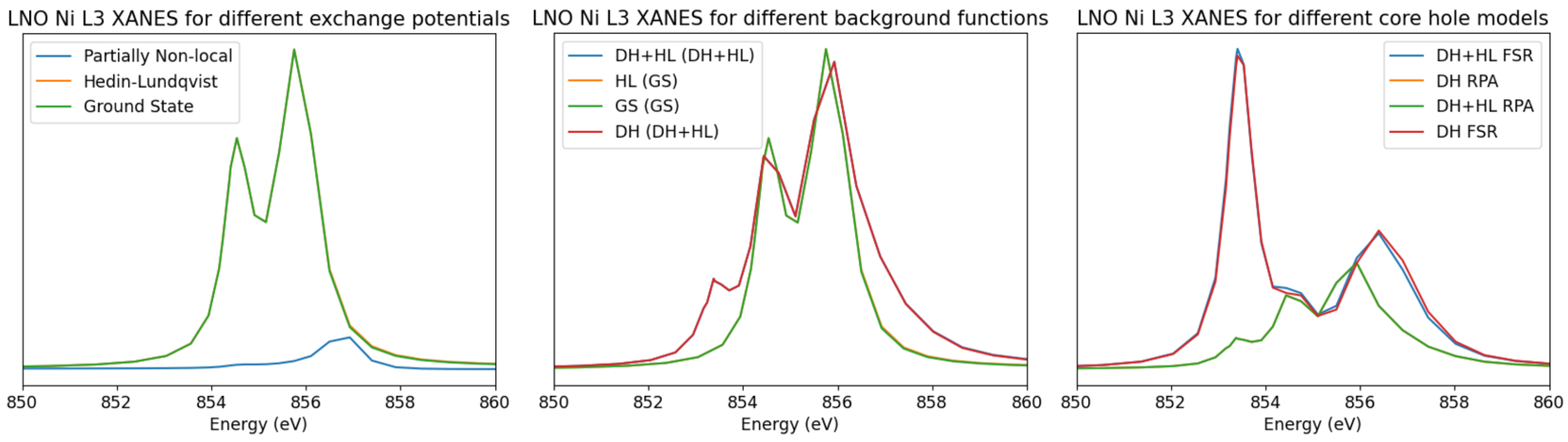
- NMC-111 belongs to a family of layered transition-metal (TM) oxides. They have generated substantial interest due to their high energy density as cathode materials for next-generation Li-ion batteries.
- Density functional theory (DFT) is the most prominent many-body electronic structure method currently in use, based on approximations for the exchange correlation functional which describes how electrons interact.
- Elevated voltages and temperatures induce cathode material degradation by singlet oxygen evolution. We aim to investigate this mechanism by studying near edge X-ray absorption (XANES) edges using ab-initio multiple scattering methods and by simulating the density of states (DoS) using beyond-DFT methods in VASP5, at different states of charge (SoC).

FEFF XANES Methodology

- We employed beyond-single particle perturbation theory using FEFF, an ab-initio multiple scattering method to implement the GW approximation. Based on Green's functions, the code builds in inelastic losses in terms of a GW self-energy, something DFT entirely lacks.
- We explored the phase space of FEFF parameters, experimenting with the exchange potentials (to include photoelectron self-energy) and core hole models using LNO as a test case to develop our methodology.
- Our successful modelling of *K*-edge spectra boosted confidence in our methodology. However, to achieve more accurate insights into oxidation states, we shifted our focus to TM *L*-edges as they provide a superior description of hybridisation between p and d orbitals within the material.

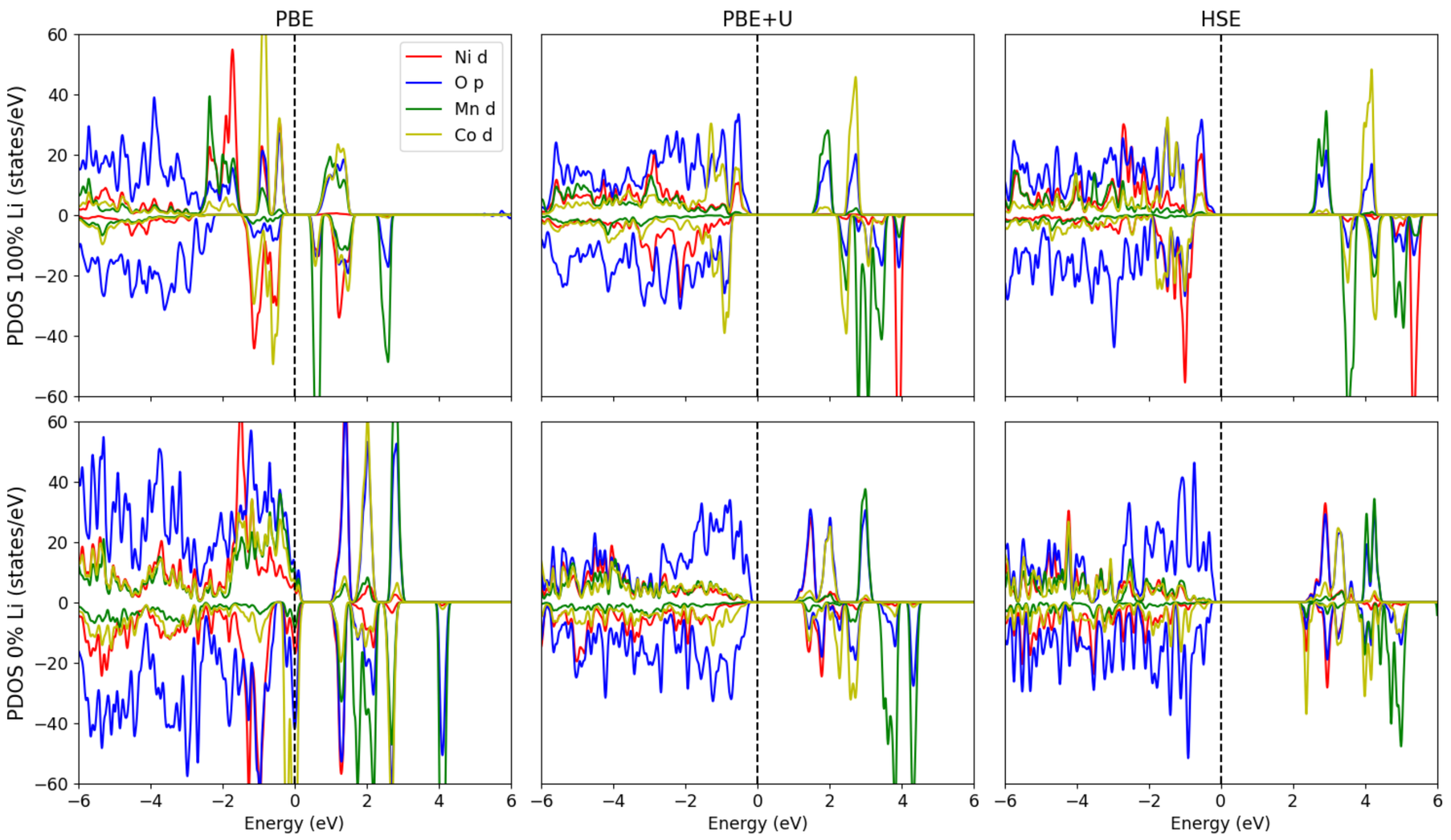
LNO XANES Investigation

1. First investigated the LNO Ni *L3* edge using standard parameters; this produces sensible double peak spectra for HL and GS self-energies for a GS background.
2. DH and DH+HL with a DH+HL background also recreates the original peaks successfully but also produced a third rising edge peak.
3. Using the FSR core hole produces a substantially different spectrum for the DH and DH+HL exchange potentials.



Density of States Investigation

- First the structures were relaxed, whereby ion positions and lattice parameters are optimised to reduce the maximum force to below 0.01 eV/Å. Working in the Generalised Gradient Approximation (GGA), the energy was minimised using the PBE functional according to the self-consistent field (SCF) method.
- DoS plots show the hybridisation of TM d orbitals with O p orbitals at both extremes of the SoC. A major challenge for DFT is the accurate description strongly correlated systems. Here DFT erroneously predicts a metallic state for 0% Li NMC-111.



- The insulating state can be recovered by adding a static Hubbard U correction (PBE+U) which implements a renormalised Coulomb potential that accounts for on-site Coulomb interactions between electrons in the same orbital.
- A hybrid functional such as HSE06 (25% non-local Fock exchange and 75% PBE exchange) provides a more accurate treatment of long-range electron interactions and charge redistribution, thus increasing the band gap further.
- However, these higher-order methods come with significantly increased computational cost.
- Comparing the two allows us to investigate the effect of different degrees of localisation.

Next steps

- Determining the DoS in the GW approximation using VASP5 and FEFF to compare.
- Simulating XANES TM edges using VASP6 to corroborate features of FEFF spectra before experimentally validating the rising edge peak.
- Investigating intermediate SoC levels to gain a more comprehensive understanding and to explain relative stabilities of NMCs.

References

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Intern Biography

- Aditya is a 3rd year Natural Sciences undergraduate at the University of Cambridge specialising in Physics.
- He completed this FUSE internship in the Grey Group at the University of Cambridge supervised by Dr Hrishit Banerjee.
- Outside his studies he is a keen squash player.

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