Convergence

August 26, 2022

1 Convergence tests

1.1 Supplemental material for *The 8Li+ site in -Al2O3*

W.A. MacFarlane,1,3,5 Z. Salman,2 J.K. Shenton,4,* A. Chatzichristos,3,5,7,9 D.L. Cortie,6 M. Dehn,3,5,7 D. Fujimoto,5,3,7 V.L. Karner,1,3,5 R.F. Kiefl,3,5,7 D. Koumoulis,8 C.D.P. Levy,5 R.M.L. McFadden,1,3,5 I. McKenzie,5,10,11 G.D. Morris,5 M.R. Pearson,5 M. Stachura,5 J.O. Ticknor,1,3

1 Chemistry Department, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada 2 Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland 3Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada 4Scientific Computing Department, Science & Technology Facilities Council, Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom 5TRIUMF, Vancouver, BC, V6T 2A3 Canada 6Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales 2234, Australia 7Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada 8Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA 9Physics Department, Khalifa University, United Arab Emirates 10Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A 1S6, Canada 11Department of Physics and Astronomy, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada

*For queries about the supplemental material in this repository contact J. Kane Shenton.

1.1.1 Contents

1. EFG
2. Structural distortion

1.1.2 1. Summary

Supercell tests

The effect of the finite supercell size on predicted EFG tensor of Li in the octahedral interstitial site was found to be negligible going from a 2x2x2 to a 3x3x3 supercell:

ν_Q (2x2x2 supercell) = 71.9782 kHz
ν_Q (3x3x3 supercell) = 71.7927 kHz

This is a 0.258% change

Similarly, we find that the displacement of the ions decays rapidly with the distance from the Li ion:

1.1.3 2. Computational details

Notebook setup We take our initial strucutre from the low-temperature (120 K) experimental structure from Pillet et al. as obtained from the ICSD, collection code 92631.

This structure has cell parameters:
a = b = 4.7602(4)
c = 12.993(2)
$\alpha = \beta = 90°$
$\gamma = 120°$

To avoid any licensing issues, we include a crystal structure that is heavily based on the experimental structure called: `experimental_structure.cell`.

Convert the experimental structure to the rhombohedral cell setting:

To run the calculations, we used the atomic simulation environment (ASE). We define a function here to run a CASTEP geometry optimisation for a given structure:

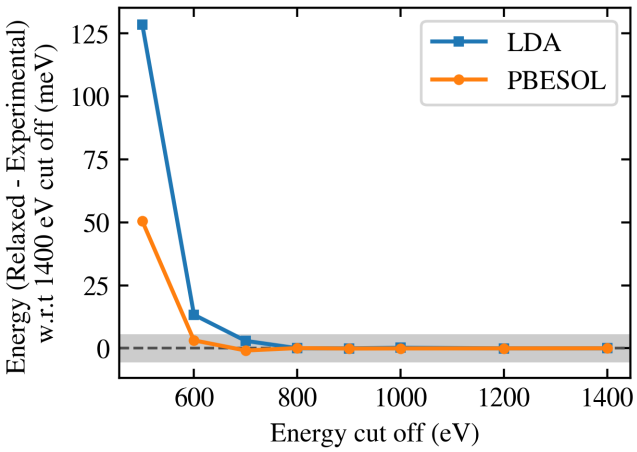
1.1.4 3. Plane wave cut off

Read in the results Now we extract key information from the results of each geometry optimisation.

```
LDA
PBESOL
```

3.1 Energy differences If we plot the different in total energy between the relaxed and unrelaxed structures with respect to that of the highest cut off energy (1400 eV), we get a sense of how well-converged energy difference are for a given cut off.

[6]: `<matplotlib.legend.Legend at 0x7faa6132e1a0>`

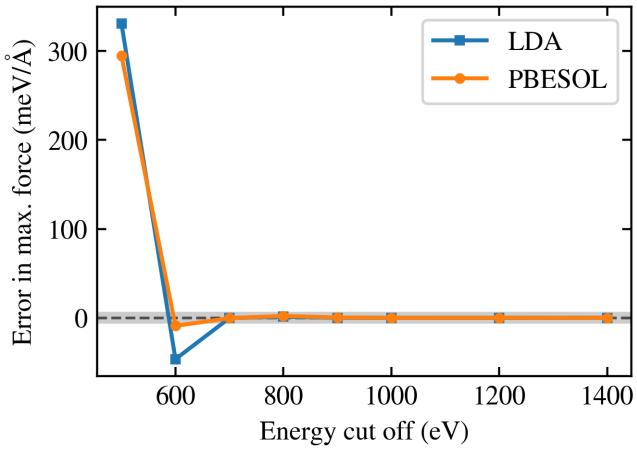


3.2 Forces Even more important than well-converged energy differences if the convergence of forces. We look at this by taking the initial forces calculated at the experimental structure (i.e. for step 1 of the geometry optimisation).

For this plot, the 'error in max. force' is defined as the max. force in the experimental structure - that calculated at a 1400 eV cut off.

By looking at how the maximum force difference due the cut off, we get a sense of the error in the forces due to the finite basis.

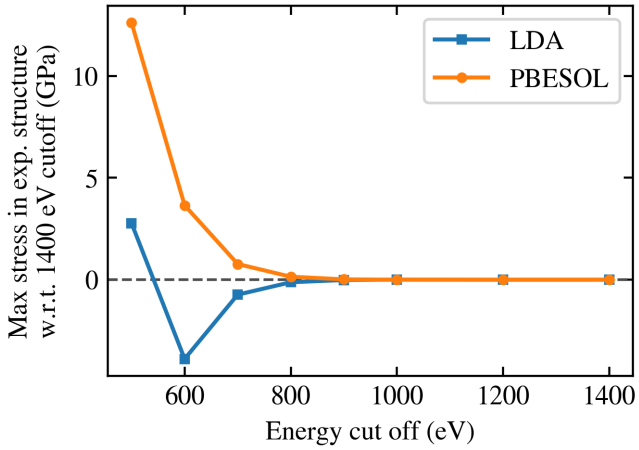
[7]: `<matplotlib.legend.Legend at 0x7faa60d1a4d0>`



3.3 Stresses We look at the convergence of stresses by taking the initial stress calculated at the experimental structure (i.e. for step 1 of the geometry optimisation) at different cut offs and comparing that to our most-converged cut off (1400 eV).

By looking at how this stress deviation due the cut off we get a sense of the error in the computed stresses due to the finite basis.

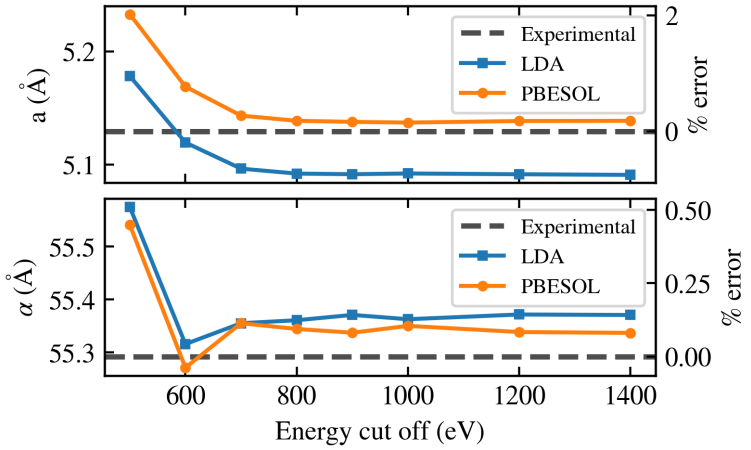
[8]: `<matplotlib.legend.Legend at 0x7faa60d72b60>`



3.4 Final structure Finally, we look at how the optimised unit cell depends on the plane wave cut off. We see that the unit cell parameters are certainly well-converged at a cut-off of 900 eV.

Note that this only tells us about the error in the unit cell due to finite basis set – not the final converged unit cell. For that we must also converge w.r.t. e.g. k-points (see below).

[9]: `<matplotlib.legend.Legend at 0x7faa61213070>`

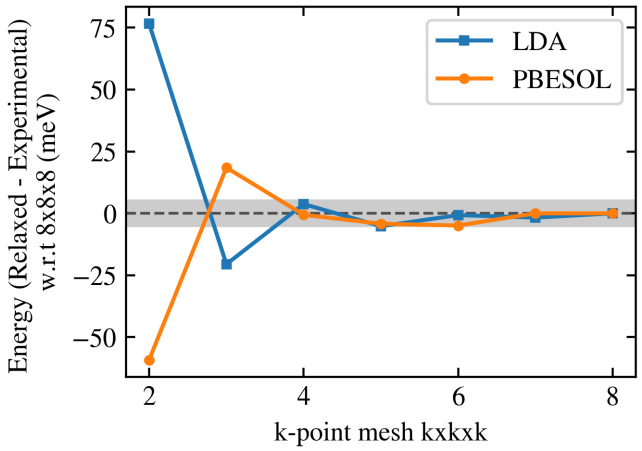


1.1.5 4. *k*-points

Read in the results Now we extract key information from the results of each geometry optimisation.

4.1 Energy differences If we plot the different in total energy between the relaxed and unrelaxed structures with respect to that of the highest cut off energy (1400 eV), we get a sense of how well-converged energy difference are for a given cut off.

[12]: `<matplotlib.legend.Legend at 0x7faa5e516080>`

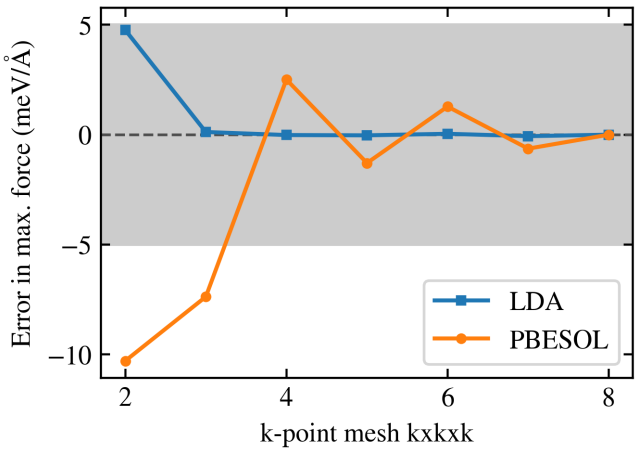


4.2 Forces Even more important than well-converged energy differences if the convergence of forces. We look at this by taking the initial forces calculated at the experimental structure (i.e. for step 1 of the geometry optimisation).

For this plot, the 'error in max. force' is defined as the max. force in the experimental structure - that calculated at an 8x8x8 *k*-point mesh.

By looking at how the maximum force difference due the *k*-point sampling, we get a sense of the error in the forces due to the finite sampling.

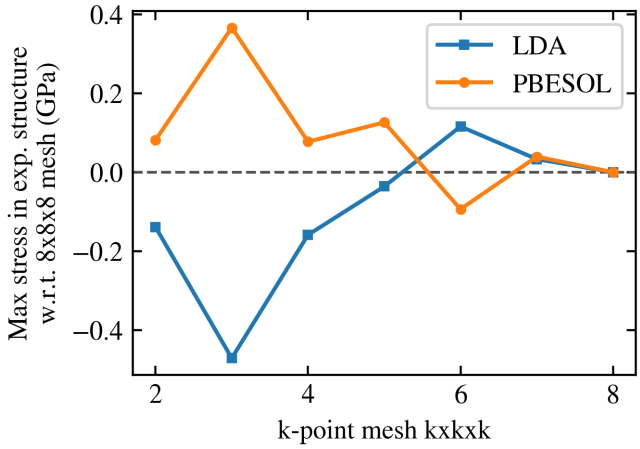
[13]: `<matplotlib.legend.Legend at 0x7faa60f9dcf0>`



4.3 Stresses We look at the convergence of stresses by taking the initial stress calculated at the experimental structure (i.e. for step 1 of the geometry optimisation) at different k-point meshes and comparing that to our most-converged mesh of 8x8x8.

By looking at how this stress deviation due the k-point mesh we get a sense of the error in the computed stresses due to the finite sampling.

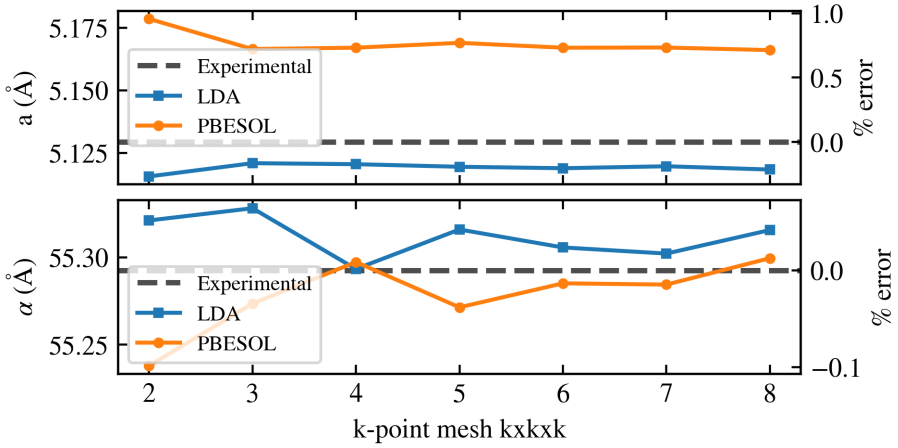
[14]: `<matplotlib.legend.Legend at 0x7faa5e36af80>`



4.4 Final structure Finally, we look at how the optimised unit cell depends on the k-point mesh. We see that the unit cell parameters are certainly well-converged at a k-point mesh of 3x3x3.

Note that this only tells us about the error in the unit cell due to finite k-point sampling – not the final converged unit cell. For that we have to use a larger plane-wave cut off (see above)!

[15]: <matplotlib.legend.Legend at 0x7faa5e6ba0b0>



1.1.6 5. Supercell

The CASTEP input and output files for a supercell size test are available in the subsirectory ./convergence/supercell

We ran a geometry-optimisation (with a fixed unit cell) for a $^{8}Li^{+}$ ion in a 2x2x2 and a 3x3x3 unit cell starting at the octahedral interstitial position. We then calculated the electric field gradient tensors in these two cases.

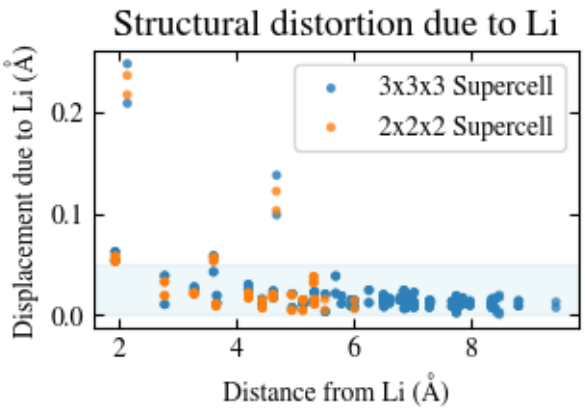
Note that due to a CASTEP bug, there was no space between the atom label and its index for indices larger than 99 in the .magres file produced. These spaces have been manually added in to allow ASE to parse the file correctly.

5.1 EFG Note also that these are not quite converged values of ν_Q, but they do allow us to assess the effects of the supercell size on the calculated.

```
 _Q(2x2x2) = 71.9782 kHz
 _Q(3x3x3) = 71.7927 kHz
This is a 0.258% change
```

5.2 Structural distortion

```
Net ionic drift: [-1.21871248e-06 -3.09585657e-06 -2.93822360e-02] A
Net ionic drift: [-1.03703704e-06 -1.82716049e-06 -1.94176790e-02] A
```


Structural distortion due to Li
Displacement due to Li (Å)
0.0
0.1
0.2
2
4
6
8
Distance from Li (Å)
3x3x3 Supercell
2x2x2 Supercell