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Li-ion diffusion in LiFePO_4 for battery applications

Version: 2016.3

Downloads & Links

- PDF version
- Tutorial Synopsis
- [Basic QuantumATK Tutorial](#)
- [ATK Reference Manual](#)
- [Calculating reaction rates using harmonic transition state theory](#)
- [Pt diffusion on Pt surfaces using NEB calculations](#)

LiFePO_4 is among the typical rechargeable Li-ion battery cathode materials with high energy density and low cost, while also being environmentally friendly ^{[1][2]}. In this tutorial you will use ATK-DFT to estimate the Li-ion diffusion rates along different crystallographic directions in LiFePO_4 .

In particular, you will:

- Import the LiFePO_4 bulk structure.
- Optimize the LiFePO_4 lattice parameters.
- Create the $\text{Li}_{1-x}\text{FePO}_4$ structures.
- Optimize the initial and final configurations.
- Create initial NEB trajectories (IDPP interpolation).
- Optimize the Li diffusion path.
- Calculate the reaction rates using harmonic transition state theory (HTST).

Import LiFePO_4 bulk structure

The LiFePO_4 structure can be imported from the **Crystallography Open Database** plugin in QuantumATK.

1. Click the **Builder**.
2. Open the From Plugin ► Crystallography Open Database.
3. Select *Li*, *Fe*, *P*, *O* as elements and click the **To results** button.
4. Choose *Lithium Iron Phosphate(V), Simple Orthorhombic(Pnma)*.
5. Click **Add to stash** button.

It will be automatically loaded in the **Builder** stash.

Crystallography Open Database

Basic Advanced Expert Help

Lattice

Type: All

a (Å): 0.00 - 100.00

b (Å): 0.00 - 100.00

c (Å): 0.00 - 100.00

α (°): 0.00 - 100.00

β (°): 0.00 - 100.00

γ (°): 0.00 - 100.00

Selected elements: Li, O, P, Fe

Only selected elements

To results

Crystallography Open Database

Filter...

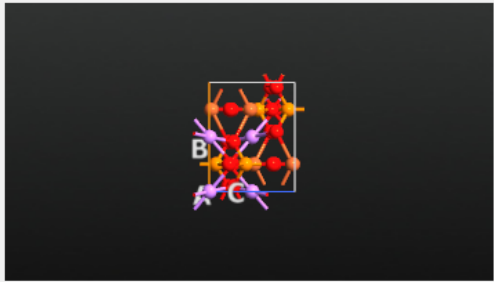
Index	Name	Crystal type	Cell volume	H-M symbol	Publication Year
1	Lithium iron(III) d...	Simple Monodinic	255.2	P 1 21 1	1990
2	Lithium iron(III) p...	Simple Orthorho...	286.7	P b n m	1938
3	Lithium Iron Phos...	Simple Orthorho...	291.45	P n m a	
4	Fe1.006 Li1.006 ...	Simple Orthorho...	297.91	P n m a	2011
5	Fe Li O4 P	Simple Orthorho...	291.4	P n m a	1993
6	Lithium Iron Phos...	Simple Orthorho...	290.383	P n m a	2012
7	Fe Li O4 P	Simple Orthorho...	291.34	P n m a	2013
8	Fe Li1.1 O4.126 P	Simple Orthorho...	291.34	P n m a	2013
9	Fe Li O4 P	Simple Orthorho...	290.84	P n m a	2013
10	Fe1.004 Li O4.12...	Simple Orthorho...	290.84	P n m a	2013
11	Lithium iron phos...	Simple Orthorho...	291.31	P n m a	2013
12	Li3 Fe2 (P O4)3	Rhombohedral	1345.15	R -3 :H	2000

FeLiO₄P (Lithium Iron Phosphate(V))

Chemical formula: FeLiO₄P
Number of elements: 4

Lattice


- Simple Orthorhombic
- a = 10.3328 Å
- b = 6.0043 Å
- c = 4.6977 Å
- α = 90.0°
- β = 90.0°



18 result found.

Back to search Download file(s)... Add to Stash

New functionality in QuantumATK 2017:

From the QuantumATK 2017 version, crystal structures such as LiFePO₄ can be imported by the QuantumATK Databases tool as follows: Click the  **Databases**. See COD (Crystallography Open Database) and Materials Project. Both are possible to get the LiFePO₄ structure. In the COD case, select Li, Fe, P, O as elements and click the **Search** button.

You can also use the **Materials Project** database. Choose the Materials Project. Select elements or type LiFePO₄. Select one and click the **import** button, it will be automatically loaded in the **LabFloor** in the same way as the COD. In this case, you can get more calculation information including the structure from the Material Project database.

tutorial (C:\tutorial) - Virtual NanoLab

File Projects View Tools Windows Help

Project Files

Filter... Text File types

Name

- ☐ LiFePo4_opt.log
- ☐ LiFePo4_opt.nc
- ☐ LiFePo4_opt.py

LabFloor

Group by Filename

Lithium Iron Phosphate(V)

mp-19017

$\{\epsilon_i(\mathbf{k})\}$

$D(\epsilon)$

$\frac{\partial \sigma_i}{\partial \epsilon_j}$

Materials Project

File Upload Help

Filter...

Formula	Crystal System	# of K-points	Stability (Energy above hull - eV)	Final Energy (eV)
LiFePO4	Orthorhombic	6	0	-191.338
LiFePO4	Orthorhombic	4	0.0150521	-572.75
LiFePO4	Monoclinic	12	0.0107254	-191.038
LiFePO4	Monoclinic	6	0.0522523	-569.625
LiFePO4	Orthorhombic	6	0.00878631	-191.092
LiFePO4	Monoclinic	4	0.00951795	-764.286
LiFePO4	Monoclinic	4	0.00689504	-764.58
LiFePO4	Trigonal	12	0.00963255	-286.603
LiFePO4	Orthorhombic	6	0.0154661	-572.715
LiFePO4	Monoclinic	2	0.0975582	-565.819
LiFePO4	Orthorhombic	6	0.0446599	-190.088
LiFePO4	Monoclinic	24	0.0379195	-190.276

LiFePO₄ (mp-19017)

Structure

- Crystal System: Orthorhombic
- Spacegroup Symbol: Pnma
- Density: 3.47 g/cm³
- Volume: 302.30 Å³

Calculation Details

- # of K-points: 6
- Energy Cutoff: 520.00 eV

60 results found.

Back to search Download file(s)... Import

For more options, see also [Import XYZ, CIF, CAR, VASP files in QuantumATK tutorial](#).

Optimize LiFePO₄ lattice parameters

You can import the LiFePO₄ structure to the **Builder** to have a deeper look into the structure.

Note

In order to better compare with the results of reference ^[3] you can use the Bulk Tools ► Swap Axes tool to swap C↔A and Z↔X. However, by doing so, the configuration will lose the information about the symmetry type, in this case *Simple orthorhombic*. Use the Bulk Tools ► Lattice Parameters tool to set the *Lattice type* to *Simple orthorhombic*.

In order to optimize the lattice parameters, send the LiFePO₄ structure from the **Stash** to the **Scripter** to set up a new DFT calculation as follows:

1. Add the **New Calculator** block and modify the following parameters:

- SGGA-PBE exchange correlation potential
- 7x5x3 k-point sampling

(We will use the the default FHI pseudopotentials and DZP basis set).

2. Add an **OptimizeGeometry** block and modify:

- Max forces 0.02 eV/Å
- Max stress 0.1 GPa
- Remove check from **Constrain cell** to allow for cell optimization
- Check **Save trajectory** and specify the file `LiFePo4_opt.nc`

3. Change default output file name to `LiFePo4_opt.nc`

4. Finally, send the script to the **JobManager** and run the calculation.

It takes about 30 minutes on 8 cores. After finishing the job, open the optimized *BulkConfiguration* with object ID `g1D002` with the **Builder**. Check the new optimized lattice parameters which agree to within 0.1 percent with the experimental data.

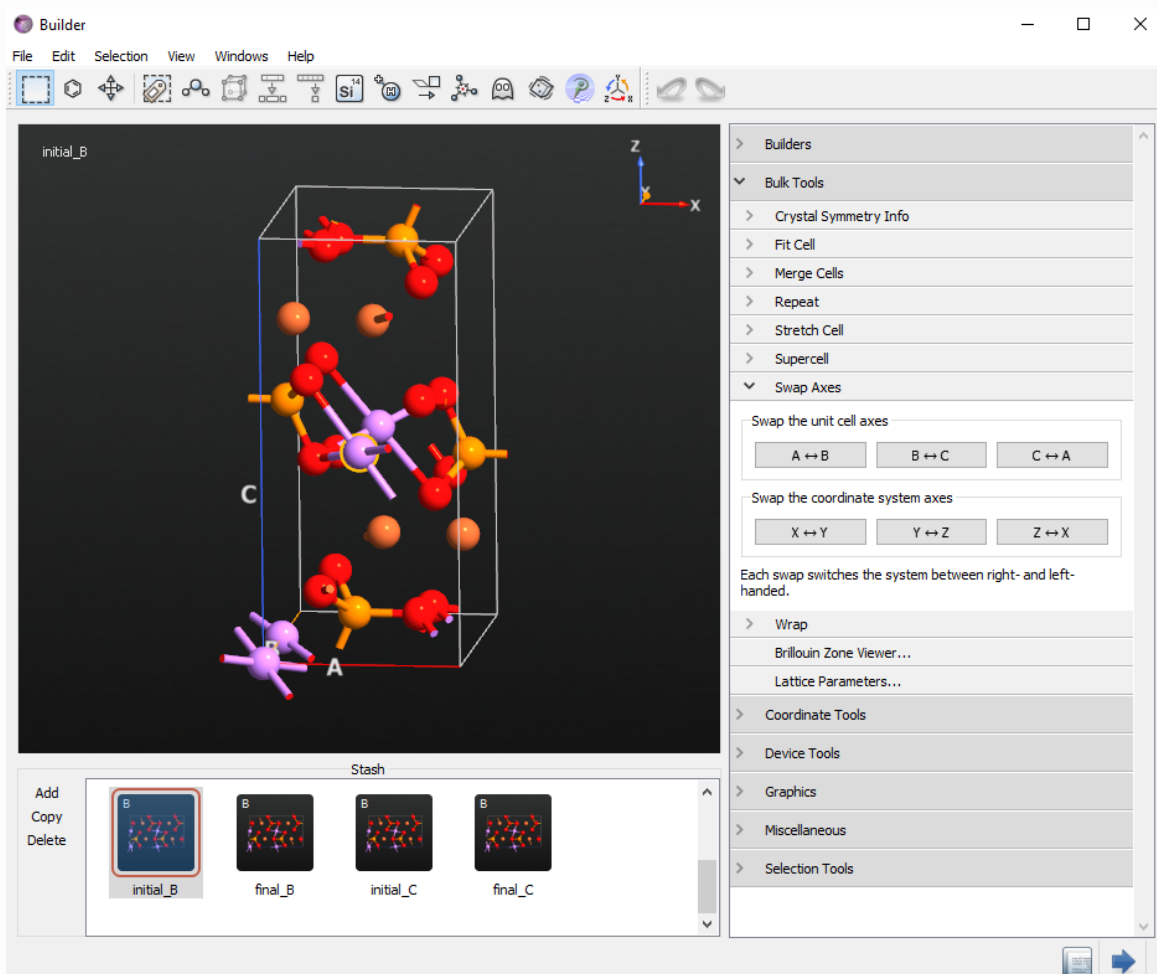
Create the Li_{1-x}FePO₄ structures

In this tutorial you will study the diffusion of one Li atom for a Li-deficient structure such as Li_{1-x}FePO₄. In particular, you will remove one of the four Li atoms from the bulk configuration. Note that the diffusion energy barriers depend on the Li concentration [4].

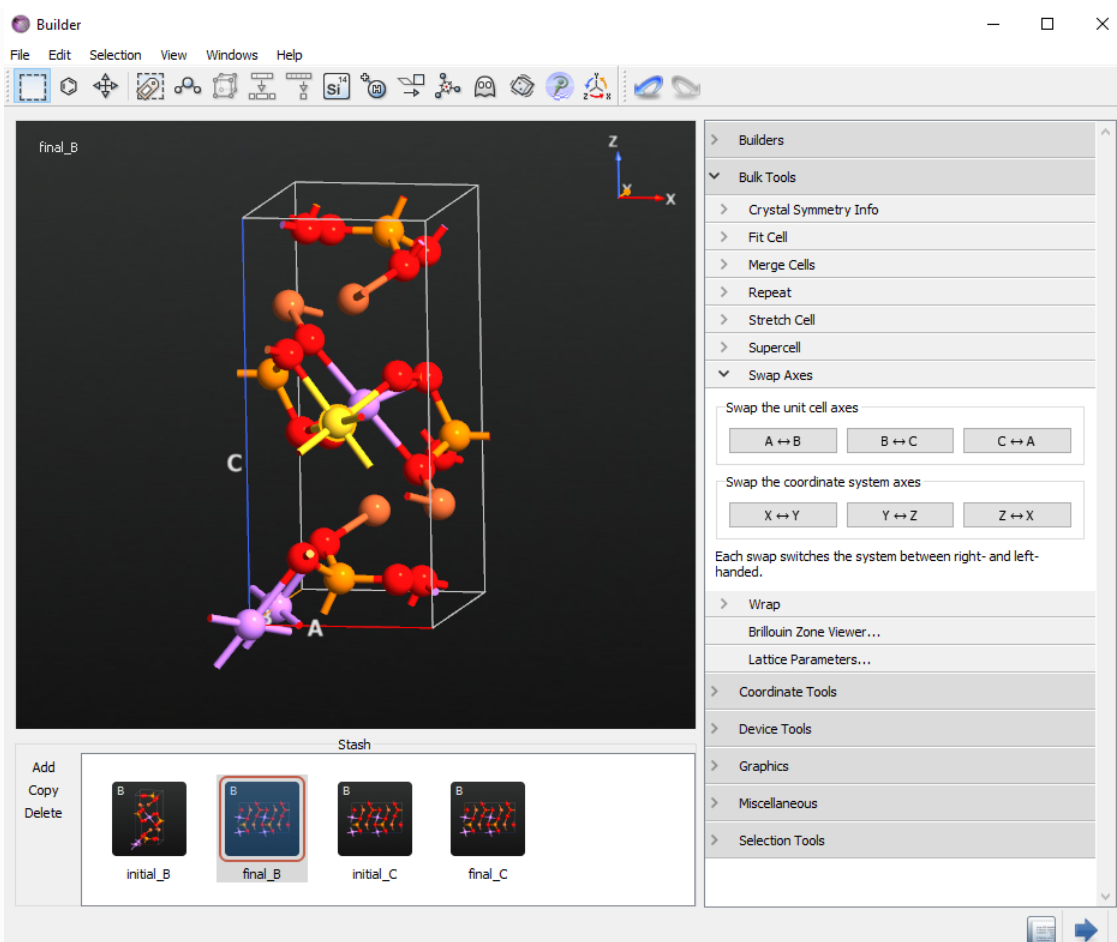
In the next section you will set up the calculation for the diffusion of a Li atom along two different directions. You thus need to create initial configurations and final configurations for the same Li atom diffusing along the B and C directions.

Create initial and final structures for diffusion along B direction

1. Right-click on the configuration on the **Stash** and make three copies such that you have 4 identical configurations. We will make initial and final structures for the B and C directions.
2. From the first configuration, delete one Li atom as in the figure below. This will be your initial structure for the B direction NEB calculations and you can rename it *initial_B*.




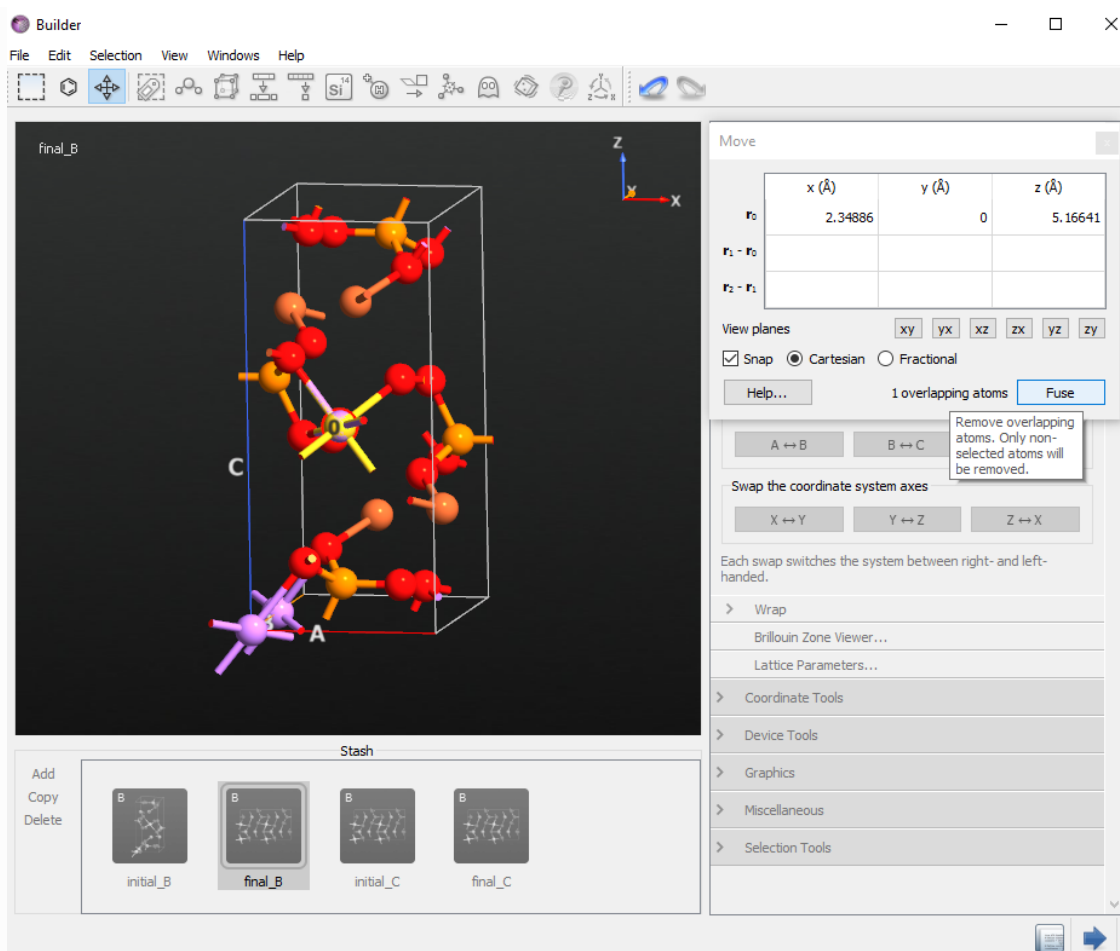
3. Double click the second configuration to make it active. Next rename it *final_B*. Select the same Li atom you just deleted from the initial configuration and open the **Si** **Periodic Table** tool. Click on **Gold** (Au) element to change the Li atom to Gold.



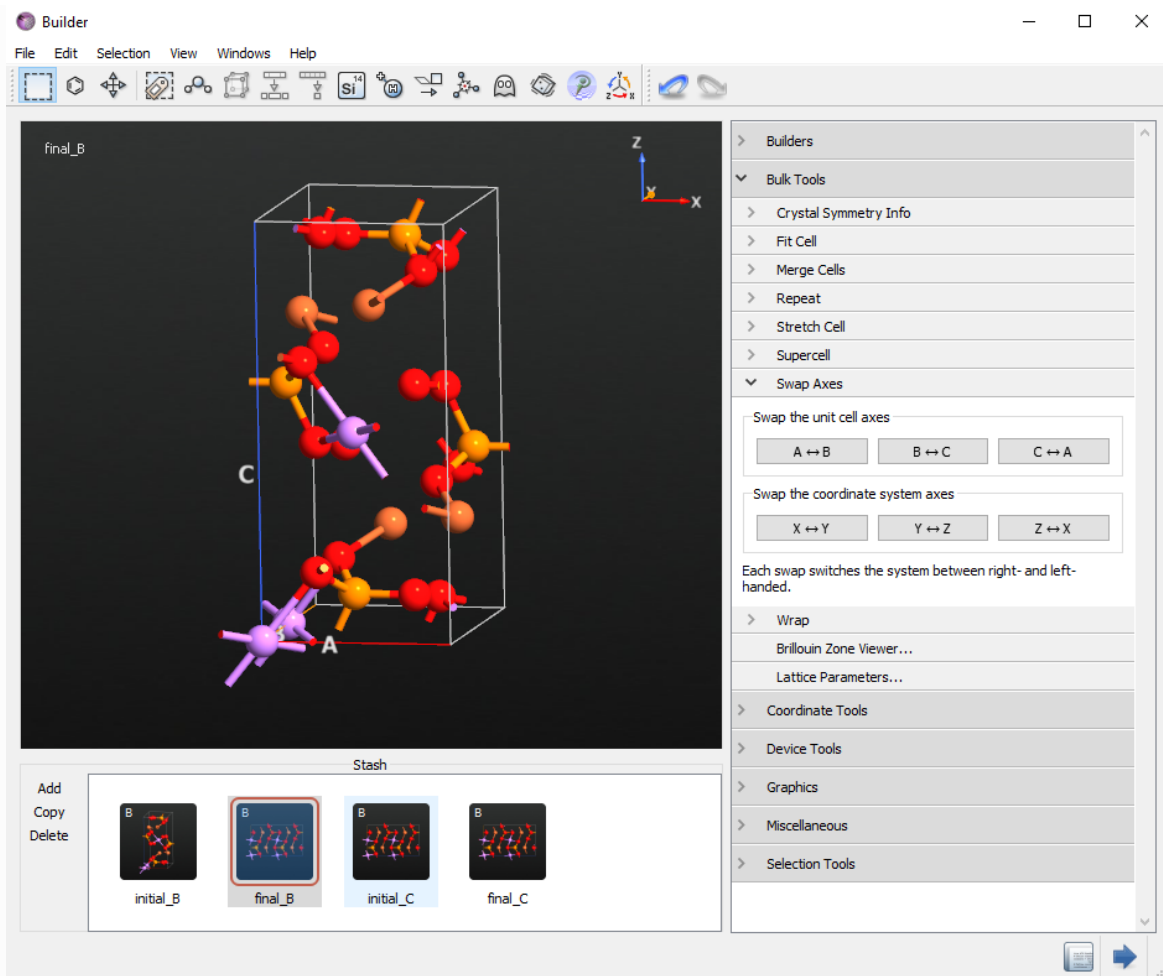
Tip

You are applying this trick to be able to move the Li atom into a specific position. In this case, the position of the Li vacancy defined by the Gold atom. There are indeed several other workarounds to build this final configuration, e.g. by copying the coordinates of the original Li atom you removed. You are welcome to use here the procedure that you find more relevant and intuitive for you.

4. Select Li atom number 7 (the one next to the Gold atom along the B direction) and use the  **Move** tool to move it on top of the Gold atom. Be sure that the *Snap* option is enabled.

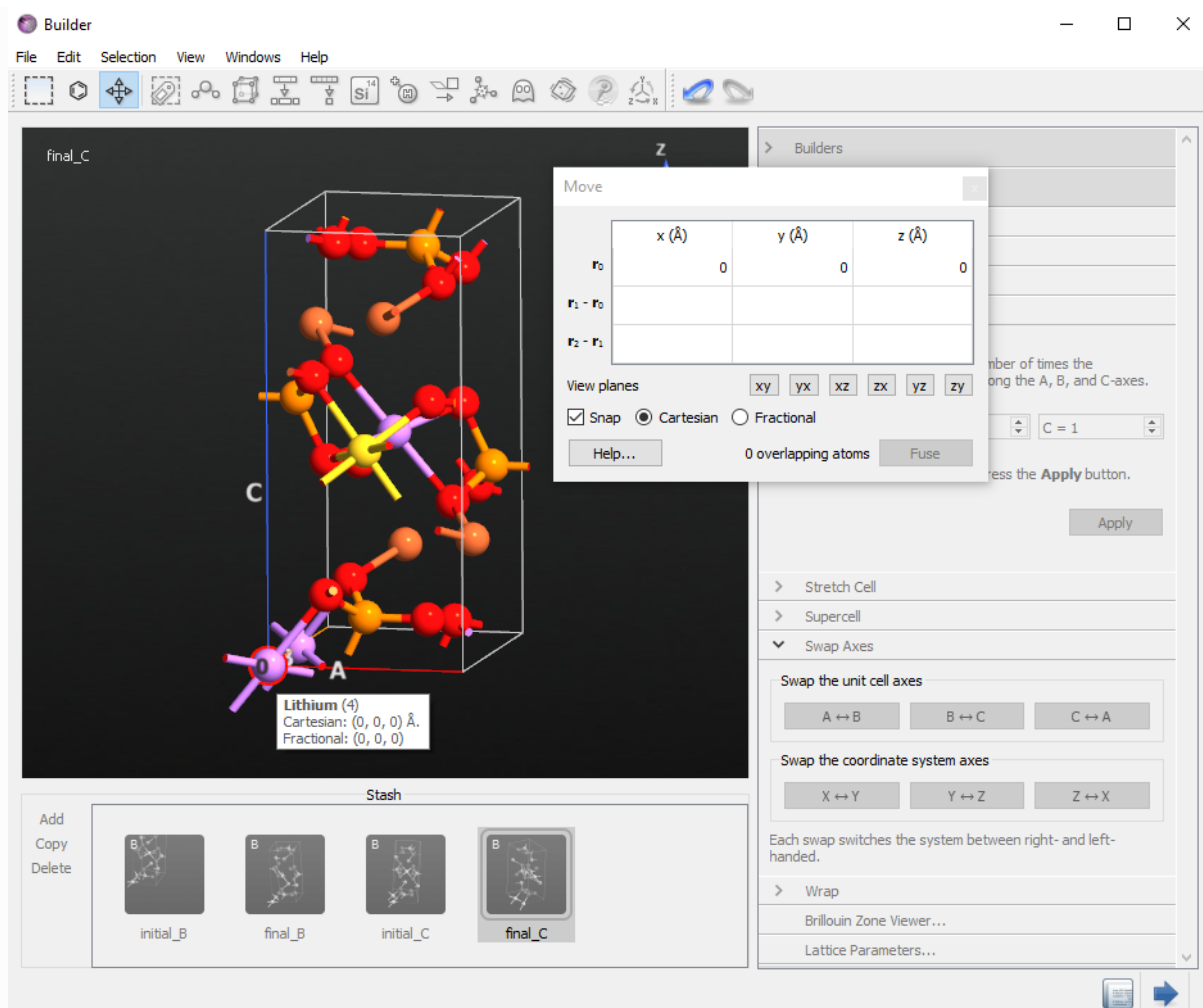


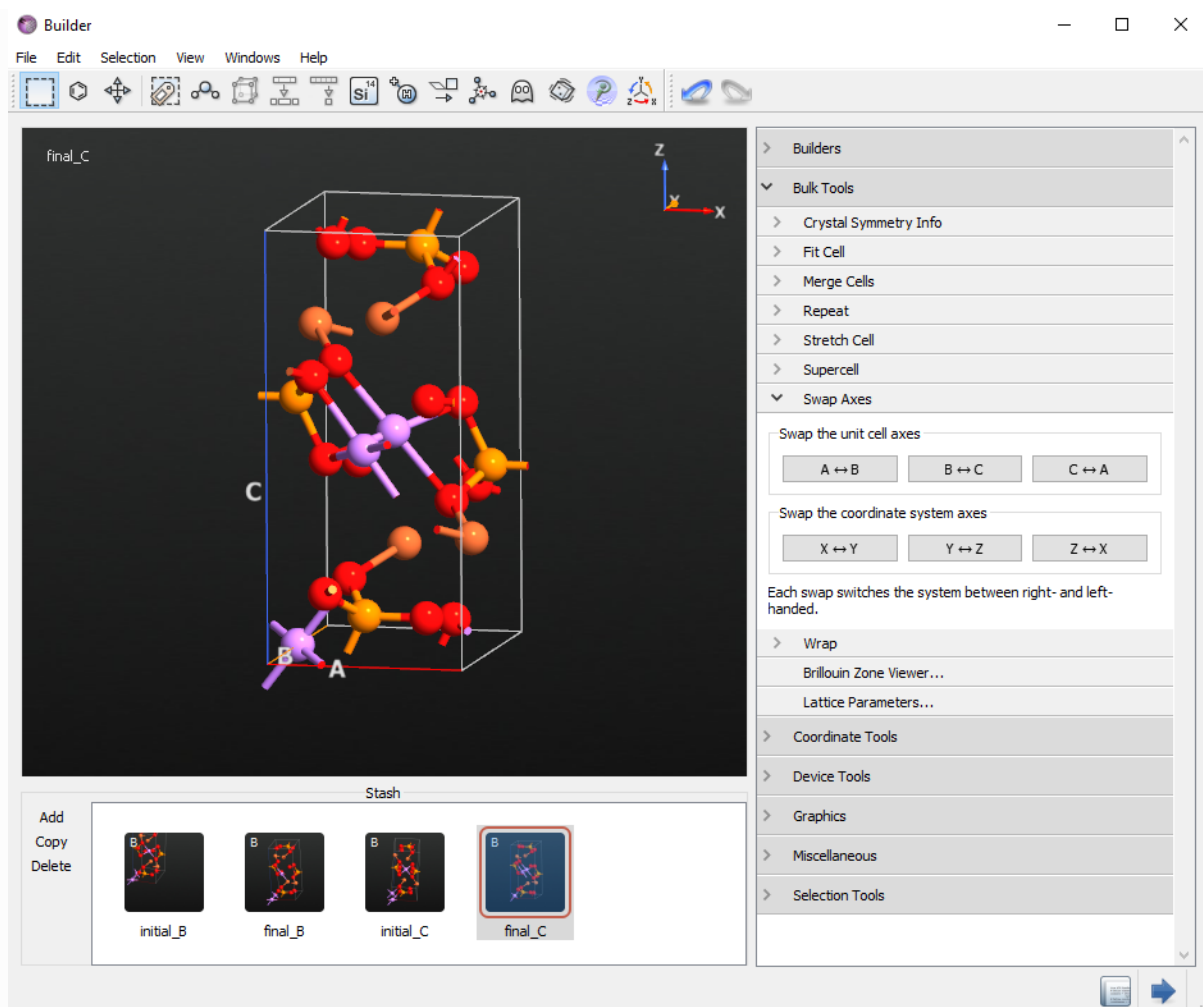
5. Use the *Fuse* option to remove the Gold atom and your final structure is now ready.
6. Finally, check the Li atom number 6 in the *initial_B* and *final_B* configurations. Li atom number 6 should be moved in the B direction.



Create initial and final structures for diffusion along C direction

Follow the same procedure as above to create the configuration along the C direction. The initial structure for the C direction is the same as the *initial_B* structure. Rename it *initial_C*. In this case, the final structure moves Li atom number 4 to the removed Li position (substituted Gold) in the *initial_C* structure. Rename the final structure, *final_C*.





Optimize initial and final configurations

Send each structure, *initial_B*, *final_B*, *initial_C* and *final_C*, to the **Scripter** and set up a geometry optimization calculation with the same parameters as for the LiFePO_4 structure. However, in this case you will not optimize the lattice parameters. Check the *Constrain cell* option as indicated below.

Optimize Geometry

Force tolerance: 0.05 eV/Å

Stress tolerance: 0.1 GPa

Maximum number of steps: 200

Maximum step size: 0.2 Å

Optimizer Method: LBFGS

Lattice Constraints

☒ Constrain Lattice Vectors ☒ x ☒ y ☒ z

☒ Constrain Bravais Lattice: Unit Cell

Target Stress

☒ Isotropic pressure: 0

Stress Tensor:

0	0	0
	0	0
		0

Unit: GPa

Atomic Constraint Editor

☒ Save trajectory: initial_B.nc

IO

☒ Save ☒ Print

File: initial_B.nc Label:

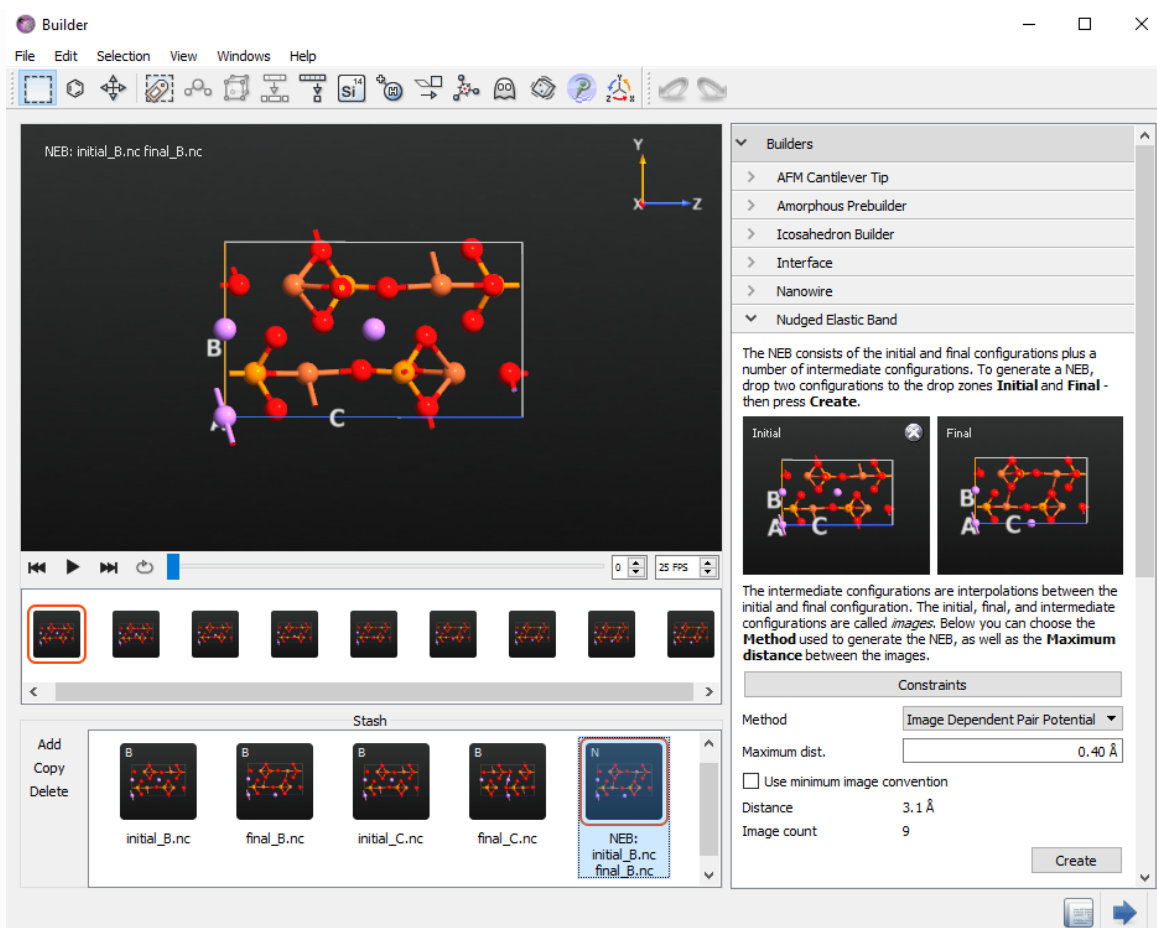
OK

Moreover, in this case you can use the unpolarized GGA.PBE functional. This will allow you to run your calculation much faster. Here you can download the four input scripts: [initial_B.py](#), [final_B.py](#), [initial_C.py](#) and [final_C.py](#).

Create initial NEB trajectories

The tutorial [Pt diffusion on Pt surfaces using NEB calculations](#) will teach you how to set up the NEB object. Here we will highlight only the main steps.



1. When the optimization of the end points are done you will find the optimized configurations loaded in the LabFloor with object ID equal to *g/D002*. Drag and drop these *BulkConfiguration* objects directly into the **Builder**.
2. In the **Builder** open the Builders ► Nudged Elastic Band plugin and drag and drop from the **Stash** the initial and final configurations corresponding to the diffusion of a Li atom along the B direction, `initial_B.nc` and `final_B.nc` configurations.



3. Select the *Image Dependent Pair Potential* interpolation method and use 9 images including the end points.
4. Create the initial Li diffusion path along C direction with the `initial_C.nc` and `final_C.nc` configurations. Use 9 images with 0.8 Å maximum distance including the end points .

Optimize Li diffusion path

You are now ready to set up and optimize the Li diffusion path in LiFePO_4 .

1. Send the two NEB objects from the **Stash** to the **Scripter**.
2. Add and set up a  **New Calculator** with the same settings as for the calculators of the end points.
3. Add a  **OptimizeGeometry** block and be sure to select the *Climbing Image Method*.
4. Finally, run the two NEB calculations [neb_B.py](#) and [neb_C.py](#).

Note that as described in the [Pt diffusion on Pt surfaces using NEB calculations](#), you can run this calculation in parallel over many MPI processes. In particular, a NEB run is parallelized over the internal images. ATK will try to detect the best parallelization strategy and it will write a small report at the beginning of your log file.

In this example, you will immediately see that a load balance problem has been detected. However, 2 out of 16 cores will be idle, so it is a rather small loss of efficiency, not “greatly reduced” as it says in the log file below. It takes about 2 hours in 16 processes. You can also change the number of MPI processes you are using to achieve the best performance.

```

+-----+
| NEB image level parallelism enabled. |
+-----+
| Total number of interior images: 7 |
| Total number of processes: 16 |
| Processes per image: 2 |
| Images calculated in parallel: 8 |
|
| Process group # 0 will calculate images: 1 |
| Process group # 1 will calculate images: 2 |
| Process group # 2 will calculate images: 3 |
| Process group # 3 will calculate images: 4 |
| Process group # 4 will calculate images: 5 |
| Process group # 5 will calculate images: 6 |
| Process group # 6 will calculate images: 7 |
| Process group # 7 will be idle! |
| WARNING: Load balance problem detected. |
|     The number of interior images calculated in parallel is not a |
|     divisor of the number of interior images. This will greatly |
|     reduce parallel performance. Either modify the parameter |
|     "processes_per_image" or the number of MPI processes. |
|
|     With 2 processes_per_image ideal performance will be obtained |
|     by using 14 MPI processes. |

```

Tip

You can speed up the optimization by first running a simple NEB calculation with a high force tolerance, e.g. 0.08 eV/Å, and without using the *Climbing Image Method*. This will in general be a faster calculation giving you a rough estimate of the energy barrier and the diffusion path. After this step, you can set up a more precise NEB run and also use the climbing method to finalize your results.

Analyze the results

Once the calculation is properly converged you will find the optimized *NudgedElasticBand* object loaded in the **LabFloor**

Tip

Always remember to check the log file at the end of your simulation. In particular, check that convergence is achieved:

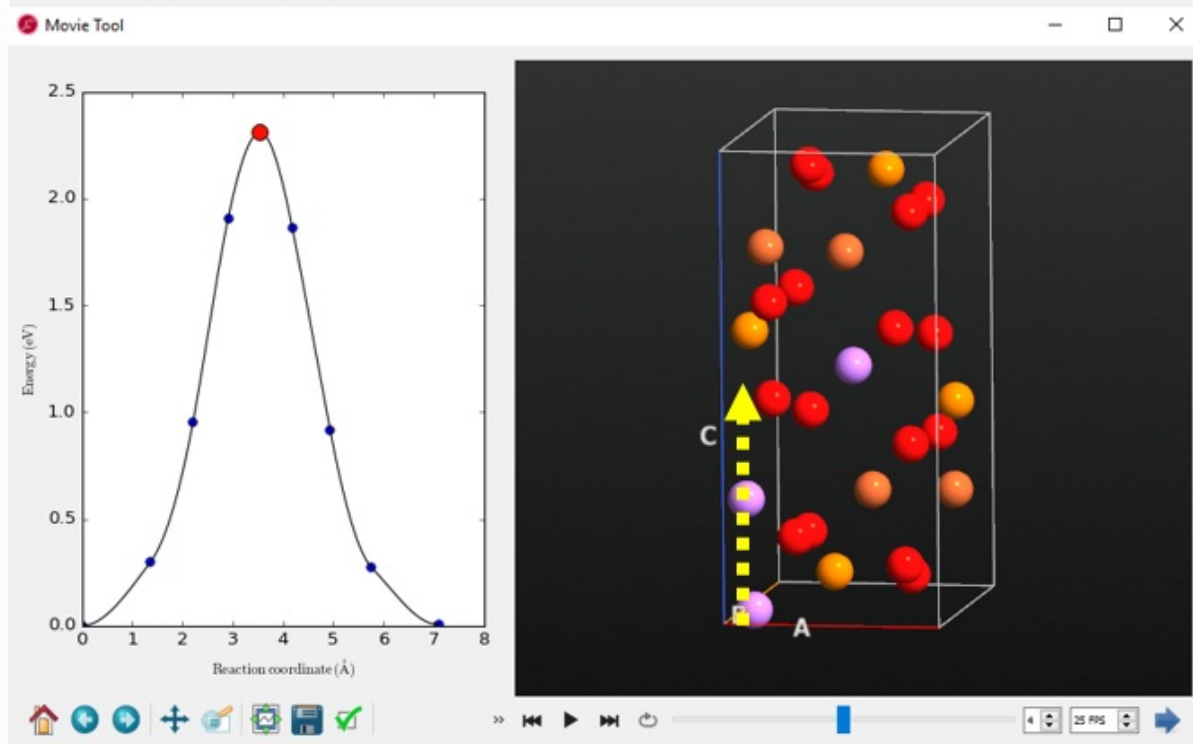
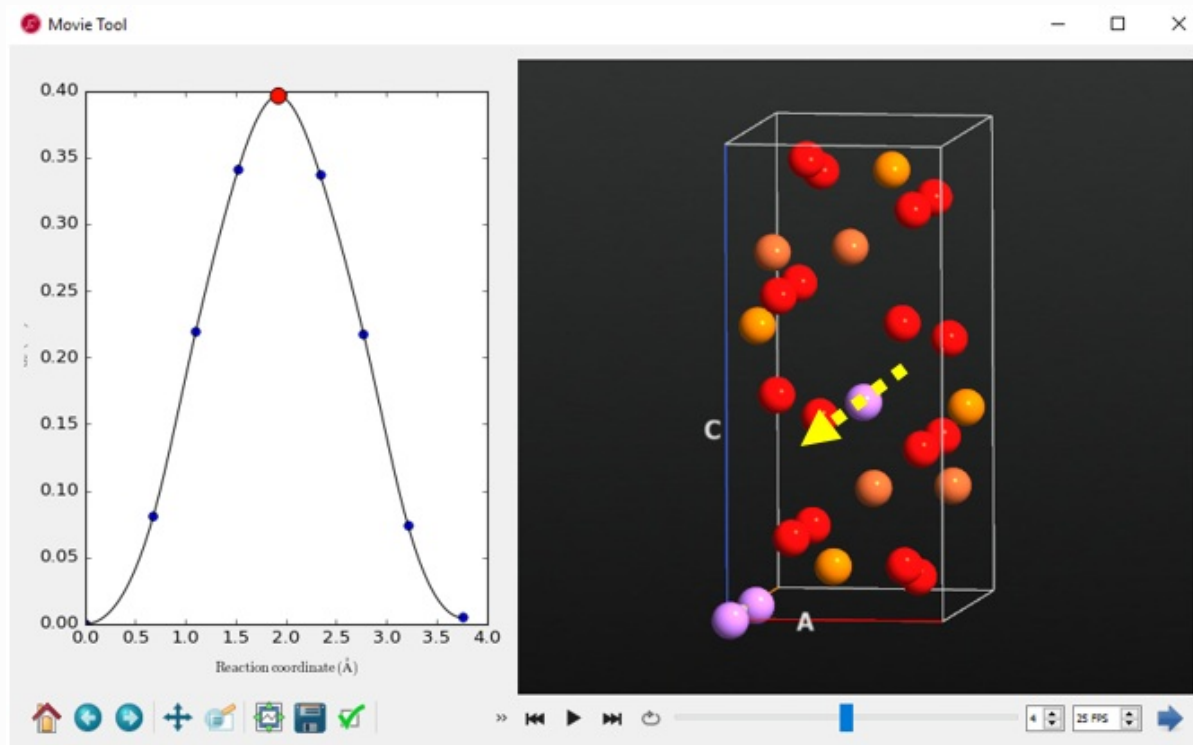
```

+-----+
| NEB Optimization using the LBFGS optimizer |
+-----+
| Iteration   Step Length   Max. Force   Max. Energy Image   Max. Energy |
+-----+
|           0   0.000e+00   1.473e+00           4   0.925917 |
|           1   4.825e-02   1.362e+00           4   0.794101 |
|           ... |
|          23   1.220e-02   2.772e-01           4   0.405770 |
|          24   3.731e-03   4.938e-02           4   0.404796 |
+-----+
| NEB optimization converged after 24 steps. |
+-----+

```

In the two figures below, the optimized Li diffusion process for the Li atom moving along the B and C

directions are illustrated by using the Movie Tool plugin.



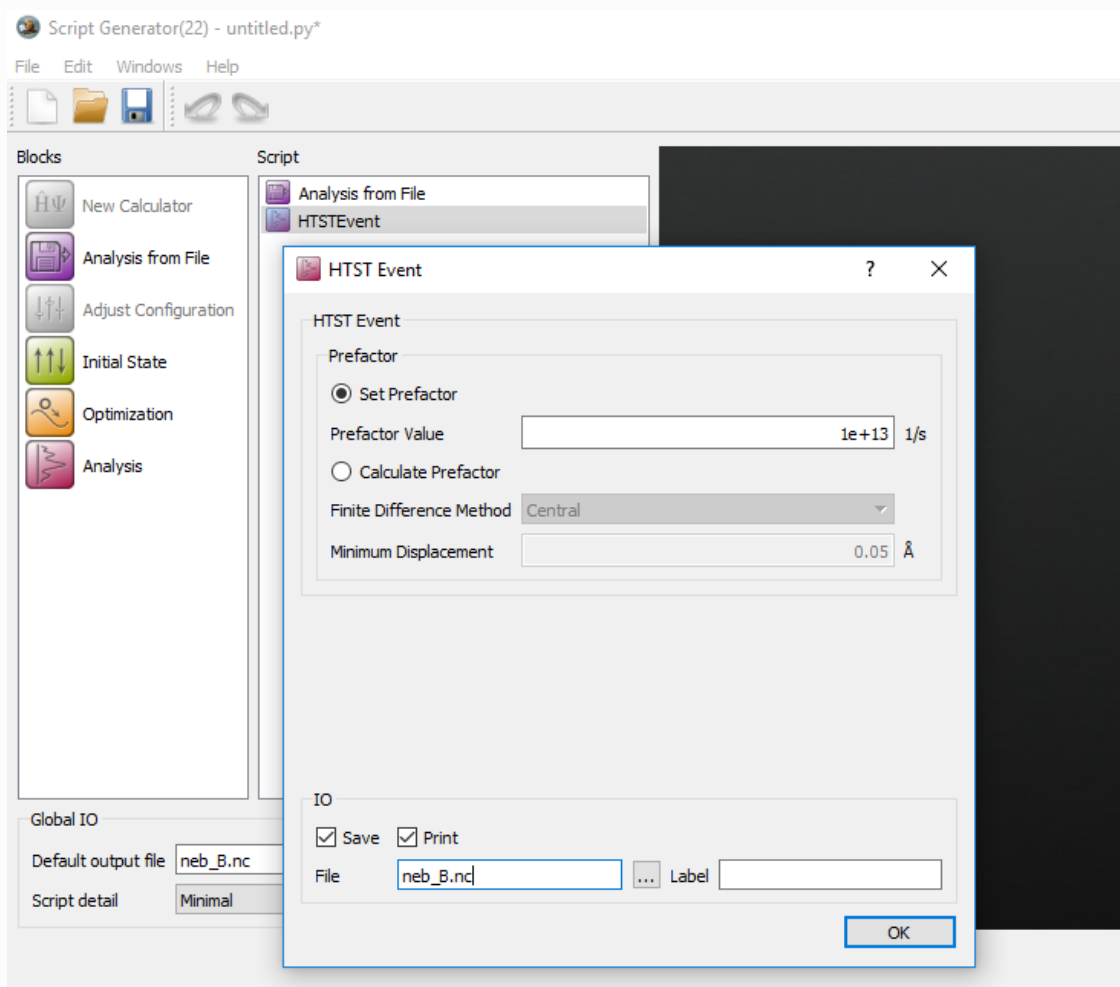
While the Li atom can more easily move along the B direction with 0.39 eV energy barrier, you found a high energy barrier, 2.3 eV for the Li atom moving along the C direction. The results are in agreement with reference [4].

Calculate the reaction rates using harmonic transition state theory

For detailed information about how reaction rates are calculated and the theory behind the harmonic transition state theory please refer to the [Calculating reaction rates using harmonic transition state theory](#).

To set up the analysis:

1. Open the **Scripter**.
2. Double click on **Analysis from file** and select the `neb_B.nc` configuration with object ID *g/D001*.
3. Add the **HTSTEvent** analysis and set the prefactor to $1e+13$ 1/s.



4. Run the analysis which will only take a minute. Here is the input script. [HTST_analysis.py](#)

Note

The time required for an HTSTEvent analysis strongly depends on whether or not the prefactor is assumed or calculated. If you need to calculate the prefactor, it can take a long time, depending on the method and system. Therefore, it is usually a very good approximation to assume the prefactor for solid state reactions like bulk diffusion.

In order to visualize the results from the **HTSTEvents** analysis, select the corresponding object from the **LabFloor** and select the *HTST Rates* plugin on the right hand side.

HTST Event Information

Forward Event

Prefactor

1.000e+13 1/s

Barrier

0.3962 eV

Reverse Event

Prefactor

1.000e+13 1/s

Barrier

0.3915 eV

Rate

Temperature

300.0 K

Forward Rate

2.213e+06 1/s

Reverse Rate

2.646e+06 1/s

Plot Options

Min. Temperature

200 K

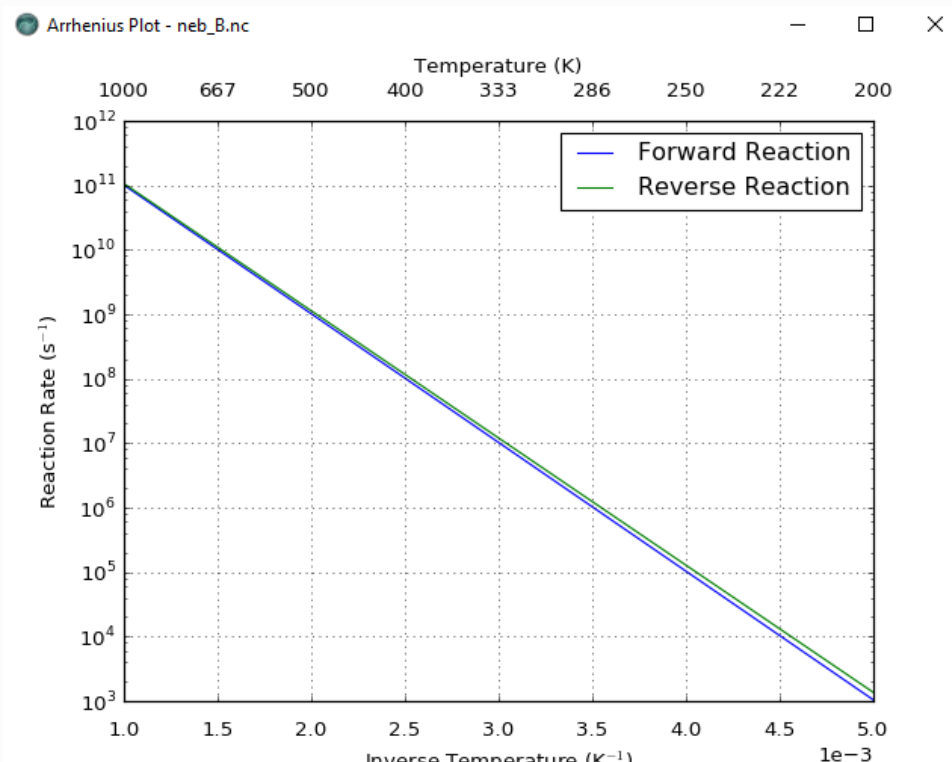
Max. Temperature

1000 K

Arrhenius Plot

Here, you can calculate the forward and reverse reaction rates for your diffusion mechanism. In this case you will find these two values to be very close to each other because the initial and final states are essentially equivalent.

Here, you can also set the options for an Arrhenius plot:



The table below summarized the results found in this tutorial.

Table 2 Table: energy barriers (eV) and reaction rates (s⁻¹) calculated at 300 K for Li diffusion in Li_{1-x}FePO₄ along the B and C directions.

Direction	Barrier	k <i>HTST</i>
B	0.39	2.6×10^6
C	2.30	1.9×10^{-26}

References

[1]

M. Saiful Islam and Craig A. J. Fisher. Lithium and sodium battery cathode materials: computational insights into voltage, diffusion and nanostructural properties. *Chem. Soc. Rev.*, 43(1):185, 2014. [doi:10.1039/C3CS60199D](https://doi.org/10.1039/C3CS60199D).

[2]

William Davidson Richards Yan Wang. Design principles for solid-state lithium superionic conductors. *Nature Materials*, 14(10):1026, 2015. [doi:10.1038/nmat4369](https://doi.org/10.1038/nmat4369).

[3]

Dhamodaran Santhanagopalan Yuri Janssen. Reciprocal salt flux growth of lifepo 4 single crystals with controlled defect concentrations. *Chemistry of Materials*, 25(22):4574, 2013. [doi:10.1021/cm4027682](https://doi.org/10.1021/cm4027682).

[4] (1,2)

Chuying Ouyang, Siqi Shi, Zhaoxiang Wang, Xuejie Huang, and Liquan Chen. First-principles study of li ion diffusion in lifepo 4. *Physical Review B*, 2004. [doi:10.1103/PhysRevB.69.104303](https://doi.org/10.1103/PhysRevB.69.104303).

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