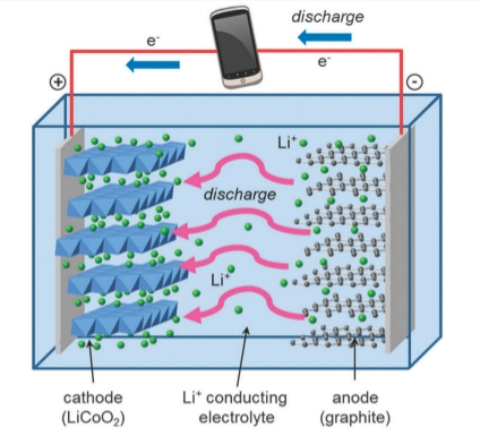
TUTORIAL SYNOPSIS

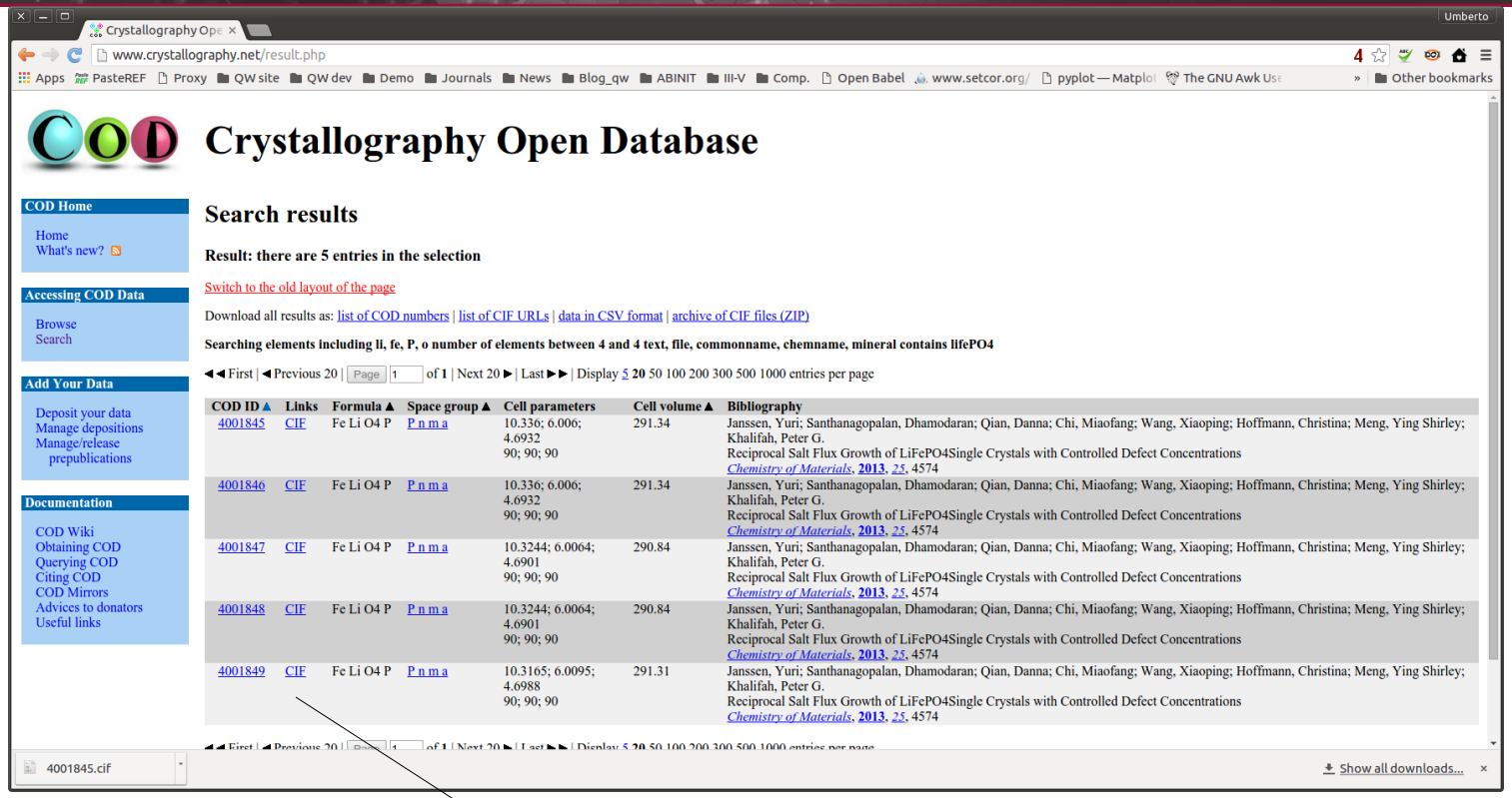
Li-ion diffusion in $LiFePO_4$ for battery applications

Quantum Wise
When every atom matters

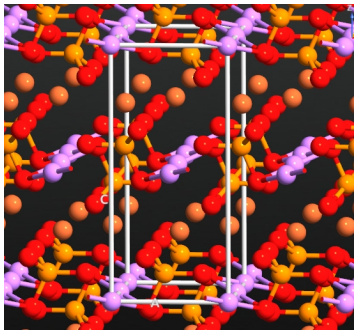


- Import $LiFePO_4$ bulk structure
- Optimize $LiFePO_4$ lattice parameters
- Create the $Li_\delta FePO_4$ structures
- Optimize initial and final configurations
- Create initial NEB trajectories (IDPP interpolation)
- Optimize Li diffusion path
- Calculate the reaction rates using harmonic transition state theory (HTST)

Import $LiFePO_4$ bulk structure



- Download CIF file
- Copy it to project folder

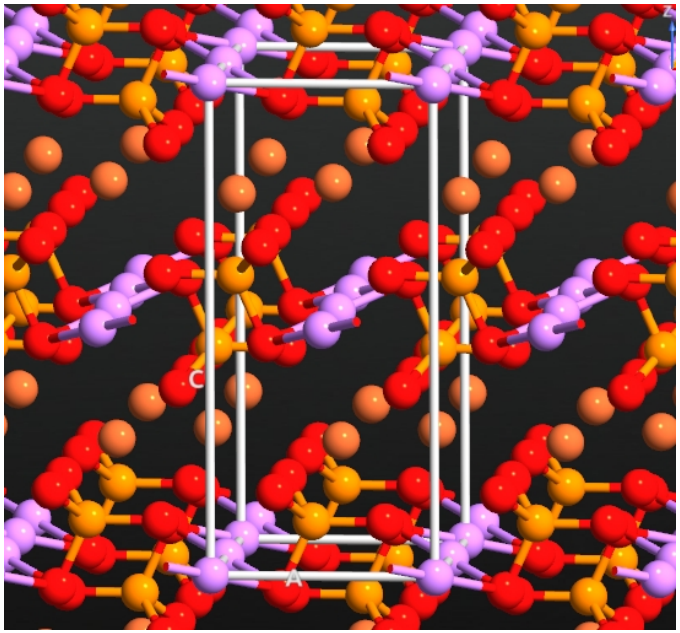


Optimize $LiFePO_4$ lattice parameters

ATK-DFT, ATK 2015.1

- GGA-PBE exchange correlation potential
- FHI pseudopotential
- DZP basis set
- 7x5x3 k-point sampling
- 75 Ha density mesh cut-off

- Geometry optimization
- Max forces 0.05 eV/Å
- Max stress 0.005 eV/Å3

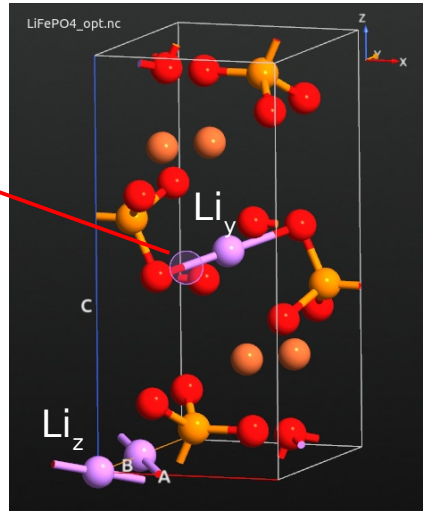


a = 4.752 Å	4.690 Å [1]
b = 6.087 Å	6.006 Å [1]
c = 10.451 Å	10.336 Å [1]

[1] Chemistry of Materials, 2013, 25, 4574

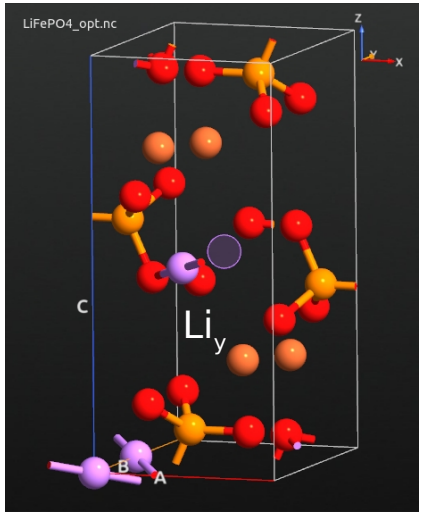
Create the $Li_{\delta}FePO_4$ structures

remove one
Li atom

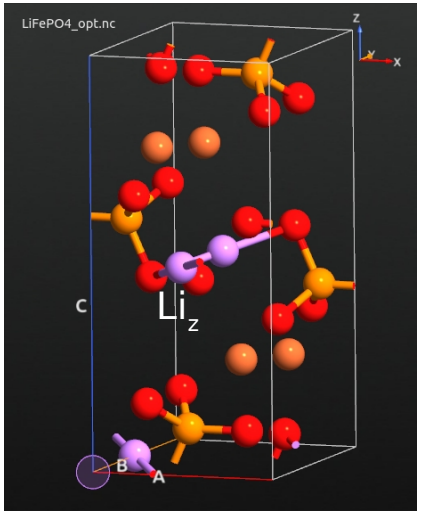


initial configuration

Li diffusion along y axes

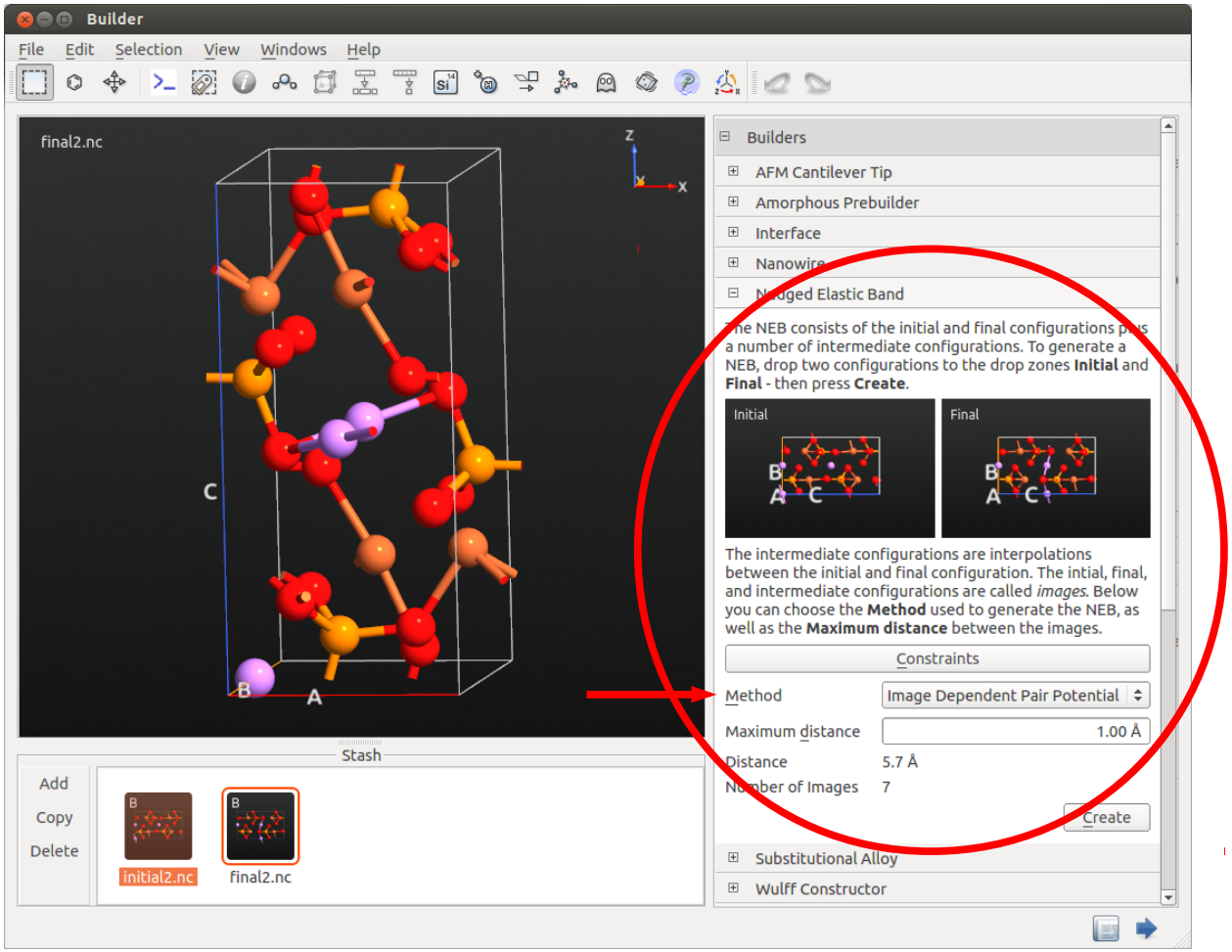


Li diffusion along z axes

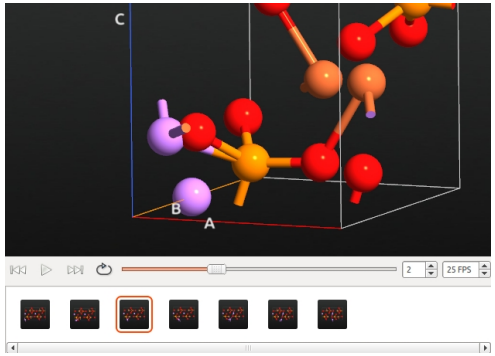


final configurations

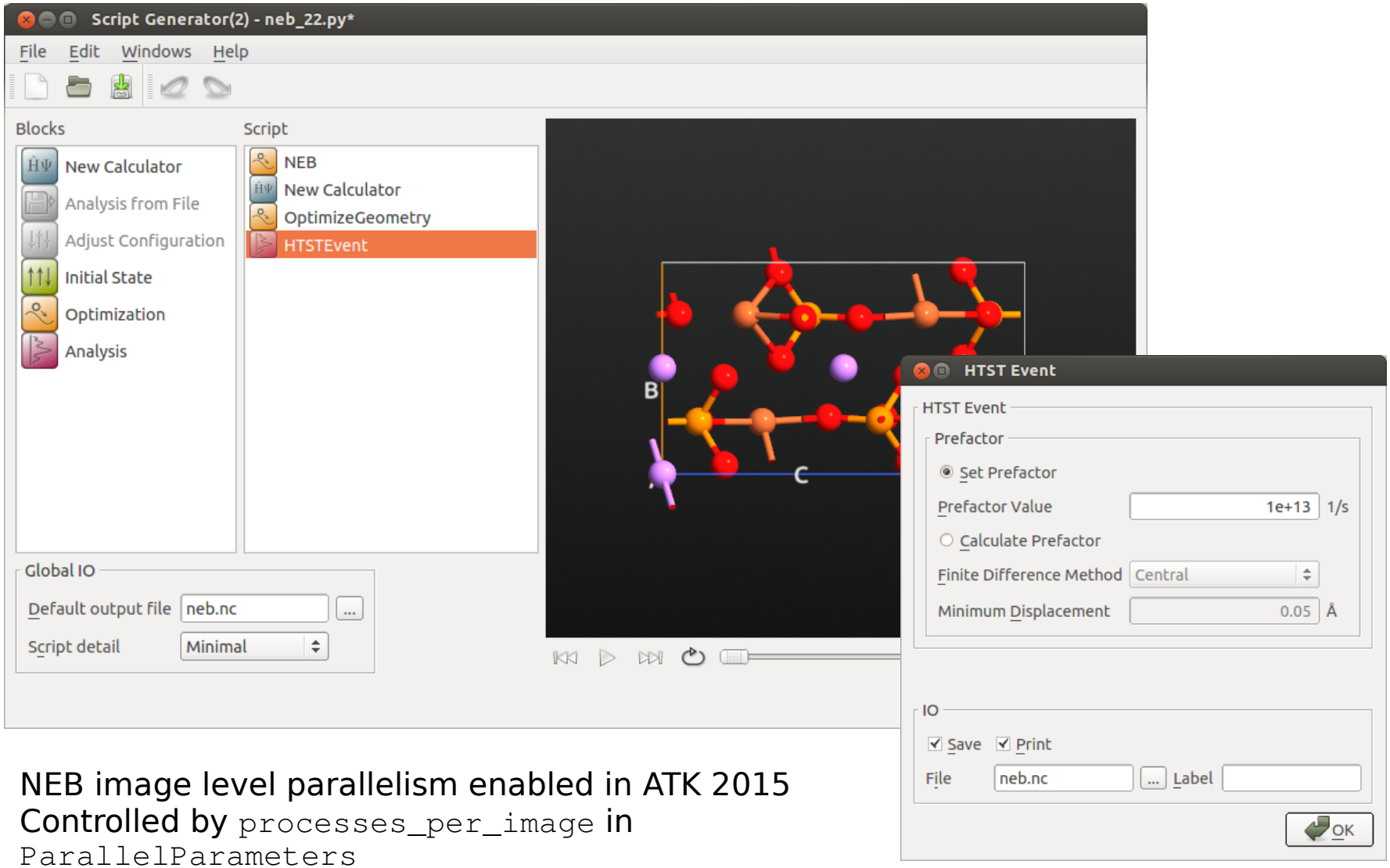
Create initial NEB trajectories (IDPP interpolation)



Linear interpolation - overlapping atoms, bad initial guess



Optimize Li diffusion path



NEB image level parallelism enabled in ATK 2015
Controlled by `processes_per_image` in `ParallelParameters`

Optimize Li diffusion path

```
+-------------------------------------------------------------------------------+
| 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.
...
```

- Information about parallelization, a warning will be printed when load balance problem is detected

```
+-------------------------------------------------------------------------------+
| NEB Optimization using the LBFGS optimizer                                    |
+-------------------------------------------------------------------------------+
| Iteration   Step Length    Max. Force  Max. Energy Image    Max. Energy       |
+-------------------------------------------------------------------------------+
|         0     0.000e+00     3.062e+01                 3       7.653375       |
|         1     1.448e-01     9.314e+00                 4       4.548878       |
...
|        75     1.659e-02     4.404e-01                 4       2.312291       |
|        76     7.696e-03     4.076e-02                 4       2.310350       |
+-------------------------------------------------------------------------------+
| NEB optimization converged after 76 steps.                                    |
+-------------------------------------------------------------------------------+
```

- Follow the convergence of the NEB trajectory

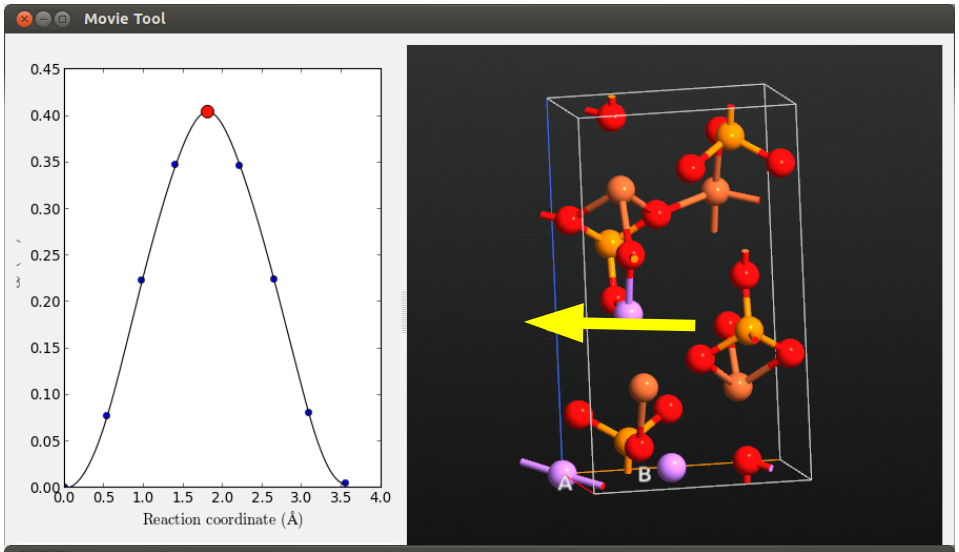
Optimize Li diffusion path

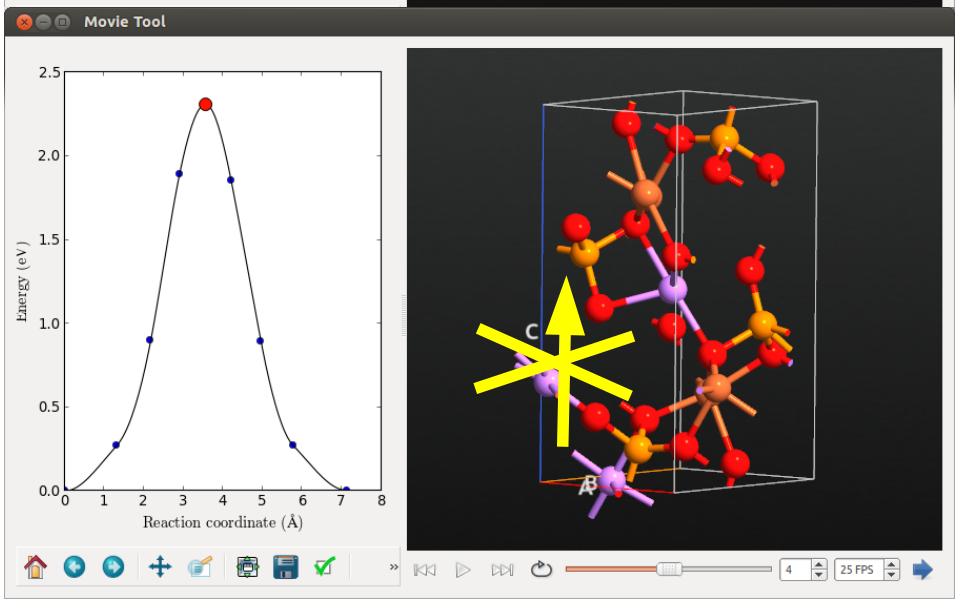
- Li diffusion along y axes:

  Barrier 0.41 eV

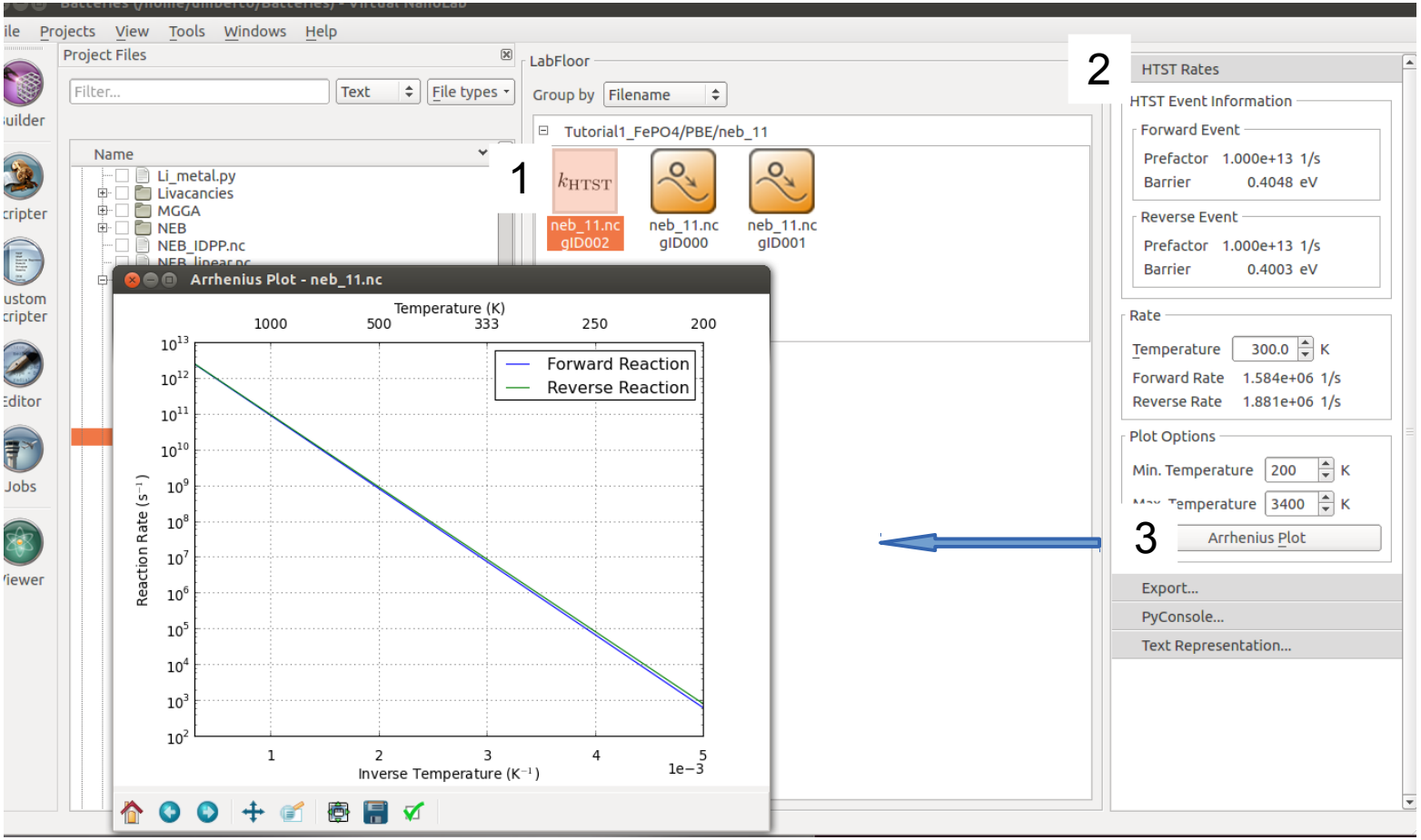
- Li diffusion along z axes:

  Barrier 2.31 eV





Calculate the reaction rates using harmonic transition state theory



	Barrier	k_{HTST} @ 300 K
y direction	0.41 eV	1.6 10^{6} s^{-1}
z direction	2.31 eV	1.5 10^{-26} s^{-1}

See Tutorial: *Calculating Reaction Rates using Harmonic Transition State Theory*
http://docs.quantumwise.com/tutorials/neb_htst.html