



Boron diffusion in Silicon

Introduction

This is a simple illustration to walk you through the steps required to perform transition state searches for diffusion of B in Silicon with MedeA-TransitionStateSearch. Please note that in general (with periodic boundary conditions) there is not an unique way to declare which atoms are moving how between initial and final structure: By displacing one or more atoms when creating the model, we can avoid complicated matching attempts as the order of atoms is unchanged and that's the first guess in the Transition State Search module.

1. Create the initial and final state

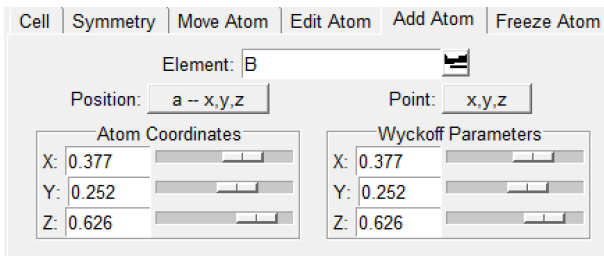
Required: *Si.sci* elemental cell of Silicon

Results: *B_in_Si_guess1.sci* B defect (with local relaxation) in Si

B_in_Si_guess2.sci B defect (with local relaxation) in Si

Let's start by building small cell with a vacancy on the Si lattice: Open the elemental cell of Si, for example from Structures/Elements/Si.sci and build a 2x2x2 supercell. Use **Edit>>Duplicate** to create working copy. Click on **Builders**, then **Build supercells...**, set the number of cells to 2, for a, b, and c direction and confirm with **OK**.

B on interstitial site

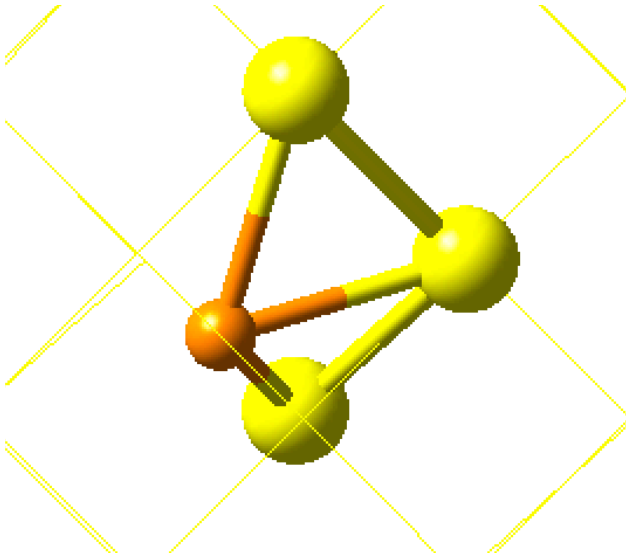


Now let's add a B atom with right-clicking and **Add atom...**. A Position close to stable configurations is for example 0.377, 0.252, 0.626 (in internal fractional cell coordinates). Please use the sliders or set the value for Wyckhoff positions, then confirm with **Apply** and **OK**.

The composition of the windows is updated, and reflects the added B atoms: Si₆₄B. This is our guess for the initial state.

With **Edit>>Rename** we can assign the name *B_in_Si_guess1*.

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Final State: B on Si lattice with Si interstitial

For the final state, we duplicate our defect model with **Edit>>Duplicate**.

| | | | | | |
|------------------|----------|--------------------|-----------|----------|---------------|
| Cell | Symmetry | Move Atom | Edit Atom | Add Atom | Freeze Atom ▶ |
| Atom: | B | Point: | x,y,z | | |
| Atom Coordinates | | Wyckoff Parameters | | | |
| X: | 0.557 | X: | 0.557 | | |
| Y: | 0.311 | Y: | 0.311 | | |
| Z: | 0.561 | Z: | 0.561 | | |
| OK | | Cancel | | Apply | |

Select the B atom, click on it to turn it white, then right-click and use **Atom>>Move** to place it at

at 0.557, 0.311, 0.561. Confirm with **Apply** and **OK**, then rename the model with **Edit>>Rename** to B_in_Si_guess2. Now we need to move the Si, which was in this local to an interstitial site, to 0.665, 0.418, 0.669.

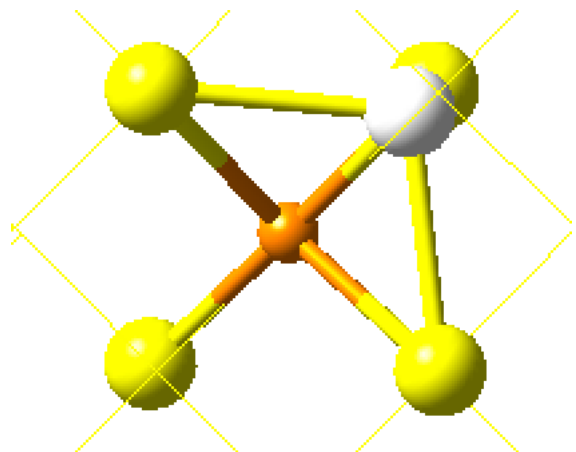
If you like to display the defect complex, recreate bonds with right-click and **Edit bonds...**, followed by **Apply** and **OK** to recreate default bonds. Select the B atom, right-click and **Selection >>Expand selection by**

one bond, then **Selection >>Invert** to select all other atoms.

Then change the display mode to “mixed mode”:



Right-click and use **Selection >>Display as Lines** to make the turn all Si-Si bonds into less prominent lines.



2. Optimize the initial and final state

Results: B_in_Si_initial.sci..... B (with local relaxation) in Si

B_in_Si_final.sci..... B (with local relaxation) in Si



With Vasp5 we can quickly relax the atoms around the vacancy. Load VASP from **Tools >>VASP5.3**. The VASP5.3 item appears in the top menu. Click on **VASP5.3**, then **Run**. Even if we are dealing with a semiconductor, we don't need a higher level method such as hybrid functionals to describe the atomic structure around a defect, we will use rather coarse settings in VASP: *Type of Calculation*: **Structure Optimization** with only **Relax atom positions** selected. In *General Setup* set *Precision*: **Low** and *Projection*: **Real space**. On the **SCF** tab under *K-mesh in Brillouin zone for SCF* set *Spacing of k-points* to 2 to ensure that only a single k-points is used. There is an optimized VASP executable for this type of calculations. Now give your calculation a proper title and click on **Run**. A dialogue window will ask you how which queue and how many cores to use.

Now select the window with the final state and click on **VASP5.3**, then **Run**. This brings up the VASP settings we just changed. No further changes needed. Assign a proper title and launch the calculation with **Run**.

After the optimizations completed, load the minimized structure from the JobServer. Click on **File>>Open>>Previous Calculation** and select the two minimized structures, bring them to the right of the Window by using the **Insert>>** bar and confirm with **OK**. To avoid confusion, rename the two structures: Select their wind in MedeA, and use **Edit>>Rename...** to change guess1 to Si_2x2x2_vac_initial. The window's name starts with composition (spacegroup) ~ and the following part, which can be changed, like the job number and minimized and the name of the original structure. Do the same for Si_2x2x2_vac_final based on guess2. As soon as you submit a calculation with these structures, they are saved on the JobServer. If you spend considerable time to create a model, but don't want to submit a calculation right now, use **File>>Export** to save the structure to your disk

3. Setting up the Transition State Search

Required: *B_in_Si_initial.sci..... vacancy (with local relaxation) in Si*

B_in_Si_final.sci..... vacancy (with local relaxation) in Si

Select **Tools>>Transition State Search** to add this time to the top menu. Select window with the initial structure, then click on **Transition State Search** to open the dialogue window to define the search:

First, you need to select the final state, and all systems with the same composition as the selected initial structure are displayed in this pull-down menu. Choose Si_2x2x2_vac_final.

The first tab, **Calculation**, does not require any changes, we'll use **Map out the minimum energy path by elastic band methods** and keep the *Initial Images* from **linear interpolation**. The next tab, **Configurations**, is used to see how much the individual atoms are apart between initial and final stage. The last tab, **Elastic Band**, requires our attention: We keep *Number of images* to 3, set *Number of refinement steps* to 1. Check *Climbing image close to Saddle point*. We speed up the calculation by requesting a less demanding *Convergence criterion* under *Parameters for elastic band optimization*: Set *Convergence* to 1, and reduce the *Maximum number of steps* to 100. We can uncheck *Start form wavefunctions of previous iteration*.

Under **VASP Settings** we set as before: In *General Setup* set *Precision*: **Low** and *Projection*: **Real space**. On the **SCF** tab under *K-mesh in Brillouin zone for SCF* set *Spacing of k-points* to 2 to ensure that only a single k-points is used.

While the calculation is running, you find information on the progress of the calculation on the Hobserver, open **Job Control>>View and Control Job** and select the number of this Job and then click on Job.out. Depending on when you click, you might see just parts of the information shown below.

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You can reload this page to get more progress information.

4. Results from the Transition State Search

Results: *transitionstate_initial.sci.... from JobServer*

neb<X>_image<N>.sci..... on JobServer as well

Job.out will be populated with the following information:

```
Nudged Elastic Band for mapping the minimum energy path between
the initial system B_in_Si_2 and the final system B_in_Si_1
with 3 intermediate images and a spring constant of 5 eV/Ang^2 and 1 refinement steps.
```

```
The initial images are created from linear interpolation.
Transition states are searched for the highest saddle point only.
Optimization of transition states is attempted.
The image closest to a saddle point is allowed to climb up into the saddle point
if the largest force on an atom is smaller than 1.0 eV/Ang.
Double nudging is applied.
```

```
Optimization parameters:
Convergence: 0.25 eV/Ang
Number of steps: 100
Diagonal elements of the inverse Hessian are initially set to 0.01 Ang^2/eV.
-----
```

VASP parameters and results from the Elastic Band calculations

After some initial steps the gradient of the chain is small enough, that the location of image with the highest energy is climbing along the path closer to the expected transition state.

```
This is a calculation based on density functional theory and the GGA-PBE exchange-correlation functional for
describing the interactions.
Since no magnetic moments are in the model, this is a non-magnetic calculation using 'low' precision and a default
planewave cutoff energy of 238.960 eV.
The electronic iterations convergence is 1.00E-06 eV using the Very Fast (RMM-DIIS) algorithm and real space
projection operators.
The requested k-spacing is 1 per Angstrom, which leads to a 1x1x1 mesh.
This corresponds to actual k-spacings of 0.580 x 0.580 x 0.580 per Angstrom.
The k-mesh is forced to be centered on the gamma point.
sing first order Methfessel-Paxton smearing with a width of 0.2 eV.
```

```
=====
Using GGA-PBE / PAW potentials:
```

```
Si
B
```

```
VASP energy of initial and final boundary images in kJ/mol per cell:
```

```
neb0_image00    -33098.439
neb0_image04    -33128.774
```

| Iter | Energy_total | max grad | image01 | image02 | image03 | Climbing | Iter_accepted |
|------|--------------|----------|------------|------------|------------|----------|---------------|
| 1 | -98923.22 | 3.69858 | -32988.816 | -32918.169 | -33016.238 | | |
| 2 | -98986.72 | 2.67156 | -33001.247 | -32951.380 | -33034.092 | 1 | |
| 3 | -99073.62 | 1.23797 | -33026.971 | -32989.463 | -33057.190 | 2 | |
| 4 | -99091.55 | 1.44191 | -33028.882 | -32999.311 | -33063.355 | 3 | |
| 5 | -99038.75 | 2.30957 | -33016.288 | -32974.039 | -33048.421 | | |
| 6 | -99093.38 | 0.55991 | -33028.053 | -33001.219 | -33064.108 | 4 | |
| 7 | -99097.02 | 1.27001 | -33029.019 | -33002.754 | -33065.244 | 5 | |
| 8 | -99110.25 | 1.20939 | -33033.264 | -33007.459 | -33069.528 | 6 | |
| 9 | -99124.45 | 1.04641 | -33036.214 | -33014.681 | -33073.555 | 7 | |
| 10 | -99135.91 | 0.55991 | -33038.276 | -33020.994 | -33076.643 | 8 | |
| 11 | -99143.15 | 0.85405 | -33039.624 | -33024.862 | -33078.663 | 2 | 9 |
| 12 | -99150.70 | 0.78363 | -33040.999 | -33028.592 | -33081.112 | 2 | 10 |
| 13 | -99150.52 | 0.66141 | -33040.937 | -33028.424 | -33081.156 | 2 | 11 |
| 14 | -99153.20 | 0.86004 | -33041.512 | -33029.238 | -33082.446 | 2 | 12 |
| 15 | -99153.32 | 0.59811 | -33041.984 | -33028.950 | -33082.385 | 2 | 13 |



| | | | | | | | |
|----|-----------|---------|------------|------------|------------|---|----|
| 16 | -99156.37 | 0.81372 | -33044.117 | -33029.283 | -33082.975 | 2 | 14 |
| 17 | -99156.90 | 0.59059 | -33044.811 | -33029.257 | -33082.827 | 2 | 15 |
| 18 | -99160.62 | 0.77829 | -33049.657 | -33030.296 | -33080.667 | 2 | |
| 19 | -99159.68 | 0.42994 | -33047.514 | -33030.103 | -33082.067 | 2 | 16 |
| 20 | -99159.36 | 0.46699 | -33048.798 | -33029.882 | -33080.678 | 2 | 17 |
| 21 | -99158.41 | 0.43936 | -33052.466 | -33029.389 | -33076.557 | 2 | 18 |
| 22 | -99157.11 | 0.40379 | -33053.995 | -33028.706 | -33074.406 | 2 | 19 |
| 23 | -99157.91 | 0.30213 | -33055.865 | -33028.941 | -33073.100 | 2 | 20 |
| 24 | -99160.06 | 0.34163 | -33057.720 | -33029.914 | -33072.424 | 2 | 21 |
| 25 | -99161.27 | 0.22432 | -33058.486 | -33030.433 | -33072.350 | 2 | 22 |

Iterations: 22 using 25 calls to the function
Energy: -99161.26964229

Refinement (with identical VASP settings)

Refinement step 1 between image 1 and image 3:

| Iter | Energy_total | max grad | image01 | image02 | image03 | Climbing | Iter_accepted |
|------|--------------|----------|------------|------------|------------|----------|---------------|
| 1 | -99066.79 | 1.12847 | -33019.052 | -33010.661 | -33037.075 | | |
| 2 | -99075.72 | 0.78759 | -33020.829 | -33014.695 | -33040.196 | 1 | |
| 3 | -99098.28 | 0.86242 | -33026.148 | -33024.330 | -33047.799 | 2 | 2 |
| 4 | -99099.45 | 0.69341 | -33026.287 | -33024.959 | -33048.202 | 2 | 3 |
| 5 | -99102.03 | 0.55976 | -33027.112 | -33026.012 | -33048.910 | 2 | 4 |
| 6 | -99106.75 | 0.62847 | -33028.534 | -33027.889 | -33050.326 | 2 | 5 |
| 7 | -99114.47 | 0.58966 | -33030.586 | -33031.102 | -33052.779 | 2 | 6 |
| 8 | -99118.69 | 0.43568 | -33031.801 | -33032.836 | -33054.050 | 2 | 7 |
| 9 | -99122.91 | 0.36931 | -33033.386 | -33034.355 | -33055.172 | 2 | 8 |
| 10 | -99124.63 | 0.43224 | -33034.361 | -33034.857 | -33055.412 | 2 | 9 |
| 11 | -99125.35 | 0.46766 | -33035.291 | -33034.860 | -33055.201 | 2 | 10 |
| 12 | -99125.58 | 0.32672 | -33035.835 | -33034.772 | -33054.971 | 2 | 11 |
| 13 | -99127.81 | 0.36245 | -33037.647 | -33035.310 | -33054.857 | 2 | 12 |
| 14 | -99128.19 | 0.36018 | -33038.379 | -33035.332 | -33054.478 | 2 | 13 |
| 15 | -99130.35 | 0.29333 | -33039.881 | -33036.003 | -33054.470 | 2 | 14 |
| 16 | -99131.32 | 0.19031 | -33040.535 | -33036.362 | -33054.418 | 2 | 15 |

Iterations: 15 using 16 calls to the function
Energy: -99131.31501298

Final Optimization

The RMM-DIIS optimizer can converge to the closest saddle point and do uphill convergence of the moving B atoms and its neighbors. This uphill effect can be overshadowed by relaxation of Si atoms farther away from the defect. If you are interested not only in the activation energy of the reaction pathway, but in the atomic structure of the transition state and its vibrational properties, this optimization should be done with better precision.

```
Results for the attempted transition state optimization:
-----
There are 1 symmetry-unique k-points
The plane wave cutoff is 238.96 eV
WARNING: The geometry optimization is not converged after 100 steps!
  VASP energy:                -342.519654 eV for Si64
  Initial VASP energy:        -342.397850 eV for Si64B
  Relaxation energy:          -0.121804 eV gained after 100 optimization steps.
Electronic contributions:
  Empirical Formula          Cell
  Si64B                      Si64B
VASP Energy                  -33048.115          -33048.115 kJ/mol
Cell parameters:
  Parameter Value
  a          10.837260
  b          10.837260
  c          10.837260
  alpha     90.000000
  beta      90.000000
  gamma     90.000000
  Volume    1272.795052 Ang^3
  Density:  2.359 Mg/m^3
```

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The pressure given below is exerted by the system according to its volume.
Positive pressure would cause expansion during full geometry optimization.

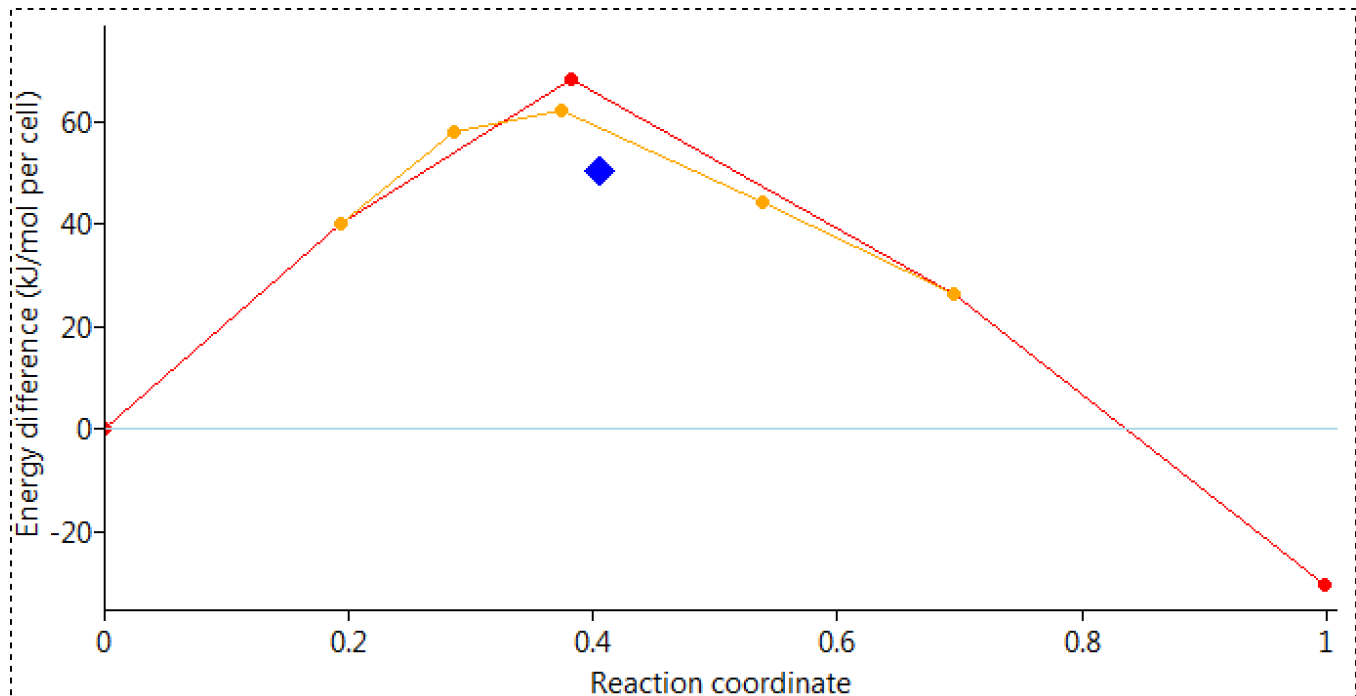
```
Pressure:      3.813 GPa
              =      38.130 kbar
Stress:
      XX      YY      ZZ      XY      YZ      ZX
      -4.785  -3.319  -3.335  0.260  -0.110  -0.360 GPa
      =
      -47.848 -33.195 -33.352  2.598  -1.100  -3.604 kbar
```

The stress tensor above is imposed on the system, i.e. negative values of diagonal components would cause expansion of the corresponding lattice parameter upon full geometry optimization. The pressure and stress include only electronic terms, i.e. the vibrational, temperature and other terms are not included here.



5. Analysis of the reaction Path

You can open this graph from **Transition State Search>>Energy Profile** and select the profile from the completed job. In this graph, the red line connects the energies from the intermediate images, the orange line shows the results from the first refinement step, between images 1 and 3, which lowers the barrier a little bit, but confirms the overall shape of path with one saddle point. The attempted optimization of the transition state does not exhibit any uphill climbing, but this is a little bit out of scope for this illustrative example.



The uphill convergence can be slow, as evidenced in the 100 steps taken without fully reaching the required convergence criterion. However, when you analyze the trajectory to the transition state optimization, the energy barely changes. This is an illustrative example and not much is gained in getting too ambitious. It's much better to take this as a starting point to look into the optimization of the transition state with higher cut-off (**Standard500**) and a finer k-mesh (e.g $k=0.5/\text{\AA}$).

6. Next steps you can take

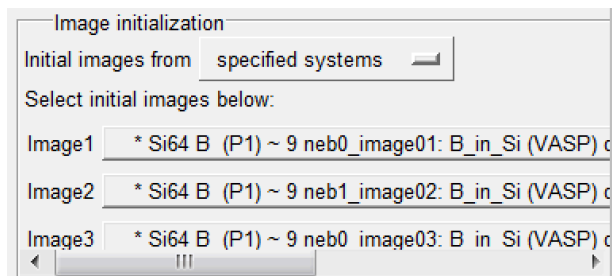
Charged defects

We can easily compare this neutral defect with a charged counterpart. MedeA-VASP has a convenient option to set the charge state of a defect. On VASP's calculation panel set *Charge State*: **+1** e.

Take the optimized structures as the input for the new Transition State Search simply change the Background Charge in **VASP Settings**: *Charge State*: **+1** e. Please note that the VASP settings in Transition State Search are independent of the general VASP settings, so don't forget the check twice.

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Higher precision



For vibrational properties of the transition state, we should use more accurate forces: Increasing *Precision* to **Normal** or, even better, **Standard 500**, which is a better choice for comparing activation energies with different defect atoms.

You can start a more accurate calculation with the images from this calculation: Open the intermediate structures through **File>>Open>>Previous**

Calculation, select the initial state, then change *Image initialization* to **specified systems**:

Modules Required:

- **VASP5.3**
- **Transition State Search**