

Table of Contents

Table of Contents	1
Using the Crystal Builder	2
Introduction	2
Crystal structure of black phosphorus	3
Phosphorene and its bandstructure	7
Bandstructure	9
References	10



Using the Crystal Builder

Version: 2016.0

Downloads & Links



PDF

[Introduction to QuantumATK](#)

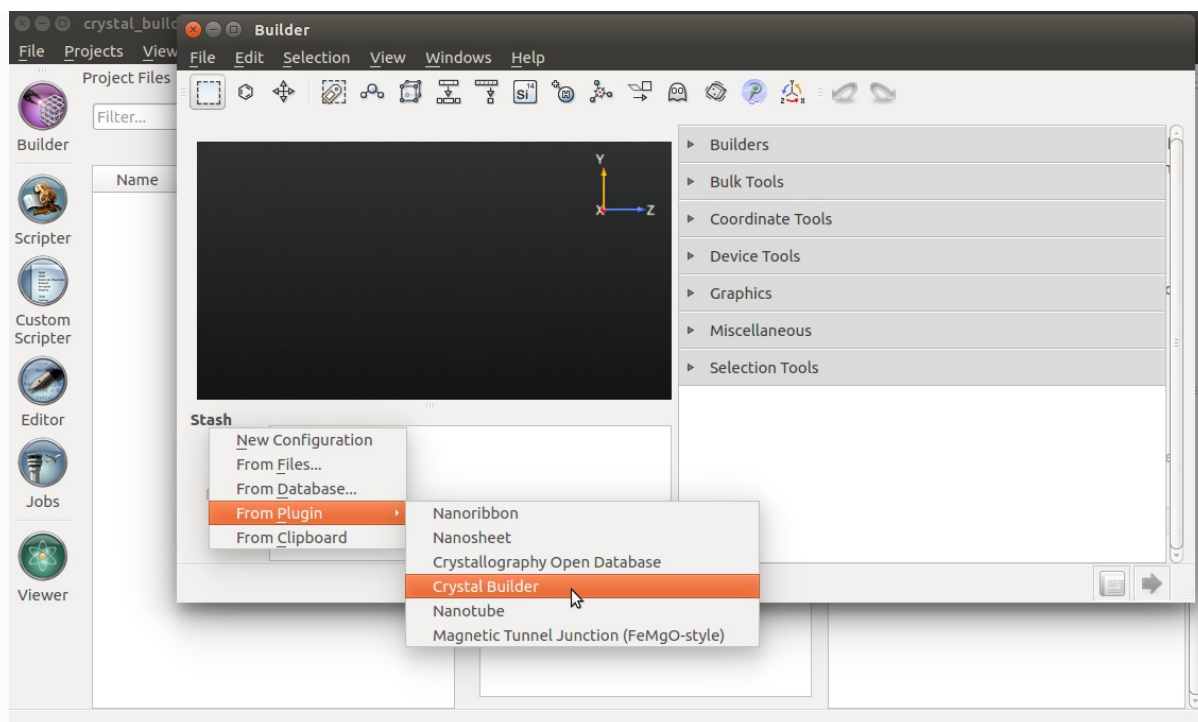
[ATK Reference Manual](#)

In this tutorial you will learn how to build a crystalline structure by knowing all the relevant information about it (space group, lattice parameters, and atomic positions). You can then use QuantumATK to perform calculations for the crystal, or export the structure as a CIF file for use with other software.



Introduction

QuantumATK has a tool, **Crystal Builder**, which makes it easy to create crystal structures by specifying parameters for the lattice and atom coordinates. The tool is a plugin for the QuantumATK **Builder** and can be found under Add ► From Plugin ► Crystal Builder.



Crystal structure of black phosphorus

As an example, this tutorial focuses on phosphorene (a monolayer of black phosphorus), which is attracting attention in electronics due to its analogy with graphene (see [chemistryworld](#) and, e.g., Refs. [LNZ+14a], [LNZ+14b], and [LYY+14].)

The table below lists the relevant information about the black phosphorus crystal [BR65]; space group and lattice constants, and Wyckoff positions for the phosphorus atoms. Based on that information, we first construct the bulk crystal, from which phosphorene is then created.

Space group	$Cmca$ (#64)
a	3.3136 Å
b	10.478 Å
c	4.3763 Å
Atom positions	
P	8f: (0, 0.10168, 0.08056)

Hint

Basics of Crystallography

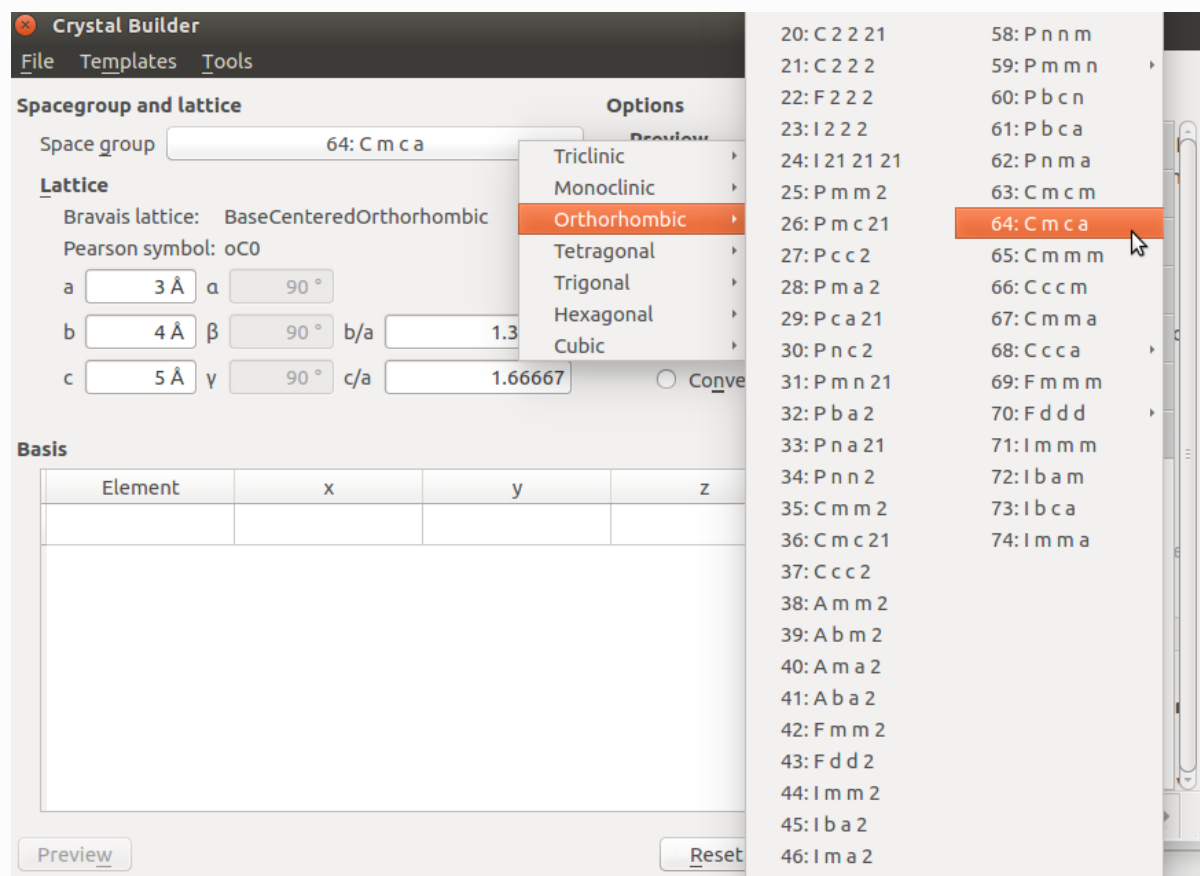
- There are in total 230 space groups, which are enumerated and symbolized in crystallography. In Hermann–Mauguin notation, the 64th group is represented by " $Cmca$ " (a new notation " $Cmce$ " is also used). See, e.g., Ref. [Hah05] for more details.
- Wyckoff positions indicate the positions that atoms are allowed to occupy in a lattice belonging to a particular space group. These are specified in fractional coordinates, e.g., (0, 0.10168, 0.08056) in the case of black phosphorus. For each space group, the Wyckoff positions are confined to certain areas in the lattice, e.g., only on the yz-plane in the case of black phosphorus, so as to give all lattice points which are transformed from one another by the symmetry operations belonging to the group.

- Wyckoff positions are denoted according to multiplicity (number of equivalent atoms in a unit cell) and Wyckoff letter (defined for each Bravais lattice). In the case of black phosphorus, the multiplicity is 8 and the Wyckoff letter is “f”.

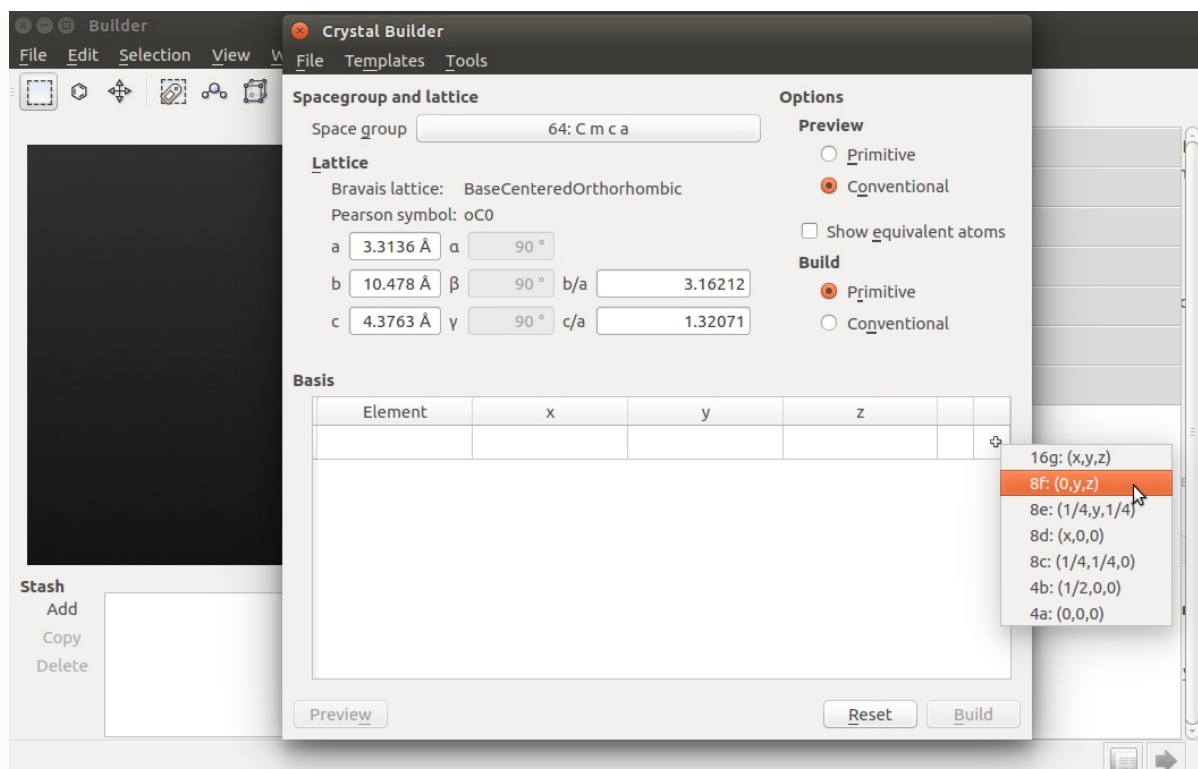
Attention

The information given in the table above is enough to fully define the black phosphorus crystal. Inserting P atoms in the Wyckoff position 8f of the lattice with space group #64 yields the black phosphorus crystal.

Let us now build the bulk configuration. First, open the **Crystal Builder** plugin, and select space group “64: C m c a”, which is orthorhombic:

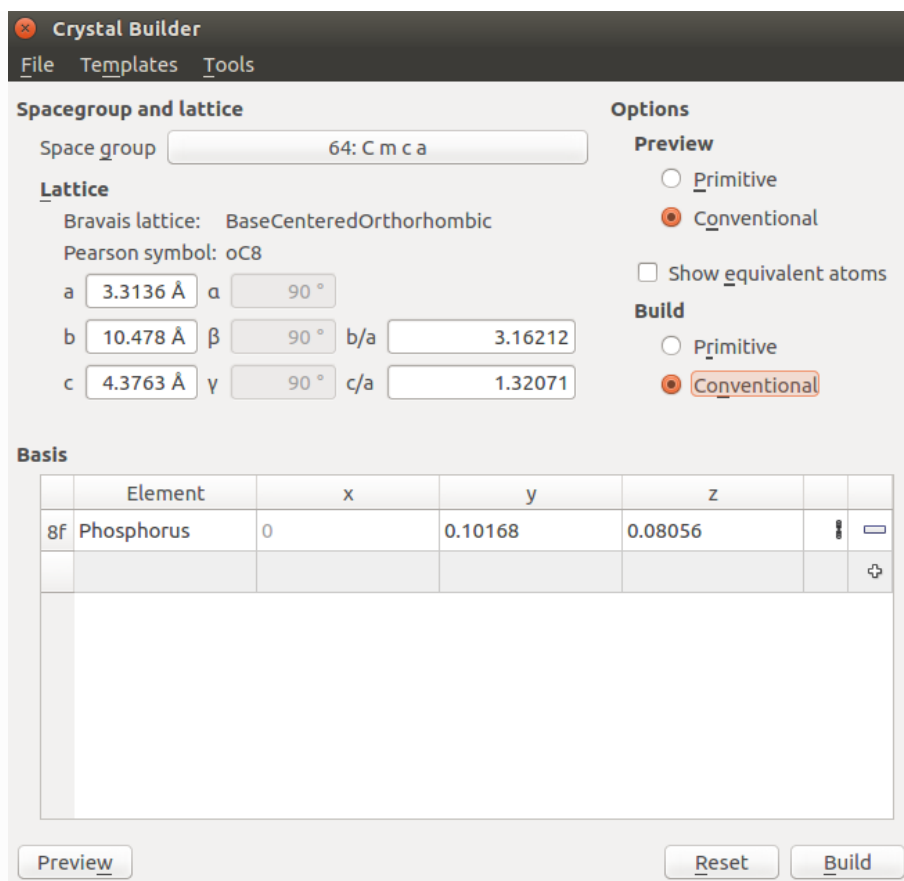


Then insert the a, b and c lattice parameters as listed in the table above, and click the “+” button to add one atom at the Wyckoff position 8f: (0,y,z).

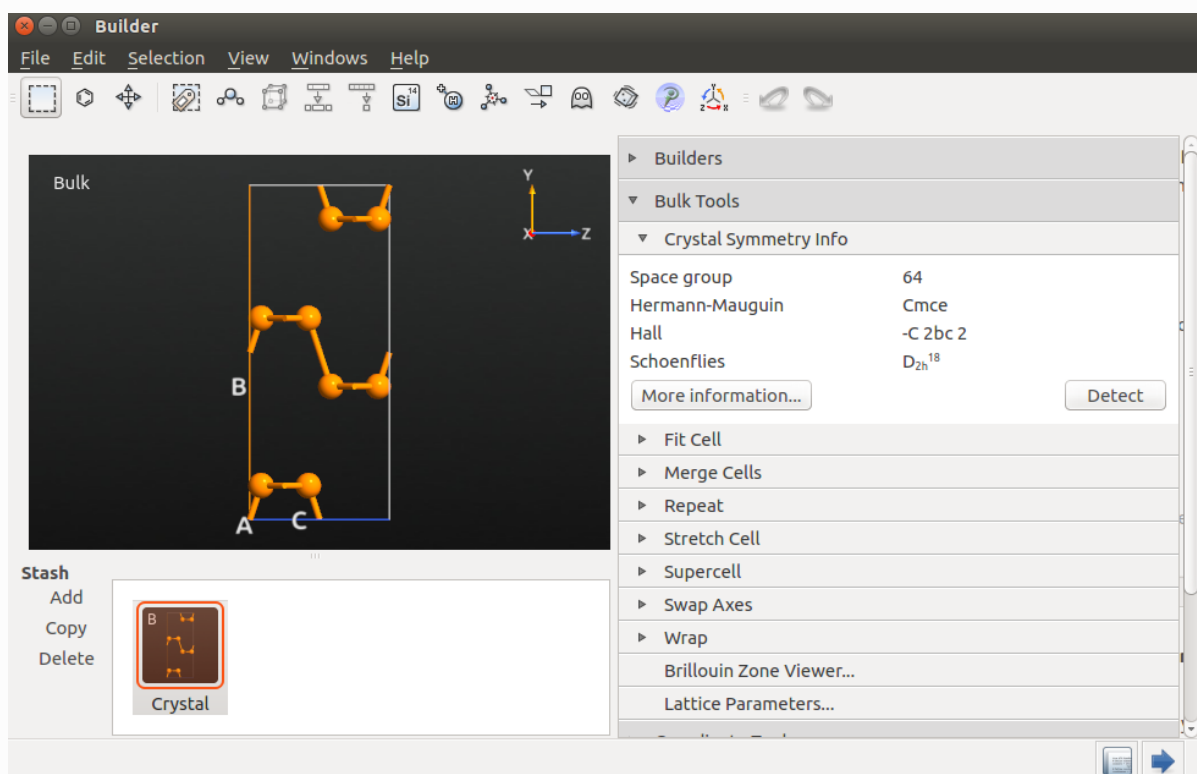


Change the newly added element from hydrogen to phosphorus, and change its y and z positions according to the table above, $y=0.10168$, $z=0.08056$ (fractional coordinates). While making these operations, you will see a preview of the structure in the Builder main window.

By default, the Crystal Builder will preview the *conventional* unit cell, but actually build the *primitive* cell. This usually has computational advantages, but in this case the conventional cell is more convenient for the subsequent manipulations needed to prepare the monolayer. Therefore, choose the conventional cell and click **Build** to create your structure.




The black phosphorus crystal is added to the Stash in the Builder, and is ready for further manipulations. Before moving on, open Bulk Tools ► Crystal Symmetry Info and check the symmetry to make sure that the system is truly black phosphorus.



Tip


You can do **3D** rotations and **2D** rotations of any configuration: Simply **click and hold down the right mouse-button** and move the cursor.

- Moving the cursor **inside the Viewer window** gives you **3D** rotations.
- Moving the cursor **outside the Viewer window** gives you **2D** rotations.
- Also note that the cursor changes when you are in rotate mode: 

Phosphorene and its bandstructure

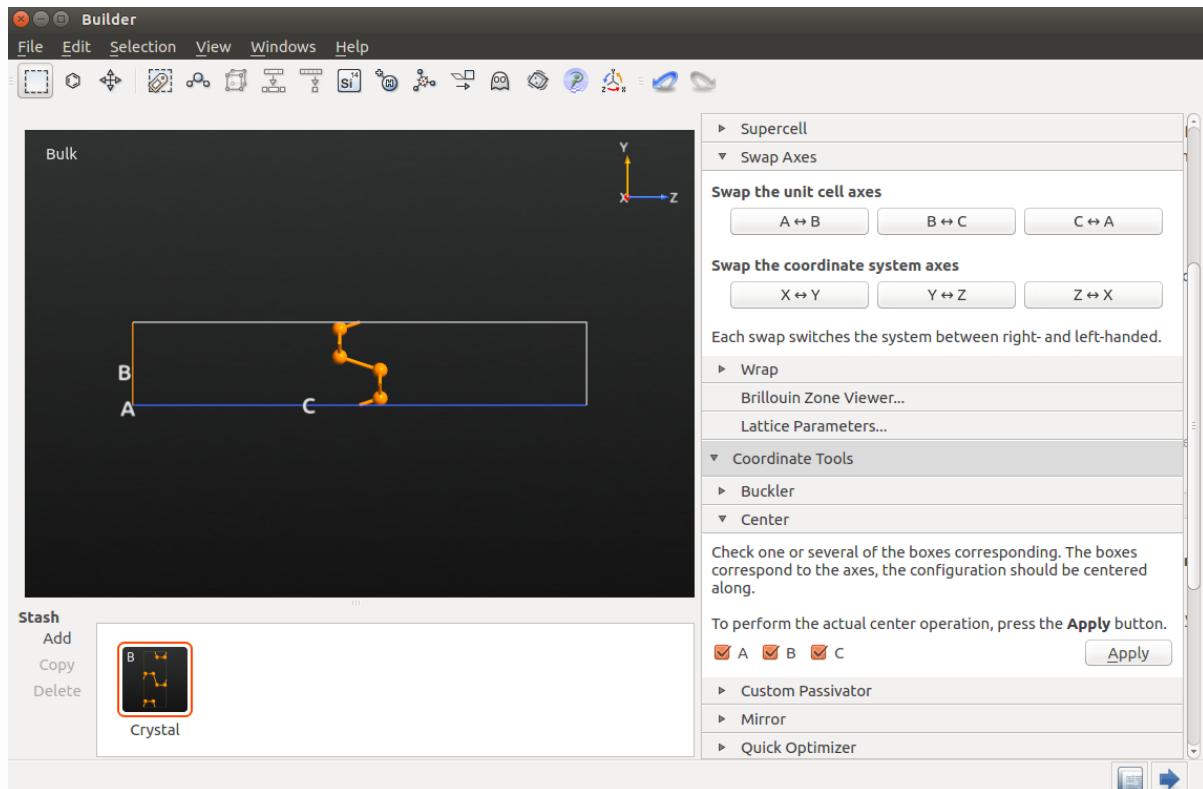
One very interesting feature of black phosphorus is the interesting electronic properties when the material is two-dimensional. The name “phosphorene” was introduced by Liu *et al.* for such a 2D p-type material [LNZ+14a].

Now that you have created black phosphorus, you can easily “exfoliate” that bulk structure, create phosphorene, and then analyze its electronic properties.

You can find many tutorials on how to use the  Builder to create and modify your system and running QuantumATK calculations, see in particular [QuantumATK tasks and workflows](#) and [Tubes, ribbons and other 1D nanostructures](#). Below is a brief example of what you can do with phosphorene – the results can be compared with Ref. [LNZ+14a].

The image below shows phosphorene, created in the QuantumATK Builder by following these steps:

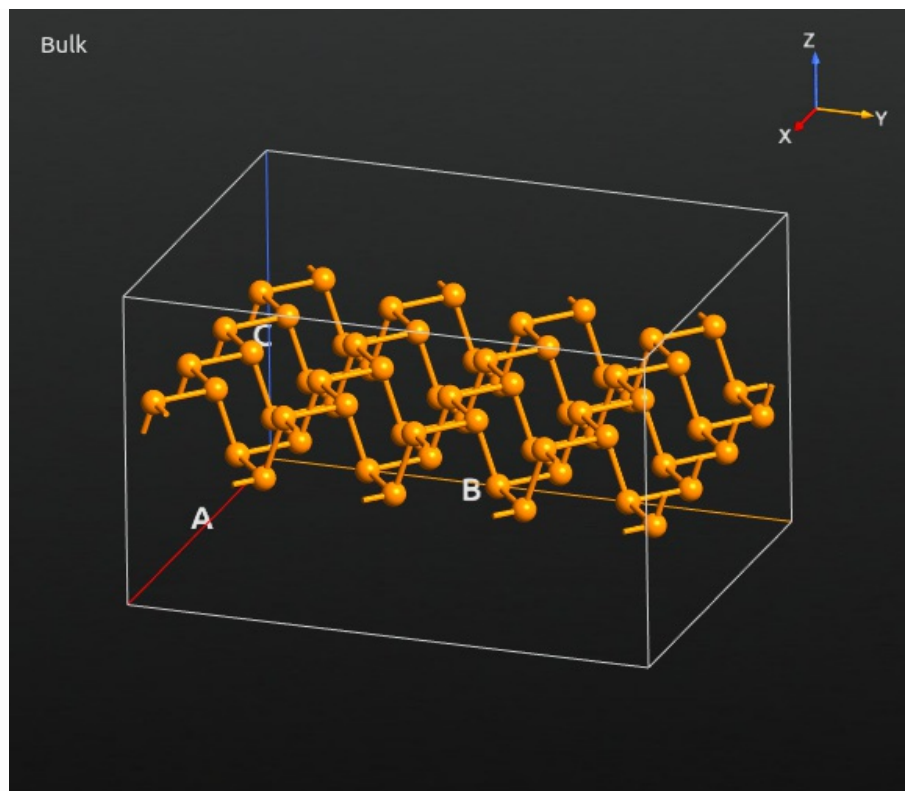
1. Open the Bulk Tools ▶ Swap Axes tool and click B-C and Y-Z in order to align the phosphorene plane perpendicular to the C axis.
2. The lattice type has now been reset. You therefore need to open Bulk Tools ▶ Lattice Parameters and select *Simple Orthorhombic* as the lattice type.
3. Delete four P atoms such that you have a monolayer.
4. Open again the Bulk Tools ▶ Lattice Parameters tool and increase the C vector length to 24 Å. This adds a vacuum region along the non-periodic C-direction.
5. Finally, use the Coordinate Tools ▶ Center tool to center the configuration in the unit cell.




Hint

Meanings of these manipulations

- Manipulation 1 sets each layer to be normal to the z axis, and the zigzag and armchair directions to be parallel to the x and y axes, respectively.
- Manipulation 3 ensures that each conventional unit cell contains a monolayer.
- Manipulation 4 then increases the distance to the repeated images of the monolayer along the C-direction, such that they are electronically decoupled. The configuration thereby represents a true monolayer.
- The snapshot below shows the monolayer obtained after manipulations 1–5 (the structure is repeated 3 times along A and B in order to clearly visualize the monolayer).
- The definition of the first Brillouin zone of the monolayer depends on the orientation of the unit cell in real space ("ABC" with respect to "XYZ"), as well as the orientation of the atoms in the cell (atom positions with respect to "ABC"). Manipulations 1–5 provide the same orientations as in Refs. [LNZ+14a] and [LNZ+14b], and therefore the same first Brillouin zone as in those references.

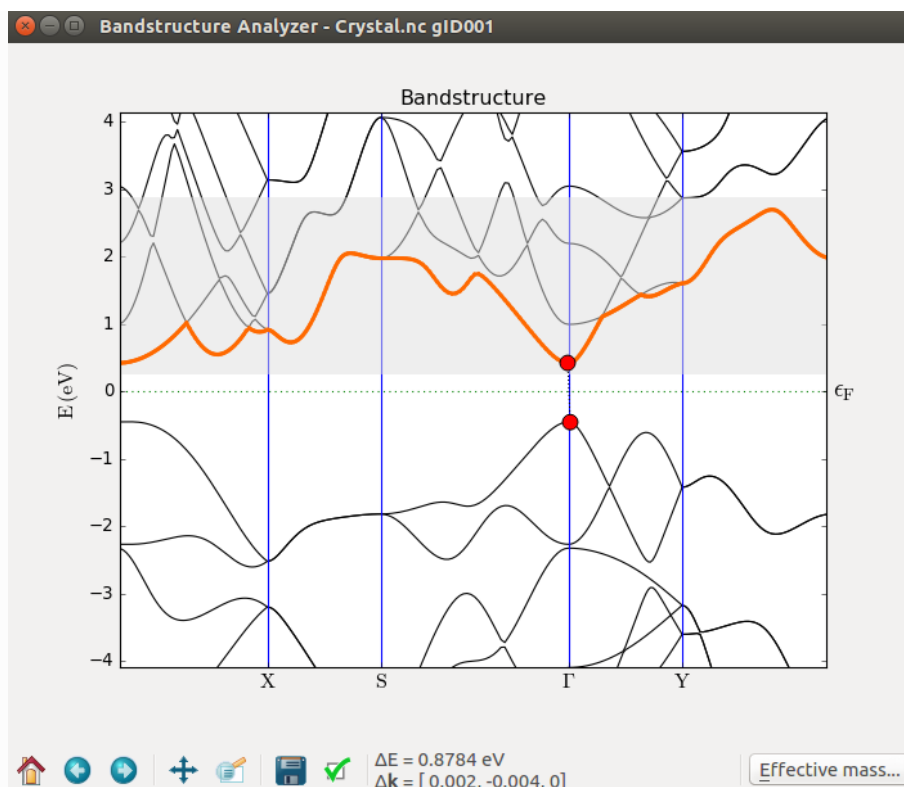


Note

You can export this configuration to a CIF file. Once you have the configuration in the  **Builder Stash**, you can use the File ► Export Configuration menu or simply right-click the configuration.

Bandstructure

Finally, calculate the bandstructure of phosphorene along the X–S–G–Y Brillouin zone path. The band structure along this path is shown in Refs. [\[LNZ+14a\]](#) and [\[LNZ+14b\]](#). You should find a band gap of about 0.87 eV, in agreement with the results in these references.



The following ATK-DFT calculator parameters have been used:

- PBE exchange-correlation functional.
- Norm-conserving FHI pseudopotential.
- *DoubleZetaPolarized* basis set.
- 90 Hartree density mesh cutoff energy.
- 8x8x1 k-point sampling grid.

References

- [BR65] A. Brown and S. Rundqvist. Refinement of the crystal structure of black phosphorus. *Acta Crystallographica*, 19(4):684–685, Oct 1965. URL: <http://onlinelibrary.wiley.com/doi/10.1107/S0365110X65004140/abstract>.
- [Hah05] T. Hahn, editor. *International Tables for Crystallography Volume A: Space-Group Symmetry*. Springer, 2005.
- [LYY+14] Likai Li, Yijun Yu, Guo Jun Ye, Qingqin Ge, Xuedong Ou, Hua Wu, Donglai Feng, Xian Hui Chen, and Yuanbo Zhang. Black phosphorus field-effect transistors. *Nat Nano*, 9(5):372–377, may 2014. doi:10.1038/nnano.2014.35.
- [LNZ+14a] (1, 2, 3, 4, 5) H. Liu, A.-T. Neal, Z. Zhu, D. Tomanek, and P.-D. Ye. Phosphorene: a new 2d material with high carrier mobility. *ArXiv e-prints*, January 2014. arXiv:1401.4133.
- [LNZ+14b] (1, 2, 3) Han Liu, Adam T. Neal, Zhen Zhu, Zhe Luo, Xianfan Xu, David Tománek, and Peide D. Ye. Phosphorene: an unexplored 2d semiconductor with a high hole mobility. *ACS Nano*, 8(4):4033–4041, 2014. doi:10.1021/nn501226z.

