2^{nd} Tutorial:

Periodic Systems

Hands-on Tutorial Workshop 2014

Lydia Nemec and Björn Bieniek

Fritz Haber Institute of the Max Planck Society

23rd July 2014

Outline of this tutorial

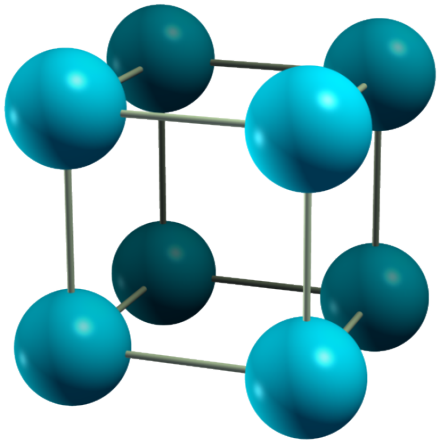
1. Periodic systems with DFT
   - The crystal structure
   - Sampling of the Brillouin zone
   - Band structure and density of states
   - Find minimal lattice constant
2. Systems of interest
   - Bulk Silicon
   - Silicon surface
3. Overview

Periodic systems with DFT

- The crystal structure
- Sampling of the Brillouin zone
- Band structure and density of states
- Find minimal lattice constant

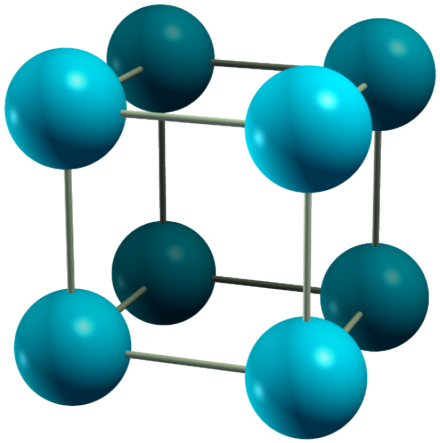
The crystal structure

The crystal lattice: First examples

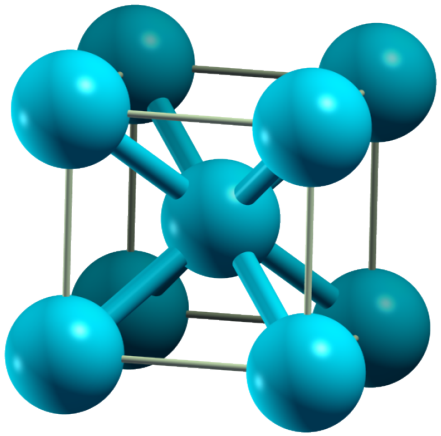


simple cubic

The crystal lattice: First examples

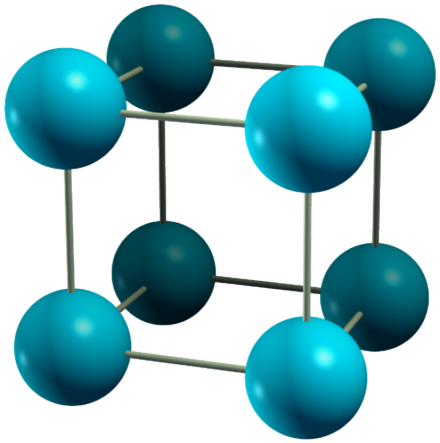


simple cubic

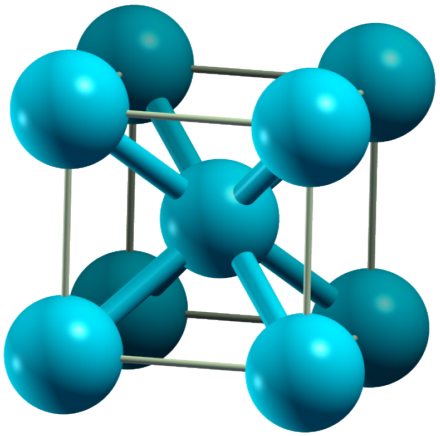


BCC

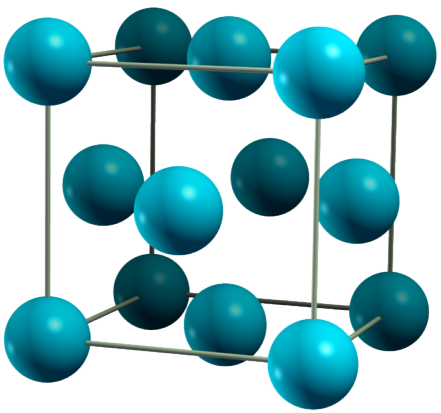
The crystal lattice: First examples



simple cubic

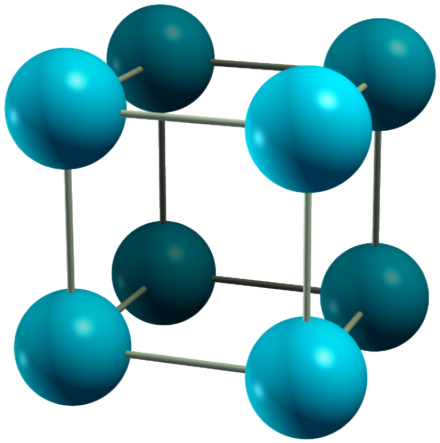


BCC

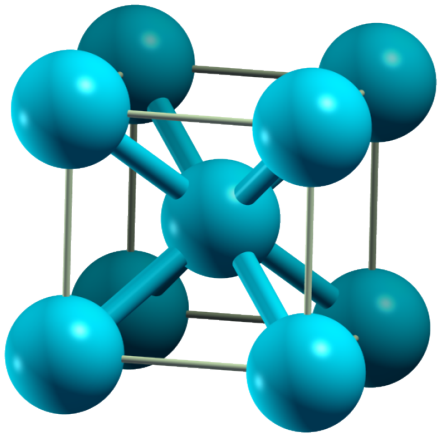


FCC

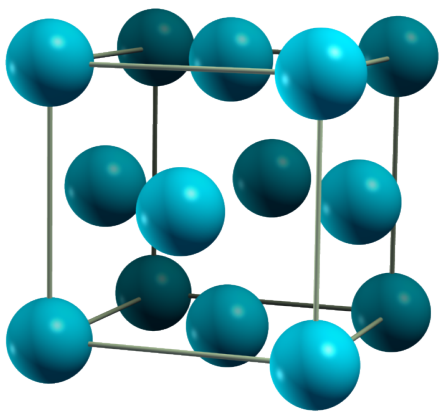
The crystal lattice: First examples



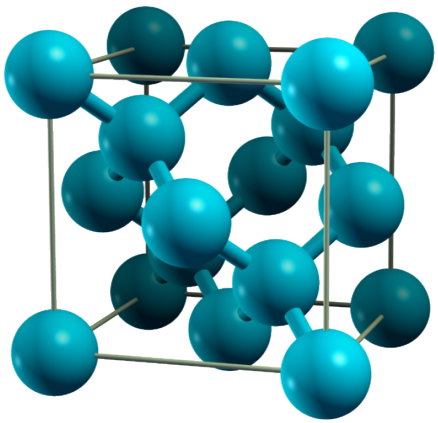
simple cubic



BCC

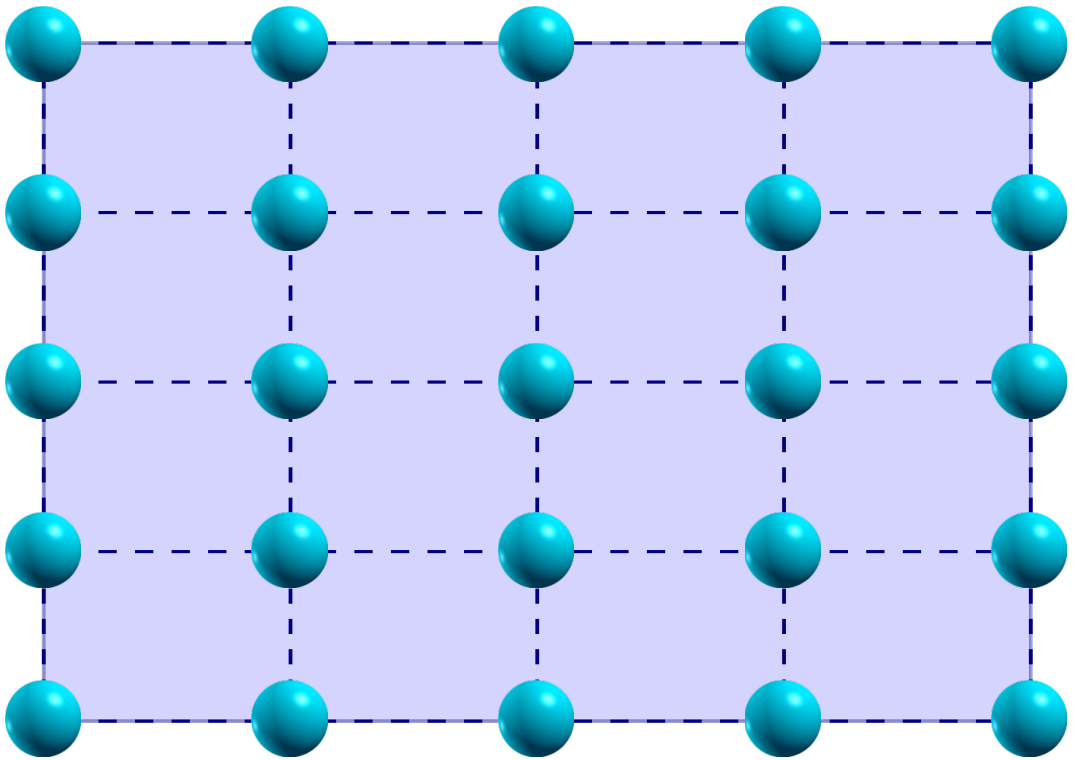


FCC



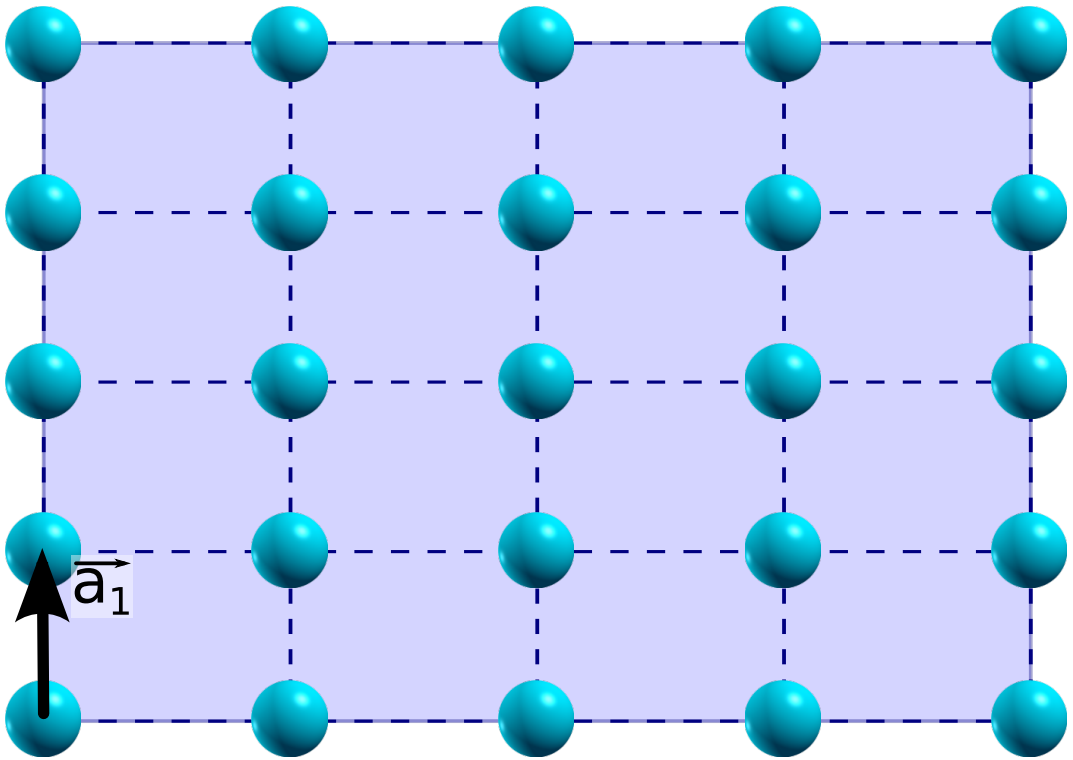
diamond

A 2-dimensional example



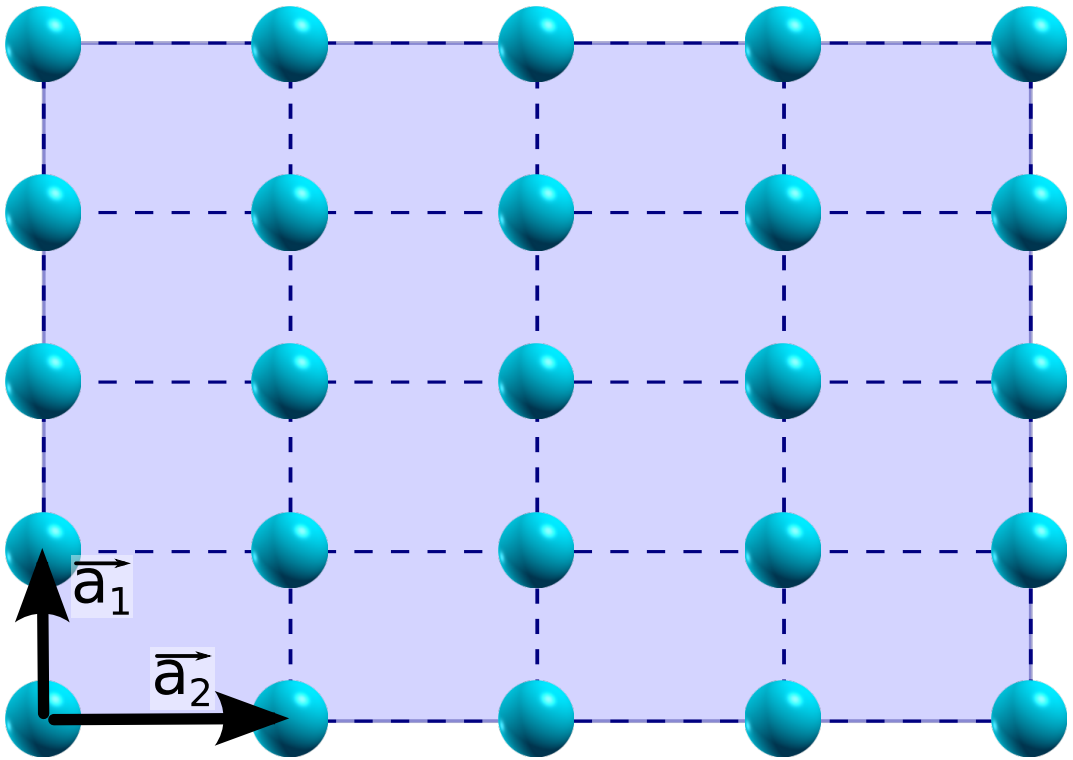
$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

A 2-dimensional example



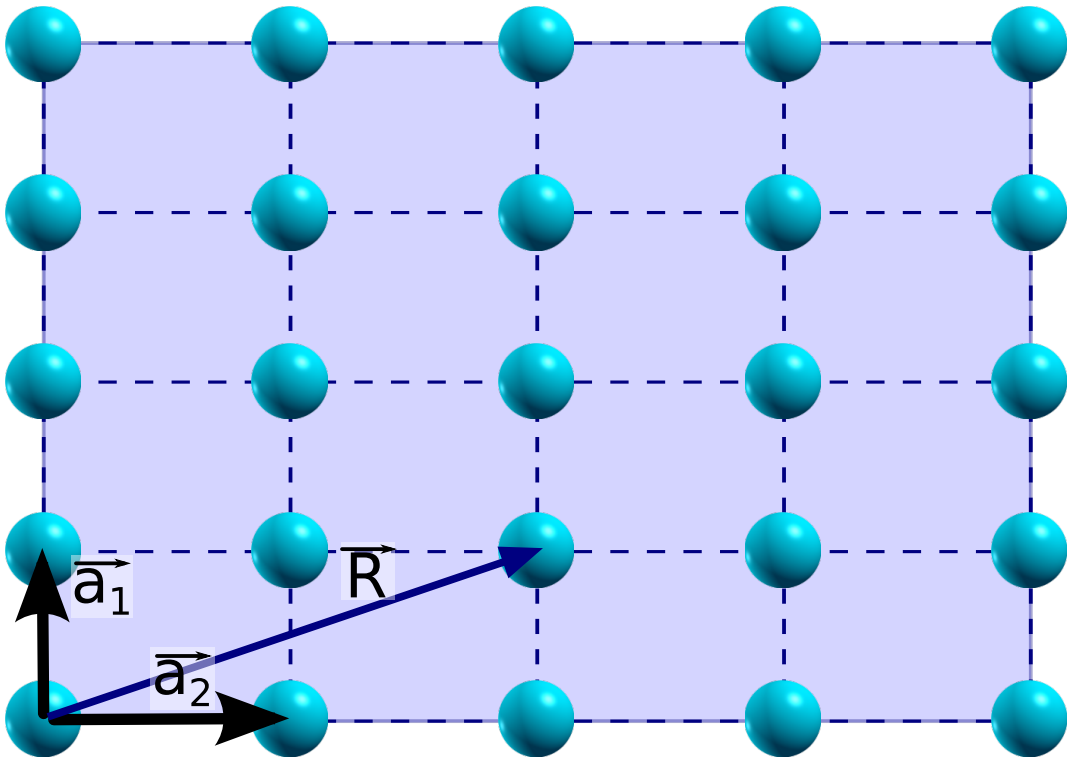
$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

A 2-dimensional example



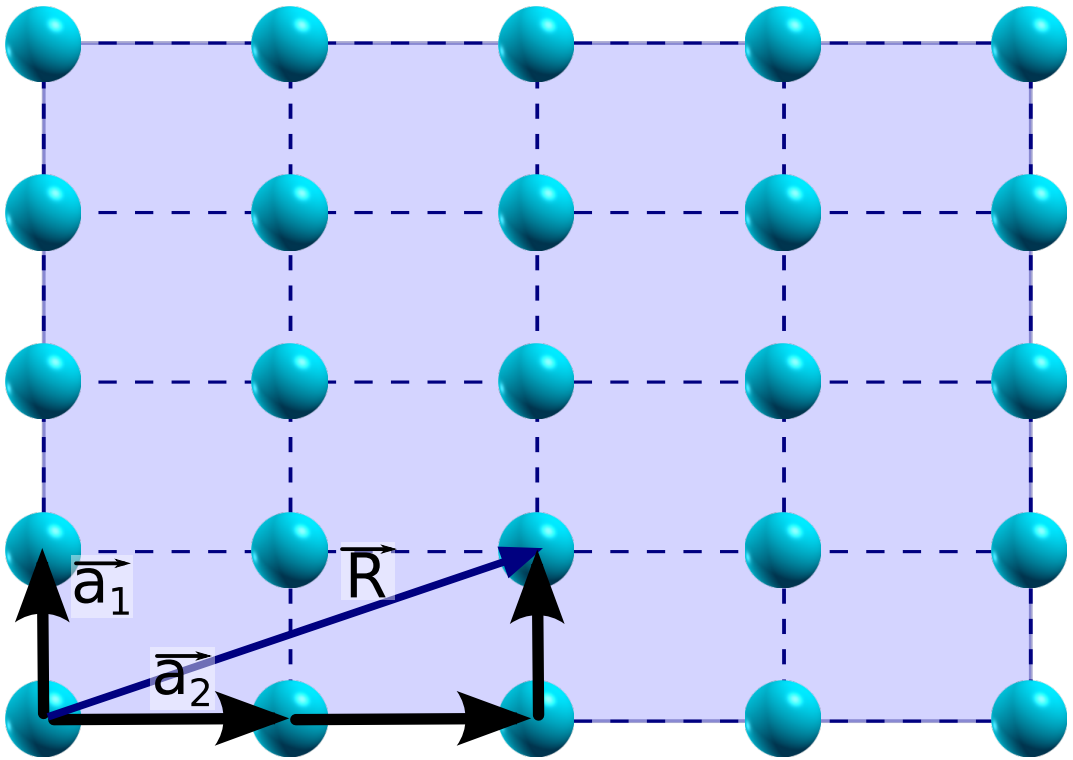
$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

A 2-dimensional example



$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

A 2-dimensional example



$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

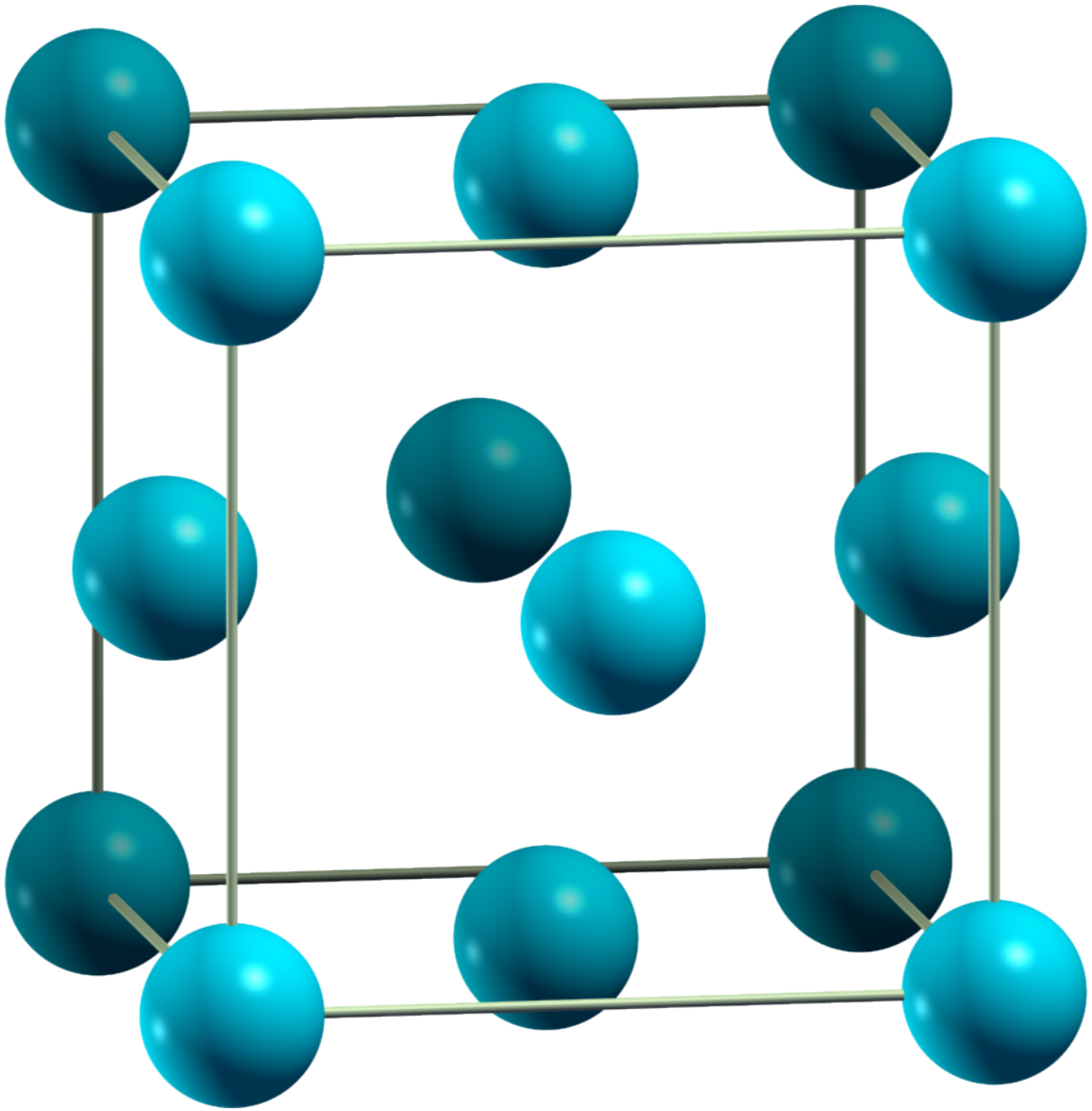
$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2$$

with

$\vec{a}_{1,2}$: primitive vectors

$n_{1,2}$: integers

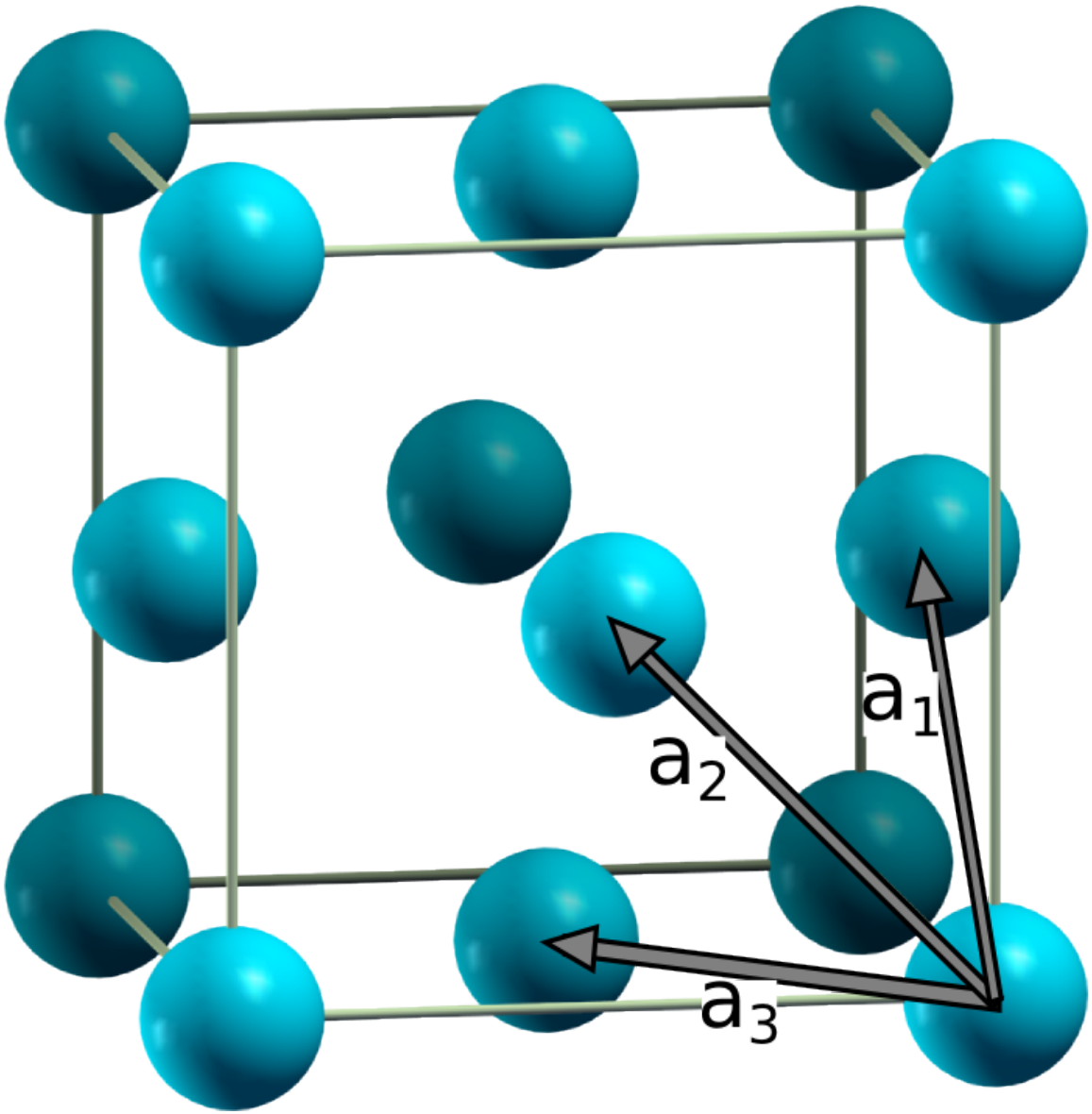
How to specify the crystal structure for a calculation?



The geometry.in file

- specify the primitive unit vectors
- give coordinates of the atoms in the basis

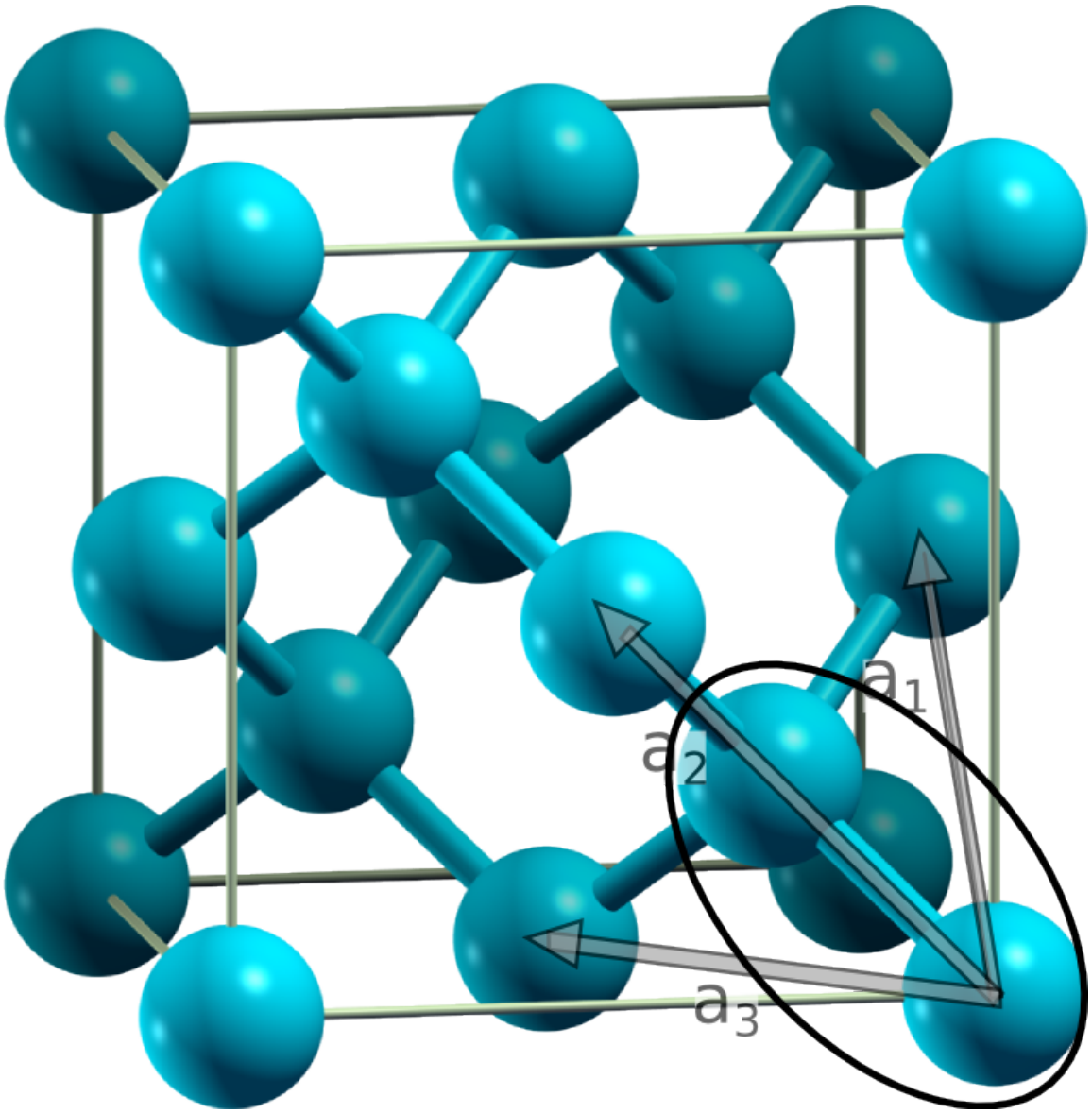
How to specify the crystal structure for a calculation?



The geometry.in file

- specify the primitive unit vectors
- give coordinates of the atoms in the basis

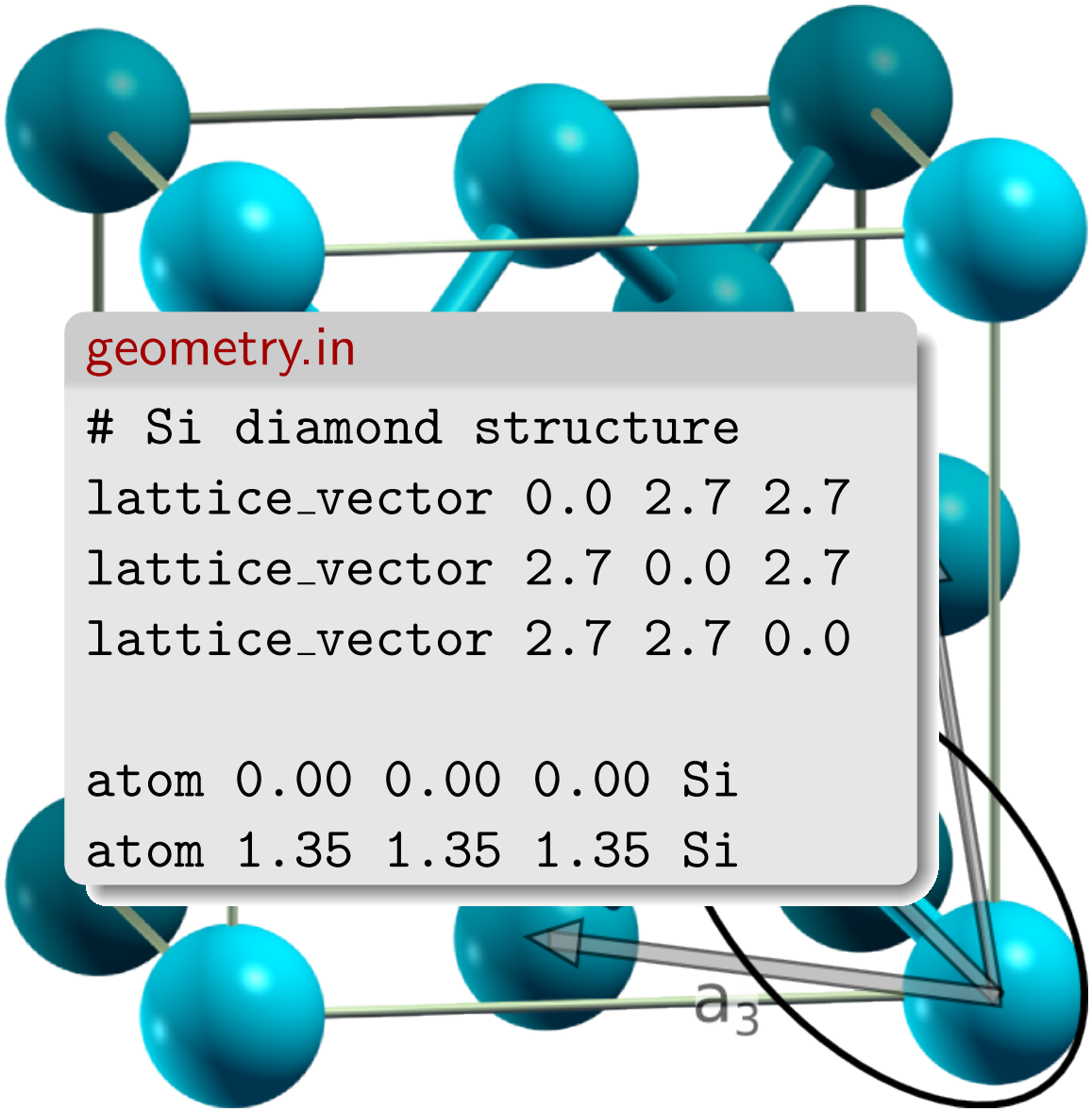
How to specify the crystal structure for a calculation?



The geometry.in file

- specify the primitive unit vectors
- give coordinates of the atoms in the basis

How to specify the crystal structure for a calculation?



geometry.in

```
# Si diamond structure
lattice_vector 0.0 2.7 2.7
lattice_vector 2.7 0.0 2.7
lattice_vector 2.7 2.7 0.0

atom 0.00 0.00 0.00 Si
atom 1.35 1.35 1.35 Si
```

The geometry.in file

- specify the primitive unit vectors
- give coordinates of the atoms in the basis

Sampling of the Brillouin zone

Bloch's Theorem

- Bloch's theorem $\Rightarrow$ give conserved quantum number k for the single particle state
- Kohn-Sham orbital $\psi_{n,k}(\vec{r})$ depends on its quantum number n and on the point k in the first Brillouin zone (1BZ)
- The quantum number n is discrete, but k is continous.

The electronic density $\rho(\vec{r})$

$$\rho(\vec{r}) = \frac{1}{V_{BZ}} \sum_{n=1}^{N_{el}} \int_{Brillouin\ zone} |\psi_{n,k}(\vec{r})|^2 \ d^3k$$

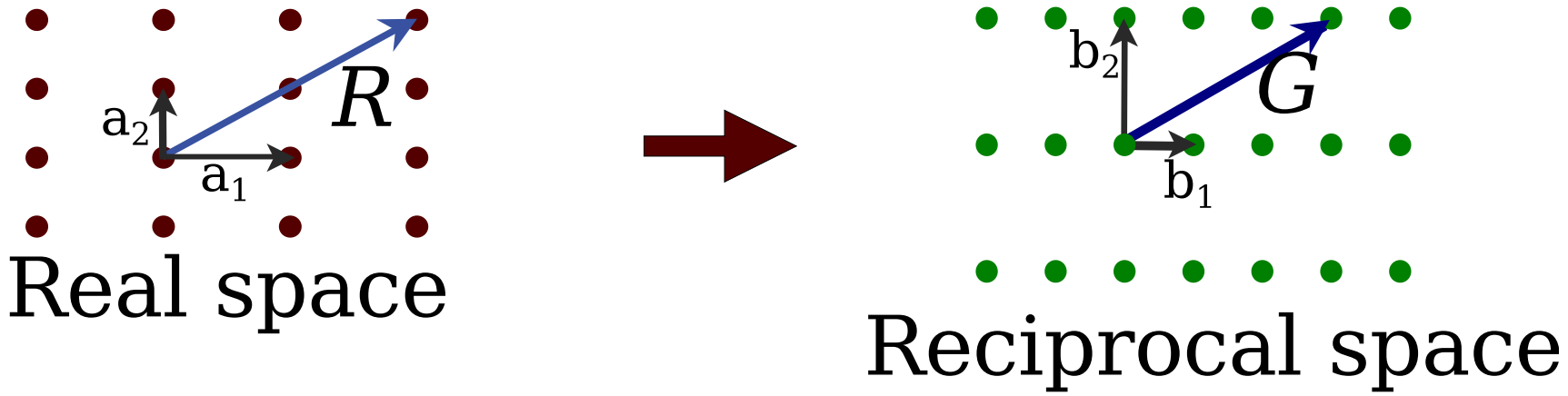
Bloch's Theorem

- Bloch's theorem $\Rightarrow$ give conserved quantum number k for the single particle state
- Kohn-Sham orbital $\psi_{n,k}(\vec{r})$ depends on its quantum number n and on the point k in the first Brillouin zone (1BZ)
- The quantum number n is discrete, but k is continous.

The electronic density $\rho(\vec{r})$

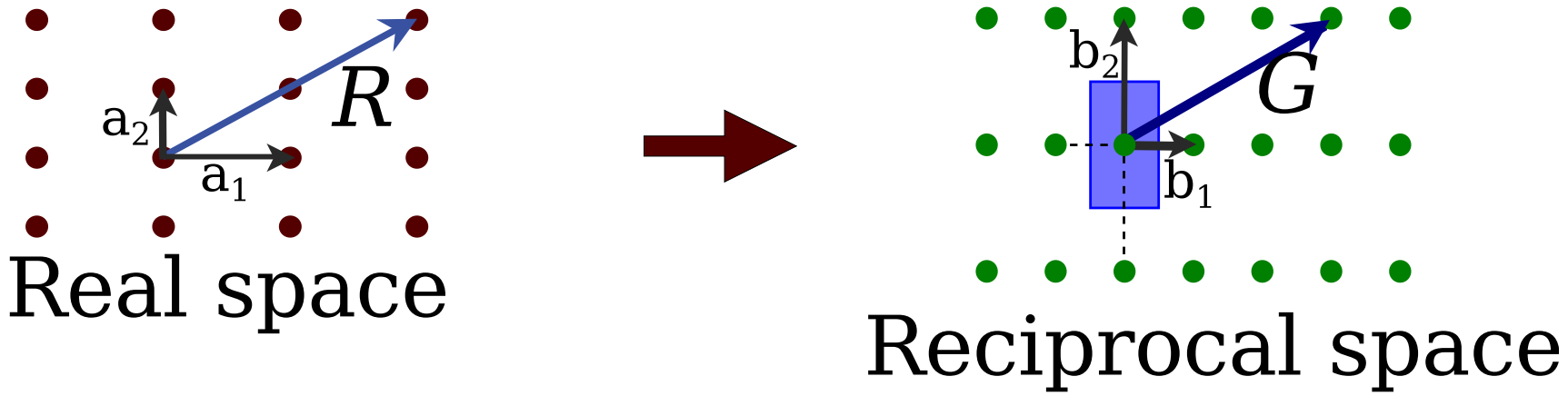
$$\rho(\vec{r}) = \frac{1}{V_{BZ}} \sum_{n=1}^{N_{el}} \int_{Brillouin\ zone} |\psi_{n,k}(\vec{r})|^2 \ d^3k$$

The Brillouin zone



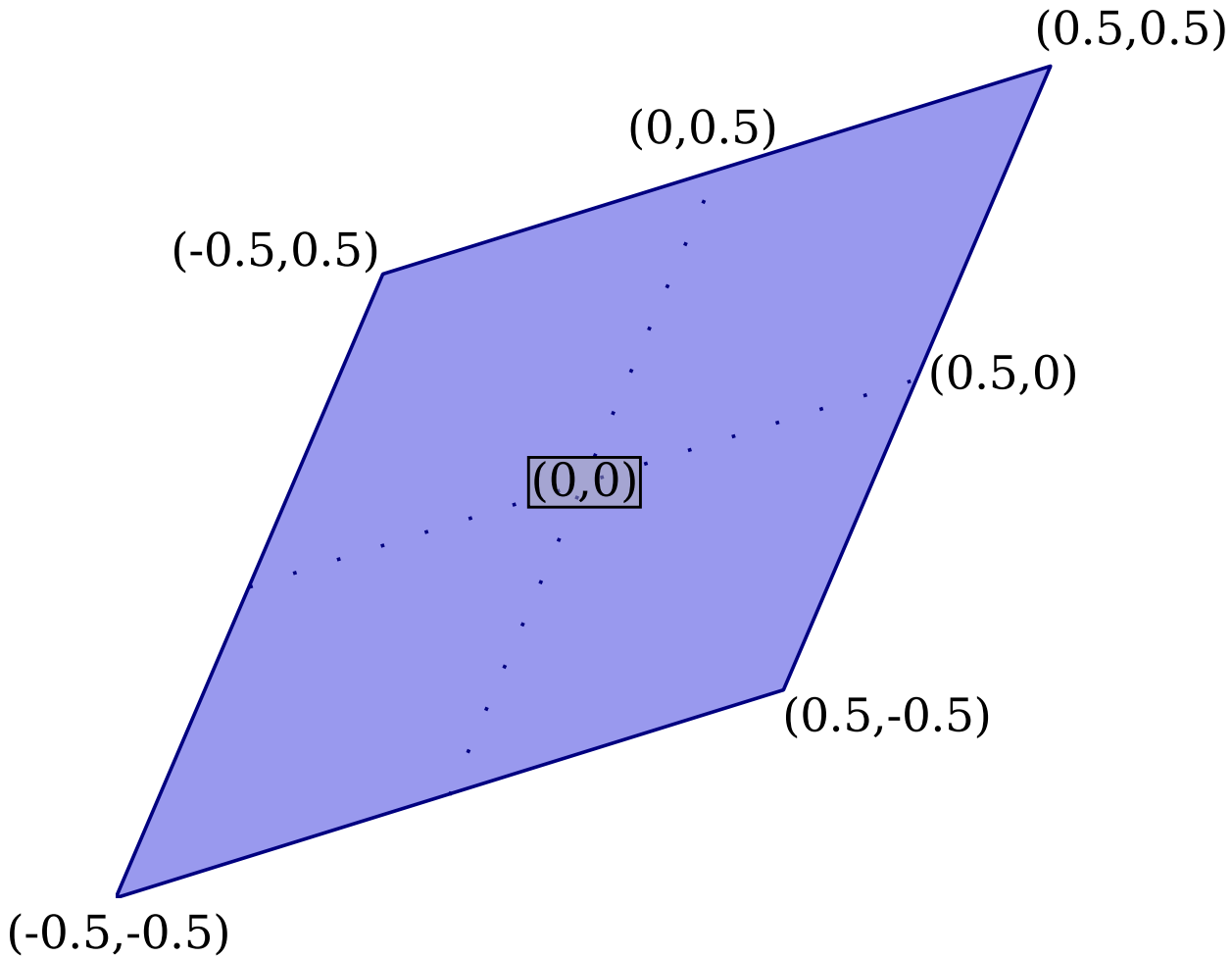
- In practice, calculations are performed on a grid of points in the 1BZ

The Brillouin zone

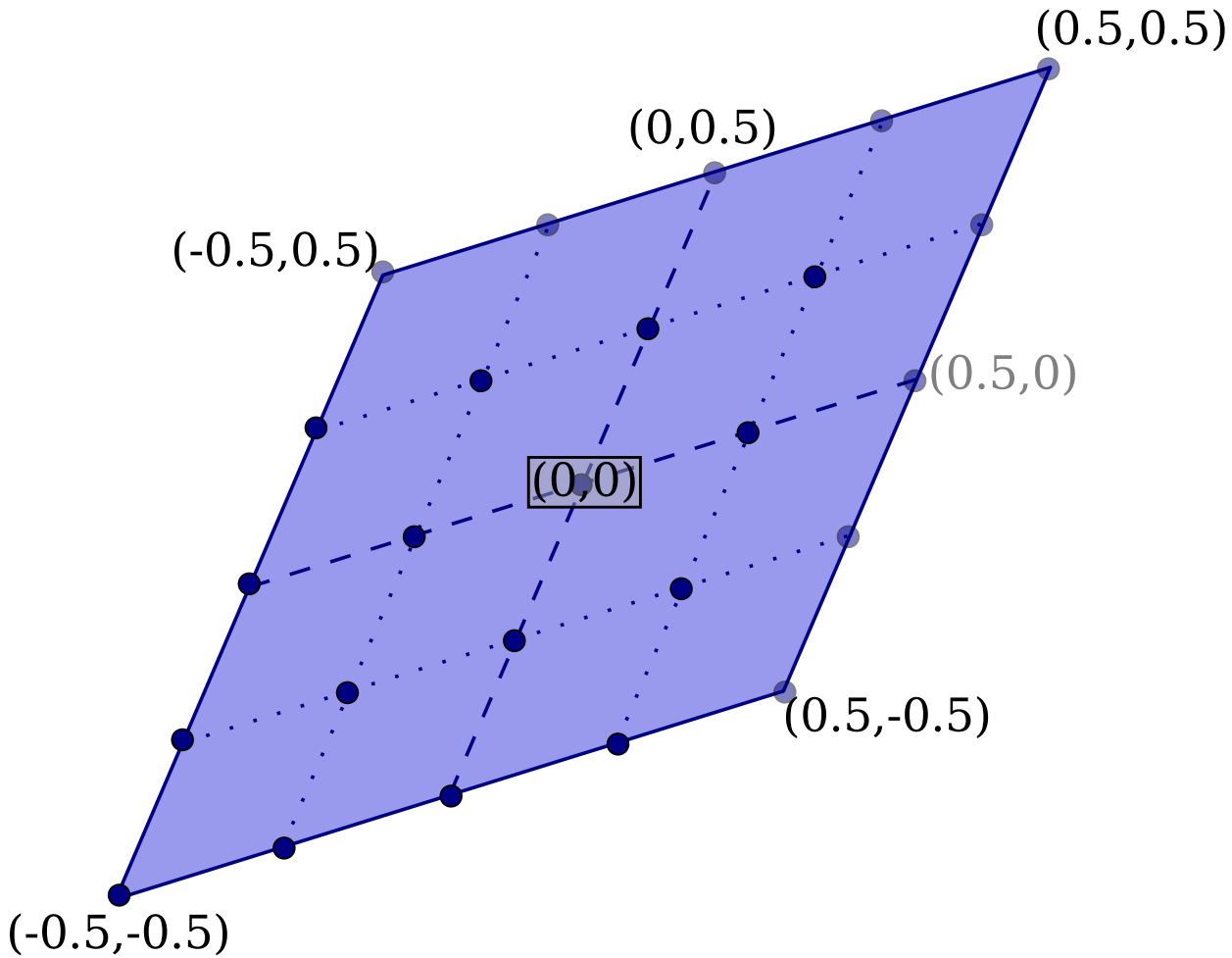


- In practice, calculations are performed on a grid of points in the 1BZ

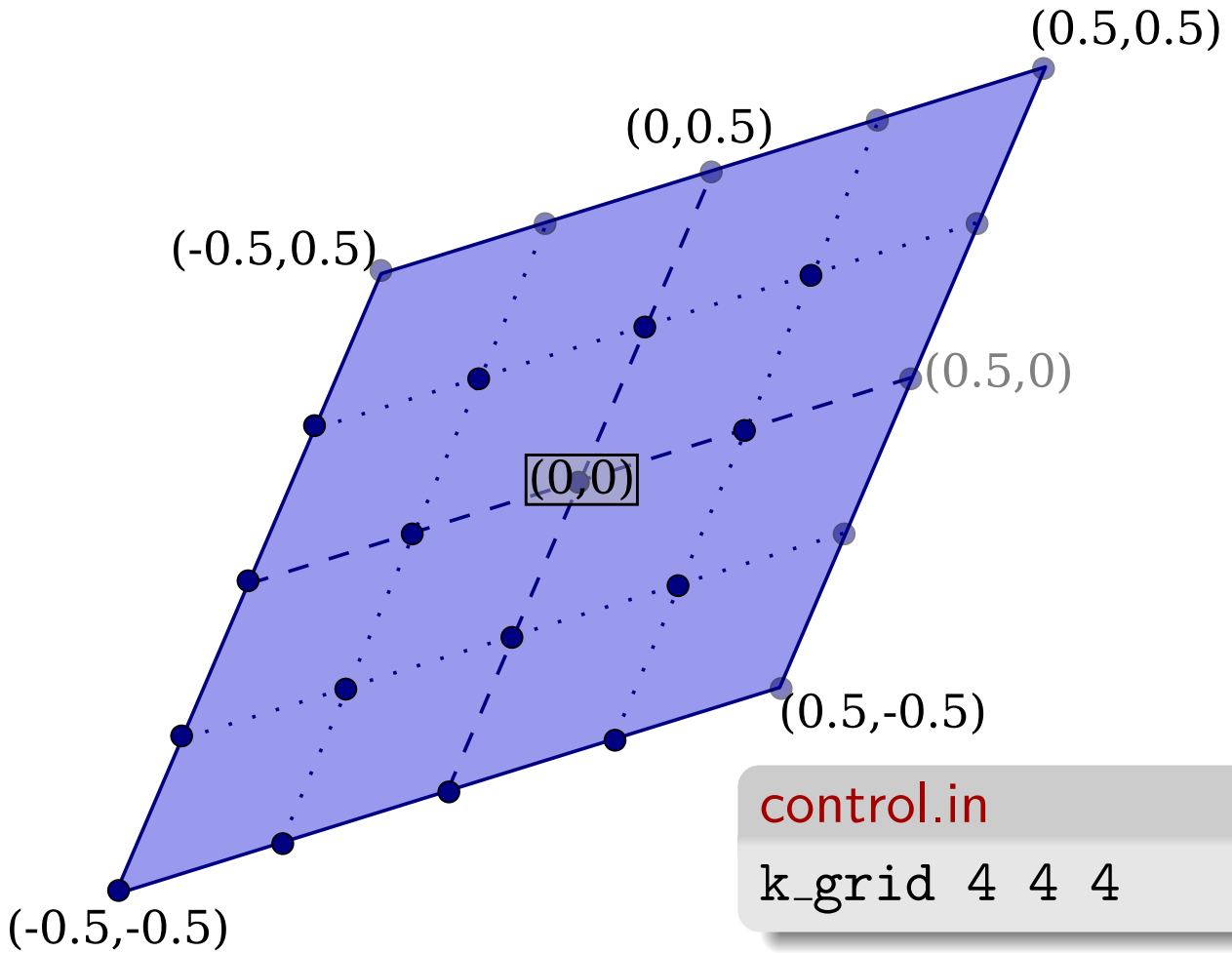
The grid in the Brillouin zone



The grid in the Brillouin zone



The grid in the Brillouin zone



control.in

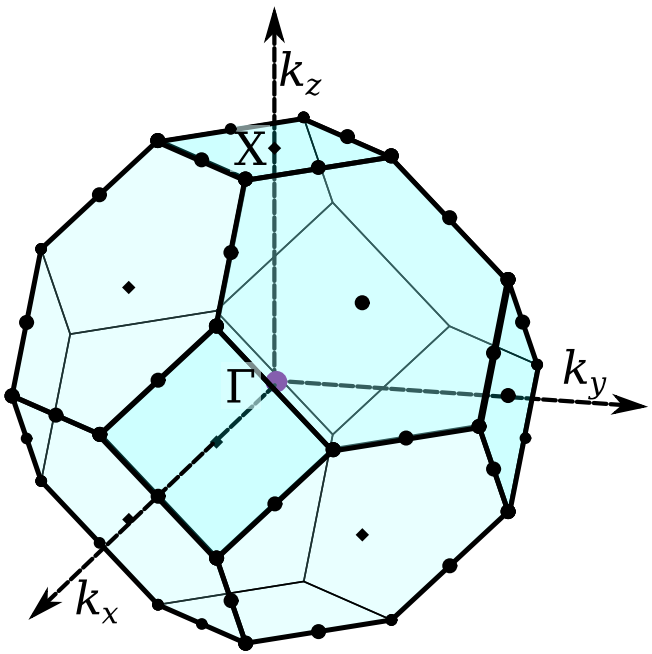
```
k_grid 4 4 4
```

Band structure and density of states

Bandstructure: example silicon

Kohn-Sham equation

$$\hat{h}_k \psi_{n,k}(\vec{r}) = \epsilon_{n,k} \psi_{n,k}(\vec{r})$$

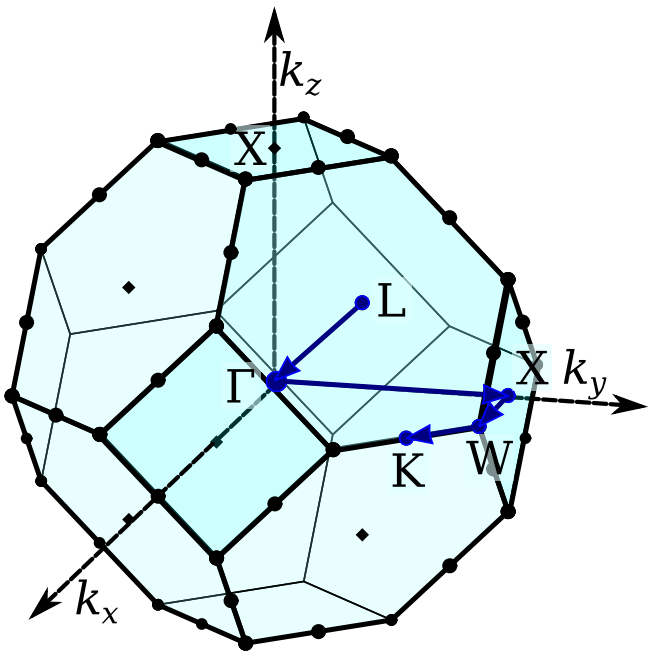


- find SCF solution
- choose a path in the Brillouin Zone
  typical: along high symmetry lines
- plot the Kohn-Sham eigenvalues ($\epsilon(k)$)

Bandstructure: example silicon

Kohn-Sham equation

$$\hat{h}_k \psi_{n,k}(\vec{r}) = \epsilon_{n,k} \psi_{n,k}(\vec{r})$$



- find SCF solution
- choose a path in the Brillouin Zone
  typical: along high symmetry lines
- plot the Kohn-Sham eigenvalues ($\epsilon(k)$)

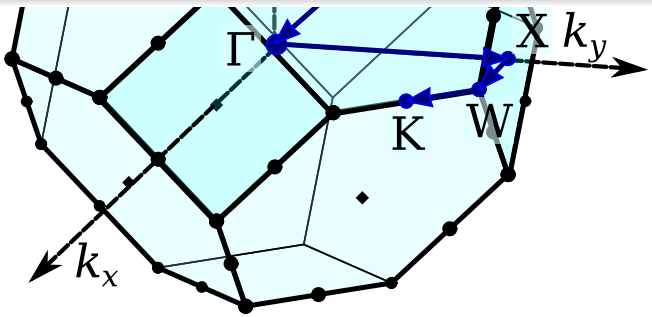
Bandstructure: example silicon

Kohn-Sham equation

$$\hat{h}_k \psi_{n,k}(\vec{r}) = \epsilon_{n,k} \psi_{n,k}(\vec{r})$$

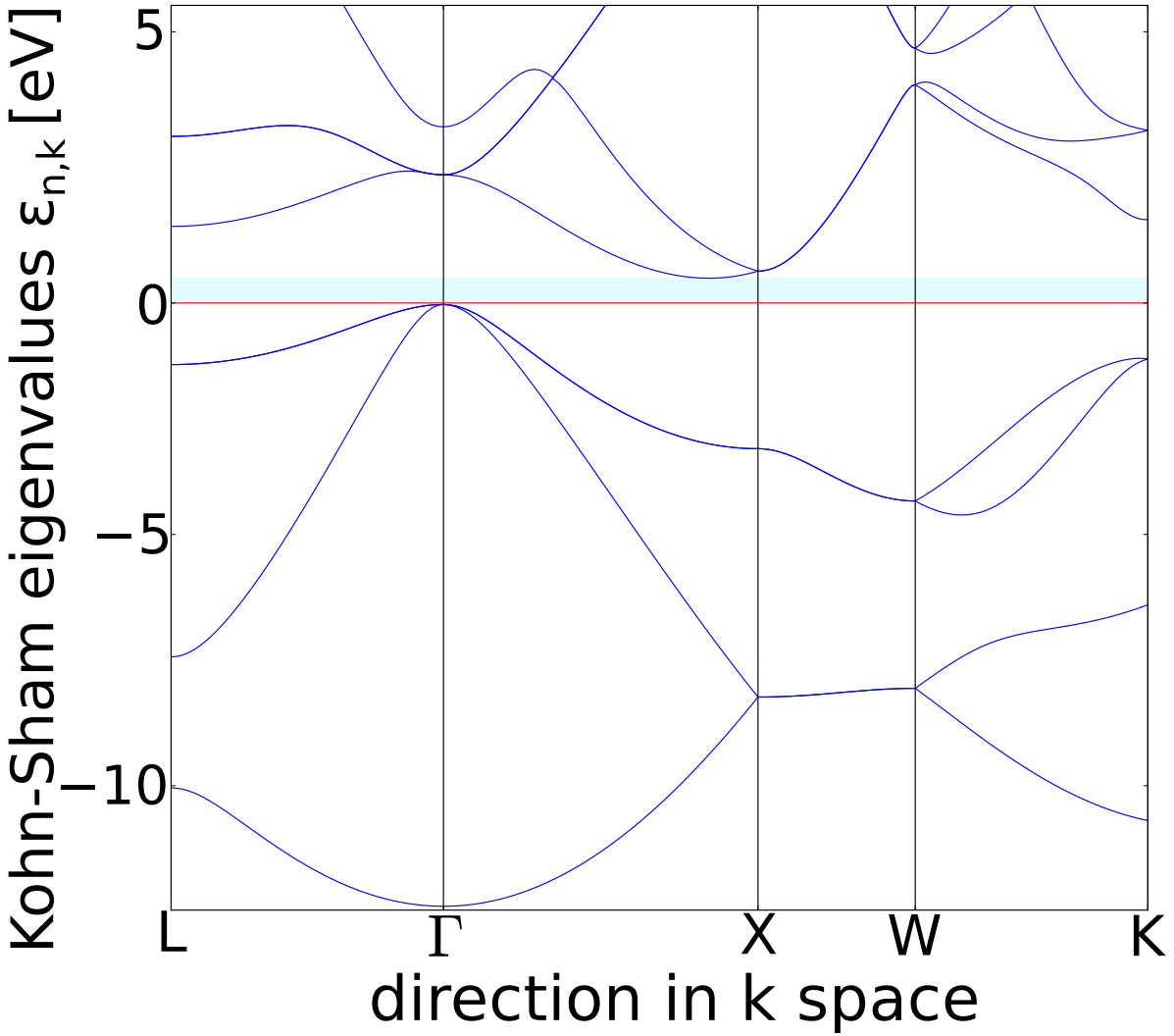
control.in

```
output band  0.5 0.5 0.5  0.0 0.0 0.0  50  L Gamma
output band  0.0 0.0 0.0  0.0 0.5 0.5  50  Gamma X
...
```



- typical: along high symmetry lines
- plot the Kohn-Sham eigenvalues ($\epsilon(k)$)

The electronic Band structure of Silicon



- semiconductor
- indirect band gap

The density of states (DOS)

- number of states n within a given energy interval $[\epsilon - \Delta\epsilon, \epsilon + \Delta\epsilon]$

$$n = \int_{\epsilon-\Delta\epsilon}^{\epsilon+\Delta\epsilon} g(\epsilon)\, d\epsilon$$

  $g(\epsilon)$ is the density of states
- $g(\epsilon)$ in a free atom or molecule is

$$g(\epsilon) = \sum_i \delta(\epsilon_i - \epsilon)$$

- in a periodic system the number of states per energy is averaged over k

$$g(\epsilon) = \frac{1}{V_{BZ}} \sum_i \int_{BZ} d^3k\ \delta(\epsilon_{i,k} - \epsilon)$$

Density of states: Broadening and k-points

Density of states (DOS)

$$g(\epsilon) = \frac{1}{V_{BZ}} \sum_i \int_{BZ} d^3k \; \delta(\epsilon_{i,k} - \epsilon)$$

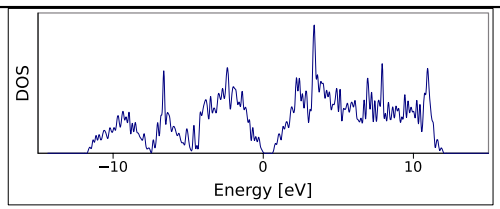
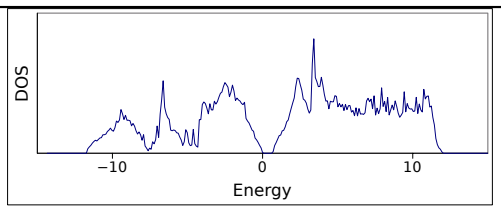
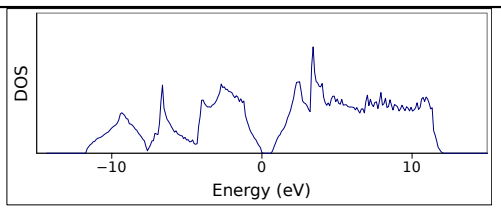
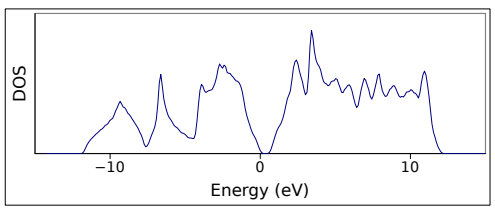
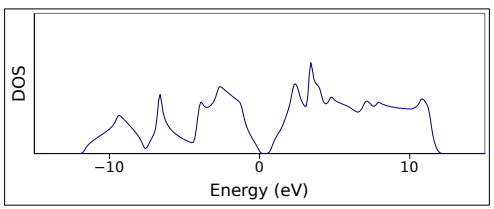
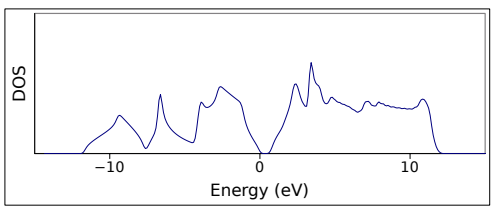
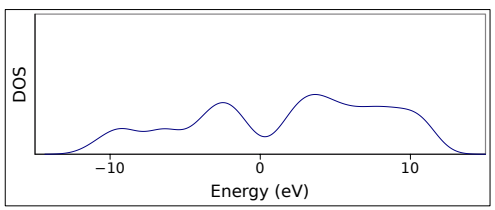
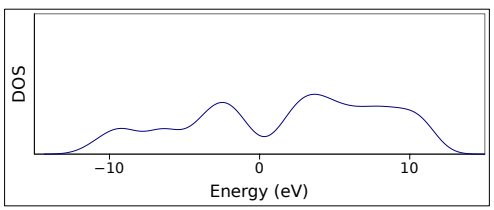
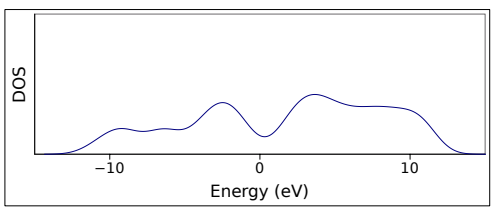
$$\approx \frac{1}{\sqrt{2\pi}\sigma} \frac{1}{N_k} \sum_i \sum_k \exp\left[-\frac{1}{2} \left(\frac{\epsilon - \epsilon_{k,i}}{\sigma} \right)^2 \right]$$

where σ is the Gaussian broadening

Density of states: Broadening and k-points

$$g(\epsilon) = \frac{1}{\sqrt{2\pi}\sigma}\frac{1}{N_k}\sum_i\sum_k \exp\left[-\frac{1}{2}\left(\frac{\epsilon-\epsilon_{k,i}}{\sigma}\right)^2\right]$$

where σ is the Gaussian broadening

σ/grid	20x20x20	40x40x40	60x60x60
0.01			
0.1			
1.0			

Find minimal lattice constant

Cohesive properties of solids

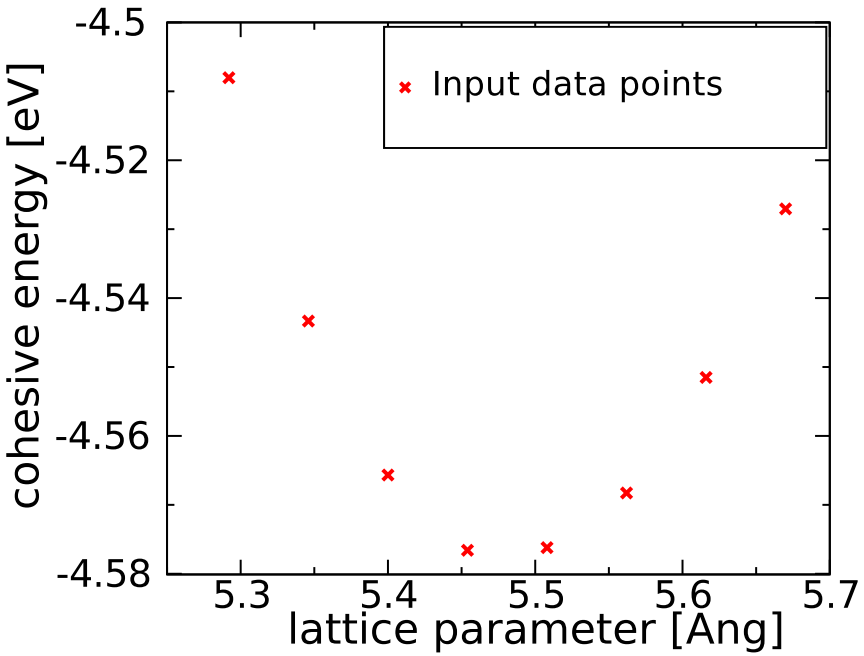
Cohesive energy:

$$E_{coh} = -\frac{E_{bulk} - N \cdot E_{atom}}{N}$$

- energy gain per atom

Find the minimal lattice constant

Birch-Murnaghan Fit versus quadratic interpolation



V : Volume

E_0 : Equilibrium energy

V_0 : optimum Volume

B_0 : Bulk modulus

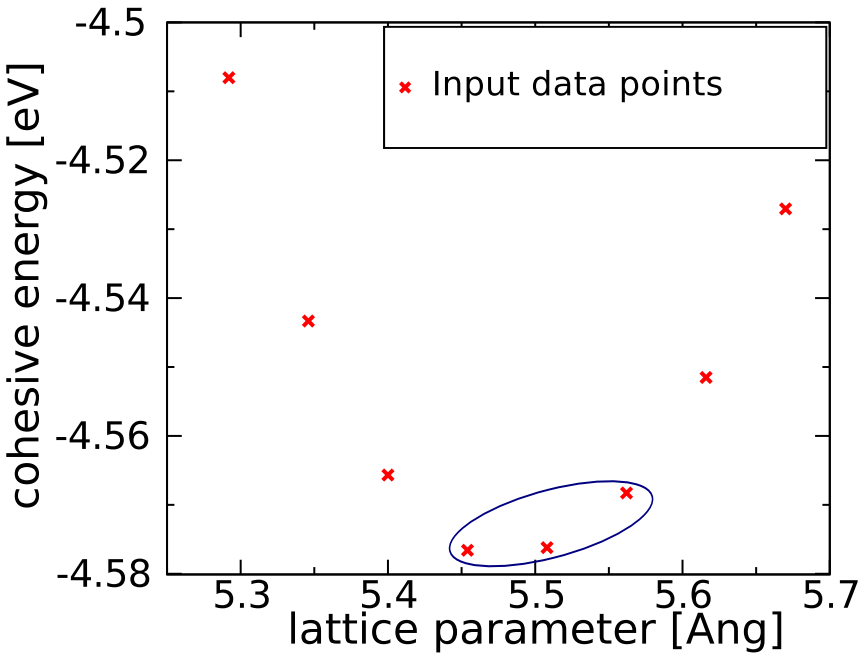
B_0' : derivative of B_0 (w.r.t. pressure)

Birch-Murnaghan equation of states

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right) - \frac{B_0 V_0}{B_0' - 1}$$

Find the minimal lattice constant

Birch-Murnaghan Fit versus quadratic interpolation



V : Volume

E_0 : Equilibrium energy

V_0 : optimum Volume

B_0 : Bulk modulus

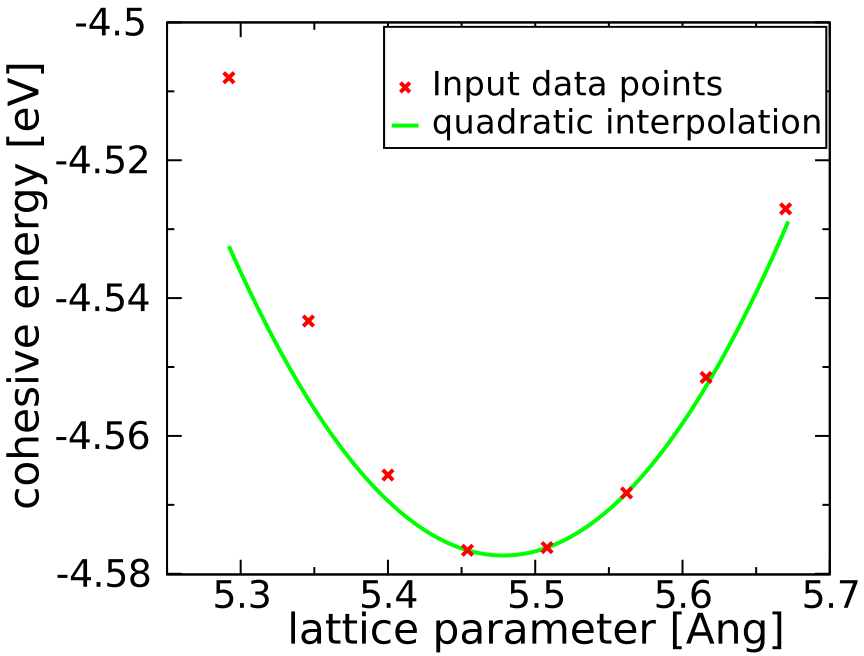
B_0' : derivative of B_0 (w.r.t. pressure)

Birch-Murnaghan equation of states

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right) - \frac{B_0 V_0}{B_0' - 1}$$

Find the minimal lattice constant

Birch-Murnaghan Fit versus quadratic interpolation



V : Volume

E_0 : Equilibrium energy

V_0 : optimum Volume

B_0 : Bulk modulus

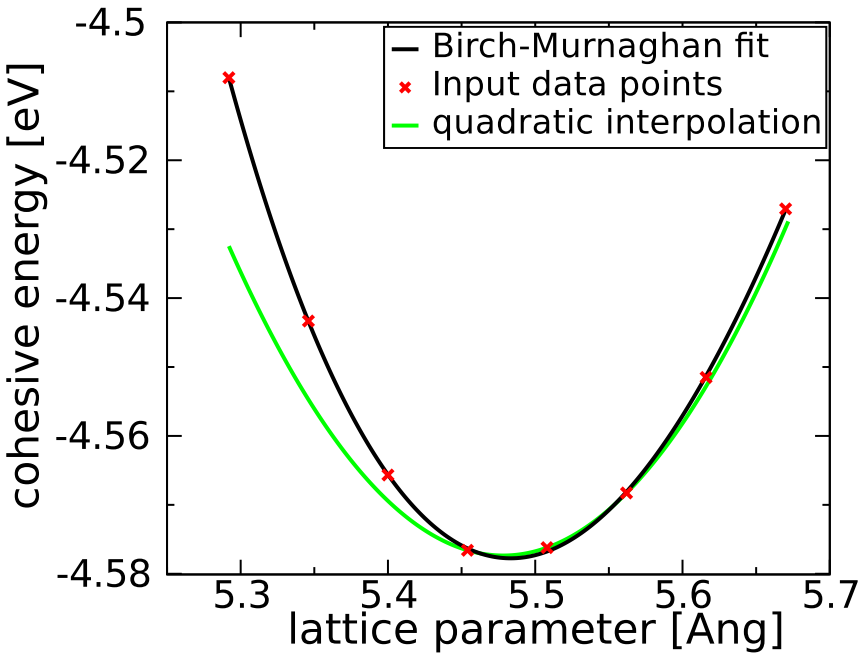
B_0' : derivative of B_0 (w.r.t. pressure)

Birch-Murnaghan equation of states

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right) - \frac{B_0 V_0}{B_0' - 1}$$

Find the minimal lattice constant

Birch-Murnaghan Fit versus quadratic interpolation



V : Volume

E_0 : Equilibrium energy

V_0 : optimum Volume

B_0 : Bulk modulus

B_0' : derivative of B_0 (w.r.t. pressure)

Birch-Murnaghan equation of states

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left(\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right) - \frac{B_0 V_0}{B_0' - 1}$$

Systems of interest

- Bulk Silicon
- Silicon Surface
- $Ga_3Mn_1As_4$

Bulk Silicon

Motivation

VOLUME 45, NUMBER 12 PHYSICAL REVIEW LETTERS 22 SEPTEMBER 1980

Microscopic Theory of the Phase Transformation and Lattice Dynamics of Si

M. T. Yin and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 14 July 1980)

An *ab initio* calculation for the solid-solid phase transformation, static structural properties, and the lattice dynamics of Si is presented. A density-functional pseudopotential scheme is used with the atomic number as the only input. The detailed properties of the diamond to β-tin transition are accurately reproduced. The phonon frequencies and mode-Grüneisen parameters at Γ and X, along with the lattice constant, bulk modulus, and cohesive energy, are calculated and found to be in excellent agreement with experiment.

PACS numbers: 63.20.Dj, 61.50.Lt

Motivation

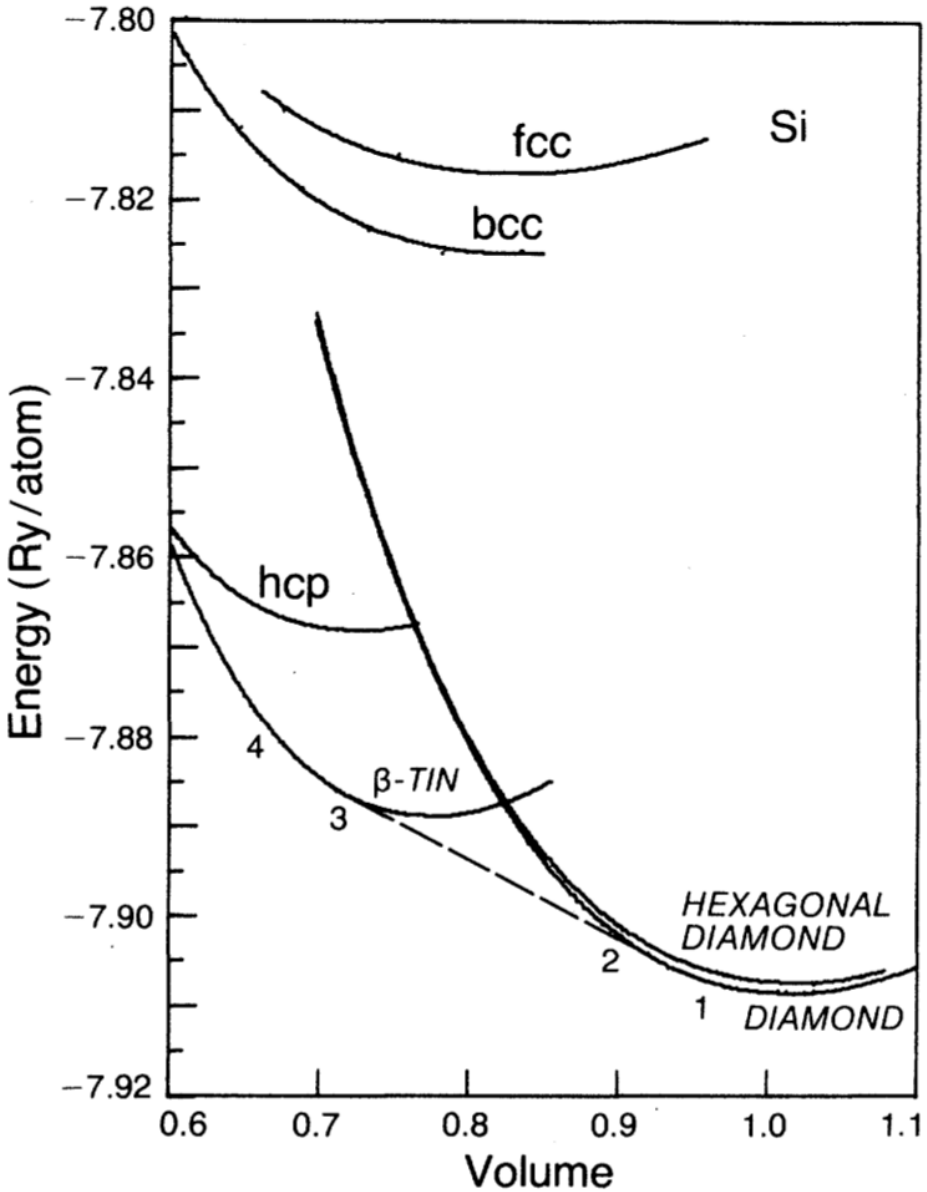
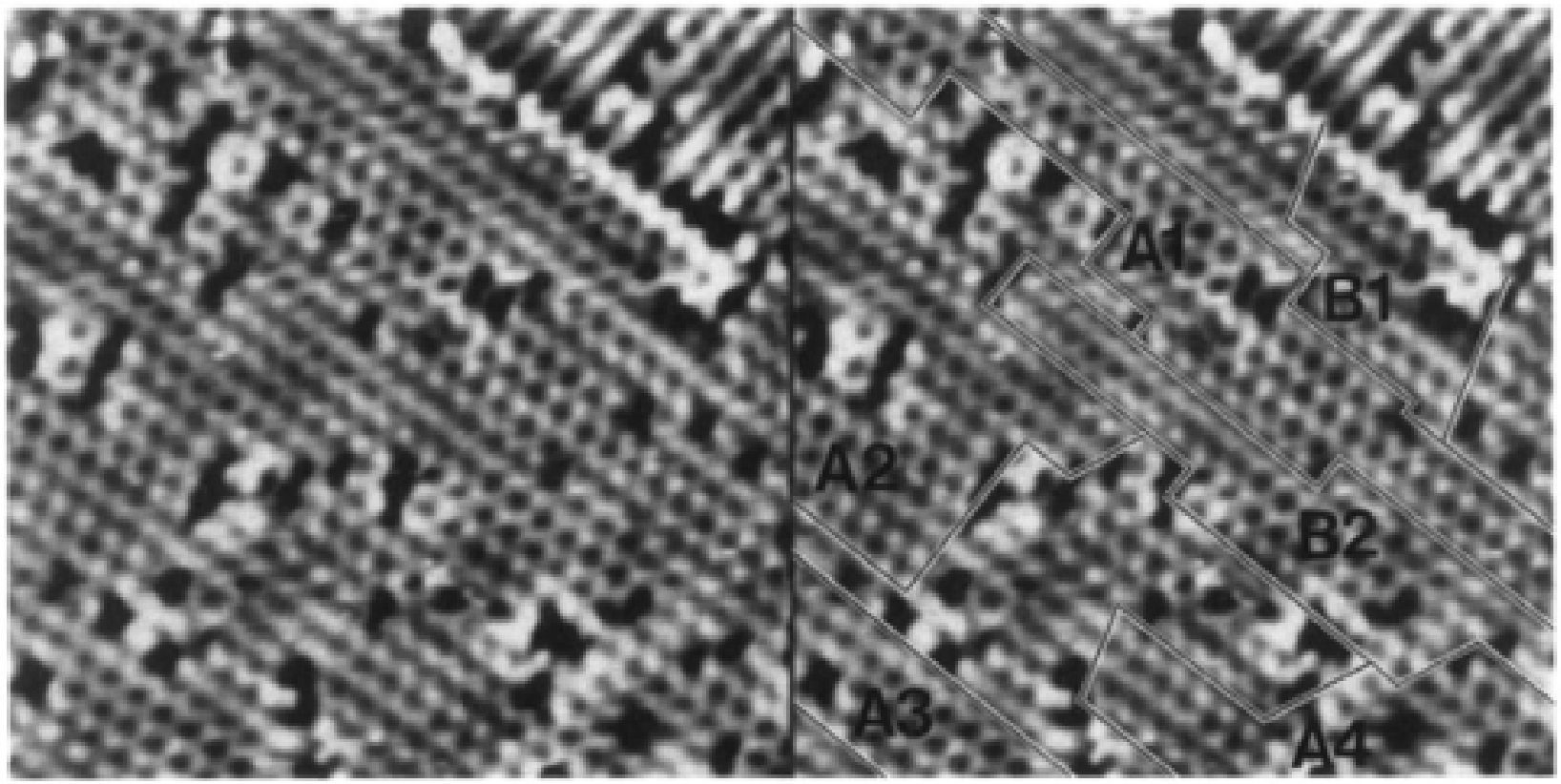


FIG. 1. The diamond, hexagonal diamond, and β-tin, hcp, bcc, and fcc structural energies (in units of Ry/atom) as a function of the atomic volume [normalized to the measured free volume (Ref. 16)] for Si. The dashed line is the common tangent of the energy curves for the diamond and the β-tin structures.

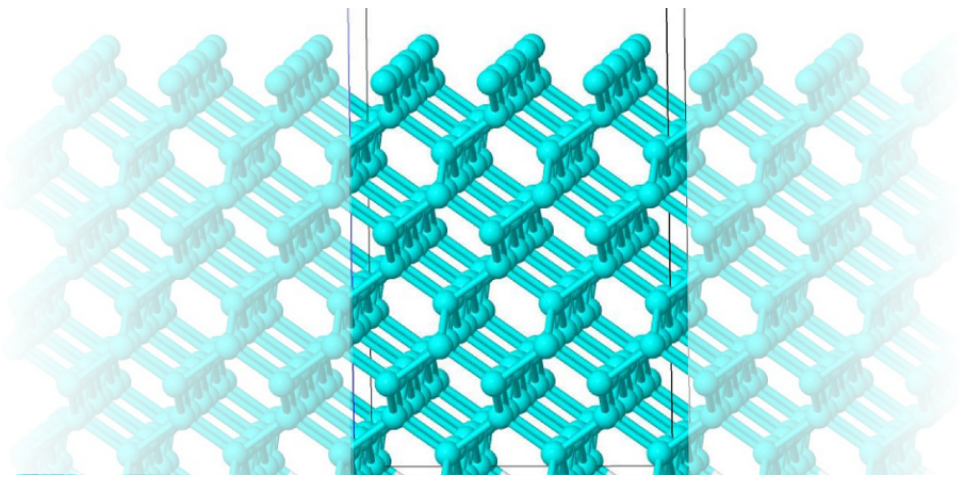
Silicon surface

Motivation



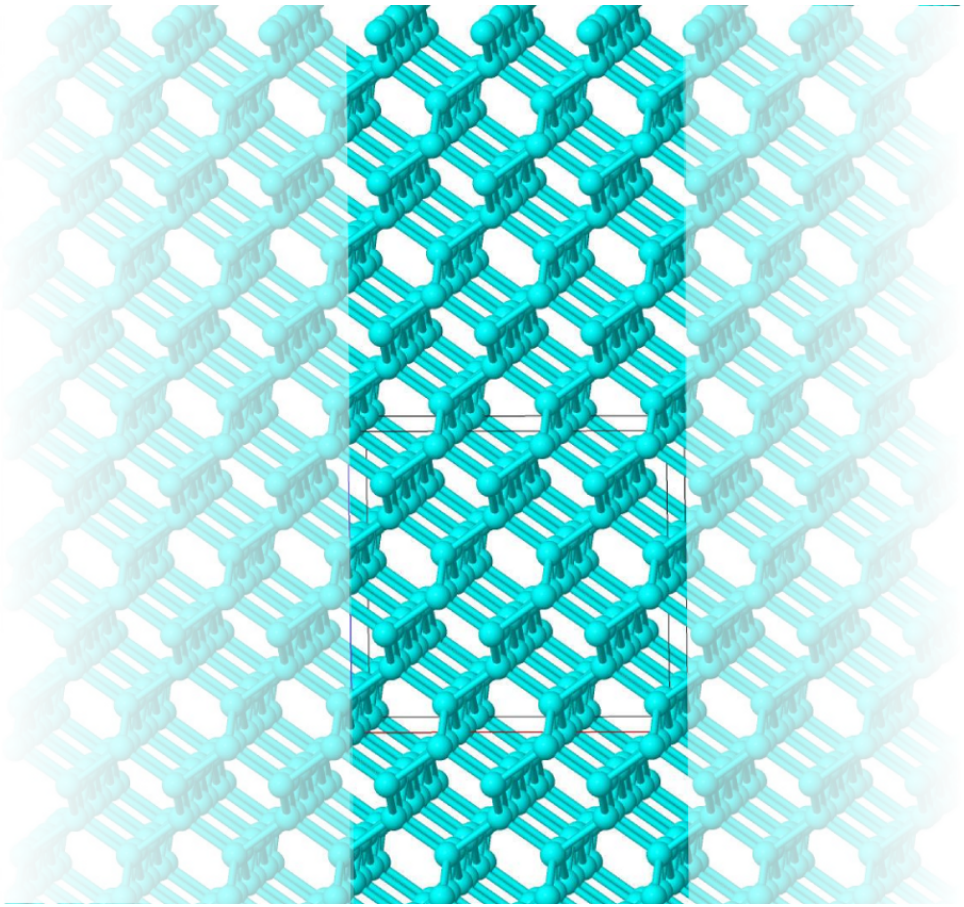
R.A. Wolkow, PRL 68,2636 (1992)

Supercell approach



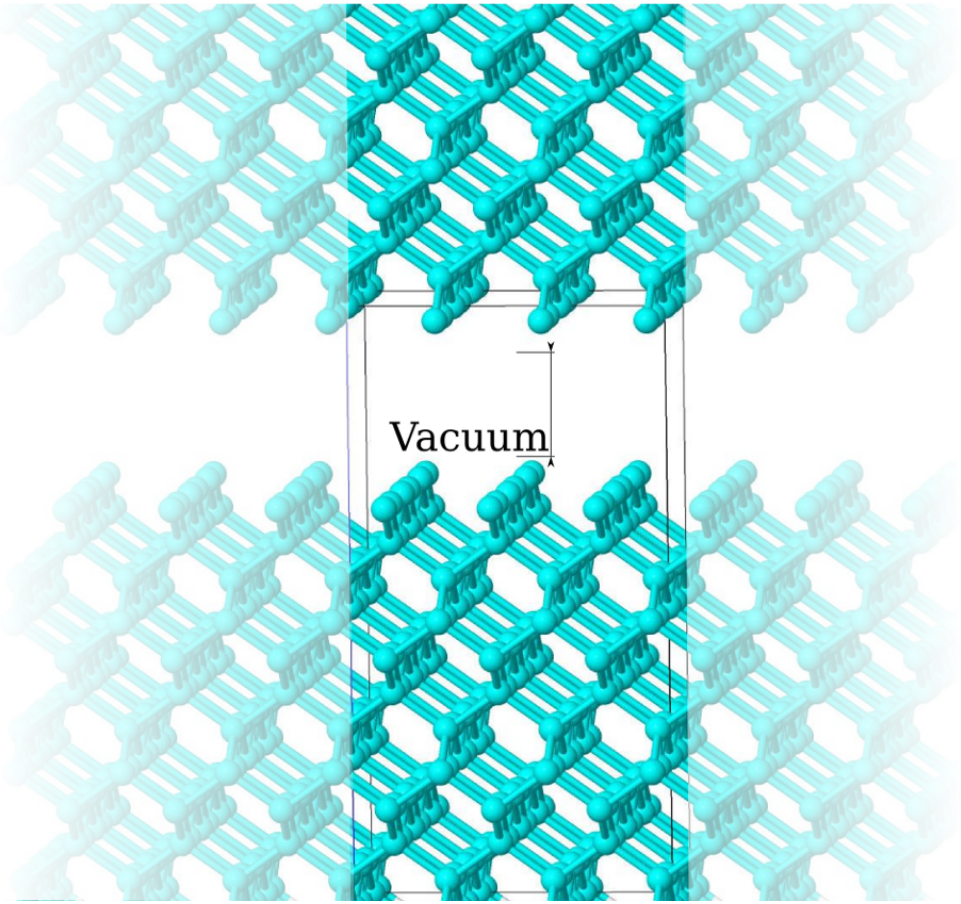
- Surface: periodic in two directions
- Start from bulk geometry
- insert vacuum
  here: increase lattice vector in z-direction
- saturate the dangling bonds on the bottom layer with hydrogen
- choose vacuum large enough (no interaction between slabs)

Supercell approach



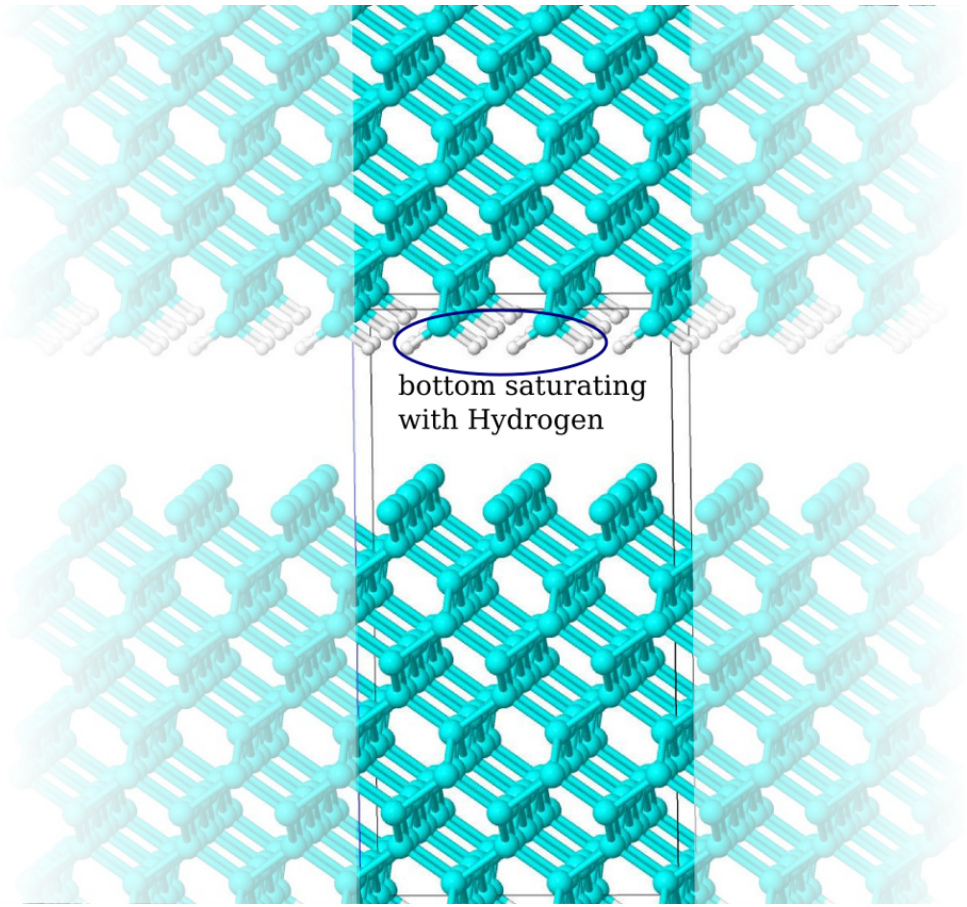
- Surface: periodic in two directions
- Start from bulk geometry
- insert vacuum
  here: increase lattice vector in z-direction
- saturate the dangling bonds on the bottom layer with hydrogen
- choose vacuum large enough (no interaction between slabs)

Supercell approach



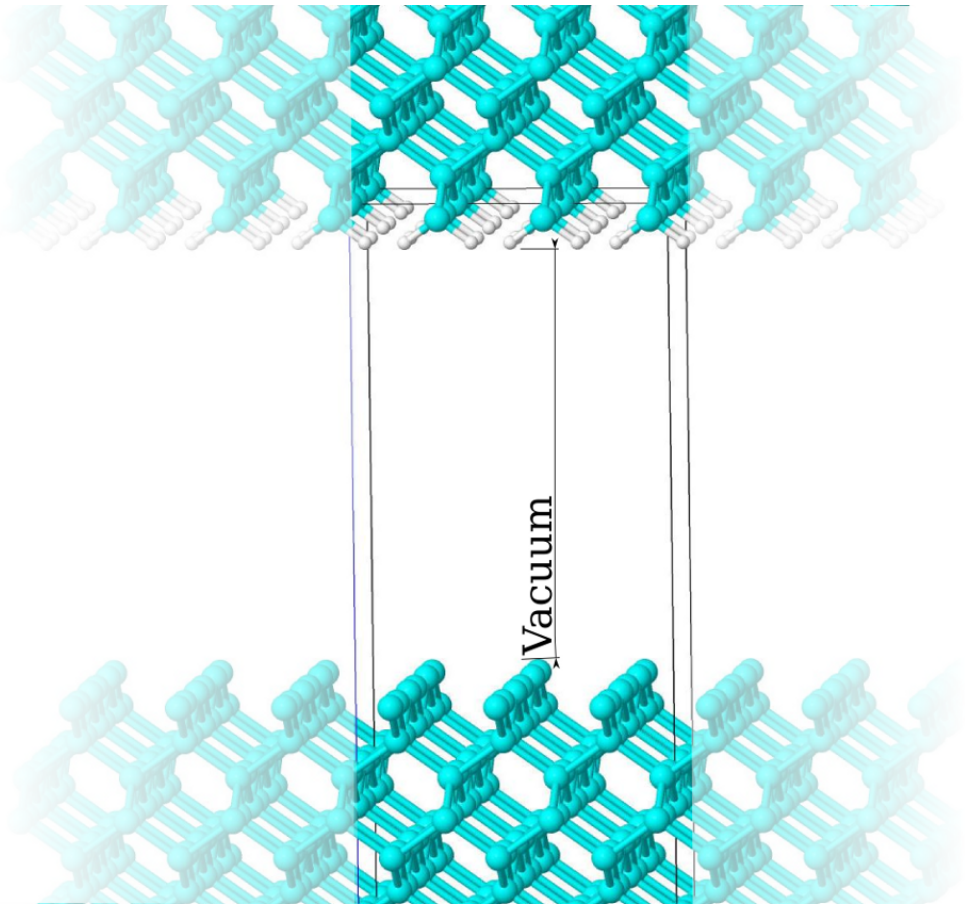
- Surface: periodic in two directions
- Start from bulk geometry
- insert vacuum
  here: increase lattice vector in z-direction
- saturate the dangling bonds on the bottom layer with hydrogen
- choose vacuum large enough (no interaction between slabs)

Supercell approach



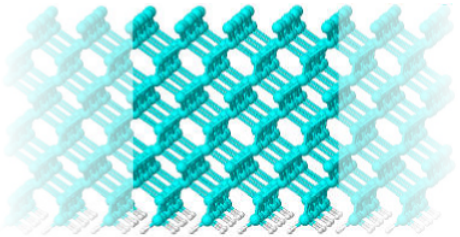
- Surface: periodic in two directions
- Start from bulk geometry
- insert vacuum
  here: increase lattice vector in z-direction
- saturate the dangling bonds on the bottom layer with hydrogen
- choose vacuum large enough (no interaction between slabs)

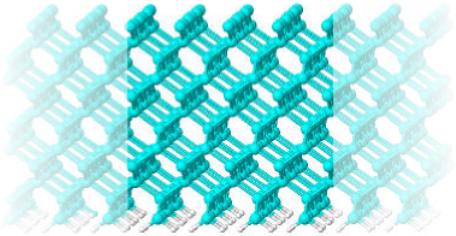
Supercell approach

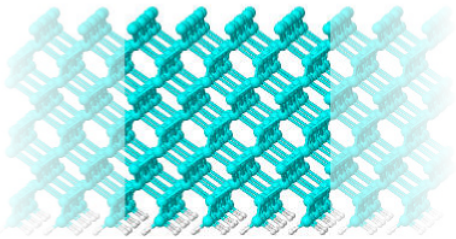


- Surface: periodic in two directions
- Start from bulk geometry
- insert vacuum
  here: increase lattice vector in z-direction
- saturate the dangling bonds on the bottom layer with hydrogen
- choose vacuum large enough (no interaction between slabs)

Supercell approach



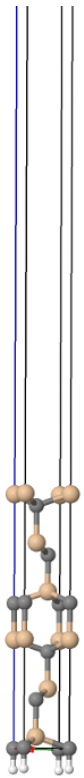


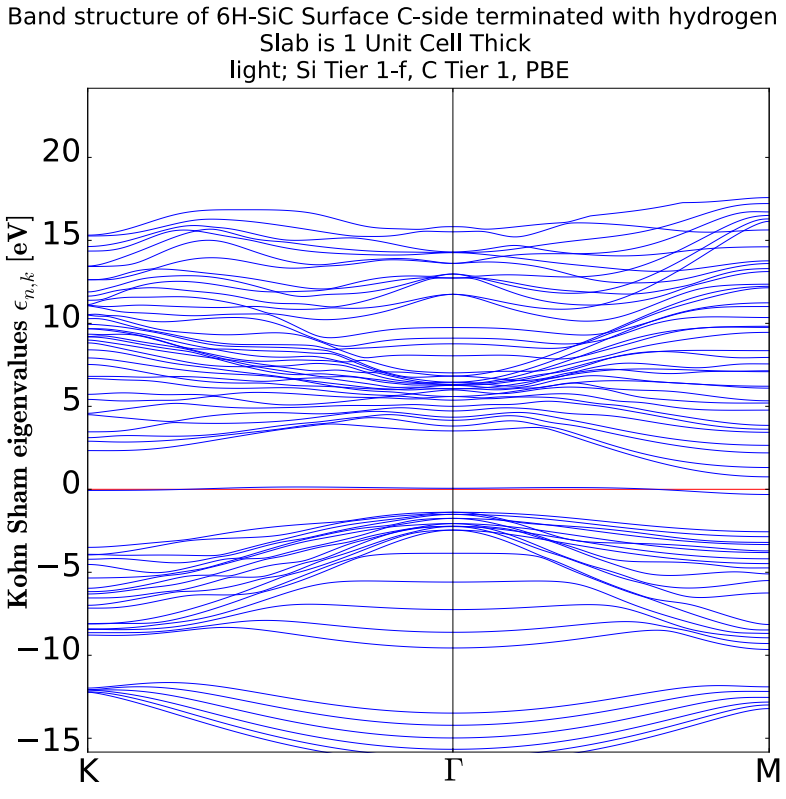


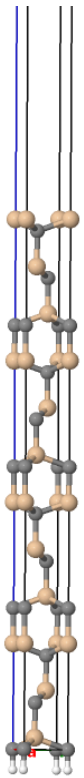
- Surface: periodic in two directions
- Start from bulk geometry
- insert vacuum
  here: increase lattice vector in z-direction
- saturate the dangling bonds on the bottom layer with hydrogen
- choose vacuum large enough (no interaction between slabs)

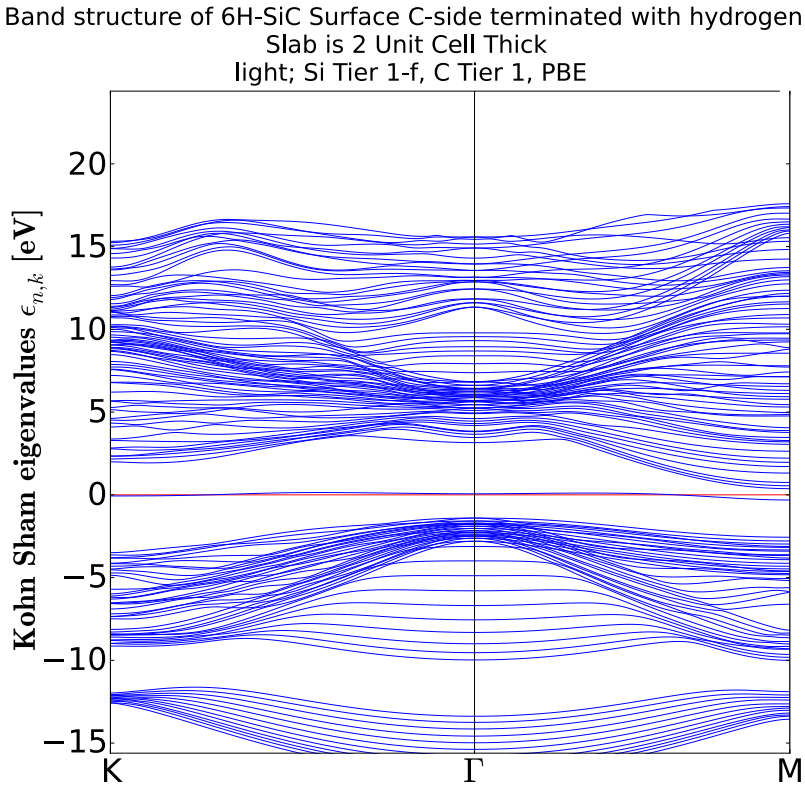
The projected band structure

An example: Hexagonal silicon carbide









Overview

1. (Problems I to V) Introduces basic bulk properties and convergence tests.
   - Problem I: Generation and visualisation of bulk structures
   - Problem II: Energy convergence tests
   - Problem III: Phase stability and cohesive properties
   - Problem IV: Unit cell relaxation
   - Problem V: Electronic band structure & density of states
2. (Problem VI and VII) Discusses surface calculations.
   - Problem VI: Electronic structure of crystal surfaces
   - Problem VII: Relaxing surface structures
3. (Problems VIII to IX) Magnetism and collinear spin calculations
   - Problem VIII: Magnetic $Ga_3Mn_1As_4$
   - Problem IX: Ferromagnetic and anti-ferromagnetic Ga0.75Mn0.25As

Practical issues

- **Each calculation one directory**

```
> mkdir tutorial2
> cd tutorial2
> mkdir Si
```

- **2 input files**

  `geometry.in`
  `control.in`

- **Launching FHI-aims calculation**

```
mpirun -n 4 aims.x > aims.out
```

- **... scripting helps !**
  (Sample scripts in the handout)

Your Tutors for the afternoon

Björn Bieniek

Lydia Nemec

Christian Carbongo

Noa Marom

Bryan Goldsmith

Arvid Ihrig