2^{nd} Tutorial:

Periodic Systems

Hands-on Tutorial Workshop 2011

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Fritz Haber Institute of the Max Planck Society

14th July 2011

Outline of this tutorial

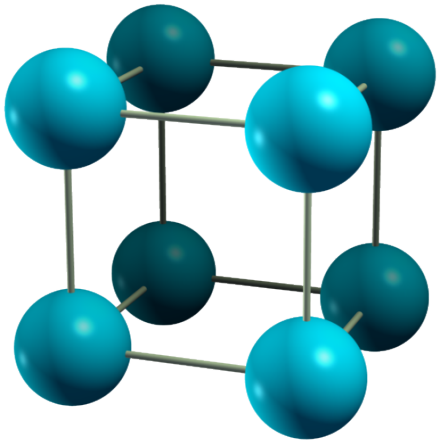
1. Periodic systems with DFT
   - The crystal structure
   - Sampling of the Brillouin zone
   - Band structure and density of states
   - Find minimal lattice constant
2. Systems of interest
   - Bulk Silicon
   - Silicon surface
   - Iron
3. Overview

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

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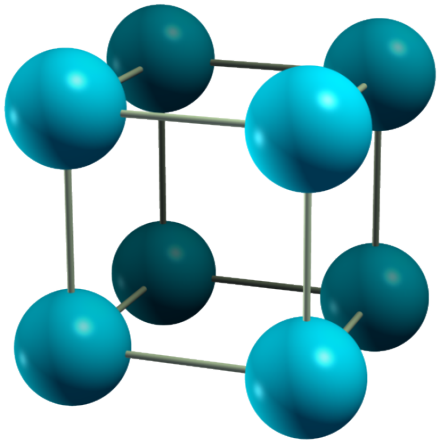

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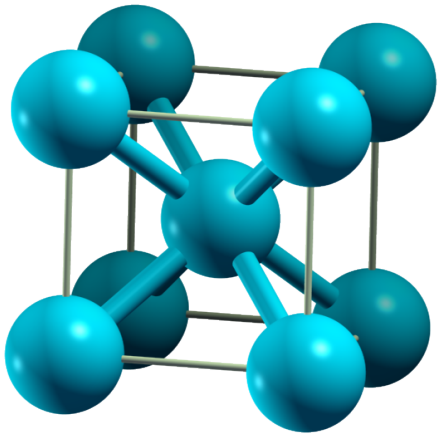

BCC

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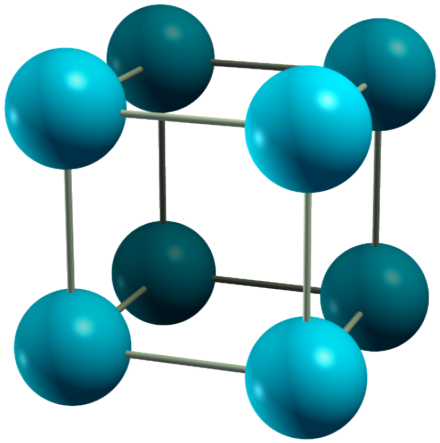

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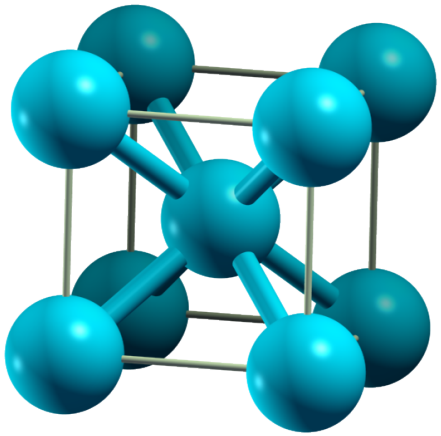

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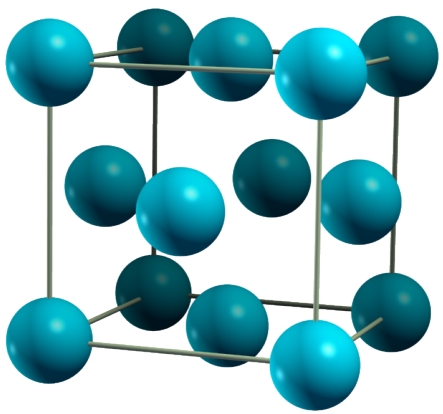

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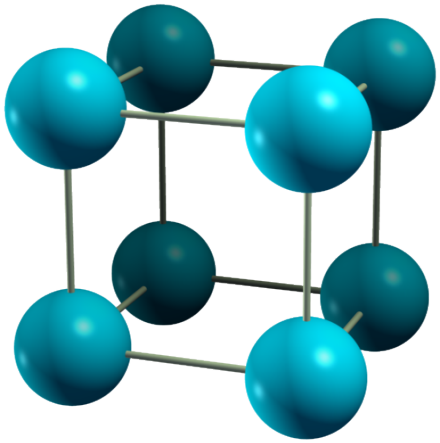

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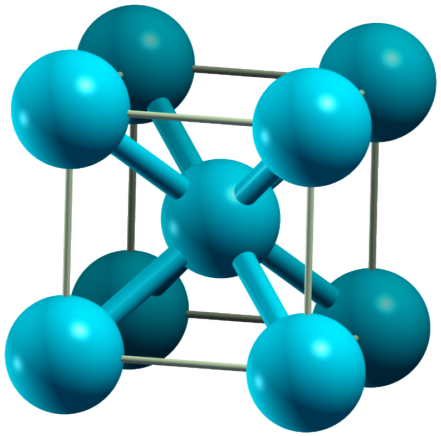

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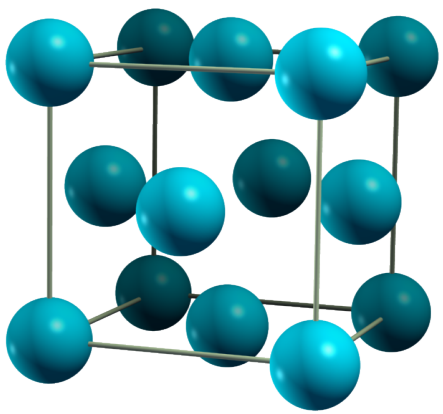

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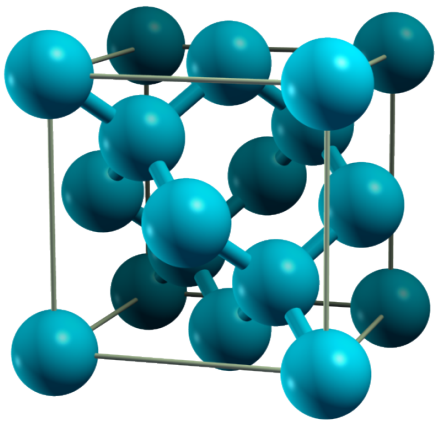
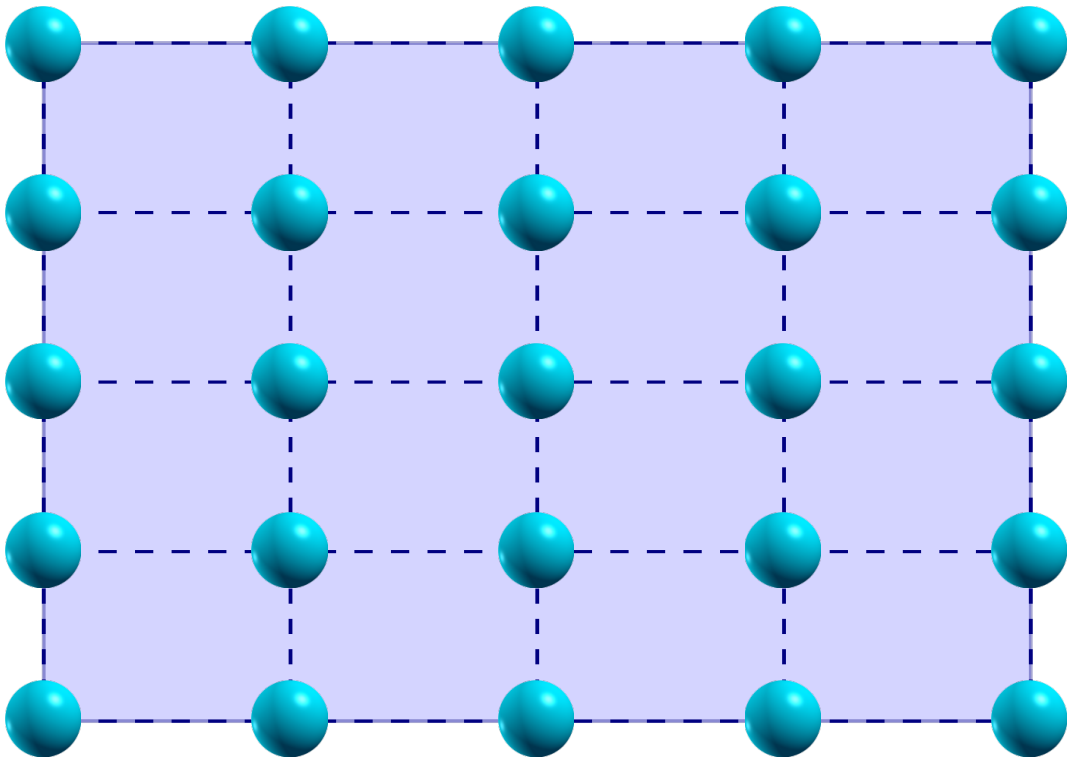


diamond

A 2-dimensional example



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

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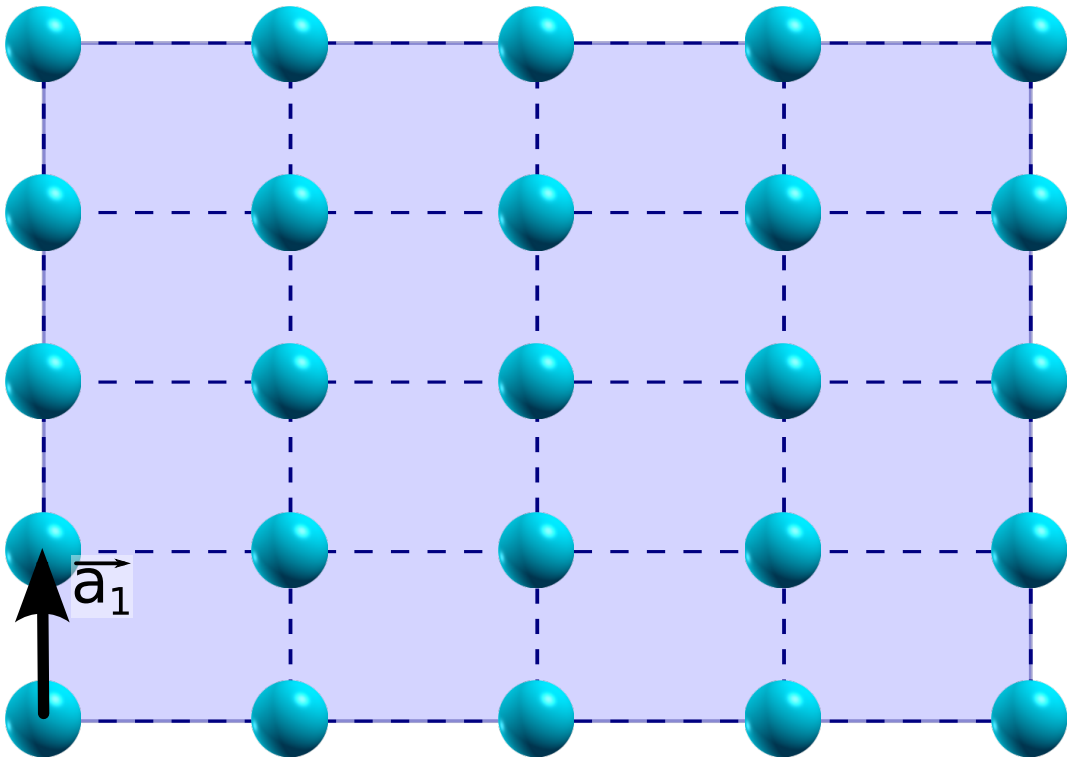

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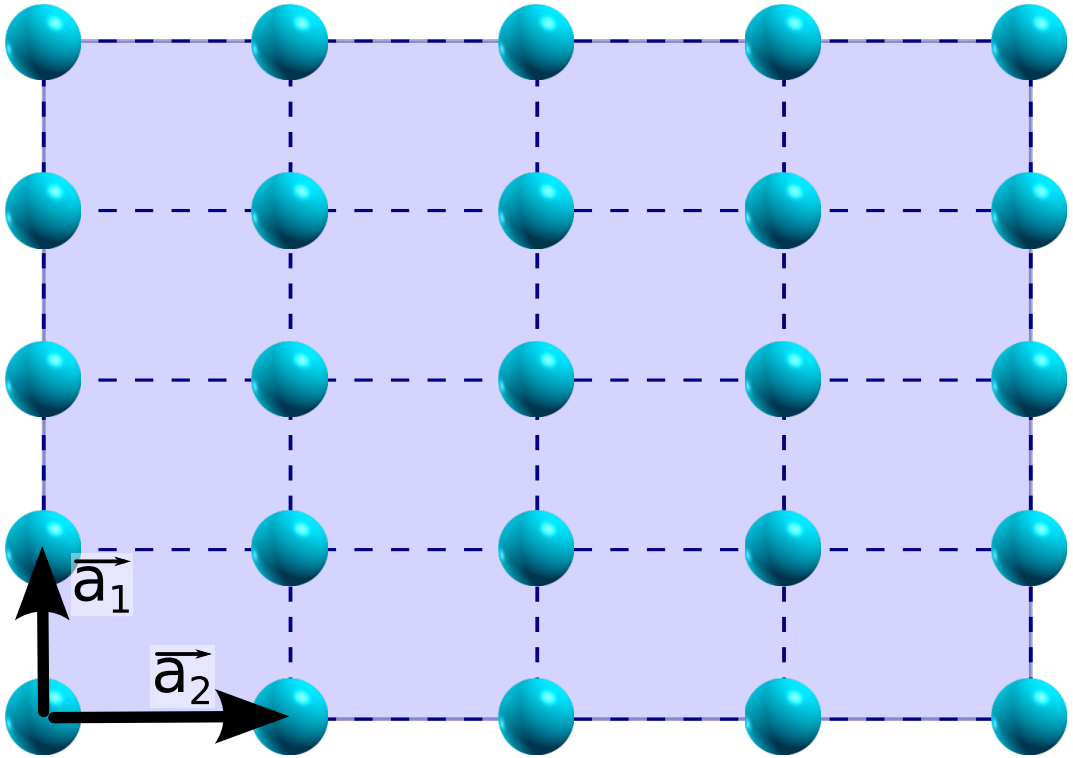

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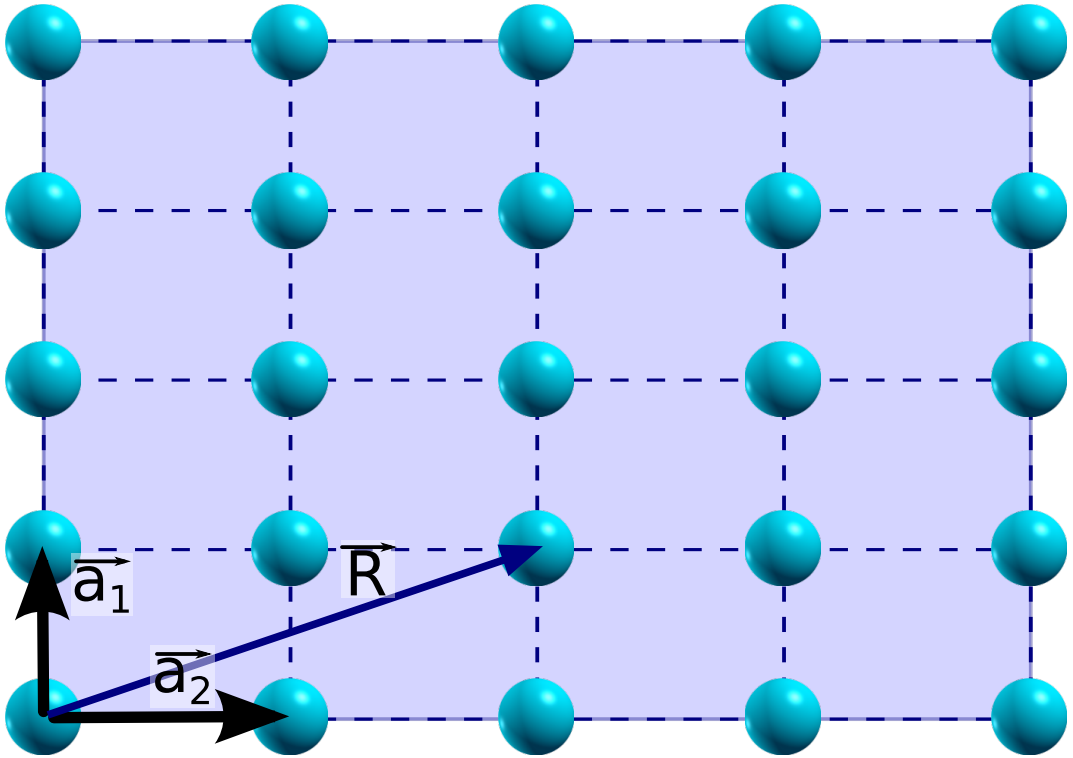

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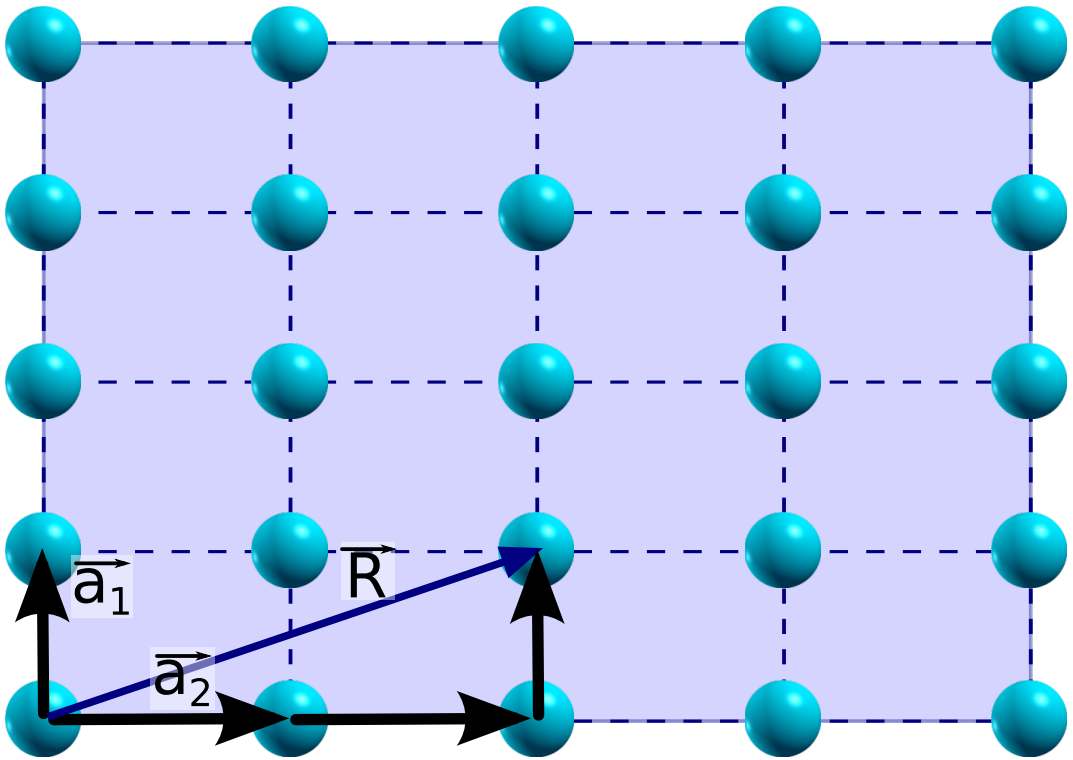


$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

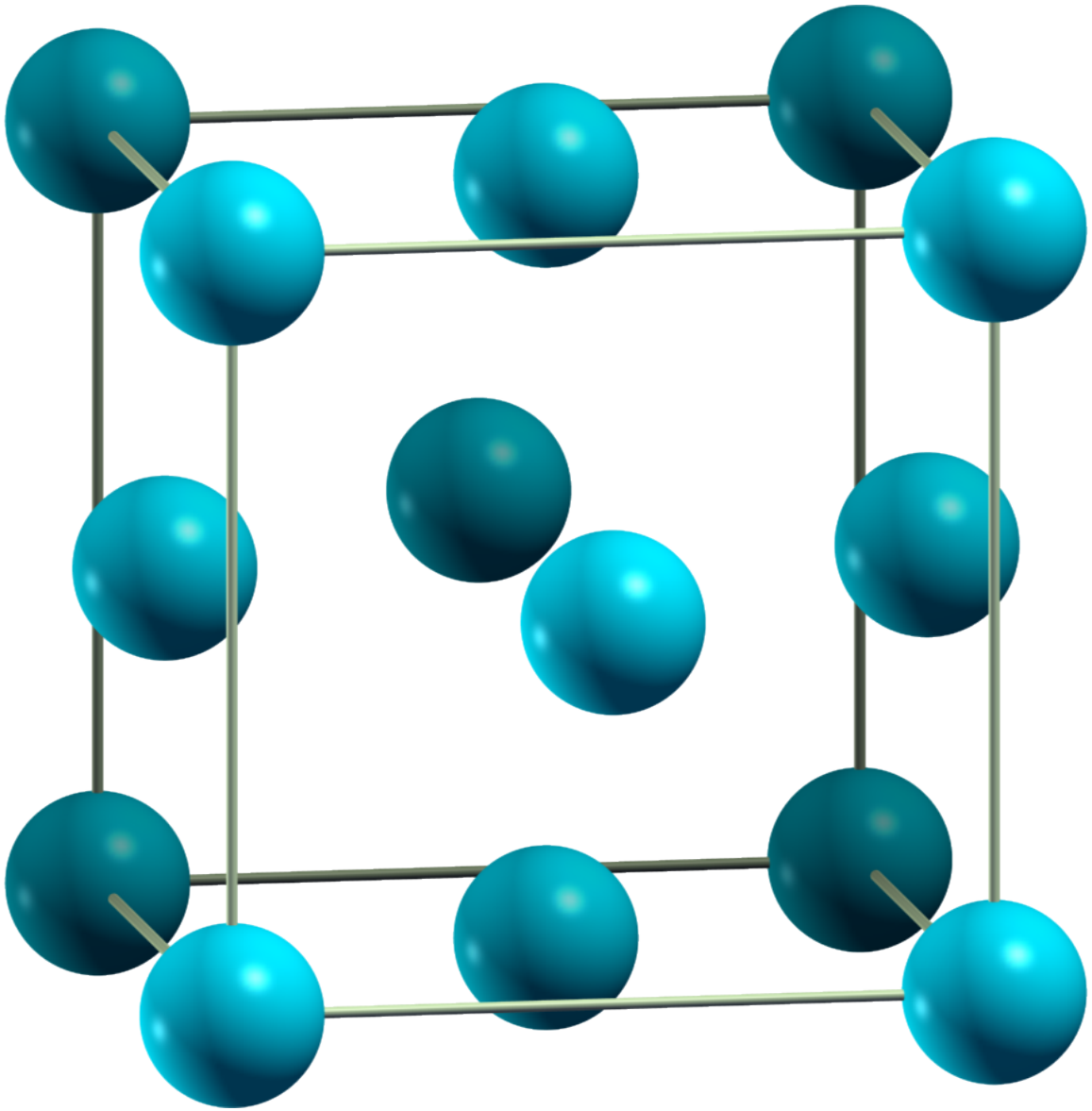
$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2$$

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

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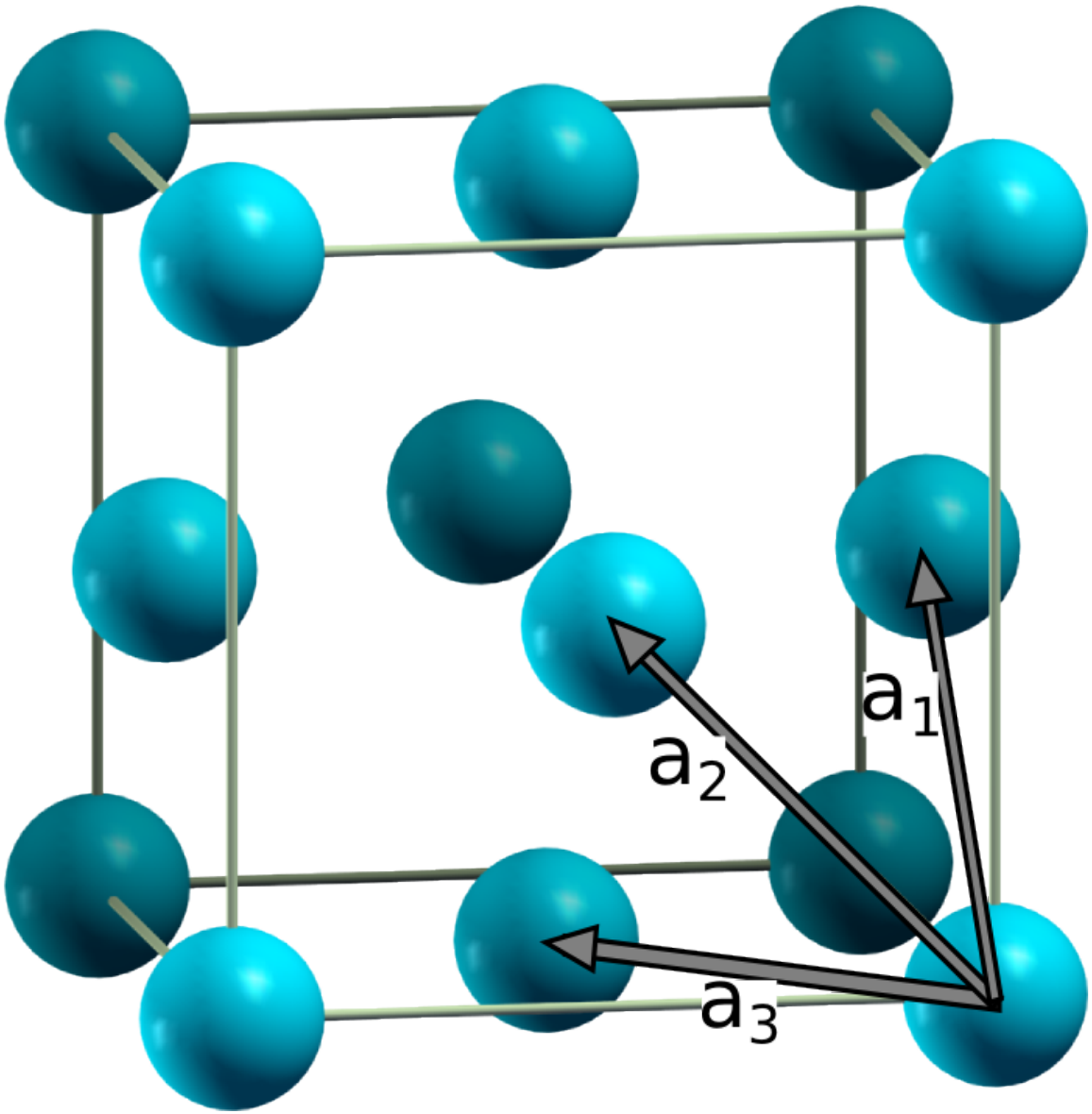

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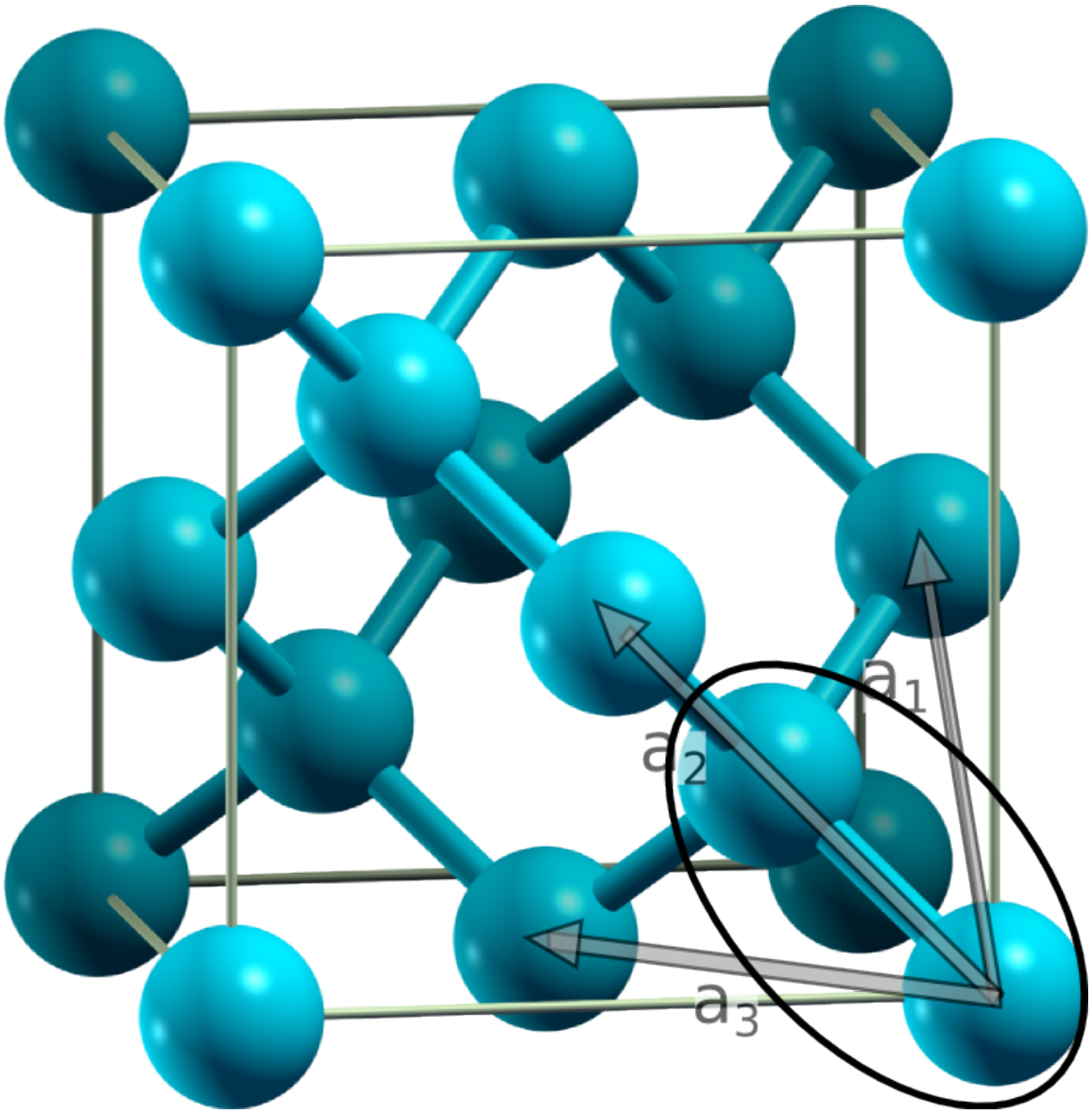

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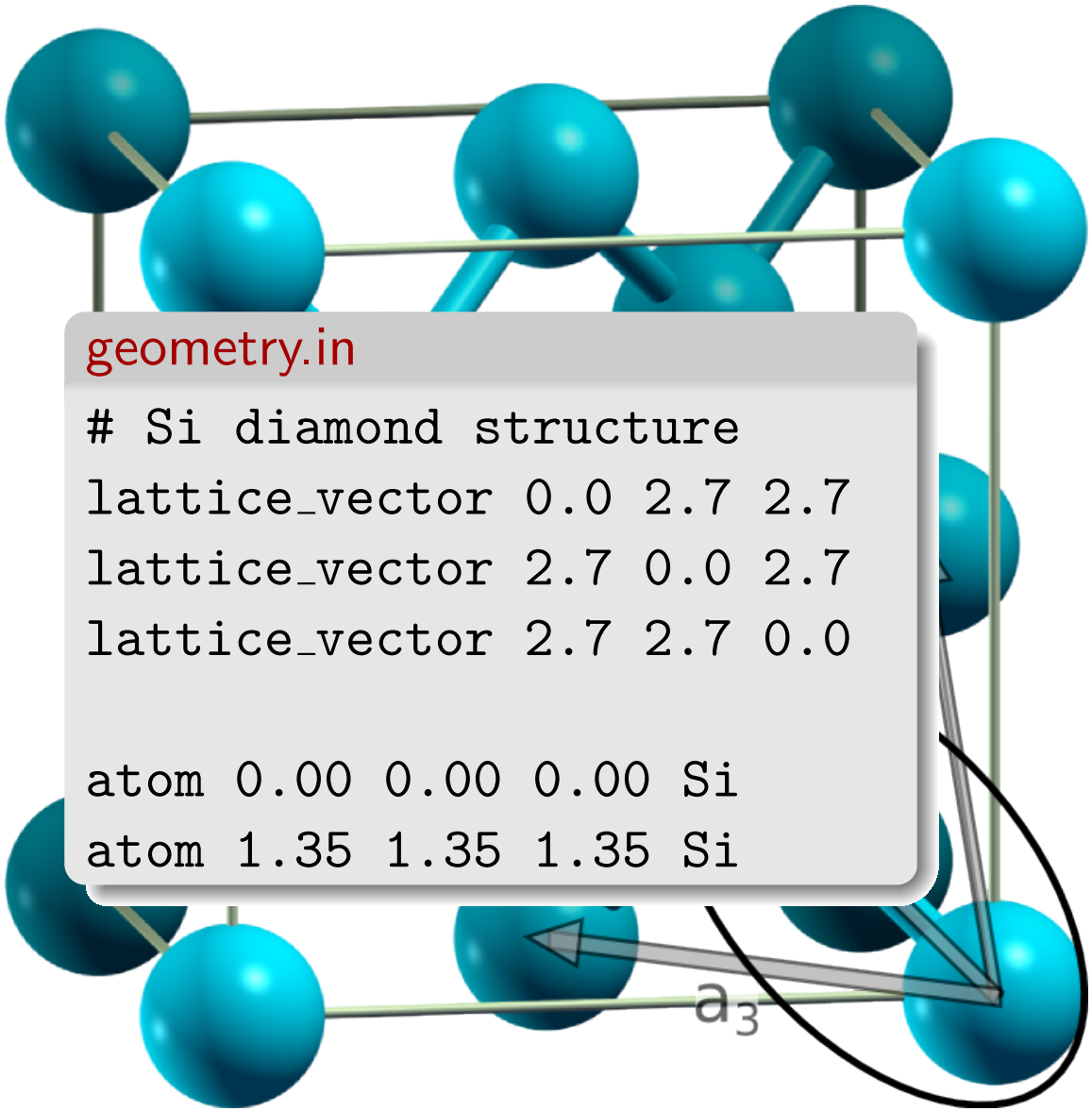

geometry.in

```
# 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 $\rho(\vec{r})$

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

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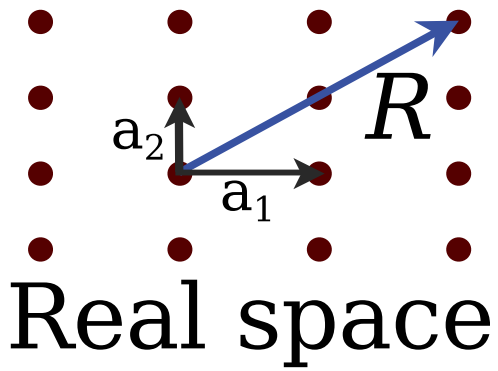

- In practice, calculations are performed on a grid of points in the 1BZ

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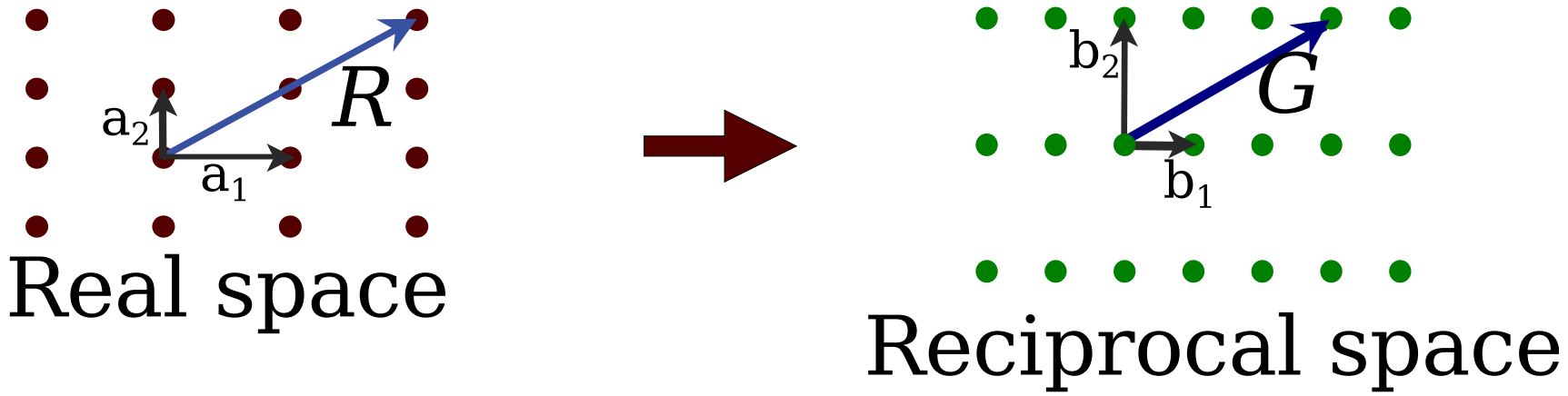

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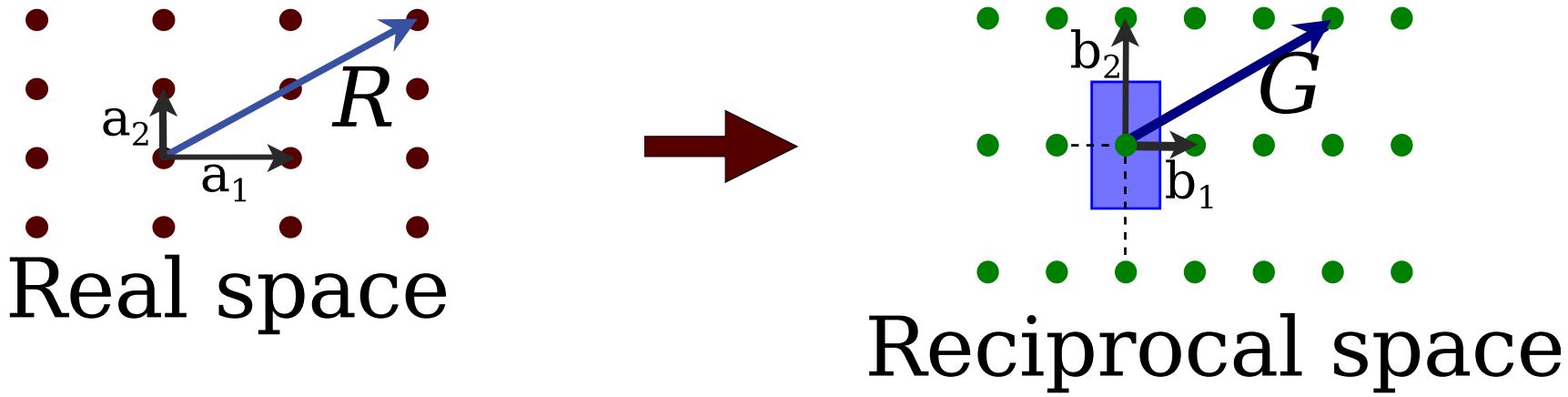

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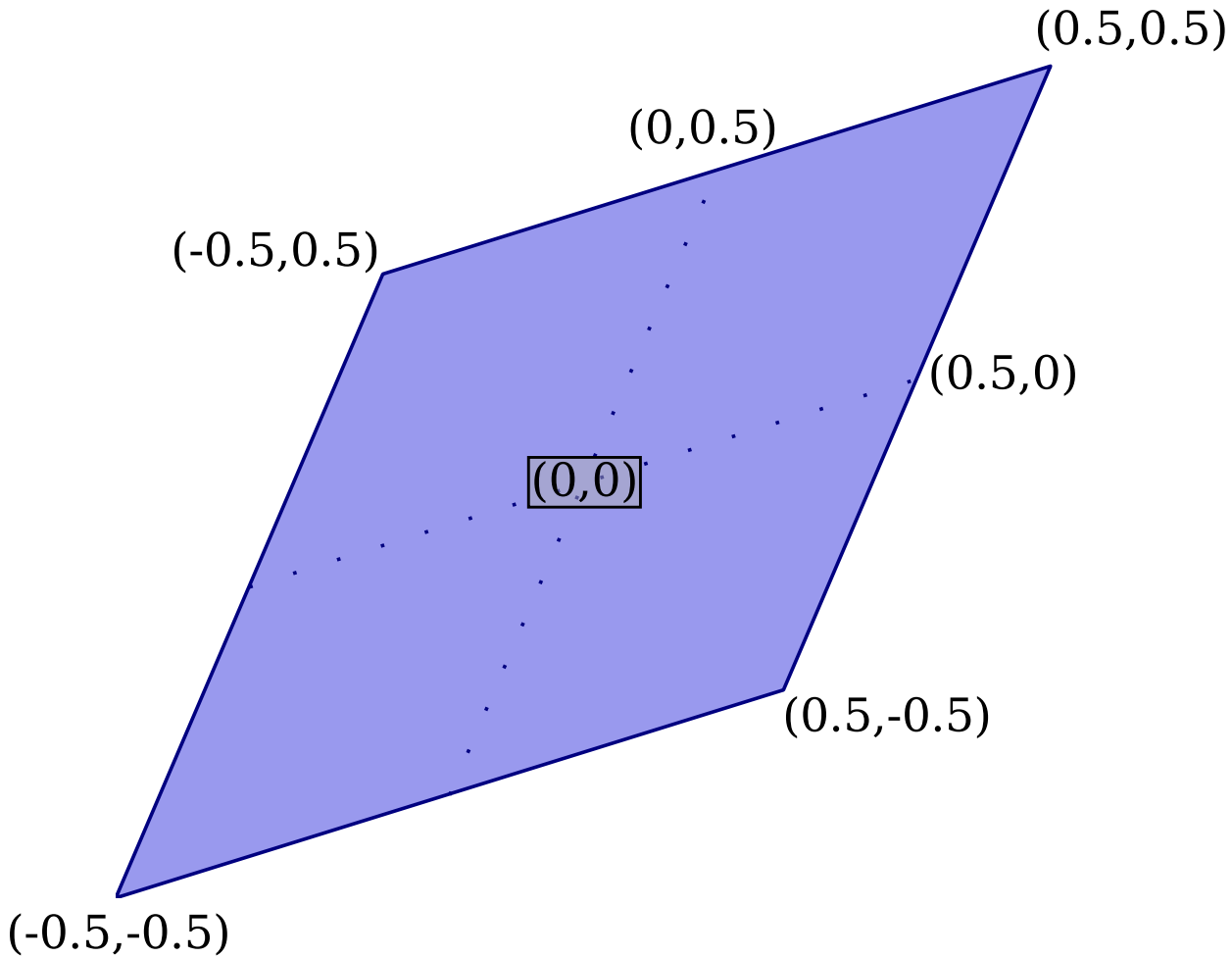
The grid in the Brillouin zone



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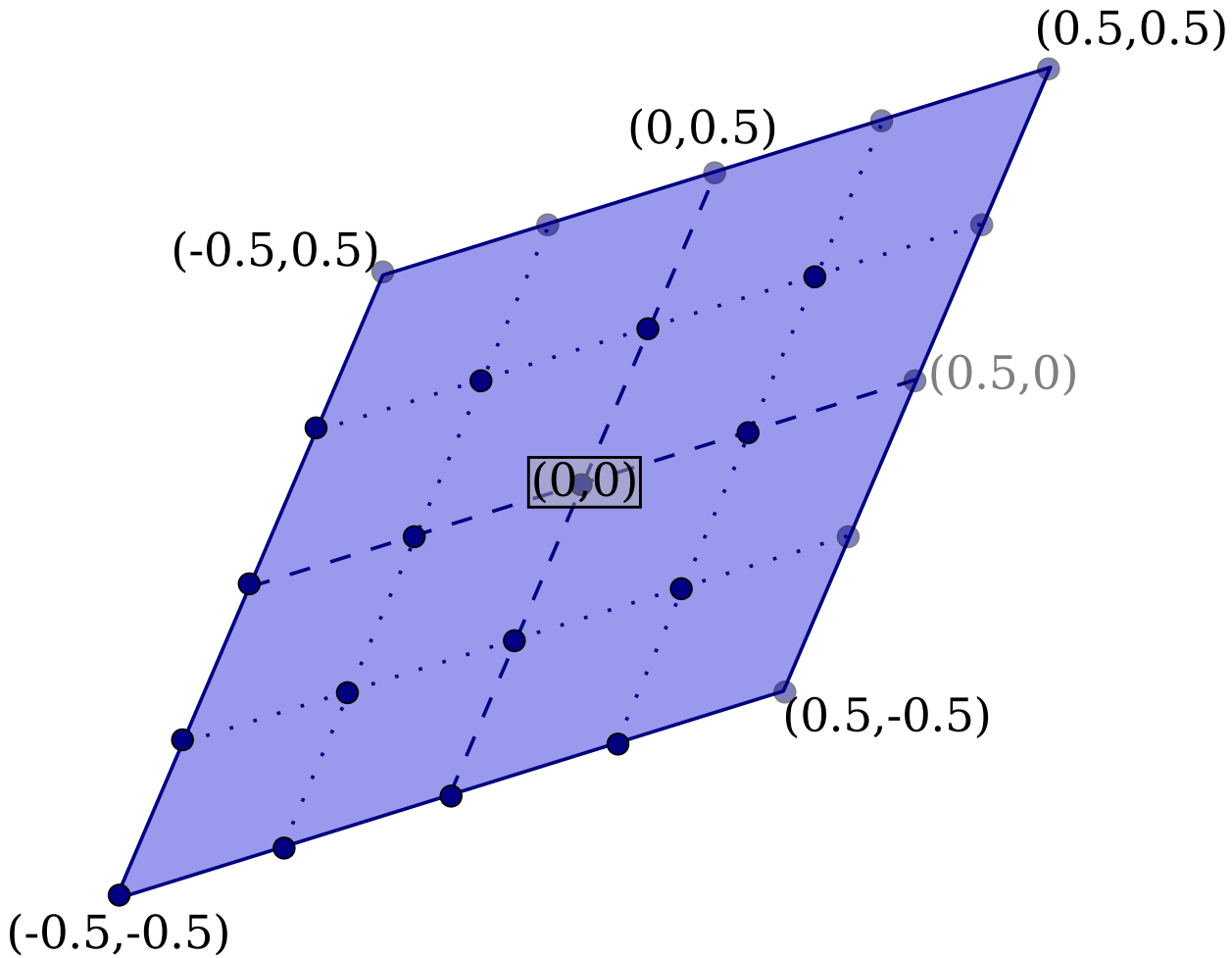

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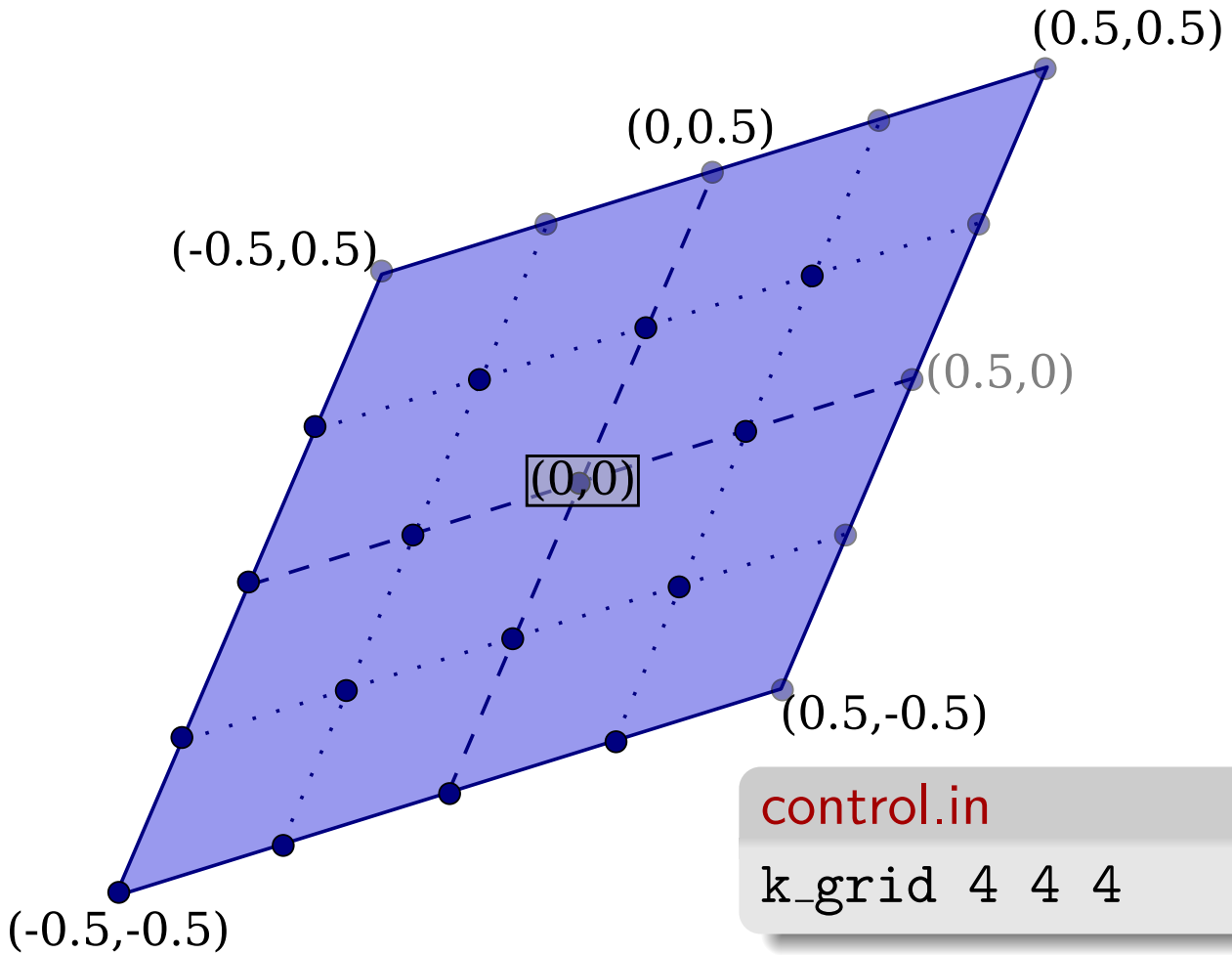


control.in

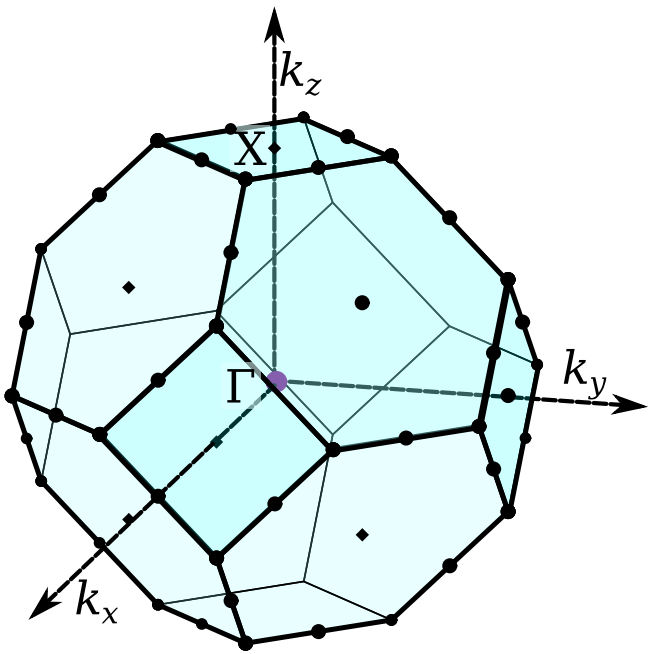
```
k_grid 4 4 4
```

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 ($\epsilon(k)$)

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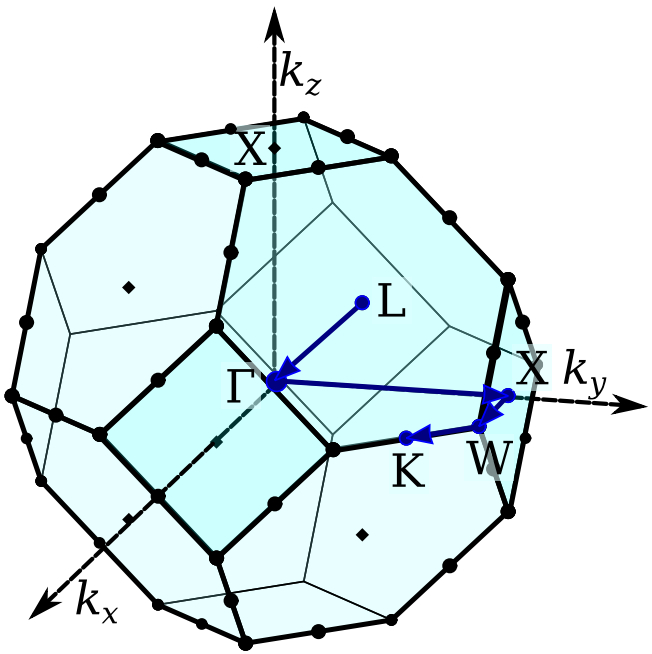

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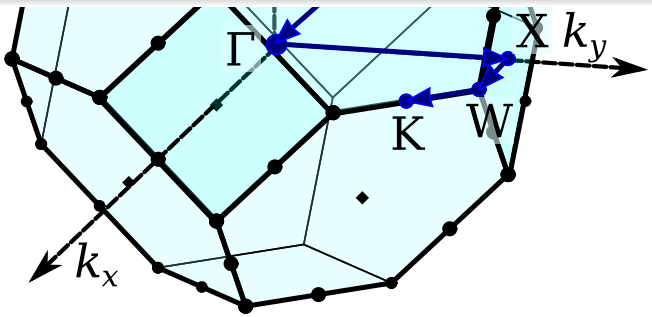
control.in

```
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
...
```



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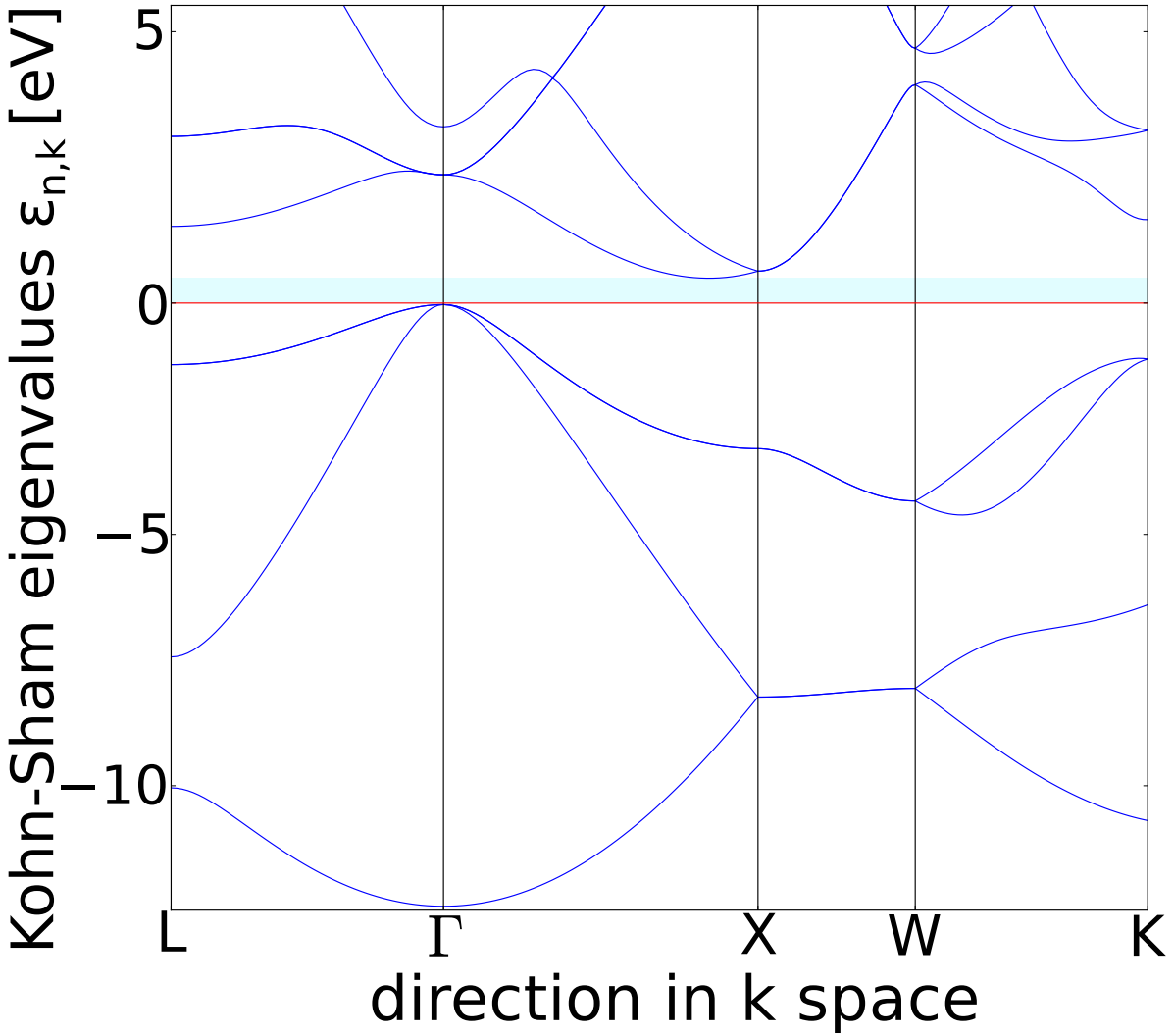
The electronic Band structure of Silicon



- 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)

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

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

where σ is the Gaussian broadening

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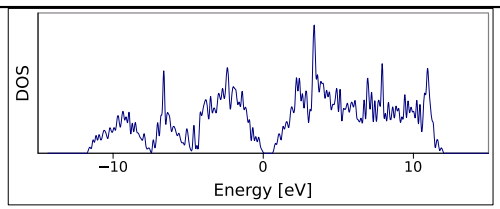
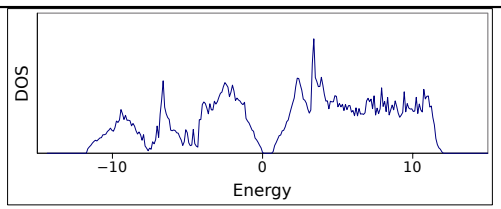
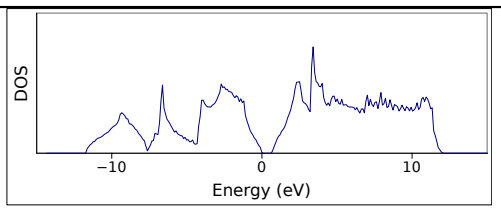
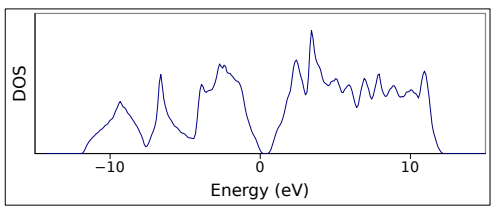
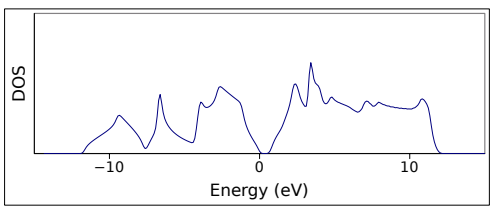
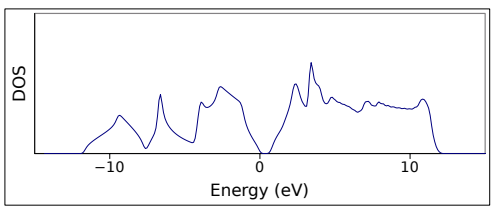
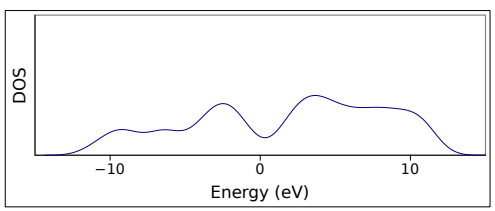
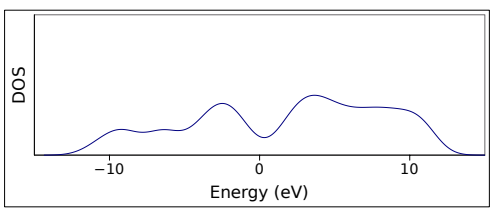
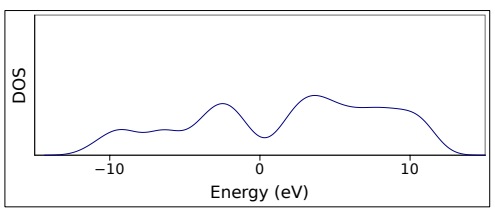
σ/grid	20x20x20	40x40x40	60x60x60
0.01			
0.1			
1.0			

Find minimal lattice constant

Cohesive properties of solids

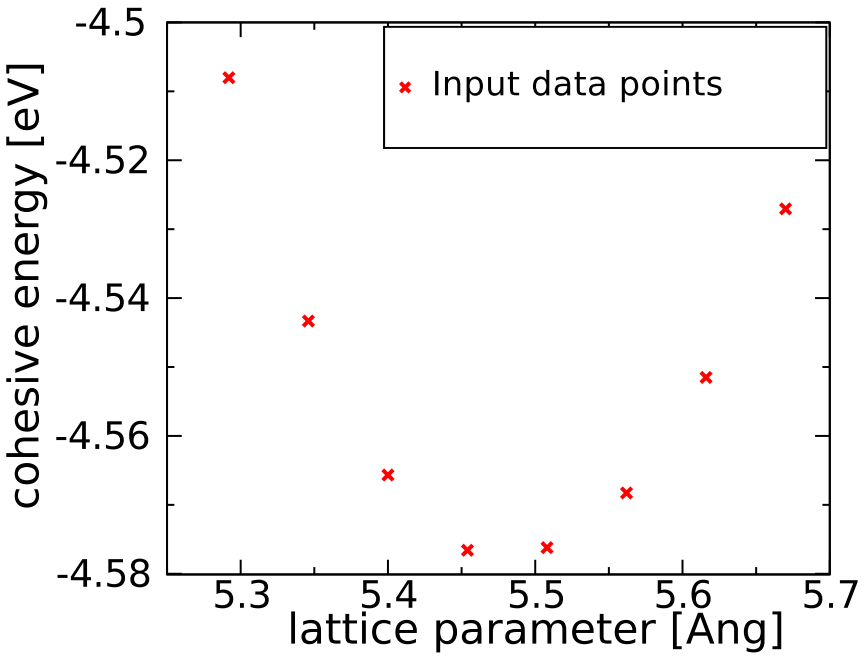
Cohesive energy:

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

- 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

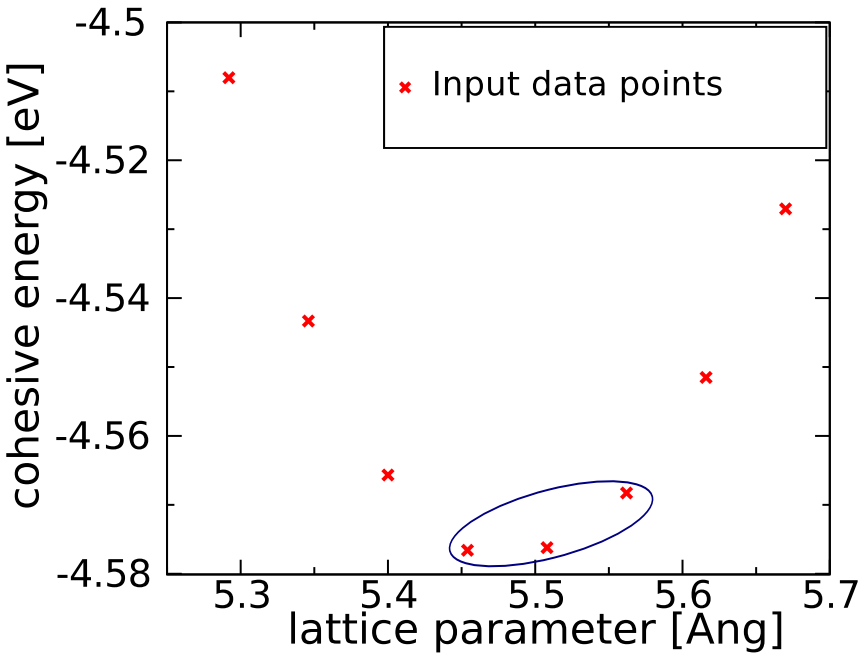
B_0' : derivative of B_0 (w.r.t. pressure)

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



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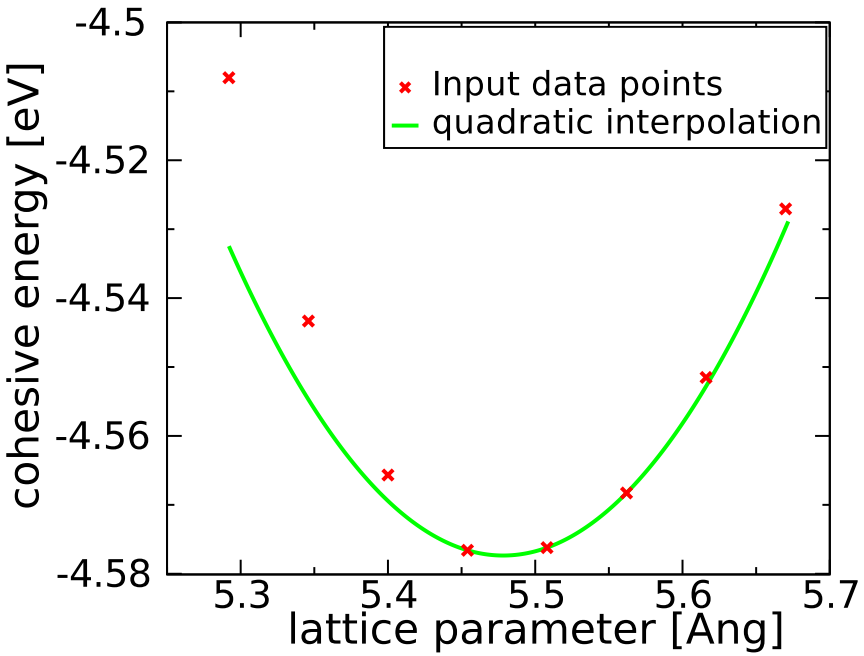

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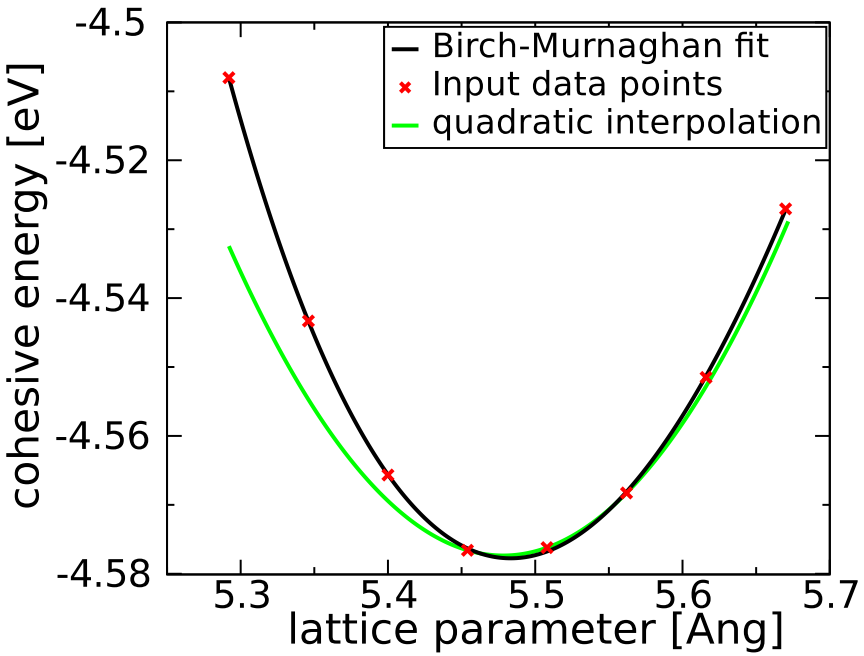

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Systems of interest

- Bulk Silicon
- Silicon Surface
- Magnetic Iron

Bulk Silicon

Motivation

VOLUME 45, NUMBER 12 PHYSICAL REVIEW LETTERS 22 SEPTEMBER 1980

Microscopic Theory of the Phase Transformation and Lattice Dynamics of Si

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(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

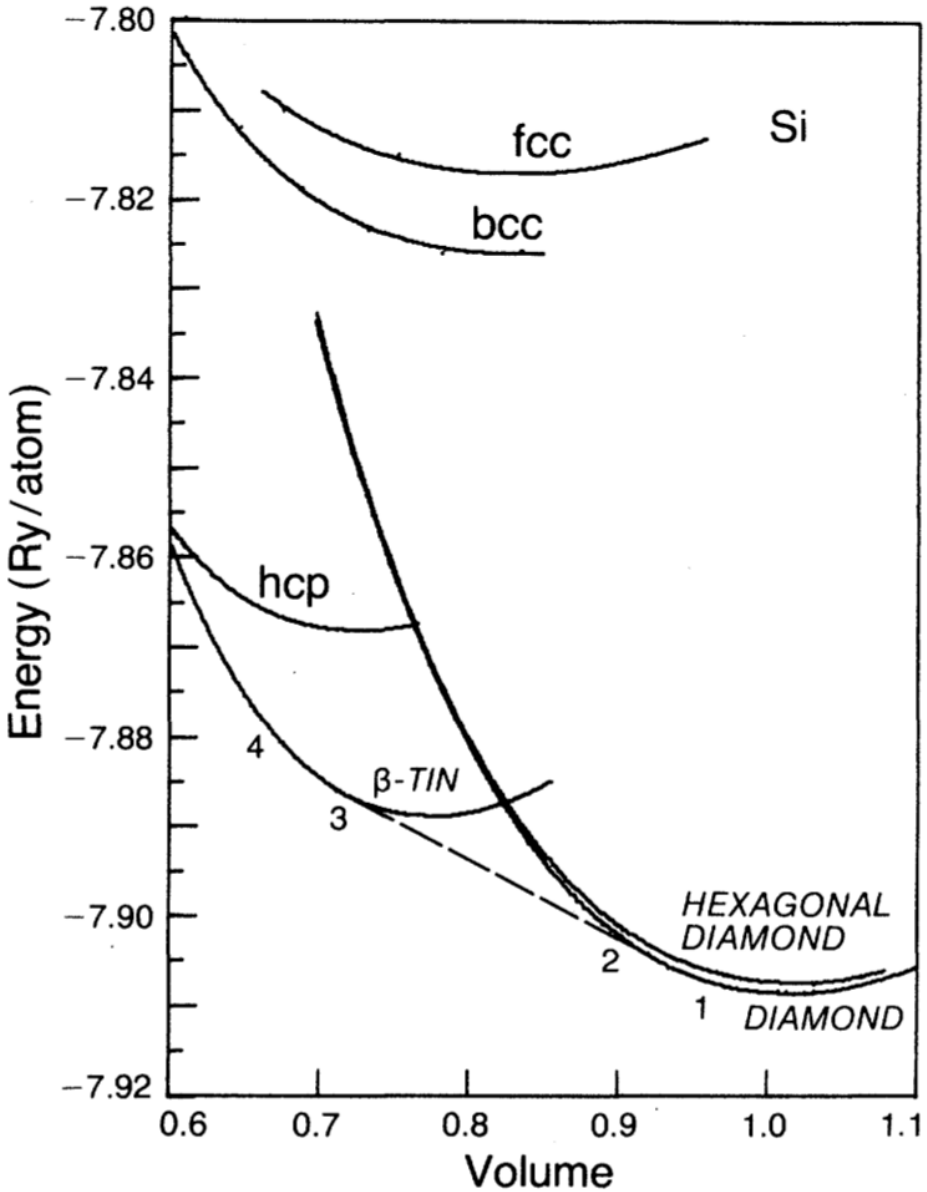
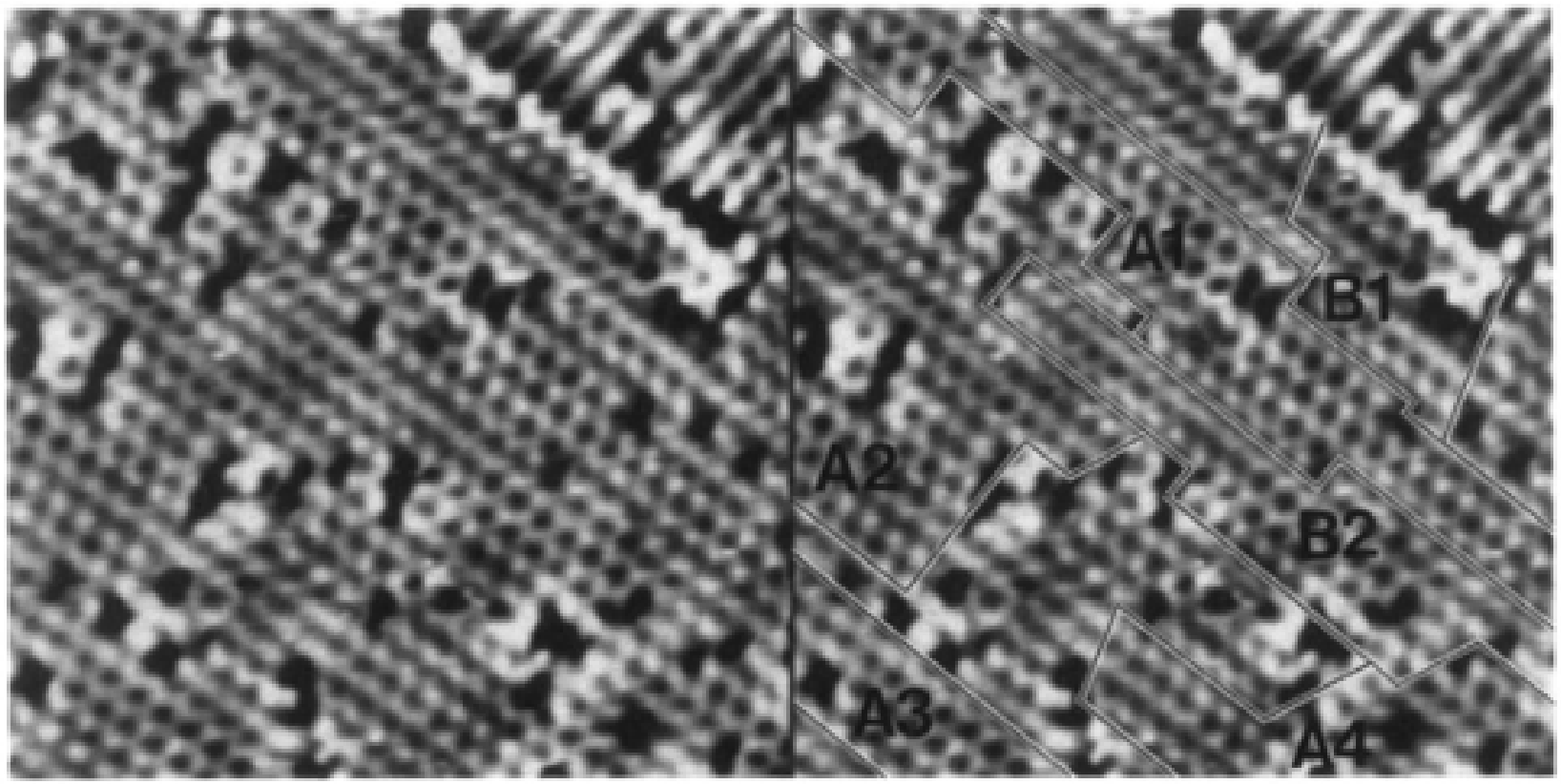


FIG. 1. The diamond, hexagonal diamond, and β-tin, hcp, bcc, and fcc structural energies (in units of Ry/atom) as a function of the atomic volume [normalized to the measured free volume (Ref. 16)] for Si. The dashed line is the common tangent of the energy curves for the diamond and the β-tin structures.

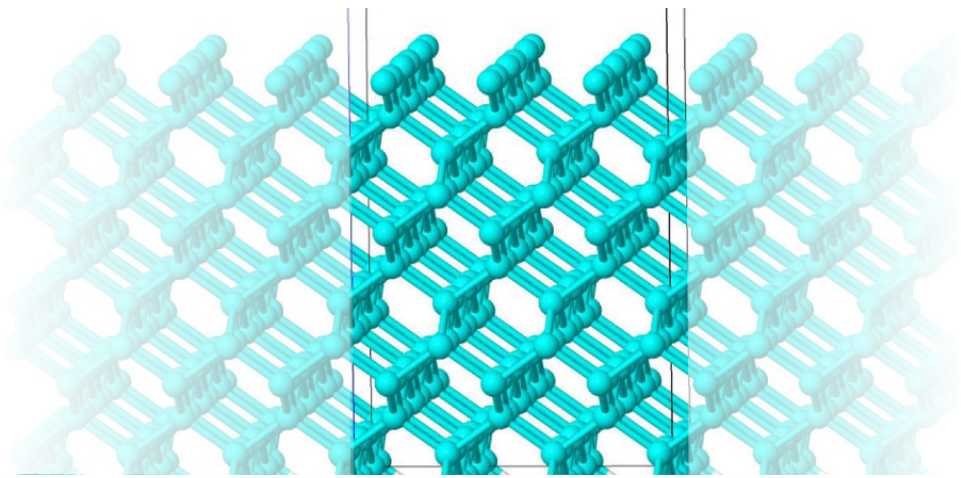
Silicon surface

Motivation



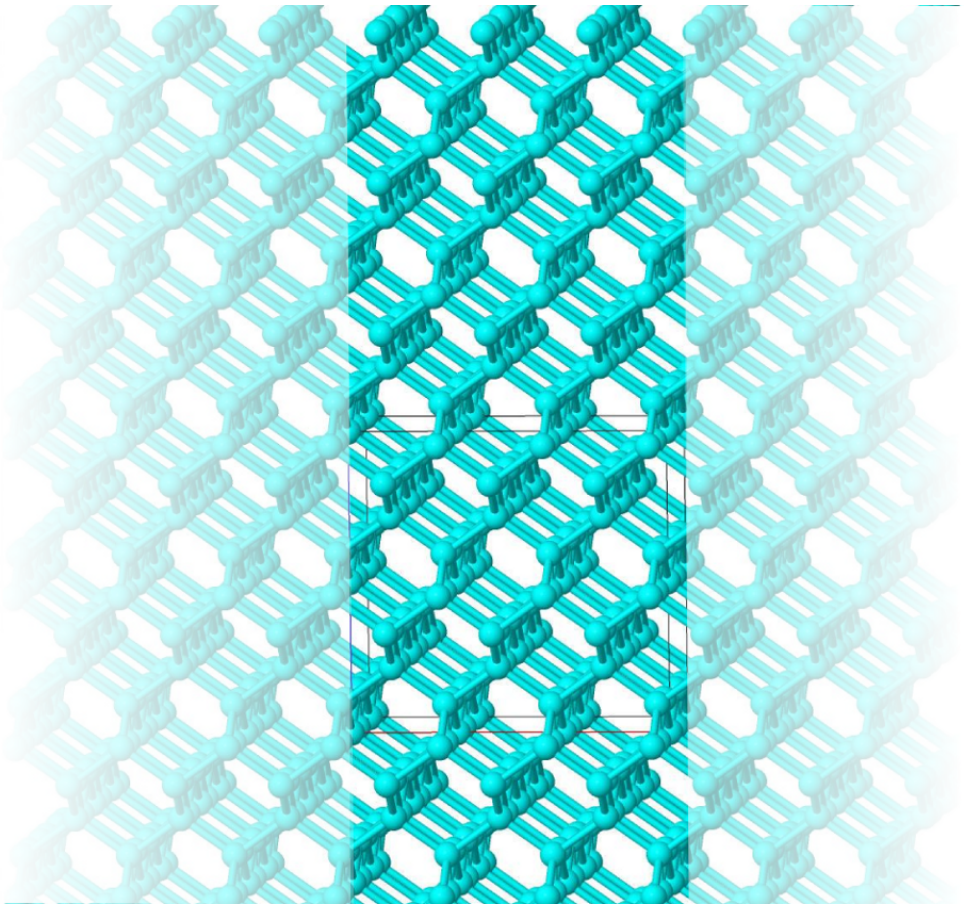
R.A. Wolkow, PRL 68,2636 (1992)

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



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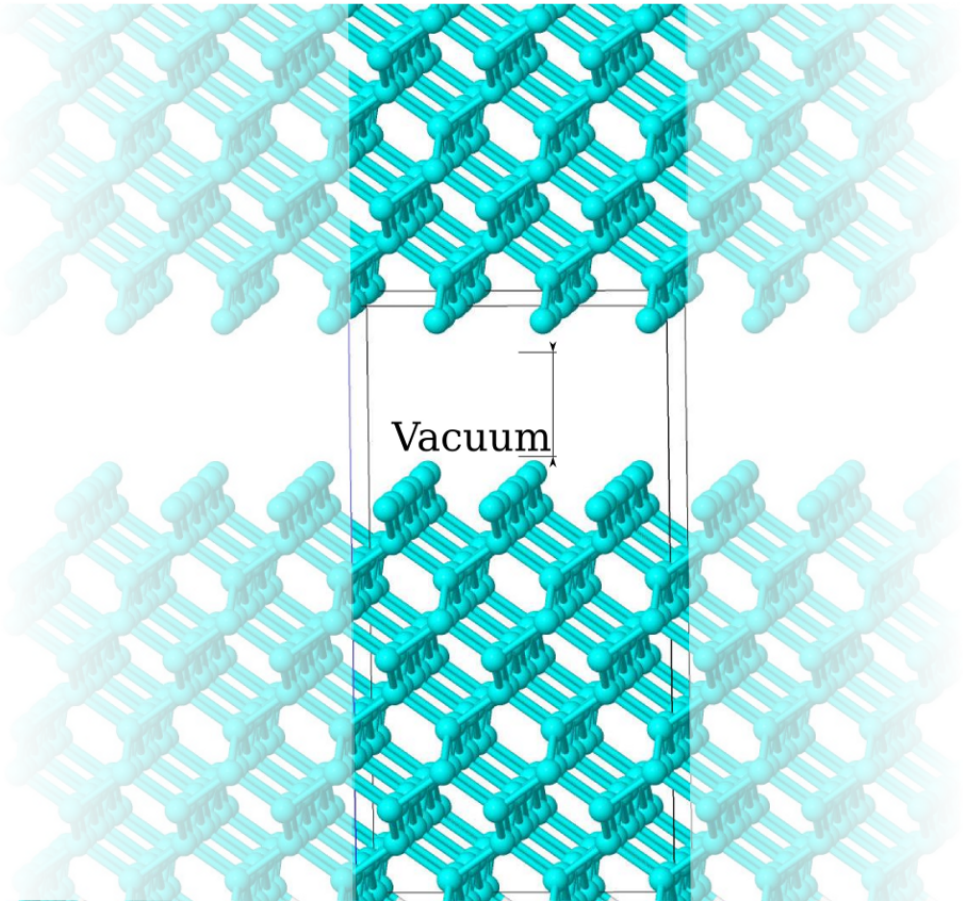

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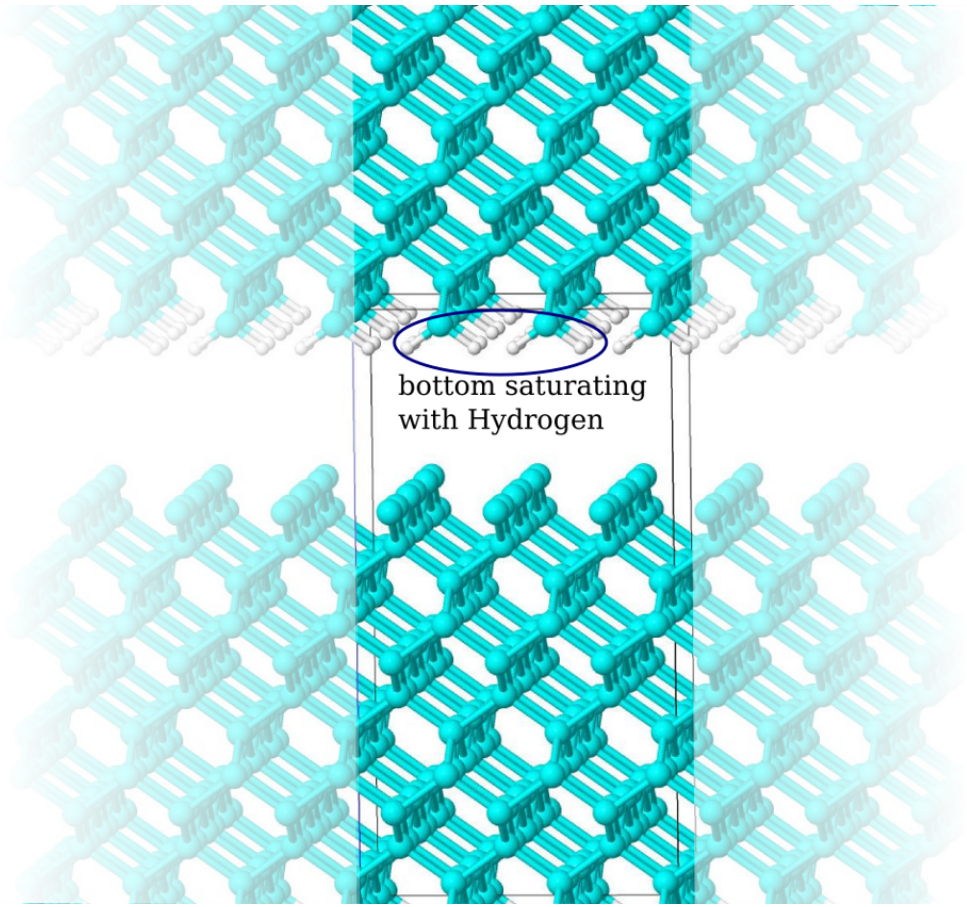

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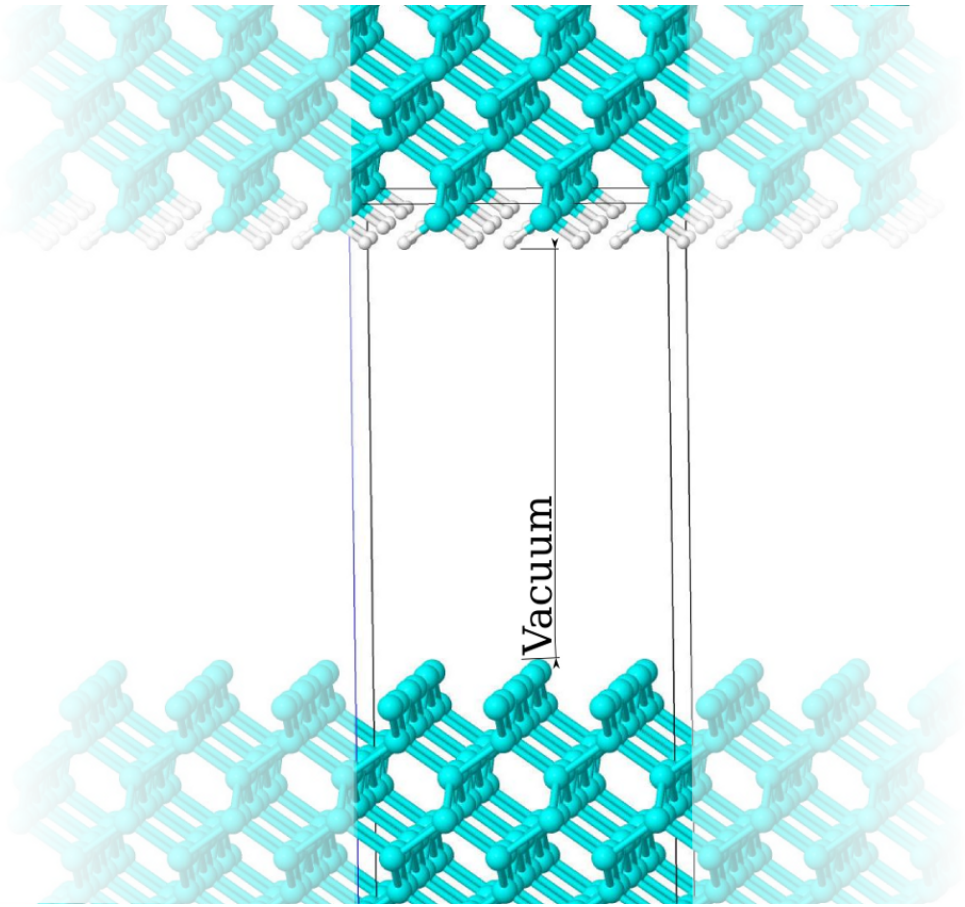

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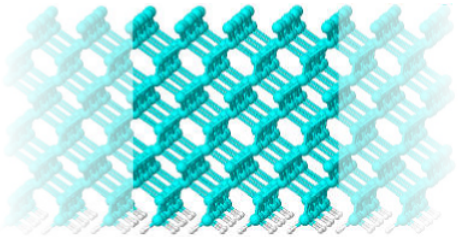

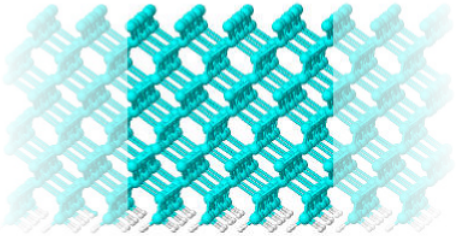

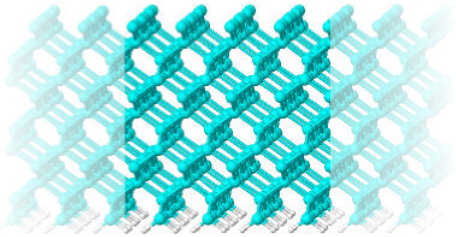

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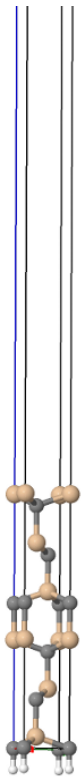
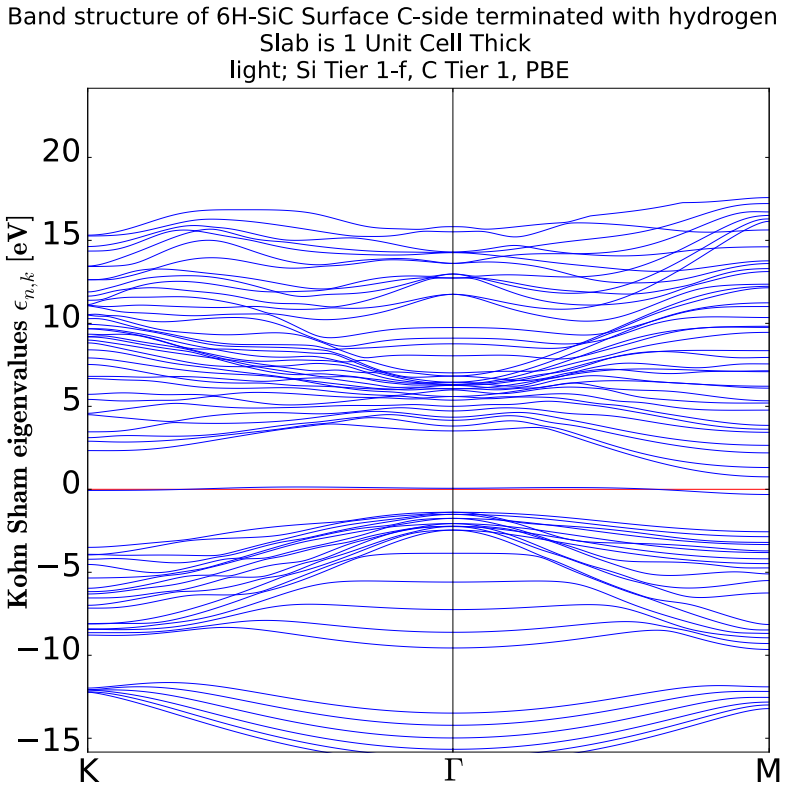
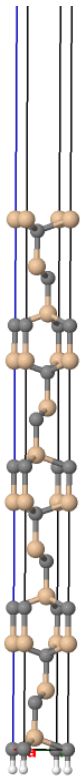
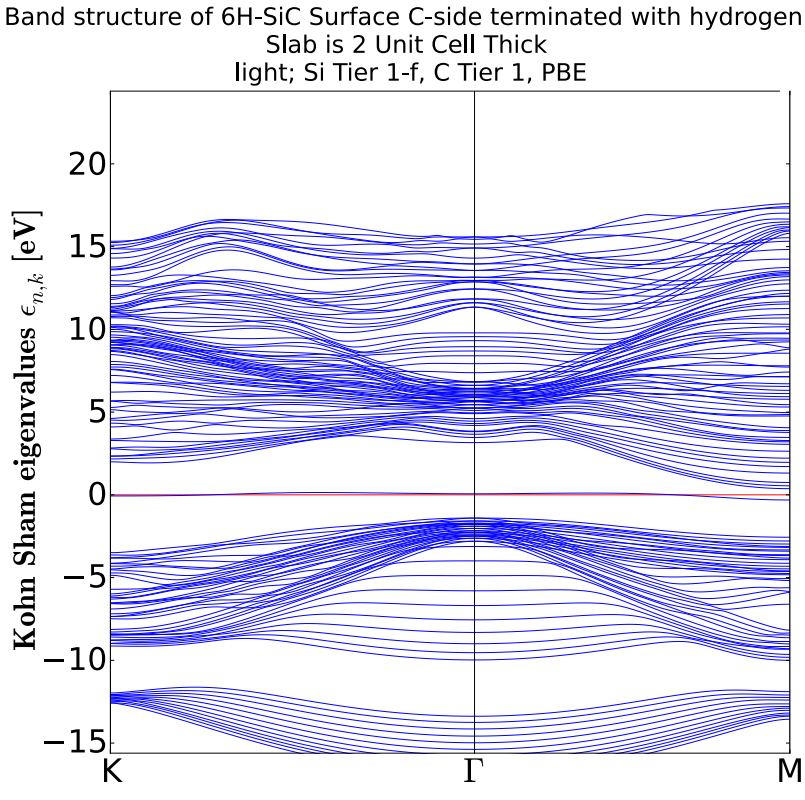
The projected band structure

An example: Hexagonal silicon carbide









Iron

Iron and steel

Properties: hard, elastic, and tensile strength

- steel is an alloy that consists mostly of iron
- carbon content between 0.2% and 2.1% by weight
- at 0.021% carbon concentration at $\sim$ 1300 K $\rightarrow$ (FCC) structure

Source: wikipedia July 2011

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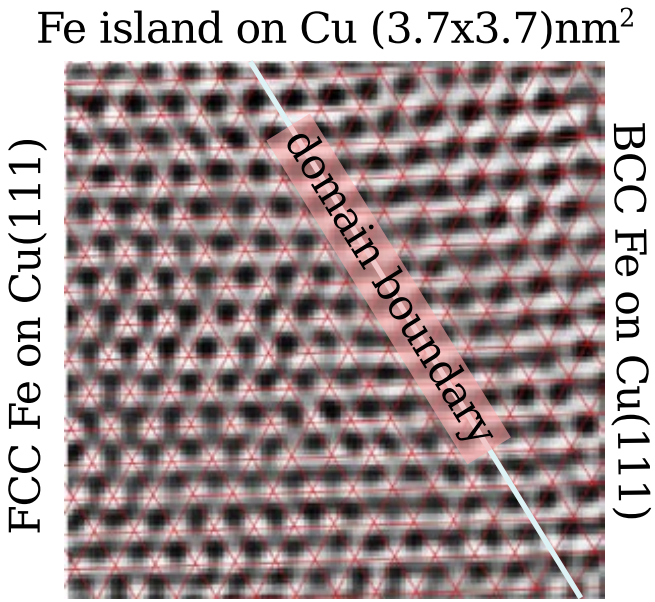
Magnetism and collinear spin calculations



L. Gerhard et all., Nature Nanotechnology 5, 792–7 (2010)
doi:10.1038/nnano.2010.214

- strong magnetoelectric coupling at the surface of thin iron films
- write and store information
- durable and high density

Magnetism and collinear spin calculations

adapted from:
L. Vočadlo et al. Physics of the Earth and Planetary Interiors 117 (2000) 123–137

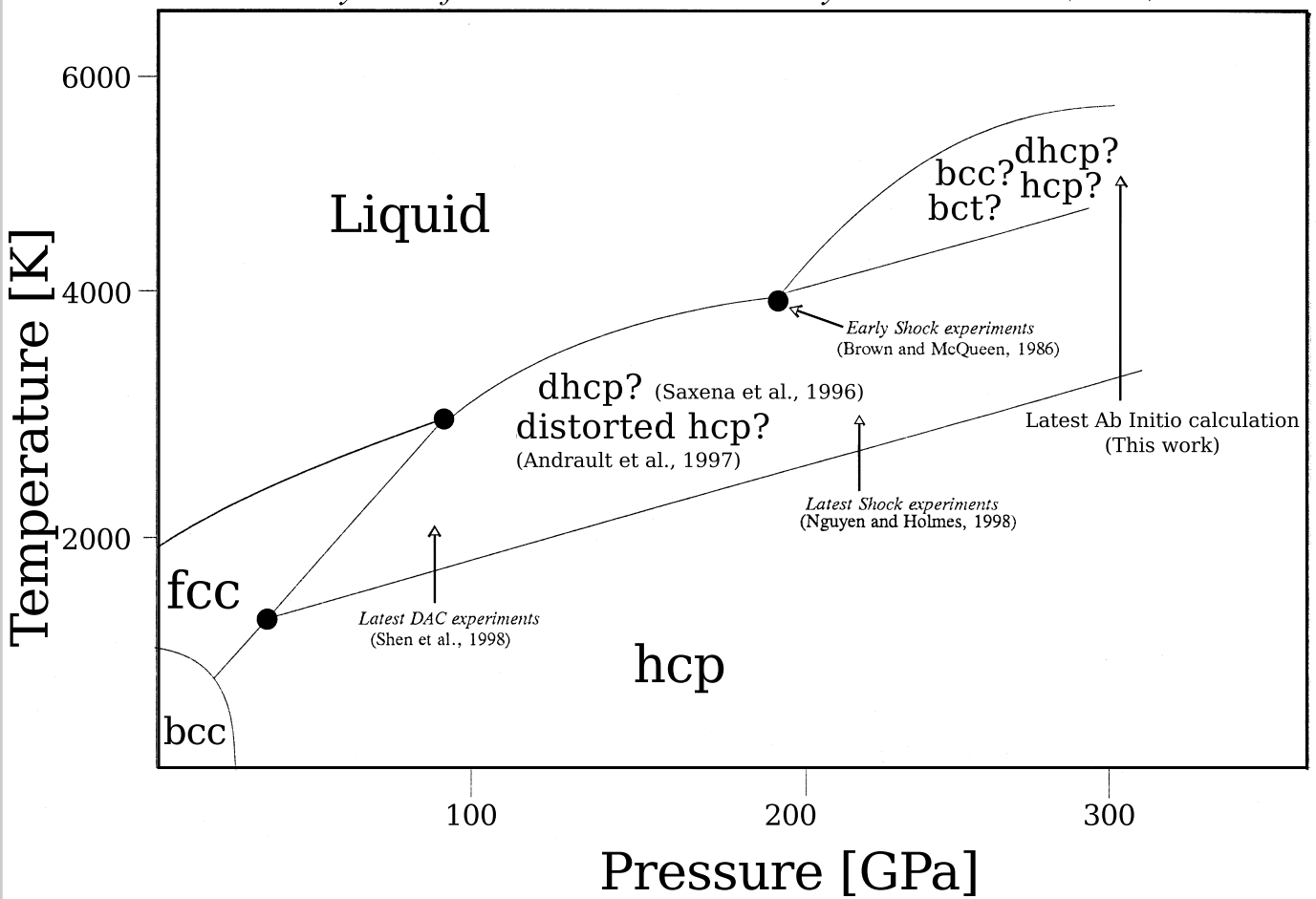
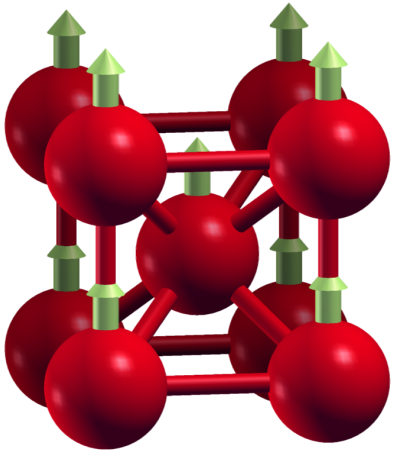
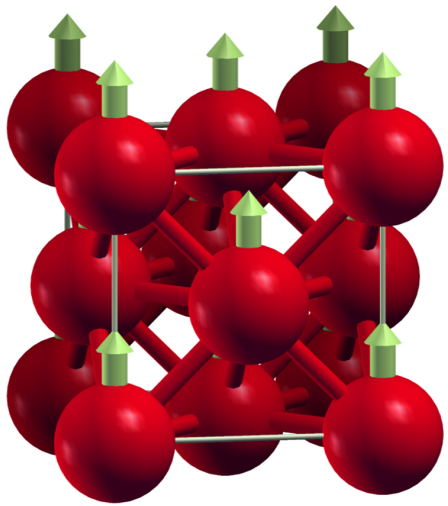


Fig. 1. The phase diagram of iron which shows the experimentally solid - solid phase transformations to high *P/T* polymorphs of unknown structure.

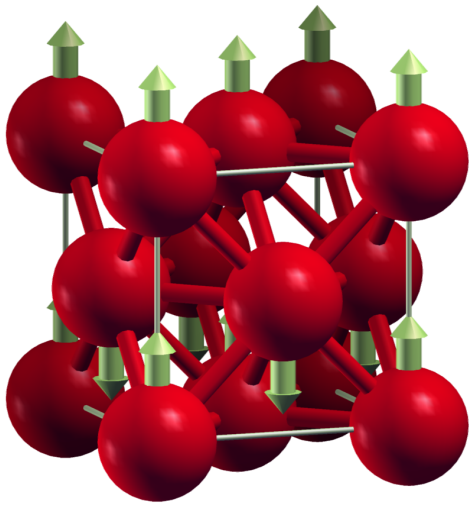
Magnetic Iron: BCC and FCC geometry



BCC iron
ferromagnetic



FCC iron
ferromagnetic



FCC iron
anti-ferromagnetic

How to set up a magnetic calculation?

The geometry.in file

- specify the initial spin moment

The control.in file

- keyword: `spin collinear`

```
# Fe FCC ferromagnetic
lattice_vector 0.00 1.74 1.74
lattice_vector 1.74 0.00 1.74
lattice_vector 1.74 1.74 0.00
#
atom 0.00 0.00 0.00 Fe
 initial_moment 2.0
```

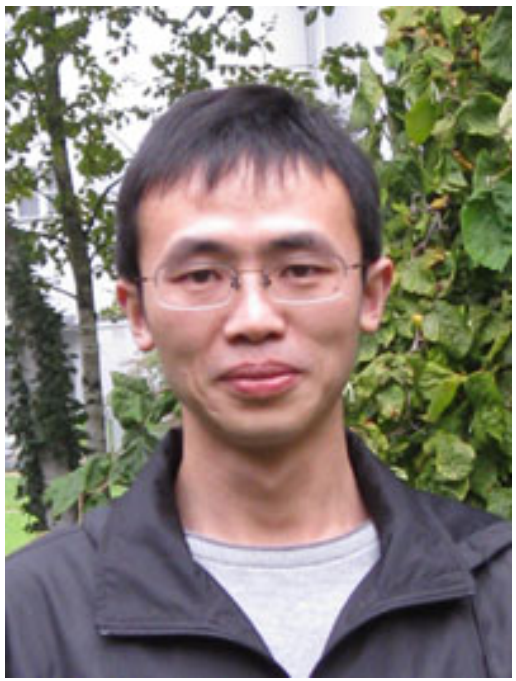
```
# control.in
spin collinear
```

Overview

1. (Problems I to IV) introduces basic bulk properties and convergence tests.
   - Problem I: Generation and visualization of bulk structures
   - Problem II: Energy convergence tests
   - Problem III: Phase stability and cohesive properties
   - Problem IV: Electronic band structure & density of states
2. (Problem V and VI) discusses surface calculations.
   - Problem V: Electronic structure of crystal surfaces
   - Problem VI: Relaxing surface structures
3. (Problems VII to IX) covers magnetism and collinear spin calculations on iron.
   - Problem VII: Lattice constant of non-magnetic iron
   - Problem VIII: *Ferro*magnetic iron
   - Problem IX: Anti-*ferro*magnetic iron

Acknowledgements

Special Thanks!



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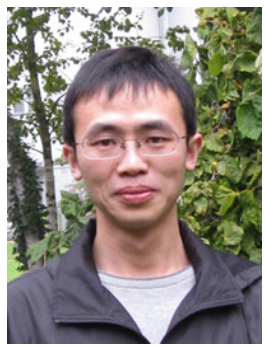
Volker Blum

Your Tutors for the afternoon

Jürgen Wieferink

Lydia Nemec



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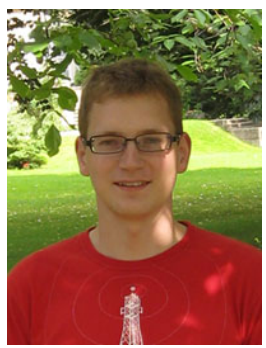
Marco Casadei



Franz Knuth

Florian Lazarevic