2nd Tutorial:

Periodic Systems
Hands-on Tutorial Workshop 2014

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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
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- simple cubic
- BCC
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- simple cubic
- BCC
- FCC
The crystal lattice: First examples

- simple cubic
- BCC
- FCC
- diamond
A 2-dimensional example

\[ V(\vec{r} + \vec{R}) = V(\vec{r}) \]
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\[ \vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 \]

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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**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
```
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 continuous.

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

$$\rho(\vec{r}) = \frac{1}{V_{BZ}} \sum_{n=1}^{N_{el}} \int_{\text{Brillouin zone}} |\psi_{n,k}(\vec{r})|^2 \, d^3k$$
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In practice, calculations are performed on a grid of points in the 1BZ.
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The grid in the Brillouin zone
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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 \( (\epsilon(k)) \)
Bandstructure: example silicon

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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

... 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 $k$
  
  $$g(\epsilon) = \frac{1}{V_{BZ}} \sum_i \int_{BZ} d^3 k \, \delta(\epsilon_i, k - \epsilon)$$
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 \( \sigma \) is the Gaussian broadening
Density of states: Broadening and k-points

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where \( \sigma \) is the Gaussian broadening
Find minimal lattice constant
Cohesive properties of solids

Cohesive energy:

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

- energy gain per atom
Birch-Murnaghan equation of states

\[ E(V) = E_0 + \frac{B_0 V}{B'_0} \left( \left( \frac{V_0}{V} \right)^{B'_0} \left( \frac{B'_0}{B'_0 - 1} - 1 \right) + 1 \right) - \frac{B_0 V_0}{B'_0 - 1} \]
Find the minimal lattice constant

Birch-Murnaghan Fit versus quadratic interpolation

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\( V \): Volume
\( E_0 \): Equilibrium energy
\( V_0 \): optimum Volume
\( B_0 \): Bulk modulus
\( B'_0 \): derivative of \( B_0 \) (w.r.t. pressure)
Find minimal lattice constant

Birch-Murnaghan Fit versus quadratic interpolation

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

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Systems of interest

- Bulk Silicon
- Silicon Surface
- Ga$_3$Mn$_1$As$_4$
Bulk Silicon
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 $\beta$-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 $\beta$-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)
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Periodic Systems

Systems of interest

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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: Relaxes surface structures

3. (Problems VIII to IX) Magnetism and collinear spin calculations
   - Problem VIII: Magnetic Ga$_3$Mn$_1$As$_4$
   - Problem IX: Ferromagnetic and anti-ferromagnetic Ga$_{0.75}$Mn$_{0.25}$As
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