FHI-vibes
Lattice Dynamics with python

Florian Knoop, Thomas Purcell, Christian Carbogno
DFT and Beyond, Tutorial 6
Barcelona 2019

VIBES

FHI-vibes

Project ID: 14103635

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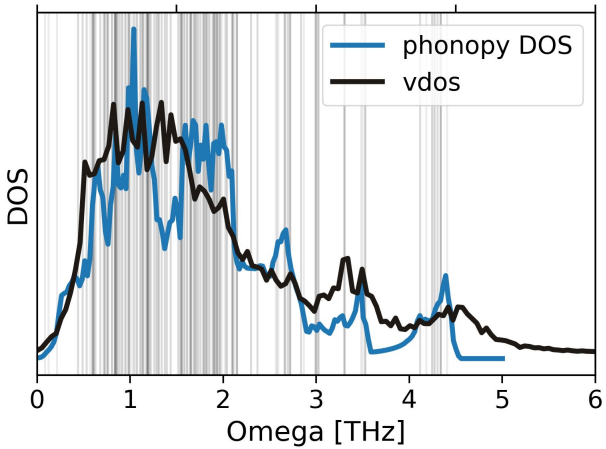
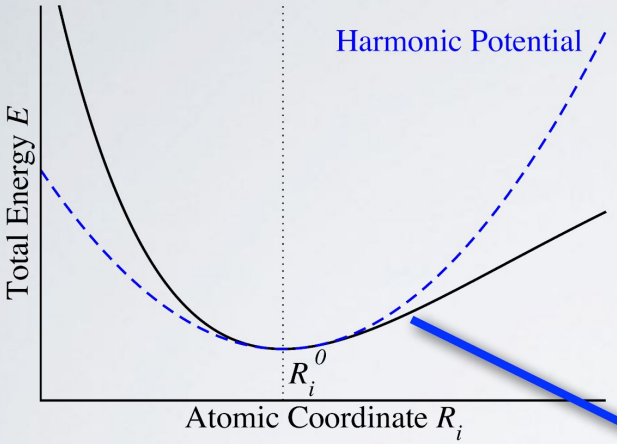
FHI vibrational simulations.

- **FHI-vibes**
  - python package for **lattice dynamics investigations with FHIaims**
  - built on top of **ase**
- Current Features
  - **phonopy** calculations ➔ Handson 2019
  - **MD + heat flux** simulations
  - **toolset** for preparing, and analyzing data
  - high throughput functionality via ***fireworks***
    - ➢ Tom



THE HARMONIC APPROXIMATION



The total energy ***E*** is a
3N-dimensional surface:

$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

Approximate by Taylor Expansion around the Static Equilibrium R_i^0

$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \left.\frac{\partial E}{\partial \mathbf{R}_i}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i + \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i \Delta\mathbf{R}_j$$

Hessian Φ_{ij}

from Christian Carbogno

THE FINITE DIFFERENCE APPROACH

K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997).
A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).

Finite differences using normalized displacements ***d***:

$$\Phi_{ij} = \frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\bigg|_{\mathbf{R}^0} = -\frac{\partial}{\partial \mathbf{R}_i}\mathbf{F}_j\bigg|_{\mathbf{R}^0} \approx -\frac{\mathbf{F}_j(\mathbf{R}_i^0 + \varepsilon\,\mathbf{d}_i)}{\varepsilon}$$

Example: Diamond Si (2 atoms in the basis):

$$\begin{pmatrix} \Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & \Phi_{12}^{xx} & \Phi_{12}^{xy} & \Phi_{12}^{xz} \\ \Phi_{11}^{yx} & \Phi_{11}^{yy} & \Phi_{11}^{yz} & \Phi_{12}^{yx} & \Phi_{12}^{yy} & \Phi_{12}^{yz} \\ \Phi_{11}^{zx} & \Phi_{11}^{zy} & \Phi_{11}^{zz} & \Phi_{12}^{zx} & \Phi_{12}^{zy} & \Phi_{12}^{zz} \\ \Phi_{21}^{xx} & \Phi_{21}^{xy} & \Phi_{21}^{xz} & \Phi_{22}^{xx} & \Phi_{22}^{xy} & \Phi_{22}^{xz} \\ \Phi_{21}^{yx} & \Phi_{21}^{yy} & \Phi_{21}^{yz} & \Phi_{22}^{yx} & \Phi_{22}^{yy} & \Phi_{22}^{yz} \\ \Phi_{21}^{zx} & \Phi_{21}^{zy} & \Phi_{21}^{zz} & \Phi_{22}^{zx} & \Phi_{22}^{zy} & \Phi_{22}^{zz} \end{pmatrix}$$

Space Group Analysis

$$\begin{pmatrix} \Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & -\Phi_{11}^{xx} & \Phi_{12}^{xy} & 0 \\ 0 & \Phi_{11}^{xx} & \Phi_{11}^{yz} & \Phi_{11}^{yz} & -\Phi_{11}^{xx} & 0 \\ 0 & \Phi_{12}^{xy} & \Phi_{11}^{xx} & -\Phi_{11}^{xz} & -\Phi_{11}^{xy} & -\Phi_{11}^{xx} \\ -\Phi_{11}^{xx} & -\Phi_{11}^{xy} & -\Phi_{11}^{xz} & \Phi_{11}^{xx} & -\Phi_{12}^{xy} & 0 \\ 0 & -\Phi_{11}^{xx} & -\Phi_{11}^{yz} & -\Phi_{11}^{yz} & \Phi_{11}^{xx} & 0 \\ 0 & -\Phi_{12}^{xy} & -\Phi_{11}^{xx} & \Phi_{11}^{xz} & \Phi_{11}^{xy} & \Phi_{11}^{xx} \end{pmatrix}$$

Hessian has **5 unique, non-zero** entries:
⇒ Only **1** displacement ***d*** required

from Christian Carbogno

THE FINITE DIFFERENCE APPROACH

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Finite differences using **normalized displacements *d***

$$\Phi_{ij} = \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}^0} = -\left.\frac{\partial}{\partial \mathbf{R}_i}\mathbf{F}_j\right|_{\mathbf{R}^0}$$

Handled by phonopy and spglib

Example: Diamond Si (2 atoms in the basis):

$$\begin{pmatrix}
\Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & \Phi_{12}^{xx} & \Phi_{12}^{xy} & \Phi_{12}^{xz} \\
\Phi_{11}^{yx} & \Phi_{11}^{yy} & \Phi_{11}^{yz} & \Phi_{12}^{yx} & \Phi_{12}^{yy} & \Phi_{12}^{yz} \\
\Phi_{11}^{zx} & \Phi_{11}^{zy} & \Phi_{11}^{zz} & \Phi_{12}^{zx} & \Phi_{12}^{zy} & \Phi_{12}^{zz} \\
\Phi_{21}^{xx} & \Phi_{21}^{xy} & \Phi_{21}^{xz} & \Phi_{22}^{xx} & \Phi_{22}^{xy} & \Phi_{22}^{xz} \\
\Phi_{21}^{yx} & \Phi_{21}^{yy} & \Phi_{21}^{yz} & \Phi_{22}^{yx} & \Phi_{22}^{yy} & \Phi_{22}^{yz} \\
\Phi_{21}^{zx} & \Phi_{21}^{zy} & \Phi_{21}^{zz} & \Phi_{22}^{zx} & \Phi_{22}^{zy} & \Phi_{22}^{zz}
\end{pmatrix}$$

Space Group Analysis

$$\begin{pmatrix}
\Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & -\Phi_{11}^{xx} & \Phi_{12}^{xy} & 0 \\
0 & \Phi_{11}^{xx} & \Phi_{11}^{yz} & \Phi_{11}^{yz} & -\Phi_{11}^{xx} & 0 \\
0 & \Phi_{12}^{xy} & \Phi_{11}^{xx} & -\Phi_{11}^{xz} & -\Phi_{11}^{xy} & -\Phi_{11}^{xx} \\
-\Phi_{11}^{xx} & -\Phi_{11}^{xy} & -\Phi_{11}^{xz} & \Phi_{11}^{xx} & -\Phi_{12}^{xy} & 0 \\
0 & -\Phi_{11}^{xx} & -\Phi_{11}^{yz} & -\Phi_{11}^{yz} & \Phi_{11}^{xx} & 0 \\
0 & -\Phi_{12}^{xy} & -\Phi_{11}^{xx} & \Phi_{11}^{xz} & \Phi_{11}^{xy} & \Phi_{11}^{xx}
\end{pmatrix}$$

Hessian has **5 unique, non-zero** entries:
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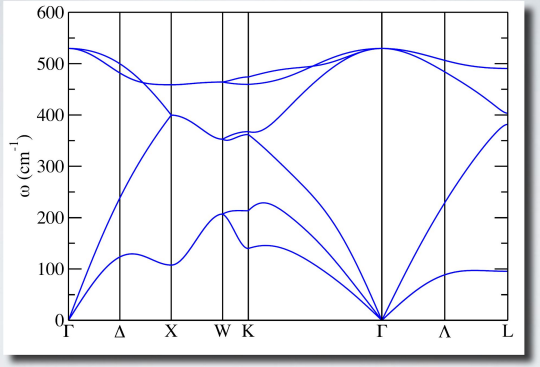
from Christian Carbogno

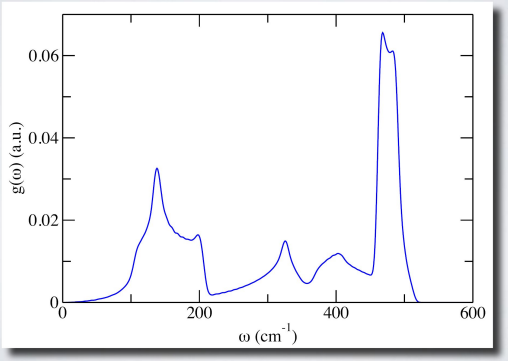
VIBRATIONAL BAND STRUCTURE



Silicon, diamond structure

VIBRATIONAL DENSITY OF STATES

$$g(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega(\mathbf{q})) = \sum_s \int_{\omega(\mathbf{q})=\omega} \frac{dS}{(2\pi)^3} \frac{1}{|\nabla\omega(\mathbf{q})|}$$



THE HARMONIC FREE ENERGY

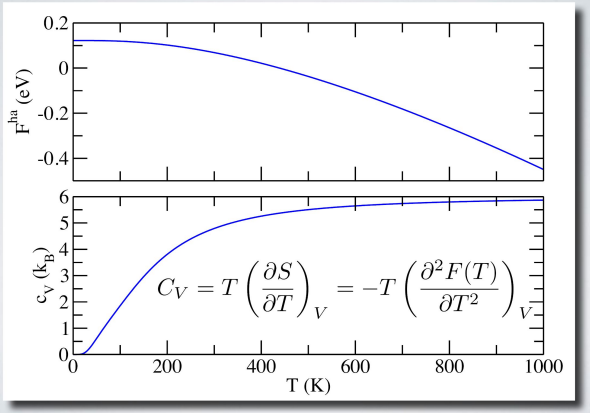
$$F^{ha}(T) = E(\{\mathbf{R}_0\}) + \int d\omega\, g(\omega) \frac{\hbar\omega}{2} + \int d\omega\, g(\omega)\, k_B T \ln\left(1 - e^{\left(-\frac{\hbar\omega}{k_B T}\right)}\right)$$

Static Equilibrium Energy

Zero-point vibration

Thermally induced vibrations

FREE ENERGY AND HEAT CAPACITY



from Christian Carbogno

THE HARMONIC APPROXIMATION

$$\mathbb{H} = \sum_i T_i + \frac{1}{2}\sum_{i,j} \Phi_{ij}\Delta\mathbf{R}_i\Delta\mathbf{R}_j \quad \Rightarrow \quad \frac{\partial \mathbb{H}}{\partial V} = 0$$

Lattice expansion vanishes in the **harmonic** approximation.

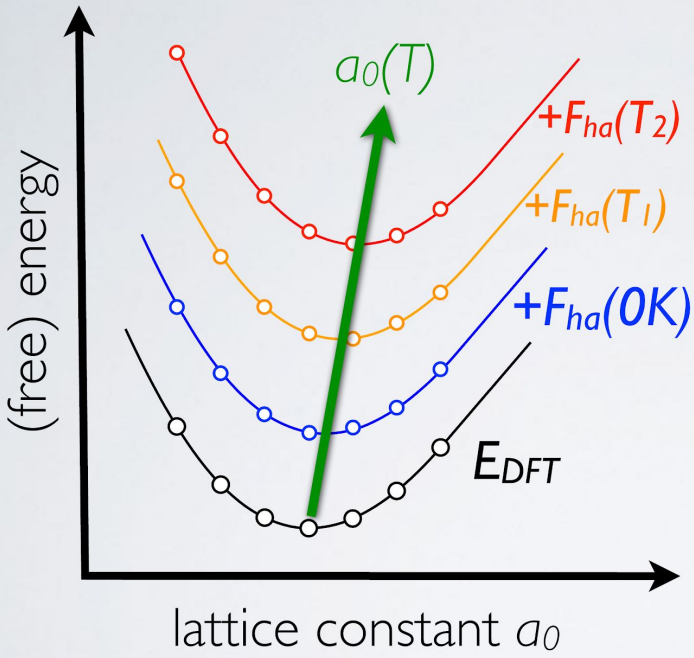
THE QUASI-HARMONIC APPROACH

$$\mathbb{H} = \sum_i T_i + \frac{1}{2}\sum_{i,j} \Phi_{ij}(V)\,\Delta\mathbf{R}_i\Delta\mathbf{R}_j \quad \Rightarrow \quad \frac{\partial \mathbb{H}}{\partial V} \neq 0$$

Assess **lattice expansion** by explicitly accounting for the ***volume dependence*** of the ***Hessian***.

from Christian Carbogno

THE QUASI-HARMONIC APPROACH



Lattice constant a_0 can be determined from *Birch-Murnaghan* fit of $E(a_0)$

cf. Victor Yu, Practical Session 2

Add **vibrational free energy** for each individual value of a_0

Repeat for **each** temperature

0K < T_1 < T_2

Birch-Murnaghan fits for **each individual temperature** allow to determine **temperature dependence of lattice constant** $a_0(T)$.

from Christian Carbogno

vibes: how to run an **phonopy** simulation?

```
$ <editor> phonopy.in
```

```
[geometry]
file:                geometry.in

[control]
xc:                  pbesol
k_grid:              [2, 2, 2]

[basissets]
default:             light

[phonopy]
supercell:           [[1, 0, 0], [0, 1, 0], [0, 0, 1]]
```

vibes: how to run an **phonopy** simulation?

```
$ vibes run phonopy
```

```
[hilde]         Run phonopy workflow in working directory
  phonopy
[hilde]         Start phonopy postprocess:
[trajectory]    Parse trajectory
[son] read file:  phonopy/trajectory.son
[watchdog]      seems we are not on a cluster, nothing to do for watchdog
[socketio]      Use SocketIO with port 12345
[backup]        ...
[trajectory]    Parse trajectory
[hilde]         Compute structure 1 of 1: working
```

vibes: how to run an **phonopy** simulation?

```
$ vibes run phonopy
```

```
[hilde]        ...
[hilde]        Compute structure 1 of 1: finished.
[hilde]        Start postprocess.
[hilde]        Start phonopy postprocess:
[trajectory]   Parse trajectory
[son] read file:  phonopy/trajectory.son
[son] process:    ||||||||||||||||||||||||||||||||||||  2/2
.. create atoms:  ||||||||||||||||||||||||||||||||||||  1/1
[trajectory]   .. done in 0.001s
[trajectory]   .. done in 0.097s
[hilde]        done.
```

CAUTION

- **vibes** was recently renamed from **hilde**
  - **hilde** still appears frequently

- Computers in **Room C** are **very slow** (factor of 4-5)
  - please try to fill up rooms **A and B first**
  - **Team up!**

Let’s go, have coffee and fun!