Crystal Relaxation, Elasticity, and Lattice Dynamics

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http://exciting-code.org
PART I: Structure Optimization

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Outline Part I

- Structure optimization
- Cell optimization
- Internal degrees of freedom
- Relaxing molecules
- HoW exciting! 2016
Structure Optimization

(a): Cell shape

(b): (Relative) atomic positions
Energy Minimization
Lattice (Cell) Optimization

\[ E = E(a, b, c, \alpha, \beta, \gamma) \]

\[ E = E(V, b, c, \alpha, \beta, \gamma) \]
Equation of State (EOS)

\[ E = E(V) \]

- Murnaghan EOS
- Birch-Murnaghan EOS
- Vinet EOS
- Polynomial EOS
Equation of State of Silver

\[-5.314788 \times 10^3\]

Energy [Ha]

Volume [Bohr\(^3\)]
Lattice Optimization in exciting

Tool: OPTIMIZE-lattice.sh

Example $E = E(V, c)$

- **STEP1:** opt. $V$ at fixed $c$: get $V_1$
- **STEP2:** opt. $c$ at fixed $V_1$: get $c_2$
- **STEP3:** opt. $V$ at fixed $c_2$: get $V_3$
- ...
Energy Minimization: Relaxation

Internal degree of freedom: atomic positions
Relaxation methods in

- **newton**
- **harmonic**
- **bfgs**
newton
newton
A parabola has a constant 2nd derivative
Broyden, Fletcher, Goldfarb, Shanno
bfgs

- Extension to N-degrees of freedom:
  - Similar to harmonic
  - Hessian matrix vs. 2nd derivative
  - Very efficient if close to minimum
  - Default in exciting
<input>
...
<structure ... />

<groundstate ... />

<relax method="bfgs"/>
<relax/>
</input>
Relaxation of Pyridine

![Graph showing relaxation of Pyridine](image)

- **Maximum force [Ha/bohr]**
- **Optimization steps**

Legend:
- **goal**
- **newton**
- **harmonic**
- **bfgs**
In exciting always 3D periodicity:

A Crystalline Solid Can Be Constructed From A “Unit Cell” Plus Translational Operators
“Isolated” 3D periodical molecules:
<input>
  ...
  <structure cartesian="true">
    ...
  </structure>
  ...
  <groundstate ngridk="1 1 1">
    ...
  </groundstate>
  <relax/>
</input>
Relaxation of Pyridine

Maximum force [Ha/bohr]

Optimization steps

- goal
- newton
- harmonic
- bfgs
Visualization
Molecular Orbitals of CO$_2$
Molecular Orbitals of CO$_2$

HOMO
Molecular Orbitals of CO$_2$

LUMO
Structure Optimization

- Volume optimization for cubic systems
- Simple examples of structure optimization
- General lattice optimization

Molecules

- How to run calculations for simple molecules
PART II: Lattice Dynamics

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A **phonon** in a crystal is a coherent collection of atomic displacements.
Phonons: Atoms Move Together
Phonons Oscillations

Oscillation in space:

$$q = \text{wavevector}$$

Oscillation in time:

$$\omega = \text{frequency} \rightarrow \text{energy}$$
Why Are Phonons Interesting

To Do Thermodynamics:
- Temperature Effects
- Entropy
- Free Energy
- Heat Capacity
...  

To Do Vibrational Spectroscopy:
- Raman Spectra
- Infrared (IR) Spectra
- Phonon-Assisted Absorption & Luminescence
...  

As a Prerequisite for Other Quantities & Phenomena:
- Electron-Phonon Coupling
- Electrical Conductivity
- Thermal Conductivity
- Thermal Lattice Expansion
...
Atomic Displacements

\[ \mathbf{R} \]

\[ \mathbf{u}(\mathbf{R}) \]

\[ \mathbf{R}' \]

\[ \mathbf{u}(\mathbf{R}') \]
Energy, Forces, and Phonons

\[{u}\} = \text{set of atomic displacements}

\[E(\{u\}) - \frac{\partial E}{\partial u} \quad F \quad \frac{\partial^2 E}{\partial u \partial u'} \quad \Phi\]
**Force Constants & Dynamical Matrix**

\[
\Phi(R - R') = \frac{\partial^2 E}{\partial u(R) \partial u(R')} 
\]

\[
D(q) = \text{Fourier transform of } \Phi(R) 
\]

\[
\det[D(q) - \omega^2(q) I] = 0 
\]
Phonon Periodicity

Equilibrium

$q = 0$

$q \neq 0$
Phonon Periodicity

Equilibrium

q = 0

q ≠ 0
Phonons at $\Gamma$ in Diamond-Structure Crystals

**Purpose:** In this tutorial, you will learn how to set up and execute a series of calculations for a crystal in the diamond structure, where the second atom in the unit cell is displaced along the cube diagonal. Additionally, it will be explained how to obtain the phonon frequency of the optical modes at $q=0$ ($\Gamma$ point), by calculating the derivatives of the energy-vs-displacement and force-vs-displacement curves at zero displacement.

**Table of Contents**

- Define relevant shell variables and download scripts
- Set up the calculations
  - Preparation of the input file
  - Generation of input files for the different structures
- Execute the calculations
- Post-processing: Extract energy derivatives
- Post-processing: Extract force derivatives
- Post-processing: Visualization tools
- Post-processing: How to derive the optical phonon frequency at $q=0$ ($\Gamma$ point)
- Exercises
Phonon Periodicity

Equilibrium

$q = 0$

$q \neq 0$
Phonon at X in Diamond Structure
Phonons at X in Diamond-Structure Crystals

**Purpose:** In this tutorial, you will learn how to set up and execute a series of calculations for a crystal in the diamond structure, where the second atom in the unit cell is displaced along the cube diagonal. Additionally, it will be explained how to obtain the phonon frequency of the optical modes at q=0 (Γ point), by calculating the derivatives of the energy-vs-displacement and force-vs-displacement curves at zero displacement.

**Table of Contents**

1. Define relevant shell variables and download scripts
2. Set up the calculations
   1) Preparation of the input file
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3. Execute the calculations
4. Post-processing: Extract energy derivatives
5. Post-processing: Extract force derivatives
6. Post-processing: Visualization tools
7. Exercises
<input>

...<phonons ngridq='2 2 2' ... />

...

</phonons>

...</input>
Reciprocal and Real-Space Cells

Brillouin zone sampling

(Super)cell
Reciprocal and Real-Space Cells

Brillouin zone sampling

(Super)cell
Reciprocal and Real-Space Cells

Brillouin zone sampling  →  (Super)cell
input.xml

```xml
<input>
  ...
  <phonons ngridq="2 2 2" ... >
    ...
    <phonondos ... > ... </phonondos>
    ...
  </phonons>
  ...
</input>
```
<input>
  ...
  <phonons ngridq="2 2 2" ...
    ...
    <phonondos ...
      ...
      <phonondispplot ...
        ...
        ...
      </phonondos>
    ...
  </phonons>
  ...
</input>
Phonon Dispersion: Diamond

Lattice parameter = 6.7468 Bohr

small ngridk + small ngridq
Phonon Dispersion: **Diamond**

Lattice parameter = 6.7468 Bohr

![Graph showing phonon dispersion with labels for different k-points and frequency on the y-axis.](image)

*larger ngridk + larger ngridq*
PART III: Elasticity

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What Is Elasticity?

- Description of **distorsions** of rigid bodies and of the energy, forces, and fluctuations arising from these distorsions.

- Describes mechanics of extended bodies from the *macroscopic* to the *microscopic*.

- Generalizes simple mechanical concepts

  
  Force  $\rightarrow$ Stress

  Displacement $\rightarrow$ Strain
Strain: State of deformation

Equilibrium:
- Zero strain
- Zero forces
- Zero stress
- Zero displacements

Shear strain

Uniaxial strain
Homogeneous strain

\[ \mathbf{r} = \text{unstrained position} \]

\[ \mathbf{r}_s = \text{strained position} \]

\[ \mathbf{r}_s = \mathbf{F} \cdot \mathbf{r} = (1 + \varepsilon) \cdot \mathbf{r} \]

\[ \mathbf{F} = \text{Deformation Matrix} \]

\[ \varepsilon = \text{Physical Strain Matrix} \]
Voigt notation

\[
\begin{pmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{yz} \\
\varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz}
\end{pmatrix}
\equiv
\begin{pmatrix}
\varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\
\varepsilon_6/2 & \varepsilon_2 & \varepsilon_4/2 \\
\varepsilon_5/2 & \varepsilon_4/2 & \varepsilon_3
\end{pmatrix}
\]

Voigt indices:

\[i, j = \{xx, yy, zz, yz, zy, xz, zx, xy, yx\}\]

\[\alpha = 1, 2, 3, 4, 5, 6\]

Representative vector:

\[\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)\]
Strain definitions

**Physical strain:**

\[ r_s = (1 + \varepsilon) \cdot r \]

\[ \eta = \varepsilon + \frac{1}{2} \varepsilon \cdot \varepsilon \]

\[ |\Delta_s|^2 - |\Delta|^2 = \Delta \cdot 2\eta \cdot \Delta \]

**Lagrangian strain:**
Linear elastic response

Low pressure expansion in terms of Lagrangian strain $\eta$:

$$E(\eta) = E_0 + \frac{V_0}{2!} \eta \cdot C^{(2)} \cdot \eta + \cdots$$

$E_0, V_0 =$ Reference (equilibrium) energy and volume

Linear elastic constant (2nd order):

$$C^{(2)} = \frac{1}{V_0} \left[ \frac{\partial^2 E(\eta)}{\partial \eta \partial \eta} \right]_{\eta=0}$$

Diamond $C_{11}, C_{12}, C_{44}$
Numerical derivatives

- Fitting a polynomial to the calculated points
Tutorials

Structure Optimization

- Volume optimization for cubic systems
- Simple examples of structure optimization
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Molecules

- How to run calculations for simple molecules

Elastic Properties

- Energy vs. strain calculations

Phonons and Thermal Properties

- Phonons at Γ in diamond-structure crystals
- Phonons at X in diamond-structure crystals
- Phonon properties of diamond-structure crystals
Tutorials

[ADVANCED]

[TOOLS]

[WHAT YOU SHOULD KNOW ABOUT]
Tutorials

ADVANCED:

Phonons and Thermal Properties

- How to visualize phonons
Animated Phonon Modes
The Last Slide: We are so Excited!

... and let’s listen now to Andris!