

Practical session II

Calculating equilibrium structure,
phase transitions, frozen phonons

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Workshop on :

Density Functional Theory Calculations for Modeling Materials and
Bio-Molecular Properties and Functions - A Hands-On Computer Course

Los Angeles October 30 - November 5 2005

Volume optimization and phase transition

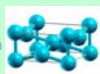
Different structure phases

StructGen™ **β-tin structure**

You have to click "Save Structure" for changes to take effect!
[Save Structure](#)

Title:

Lattice:
Type: B

[OpenStructure.htm] 

CRY [Binary Crystal Server]
CXYZ
M
L,PT

Lattice parameters in [unit: Å]
a=0.115063 b=0.115063 c=0.405343
alpha=90.000000 beta=90.000000 gamma=90.000000

Equivalent Atoms: 1
Atom 1 [x] 2=0+0.0 RMT=0.0000 [remove atom]
Pos 1 x=0.2500000 y=0.0000000 z=0.1250000 [relocate]
Pos 2 x=0.7500000 y=0.0000000 z=0.1250000 [relocate]
[add position](#)

[Add an atom](#)

Number of symmetry operations: generate


You have to click "Save Structure" for changes to take effect!
[Save Structure](#)

StructGen™ **Diamond structure**

You have to click "Save Structure" for changes to take effect!
[Save Structure](#)

Title:

Lattice:
Type: F

[OpenStructure.htm] 

CRY [Binary Crystal Server]
CXYZ
M
L,PT

Lattice parameters in [unit: Å]
a=0.357112 b=0.357112 c=0.357112
alpha=90.000000 beta=90.000000 gamma=90.000000

Equivalent Atoms: 1
Atom 1 [x] 2=0+0.0 RMT=0.0000 [remove atom]
Pos 1 x=0.1250000 y=0.1250000 z=0.1250000 [relocate]
Pos 2 x=0.8750000 y=0.1250000 z=0.1250000 [relocate]
[add position](#)

[Add an atom](#)

Number of symmetry operations: generate

You have to click "Save Structure" for changes to take effect!
[Save Structure](#)

Volume optimization

Session: Si
/wien2k/btin

Optimize volume or c/a-ratio

- x optimize | Generate structure files from btin_initial.struct
- edit optimize.job | Uncomment "x dstart" or "cp dmsum"; change options in run_lapw, save_lapw...
- run optimize.job | Type of execution: background
- plot | Plot energy curve

Session: Si
/wien2k/btin

optimizer

vary VOLUME with constant a:b:c ratio

structure changes (values on separate lines in %)

-15
-10
-5
0
5
10

Execute

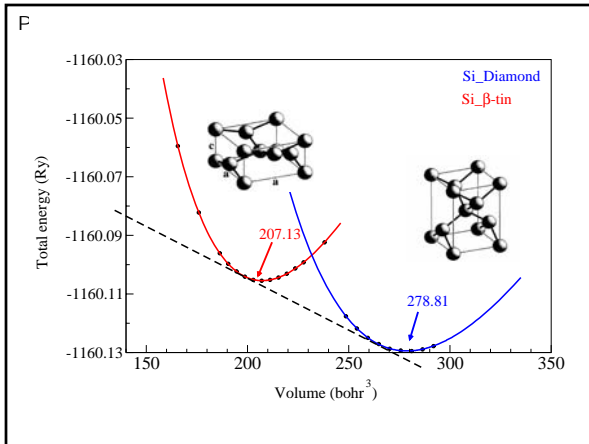
File:
/wien2k/btin/optimize.job

continue with optimizer | Save | Download this file: [x]

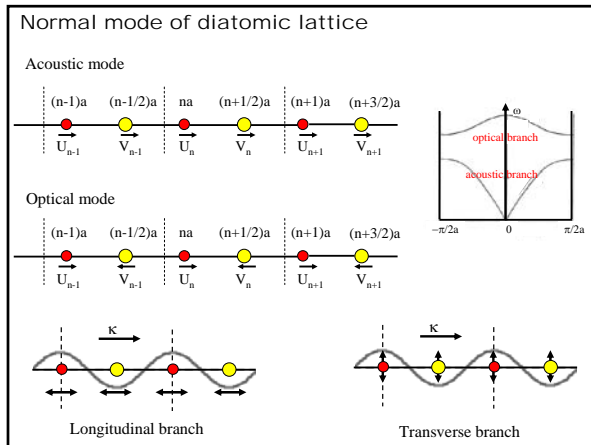
```

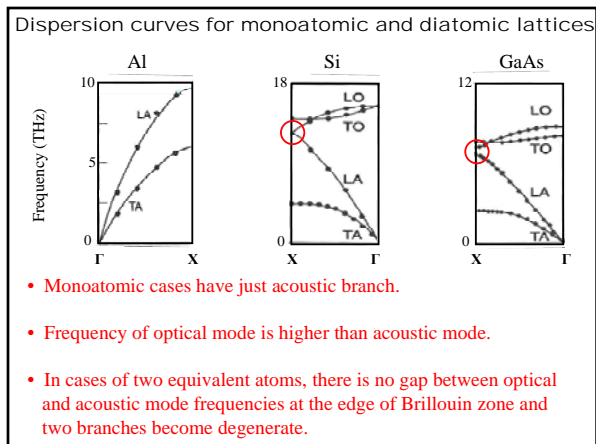
#!/bin/csh -f
# Modify this script according to your needs:
# Uncomment one of the lines ...
# Change run_lapw to runsp_lapw or use different convergence criteria
# Change save_lapw -d XXX
foreach i ( \
    btin_vol_15.0 \
    btin_vol_10.0 \
    btin_vol_5.0 \
    btin_vol_0.0 \
    btin_vol_5.0 \
    btin_vol_10.0 \
    btin_vol_15.0 \
)
    cp $i.struct btin.struct
end

# Please uncomment and adapt any of the lines below according to your needs
# cp $i.class btin.class
# x dstart
# x dstart -c
    
```



Phonon calculation





Harmonic approximation in one-dimension

$$E_0^{harm}(\{u_n\}) = E_0(0) + 1/2 \sum_{n,n'} D_{nn'} u_n u_{n'} \quad , \quad D_{nn'} = \left(\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}} \right)_0$$

Force constant matrix

$$D_{nn'} = D_{n'n} \quad \sum_{n'} D_{nn'} = 0 \quad \forall n$$

$$F_n = - \frac{\partial E_0^{harm}}{\partial u_n} = M_u \ddot{u}_n = - \sum_{n'} D_{nn'} u_{n'}$$

$$u_n(t) = A(q, \omega) e^{i(qna - \omega t)} \quad \xrightarrow{D(q) = \sum_{n'} D_{nn'} e^{iq(na - n'a)}} \quad \omega = \sqrt{\frac{D(q)}{M_u}}$$

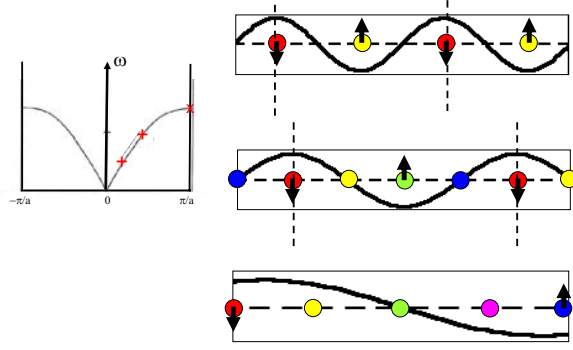
Force and frequency in 3 dimensions

$$E_0^{harm}(\{u_{nv}\}) = E_0(0) + 1/2 \sum_{n\nu\alpha, n'\nu'\alpha'} D_{n\nu\alpha, n'\nu'\alpha'} u_{n\nu\alpha} u_{n'\nu'\alpha'}$$

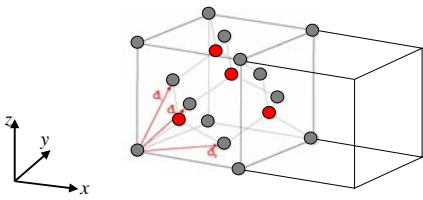
$$F_{n\nu\alpha} = - \frac{\partial E_0^{harm}}{\partial u_{n\nu\alpha}} = M_\nu \ddot{u}_{n\nu\alpha} = - \sum_{n'\nu'\alpha'} D_{n\nu\alpha, n'\nu'\alpha'} u_{n'\nu'\alpha'}$$

$$\|D_{\nu\alpha\nu'\alpha'}(q) - M_\nu \omega^2 \delta_{\nu\nu'} \delta_{\alpha\alpha'}\| = 0 \quad \xrightarrow{\text{Diagonalizing } D(q) \text{ matrix}} \quad \omega = \sqrt{\frac{D_\nu}{M_\nu}}$$

Frozen phonon method



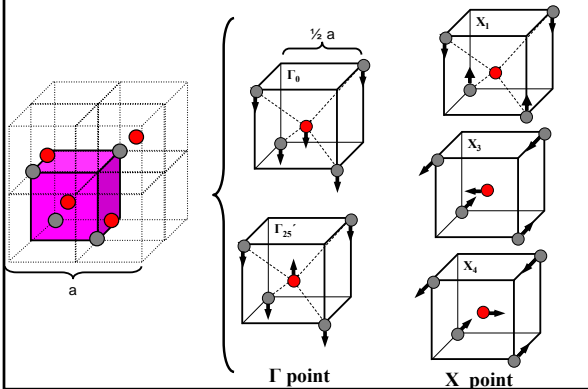
Supercell in [100] direction

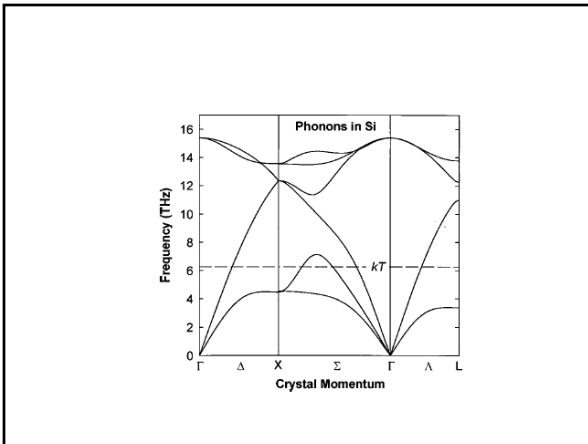


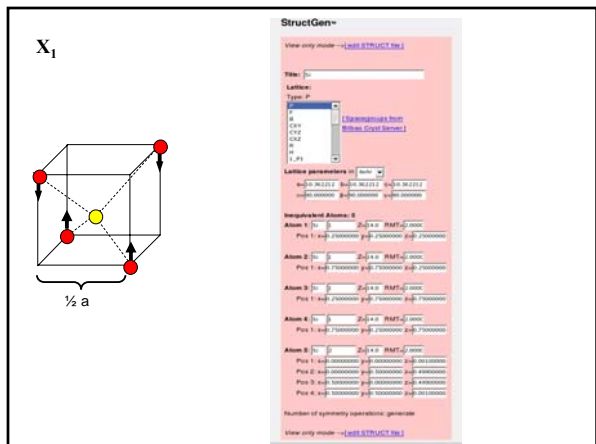
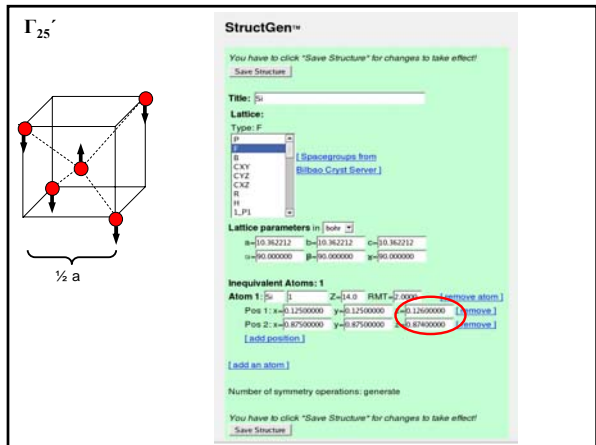
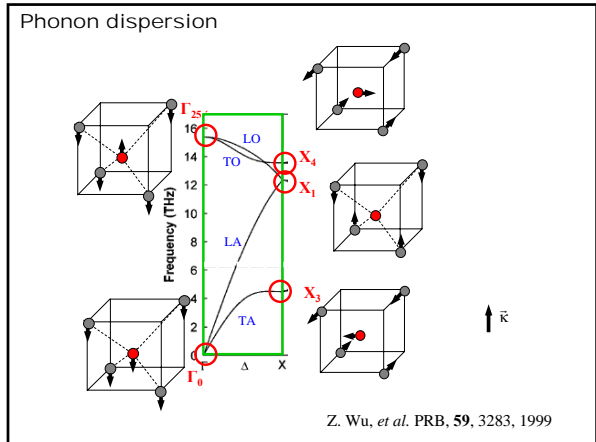
Force constants matrix :

$$D = \begin{bmatrix} D_{1x1x} & D_{1x1y} & D_{1x1z} & \dots & D_{1x4z} \\ D_{1y1x} & D_{1y1y} & D_{1y1z} & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ D_{4z1x} & \dots & \dots & \dots & D_{4z4z} \end{bmatrix}_{12 \times 12}$$

Irreducible representations





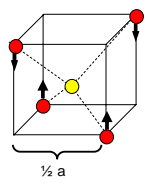


X₁

P LATTICE,NONEQUIV. ATOMS 5

MODE OF CALC=RELA unit=bohr

10.362212 10.362212 10.362212 90.000000 90.000000 90.000000



ATOM -1: X=0.25000000 Y=0.25000000 Z=0.25000000
MULT= 1 ISPLIT= 8

ATOM -2: X=0.75000000 Y=0.75000000 Z=0.25000000
MULT= 1 ISPLIT= 8

ATOM -3: X=0.25000000 Y=0.75000000 Z=0.75000000
MULT= 1 ISPLIT= 8

ATOM -4: X=0.75000000 Y=0.25000000 Z=0.75000000
MULT= 1 ISPLIT= 8

ATOM -5: X=0.00000000 Y=0.00000000 Z=0.00100000
MULT= 4 ISPLIT= 8

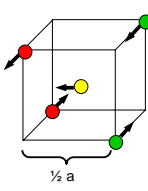
-5: X=0.00000000 Y=0.50000000 Z=0.49900000
-5: X=0.50000000 Y=0.00000000 Z=0.49900000
-5: X=0.50000000 Y=0.50000000 Z=0.00100000

X₃ , X₄

P LATTICE,NONEQUIV. ATOMS 6

MODE OF CALC=RELA unit=bohr

10.362212 10.362212 10.362212 90.000000 90.000000 90.000000



ATOM -1: X=0.00000000 Y=0.99900000 Z=0.00000000
MULT= 1 ISPLIT= 8

ATOM -2: X=0.50000000 Y=0.49900000 Z=0.00000000
MULT= 1 ISPLIT= 8

ATOM -3: X=0.50000000 Y=0.00100000 Z=0.50000000
MULT= 1 ISPLIT= 8

ATOM -4: X=0.00000000 Y=0.50100000 Z=0.50000000
MULT= 1 ISPLIT= 8

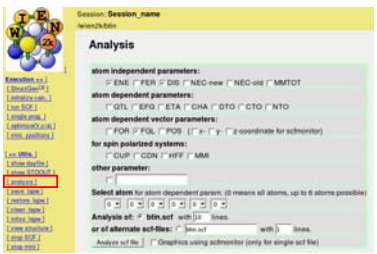
ATOM -5: X=0.24900000 Y=0.25000000 Z=0.25000000
MULT= 2 ISPLIT= 8

-5: X=0.75100000 Y=0.25000000 Z=0.75000000

ATOM -6: X=0.74900000 Y=0.75000000 Z=0.25000000
MULT= 2 ISPLIT= 8

-6: X=0.25100000 Y=0.75000000 Z=0.75000000

Analysis



$$D = \frac{\text{force}}{\text{displacement}}$$

↓

$$v = \frac{1}{2\pi} \sqrt{\frac{D}{\text{mass}}}$$

	F (mRy/bohr)	D (Ry/bohr ²)	v (THz)
Γ_{25}			
X ₁			
X ₃			
X ₄			

Effect of unharmonicity

Energy equation

$$\Delta E = \frac{D}{2} u^2 + 4D_{xyz} \left(\frac{u}{\sqrt{3}} \right)^3$$

Force equation

$$\Delta F = D u + \frac{4}{\sqrt{3}} D_{xyz} u^2$$

Phonon frequency is determined from D values.

R. Yu, *et al.* PRB, 43, 6411, 1991

THE END
