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

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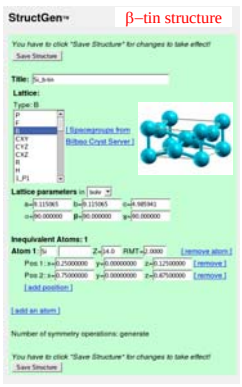
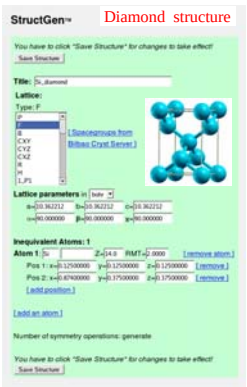
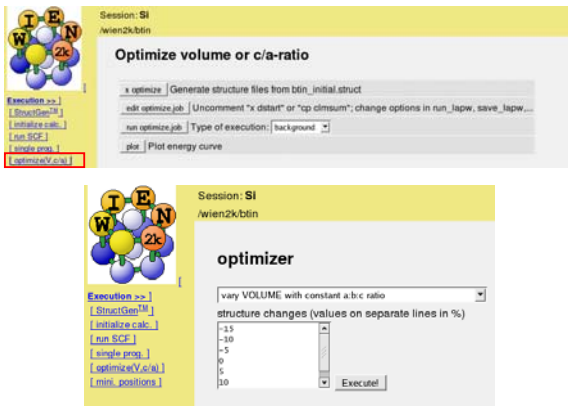
Volume optimization and phase transition

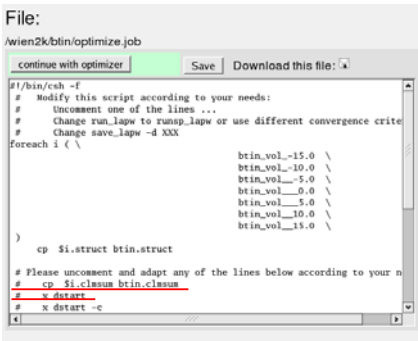
Different structure phases





Volume optimization





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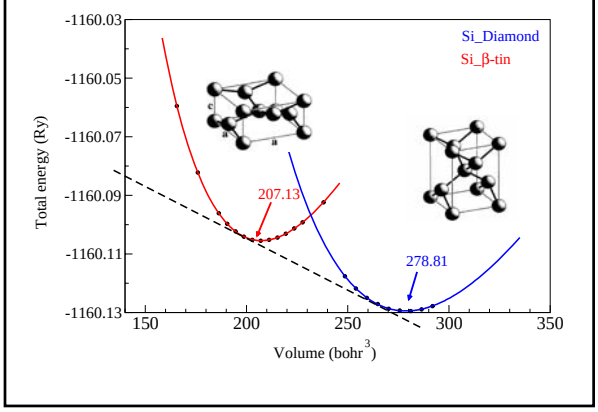
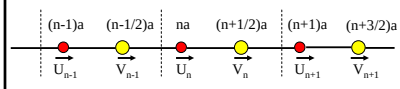
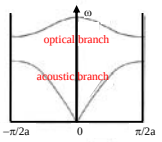


Phonon calculation

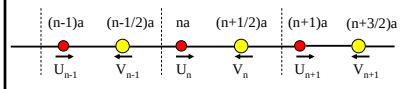
Normal mode of diatomic lattice

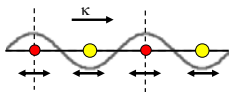
Acoustic mode



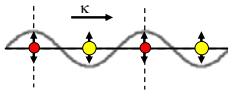


Optical mode



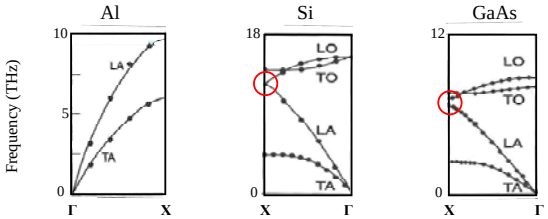


Longitudinal branch



Transverse branch

Dispersion curves for monoatomic and diatomic lattices



- Monoatomic cases have just acoustic branch.
- Frequency of optical mode is higher than acoustic mode.
- In cases of two equivalent atoms, there is no gap between optical and acoustic mode frequencies at the edge of Brillouin zone and two branches become degenerate.

Harmonic approximation in one-dimension

Force constant matrix

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

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

$$F_n = -\frac{\partial E_0^{harm}}{\partial u_n} = \mathrm{M}_u \ddot{\mathrm{u}}_\mathrm{n} = -\sum_{n'} D_{nn'} u_{n'}$$

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

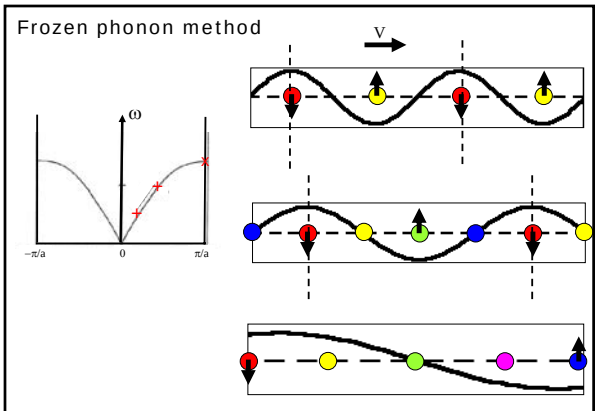
Force and frequency in 3 dimensions

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

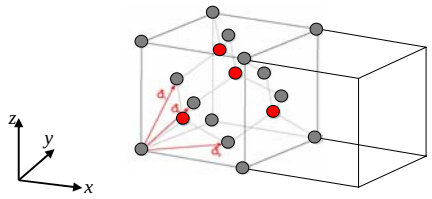
$$F_{n\nu} = -\frac{\partial E_0^{harm}}{\partial u_n} = M_\nu \ddot{u}_{n\nu\alpha} = - \sum_{n'\nu'\alpha'} D_{n\nu\alpha, n'\nu'\alpha'} u_{n'\nu'\alpha'}$$

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

Frozen phonon method



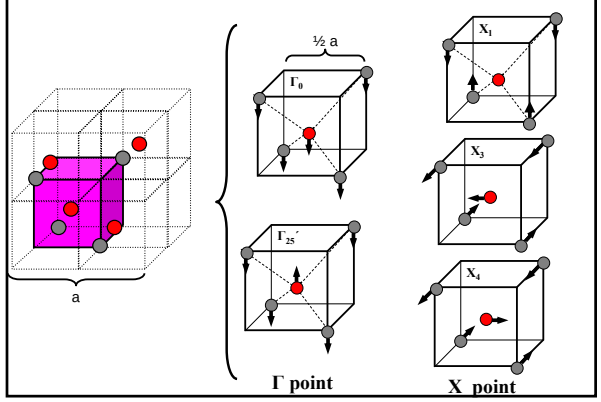
Supercell in [100] direction

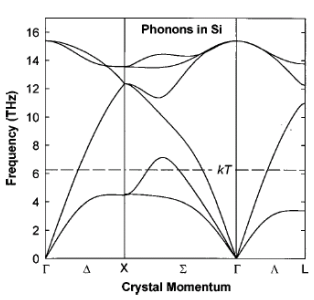


Force constants matrix :

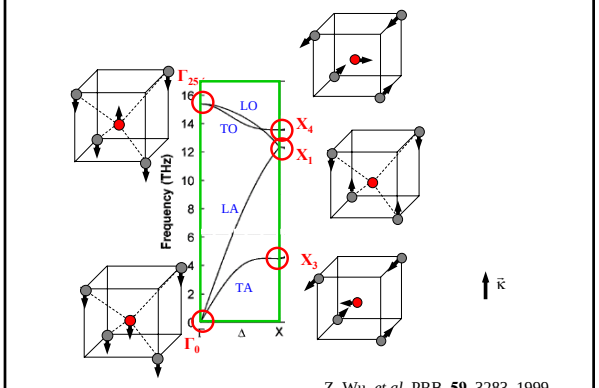
$$D = \begin{bmatrix} D_{1x1x} & D_{1x1y} & D_{1x1z} & \dots & D_{1x4z} \\ D_{1y1x} & D_{1y1y} & D_{1y1z} & \dots & \dots \\ \dots & & \dots & & \\ \dots & & & \dots & \\ D_{4z1x} & & & & D_{4z4z} \end{bmatrix}_{12\times12}$$

Irreducible representations



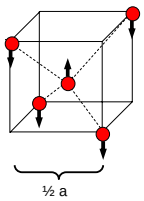


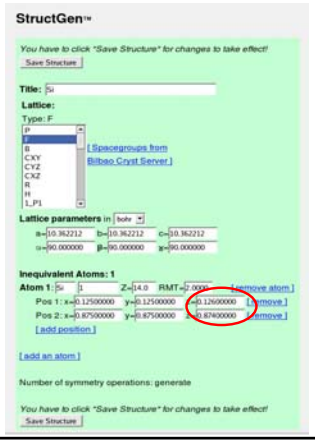
Phonon dispersion



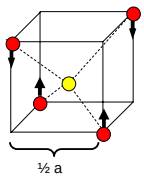
Z. Wu, *et al.* PRB, **59**, 3283, 1999

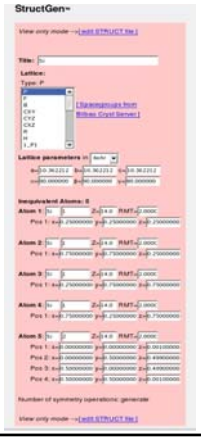
Γ_{25}'



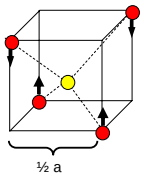


X_1





X_1



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

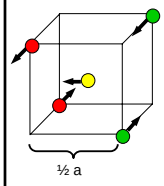
ATOM -2: X=0.75000000 Y=0.75000000 Z=0.25000000
MULT= 1 ISPLIT= 8

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

X_3 , X_4



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

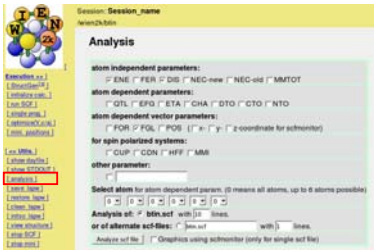
ATOM -3: X=0.50000000 Y=0.00100000 Z=0.50000000
MULT= 1 ISPLIT= 8

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



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

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

	F (mRy/bohr)	D (Ry/bohr^2)	ν (THz)
Γ_{25}			
X_1			
X_3			
X_4			

Effect of unharmonicity

Energy equation

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

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