Developing phonon dispersion code for simulated Raman spectrum by using finite difference method

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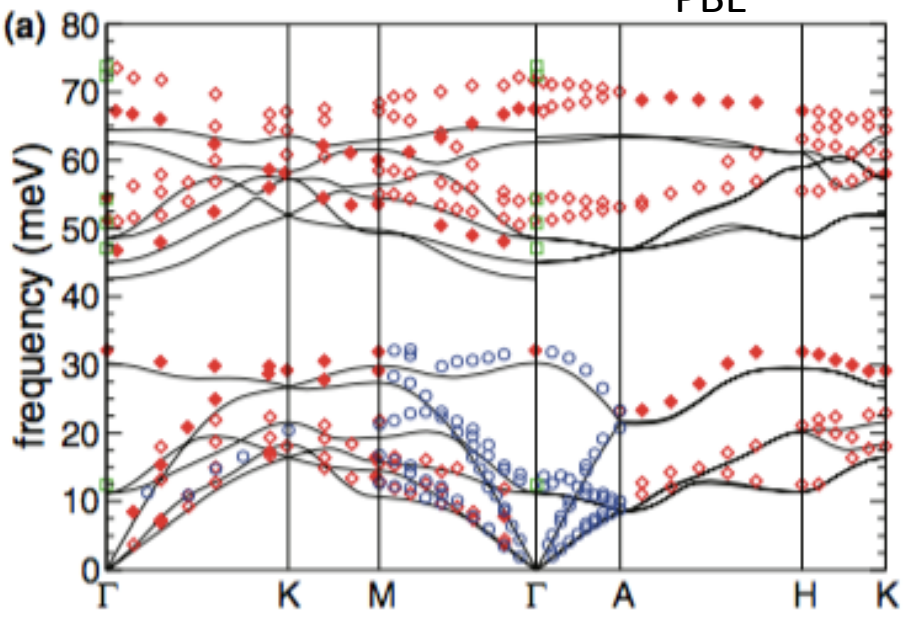
Outline

- Introduction
- Formula of phonon dispersion and Raman spectrum
- Flowchart of phonon dispersion
- Phonon dispersion Code
- Example

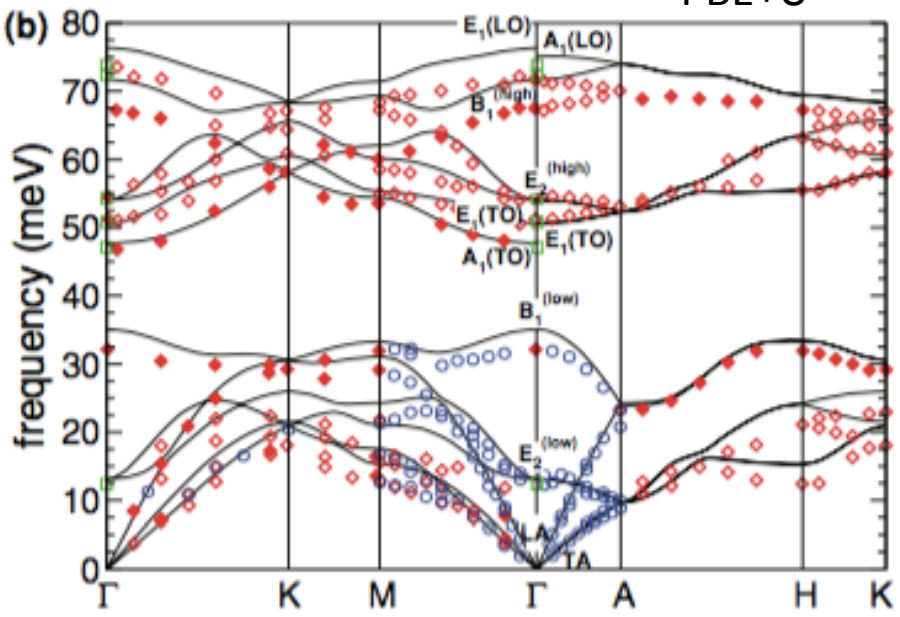
Dielectric properties and Raman spectra of ZnO from a first principles finite-differences/finite-fields approach

Arrigo Calzolari[1,2] & Marco Buongiorno Nardelli[2,3]

PBE



PBE+U



Scientific Reports **3** (2013): 2999.

Formula of phonon dispersion

Interatomic Force constants (IFCs)

$$K_{I\alpha J\beta}(R-R') = \frac{\partial^2 E_{tot}}{\partial u_{I\alpha}(R)\partial u_{J\beta}(R')} = -\frac{\partial F_{I\alpha}}{\partial u_{J\beta}(R')} \qquad (1)$$

The displacement of I-th atom along the direction α in Bravais lattice R

Dynamical matrix

$$\widetilde{D}_{I\alpha J\beta}(\vec{q}) = \frac{1}{\sqrt{m_I m_J}} \sum_{\vec{R},\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right) e^{i\vec{q}\cdot(\vec{R}'-\vec{R})} \qquad (2)$$

Mass of J-th atom

$$\omega^2(\vec{q})\vec{U}_{I\alpha}(\vec{q}) = \widetilde{D}_{I\alpha J\beta}(\vec{q})\vec{U}_{J\beta}(\vec{q}) \qquad (3)$$

Formula of Raman spectrum

The Raman intensity for a Stokes process is described by the Placzek's expression:

The Bose-Einstein distribution

$$I \propto \sum_m |e_i \cdot \alpha^m \cdot e_s|^2 \frac{(n_m + 1)}{\omega_m} \quad (4)$$

ω_m: The frequency m of optical phonon

e_i = incident polarized vector of light

e_s = scattered polarized vector of light

Raman tensor

$$\alpha_{ij}^m = \sqrt{\Omega} \sum_{I,k} \chi_{ijIk} u_{I,k}^m \quad (5)$$

$u_{I,k}^m$: the eigenvector m at atom I along k direction

The third order susceptibility tensor

The electronic polarization

$$\chi_{ijIk} = \frac{\partial \chi_{ij}}{\partial r_{I,k}} = \frac{\partial^2 P_i^{el}}{\partial r_{I,k} \partial \mathcal{E}_j} = -\frac{1}{\Omega} \frac{\partial^2 F_{I,k}^{\varepsilon}}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \quad (6)$$

The third order susceptibility tensor

$$\chi_{ijIk} = \frac{\partial \chi_{ij}}{\partial r_{I,k}} = \frac{\partial^2 P_i^{el}}{\partial r_{I,k} \partial \mathcal{E}_j} = -\frac{1}{\Omega} \frac{\partial^2 F_{I,k}^{\varepsilon}}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \quad (6)$$

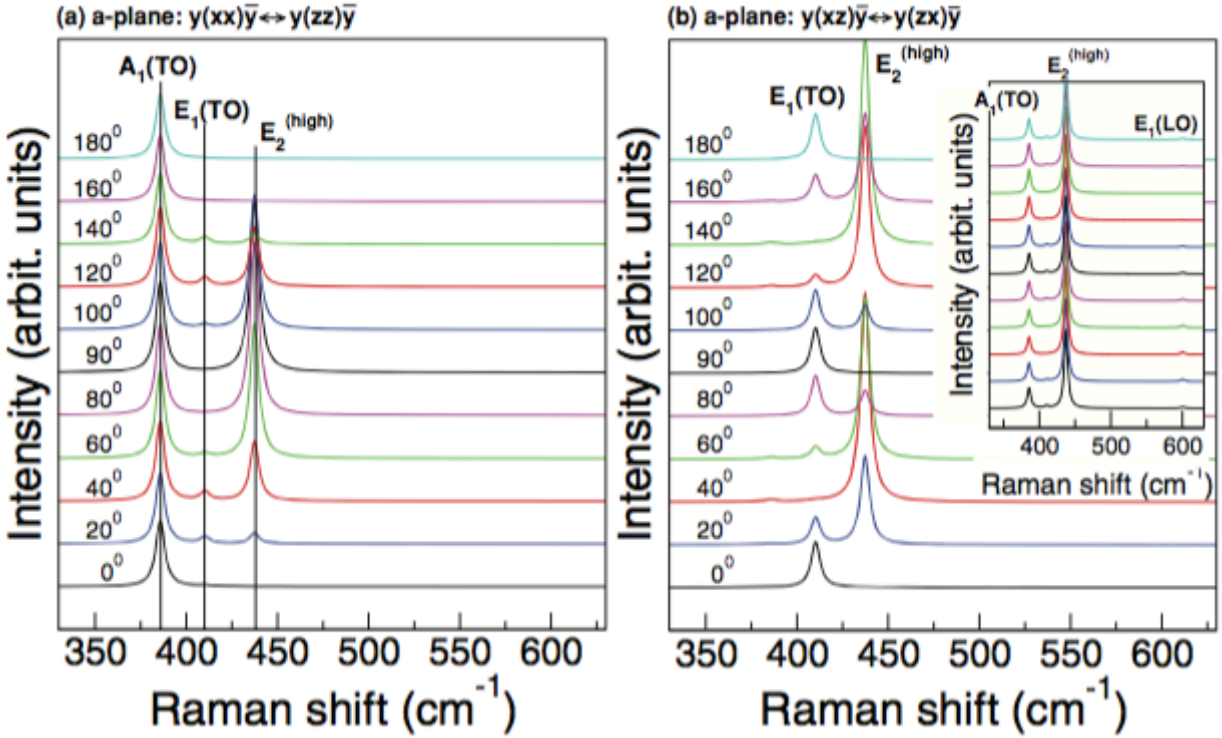
The displacement of the *I*-th atom in the k direction

The electronic polarization along the direction of electric field

$$E_{tot}^{\varepsilon}[\psi] = E^0[\psi] - \mathcal{E} \cdot (P^{ion} + P^{el}[\psi]) \quad (7)$$

The ionic polarization

$$\chi_{ij} = \frac{\partial^2 E_{tot}^{\varepsilon}[\psi]}{\partial \mathcal{E}_i \partial \mathcal{E}_j} = \frac{\partial P_i^{el}[\psi]}{\partial \mathcal{E}_j} \quad (8)$$



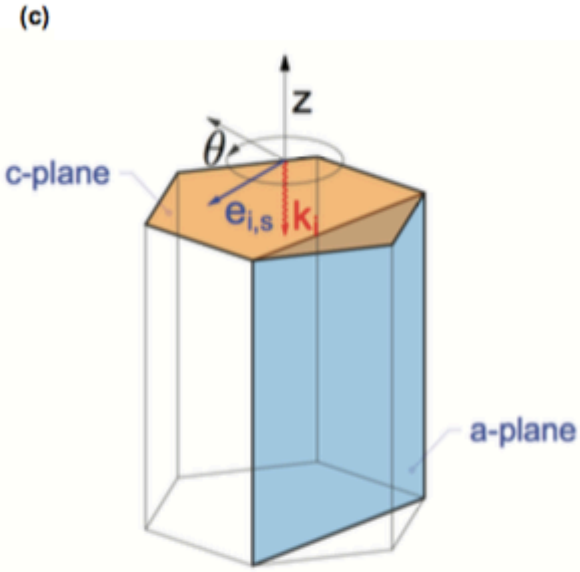


Table II | Phonon frequencies (in cm^{-1}) of ZnO at Brillouin Zone center (Γ), calculated with LDA, PBE, PBE + U and compared to experimental Raman data from Ref. 7

Mode (Γ)	LDA	PBE	PBE + U	Exp (Raman)
TA/TA	0	0	0	0
$E_w^{(low)}$	87	89	106	100
$B_1^{(low)}$	258	243	283	-
A_1(TO)	398	343	384	380
E_1(TO)	420	363	408	410
$E_2^{(high)}$	446	392	436	438
$B_1^{(high)}$	539	505	578	-
A_1(LO)	547	498	607	(584)
E_1(LO)	560	508	615	(595)

y(xz)ȳ

y =the direction of the propagation of the incident light ($\mathbf{k_i}$)

x =the direction of the polarization of the incident light ($\mathbf{e_i}$)

z =the direction of the polarization of the scatted light ($\mathbf{e_s}$)

-y =the direction of the propagation of the scatted light ($\mathbf{k_s}$)

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Born effective charge and dielectric constant

Born effective charge tensor:

$$Z^*_{I,ij} = \frac{\Omega}{e}\frac{\partial P^{el}_i[\psi]}{\partial r_{I,j}} = \frac{\partial^2 E^{\varepsilon}_{tot}[\psi]}{\partial \mathcal{E}_i \partial r_{I,j}} = -\frac{\partial F^{\varepsilon}_{I,j}}{\partial \mathcal{E}_i} \qquad (9)$$

The high-frequency dielectric constant:

$$\epsilon^{\infty}_{ij} = \delta_{i,j} + 4\pi\chi_{ij} \qquad (10)$$

The static dielectric constant:

$$\frac{\epsilon^0_s}{\epsilon^{\infty}_s} = \frac{\omega^2_s(LO)}{\omega^2_s(TO)} \qquad (11)$$

Lyddane-Sachs-Teller relation

s = electric field polarizations parallel and perpendicular to the polar axis.

Physical quantities and properties

- Force constants, phonon dispersion relation, phonon modes, PD-DOS.
- Raman tensor, susceptibility tensor
- Electronic polarization (P_{el})
- Raman spectrum
- Born effective charge and dielectric constant

The classical equation of motion-1

$$F_{I\alpha} = m_I a_{I\alpha} = m_I \frac{\partial^2 u_{I\alpha}(\vec{R})}{\partial t^2} \qquad (12)$$

$$F_{I\alpha} = -\frac{\partial E_{tot}}{\partial u_{I\alpha}(\vec{R})} = -\sum_{\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}' - \vec{R}\right) u_{J\beta}(\vec{R}') \qquad (13)$$

$$m_I \frac{\partial^2 u_{I\alpha}(\vec{R})}{\partial t^2} = -\sum_{\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}' - \vec{R}\right) u_{J\beta}(\vec{R}') \qquad (14)$$

The classical equation of motion-2

$$u_{I\alpha}(\vec{R}) = \vec{\gamma}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t} \quad (15)$$

$$\frac{\partial u_{I\alpha}(\vec{R})}{\partial t} = -i\omega\vec{\gamma}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t} \quad (16)$$

$$\frac{\partial^2 u_{I\alpha}(\vec{R})}{\partial t^2} = -\omega^2\vec{\gamma}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t} \quad (17)$$

$$m_I \frac{\partial^2 u_{I\alpha}(\vec{R})}{\partial t^2} = -\sum_{\vec{R}'} K_{I\alpha J\beta}(\vec{R}' - \vec{R})\, u_{J\beta}(\vec{R}') \quad (14)$$

Combining Eq. 14-17,

$$-m_I\omega^2\vec{\gamma}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t} = -\sum_{\vec{R}'} K_{I\alpha J\beta}(\vec{R}' - \vec{R})\,\vec{\gamma}_{J\beta}(\vec{q})e^{i\vec{q}\cdot\vec{R}'}e^{-i\omega t} \quad (18)$$

The classical equation of motion-3

$$-m_I\omega^2\vec{\gamma}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t} = -\sum_{\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)\vec{\gamma}_{J\beta}(\vec{q})e^{i\vec{q}\cdot\vec{R}'}e^{-i\omega t} \quad (18)$$

Removing signs and exp(-iwt),

$$m_I\omega^2\vec{\gamma}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}} = \sum_{\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)\vec{\gamma}_{J\beta}(\vec{q})e^{i\vec{q}\cdot\vec{R}'} \quad (19)$$

Moving exp(iqR) to the right hand side,

$$m_I\omega^2\vec{\gamma}_{I\alpha}(\vec{q}) = \sum_{\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)\vec{\gamma}_{J\beta}(\vec{q})e^{i\vec{q}\cdot(\vec{R}'-\vec{R})} \quad (20)$$

Reorganizing Eq. 19,

$$m_I\omega^2\vec{\gamma}_{I\alpha}(\vec{q}) = \sum_{\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)e^{i\vec{q}\cdot(\vec{R}'-\vec{R})}\vec{\gamma}_{J\beta}(\vec{q}) \quad (21)$$

Substituting dynamical matrix for force constant matrix,

$$m_I\omega^2\vec{\gamma}_{I\alpha}(\vec{q}) = D_{I\alpha J\beta}(\vec{q})\vec{\gamma}_{J\beta}(\vec{q}) \quad (22)$$

The classical equation of motion-4

Assume $$u_{I\alpha}(\vec{R}) = \frac{\vec{U}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t}}{\sqrt{m_I}} \quad (23)$$

$$\frac{\partial^2 u_{I\alpha}(\vec{R})}{\partial t^2} = \frac{-\omega^2 \vec{U}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t}}{\sqrt{m_I}} \quad (24)$$

$$-m_I\omega^2 \frac{\vec{U}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}e^{-i\omega t}}{\sqrt{m_I}} = -\sum_{\vec{R}'} K_{I\alpha J\beta}(\vec{R}' - \vec{R}) \frac{\vec{U}_{J\beta}(\vec{q})e^{i\vec{q}\cdot\vec{R}'}e^{-i\omega t}}{\sqrt{m_J}} \quad (25)$$

Removing signs and exp(-iwt),

$$m_I\omega^2 \frac{\vec{U}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}}{\sqrt{m_I}} = \sum_{\vec{R}'} K_{I\alpha J\beta}(\vec{R}' - \vec{R}) \frac{\vec{U}_{J\beta}(\vec{q})e^{i\vec{q}\cdot\vec{R}'}}{\sqrt{m_J}} \quad (26)$$

The classical equation of motion-5

$$m_I\omega^2\frac{\vec{U}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}}}{\sqrt{m_I}} = \sum_{\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)\frac{\vec{U}_{J\beta}(\vec{q})e^{i\vec{q}\cdot\vec{R}'}}{\sqrt{m_J}} \tag{27}$$

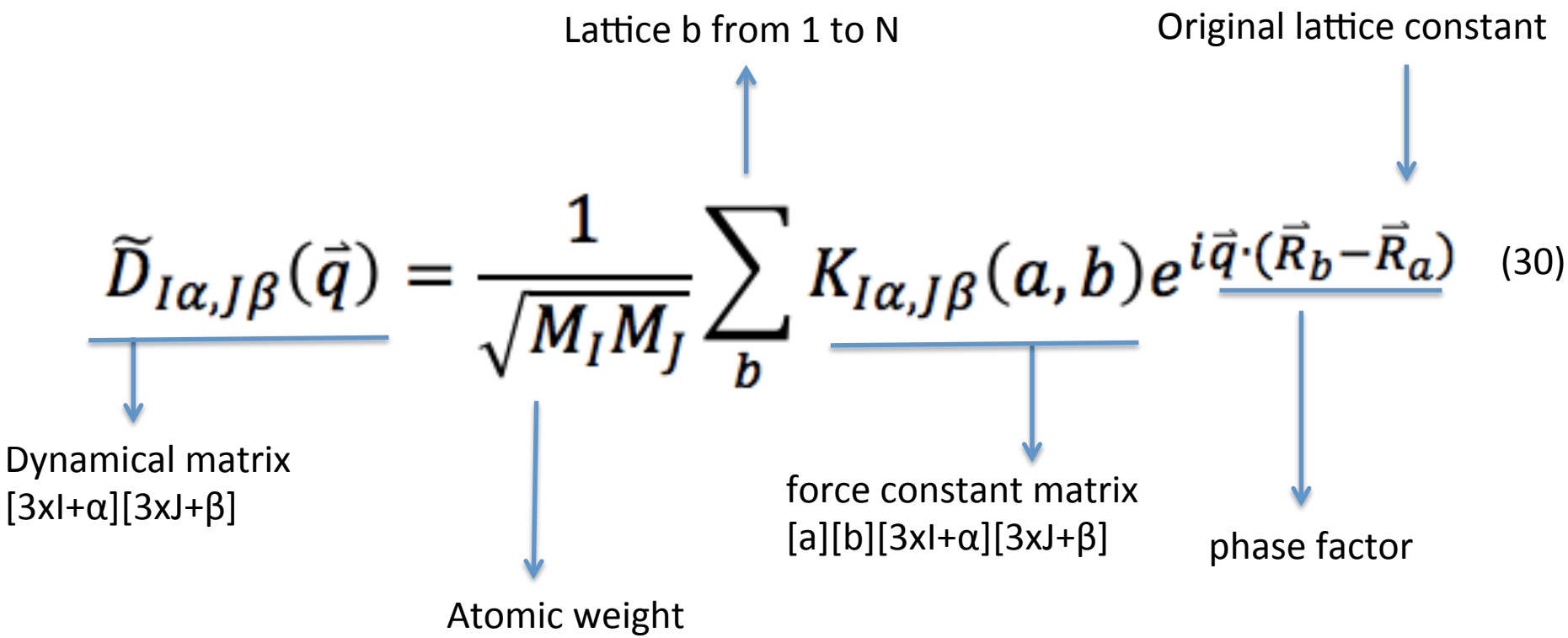
$$\sqrt{m_I}\omega^2\vec{U}_{I\alpha}(\vec{q})e^{i\vec{q}\cdot\vec{R}} = \frac{1}{\sqrt{m_J}}\sum_{\vec{R},\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)\vec{U}_{J\beta}(\vec{q})e^{i\vec{q}\cdot\vec{R}'} \tag{28}$$

$$\omega^2\vec{U}_{I\alpha}(\vec{q}) = \frac{1}{\sqrt{m_I m_J}}\sum_{\vec{R},\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)e^{i\vec{q}\cdot(\vec{R}'-R)}\vec{U}_{J\beta}(\vec{q}) \tag{29}$$

Assume $$\widetilde{D}_{I\alpha J\beta}(\vec{q}) = \frac{1}{\sqrt{m_I m_J}}\sum_{\vec{R},\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}'-\vec{R}\right)e^{i\vec{q}\cdot(\vec{R}'-\vec{R})} \tag{30}$$

LAPACK → zheev() subroutine ⟶ $$\omega^2\vec{U}_{I\alpha} = \widetilde{D}_{I\alpha J\beta}(\vec{q})\vec{U}_{J\beta} \tag{31}$$

Dynamical matrix



Force constant

$$K_{I\alpha,J\beta}(R-R') = \frac{\partial^2 E_{tot}}{\partial \mu_{I\alpha}(R)\partial \mu_{J\beta}(R')} = -\frac{\partial F_{I\alpha}}{\partial \mu_{J\beta}(R')} \quad (1)$$

Center difference approximation

$$f'(x) = \frac{f(x+\Delta x) - f(x-\Delta x)}{2\Delta x} \quad (31)$$

Displacement

Atomic coordinate x at equilibrium state

Bravais lattice vectors $\mathbf{l} = l_1 a\hat{\mathbf{i}} + l_2 a\hat{\mathbf{j}} + l_3 a\hat{\mathbf{k}}$

Reciprocal lattice vectors $\mathbf{g} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \text{(Eq. 31)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \text{(Eq. 32)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \text{(Eq. 33)}$$

The primitive vectors of the reciprocal and Bravais vectors have the property

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \qquad \delta_{ij} = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases} \quad \text{(Eq. 34)}$$

Dot product between reciprocal lattice vectors and Bravais lattice vectors

$$\mathbf{g} \cdot \mathbf{l} = (n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3) \cdot (l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3) \quad \text{(Eq. 35)}$$

$$= 2\pi(n_1 l_1 + n_2 l_2 + n_3 l_3)$$

$$= 2\pi \times \text{integer}.$$

$$e^{i\mathbf{g}\cdot\mathbf{l}} = 1 \quad \text{(Eq. 36)}$$

Flowchart of phonon dispersion

Construct a supercell (3 X 3 X 1) of graphene

↓

Displace atoms in the unit cell along 3 directions (x/y/z).

↓

Calculate all of atomic forces at each iteration

↓

$$K_{I\alpha J\beta}(R-R') = \frac{\partial^2 E_{tot}}{\partial u_{I\alpha}(R)\partial u_{J\beta}(R')} = -\frac{\partial F_{I\alpha}}{\partial u_{J\beta}(R')}$$

Construct force constant matrix(s)

↓

Applying acoustic sum rule

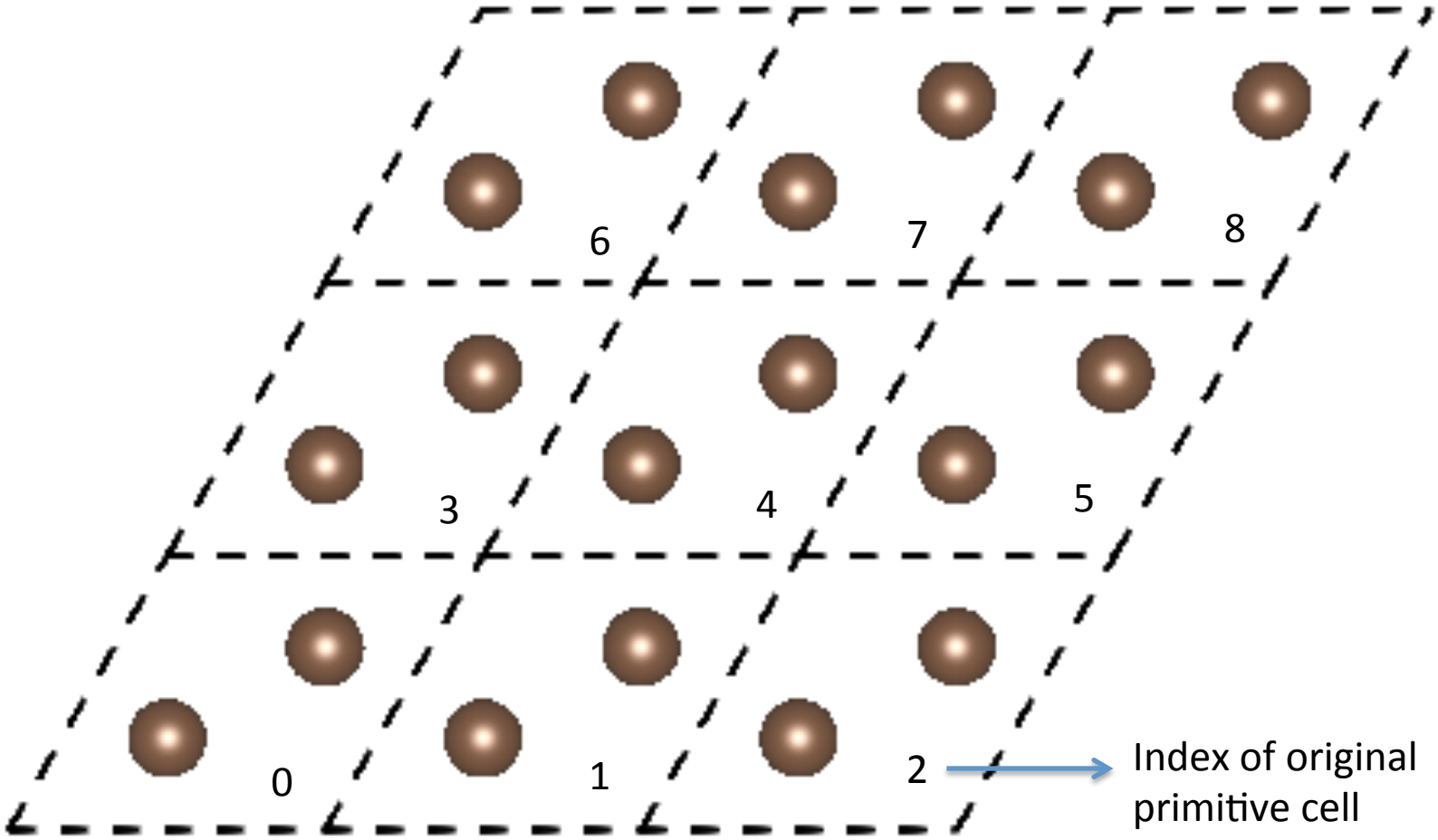
↓

$$\widetilde{D}_{I\alpha,J\beta}(\vec{q}) = \frac{1}{\sqrt{M_I M_J}} \sum_{b}^{9} K_{I\alpha,J\beta}(a,b) e^{i\vec{q}\cdot(\vec{R}_b - \vec{R}_a)}$$

Calculate real part and imagery part of dynamical matrix with wave vectors ***q***.

Construct a supercell (3x3x1) of Graphene

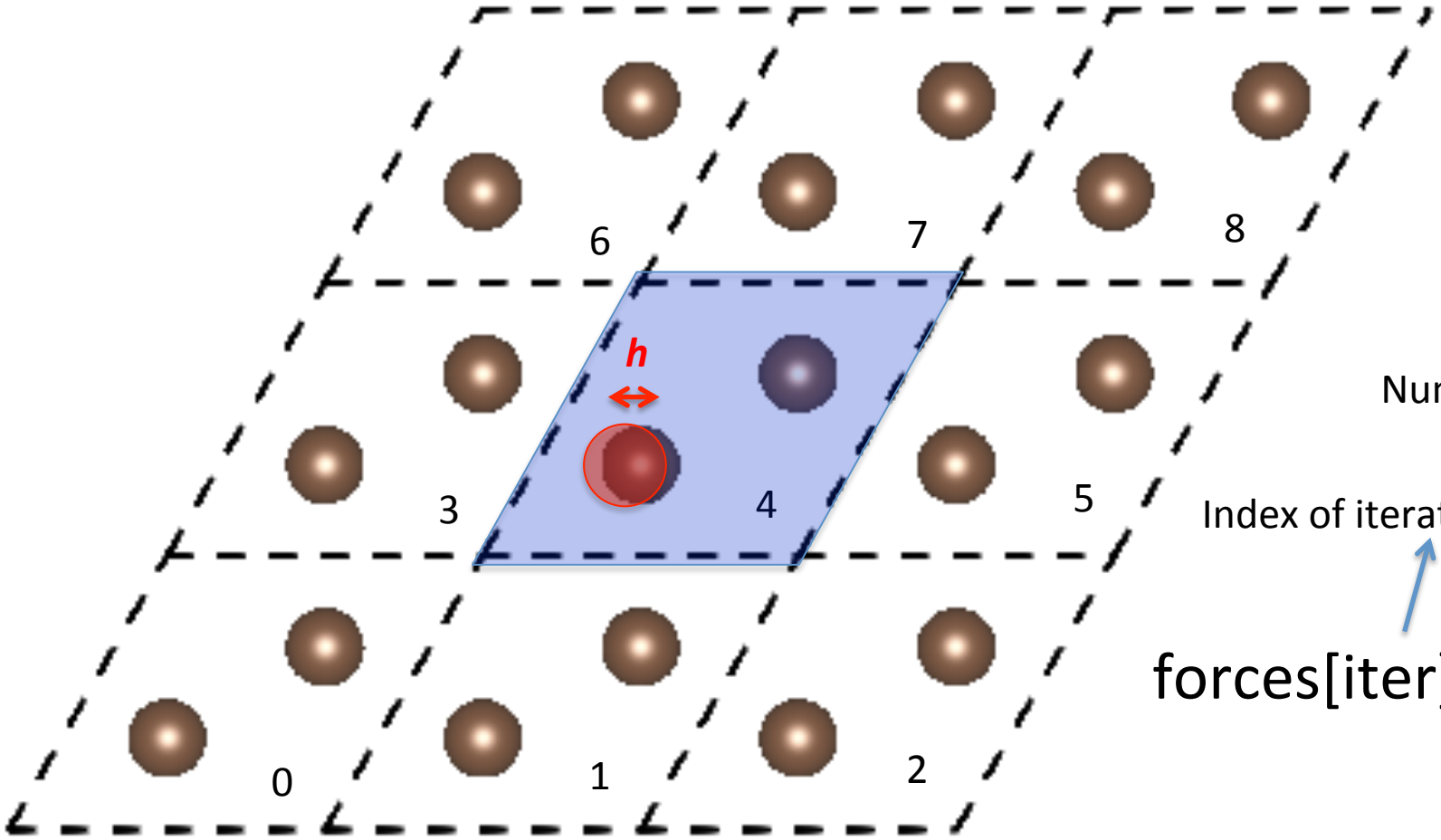
18 atoms in the supercell



Displace atomic coordinates with h

x, -x, y, -y, z, -z

Total iterations = # of atoms X 6



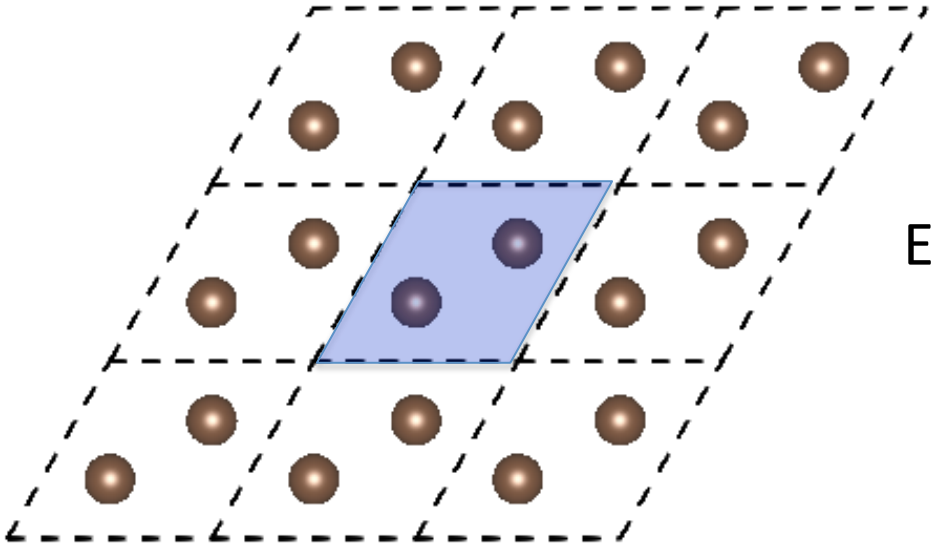
Number of atoms

Index of iteration

forces[iter][noa][3]

x, y, z

Construct 9 force constant matrixs



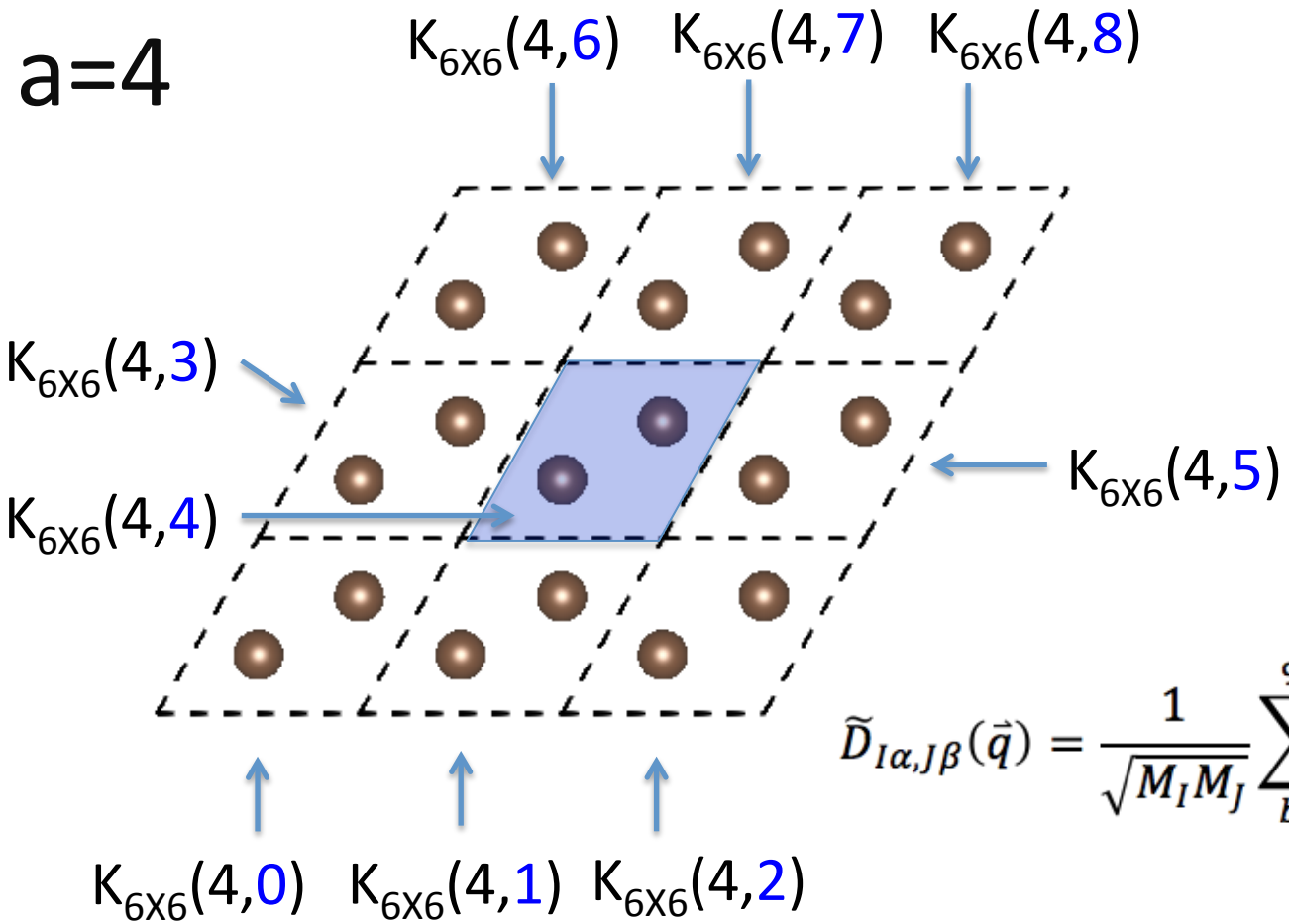
Each force constant matrix is 6 X 6.

$$K_{6X6}$$

$$\begin{bmatrix} F_{1x,1x} & F_{1x,1y} & F_{1x,1z} & F_{1x,2x} & F_{1x,2y} & F_{1x,2z} \\ F_{1y,1x} & F_{1y,1y} & F_{1y,1z} & F_{1y,2x} & F_{1y,2y} & F_{1y,2z} \\ F_{1z,1x} & F_{1z,1y} & F_{1z,1z} & F_{1z,2x} & F_{1z,2y} & F_{1z,2z} \\ F_{2x,1x} & F_{2x,1y} & F_{2x,1z} & F_{2x,2x} & F_{2x,2y} & F_{2x,2z} \\ F_{2y,1x} & F_{2y,1y} & F_{2y,1z} & F_{2y,2x} & F_{2y,2y} & F_{2y,2z} \\ F_{2z,1x} & F_{2z,1y} & F_{2z,1z} & F_{2z,2x} & F_{2z,2y} & F_{2z,2z} \end{bmatrix}$$

Force constant matrix $K_{6X6}(a,b)$

a=4



$$\widetilde{D}_{I\alpha,J\beta}(\vec{q}) = \frac{1}{\sqrt{M_I M_J}} \sum_{b}^{9} K_{I\alpha,J\beta}(a,b) e^{i\vec{q}\cdot(\vec{R}_b - \vec{R}_a)}$$

Constructing force constant matrix

FC [# of atoms X 3 X size of supercell] [# of atoms X 3 X size of supercell]

$$\widetilde{D}_{I\alpha,J\beta}(\vec{q}) = \frac{1}{\sqrt{M_I M_J}} \sum_{b}^{9} K_{I\alpha,J\beta}(a,b) e^{i\vec{q}\cdot(\vec{R}_b - \vec{R}_a)}$$

For example:

Supercell (3x3x1) → 3 X 3 X 1 = 9

Dimension of FC matrix = [2 X 3 X 9] [2 X 3 X 9] = [54] [54]

```
/* calculate force constants -24x24*/
for (i=0;i<noa3;i++){
  for (j=0;j<numberofatom;j++){
    for (k=0;k<3;k++){
      fc[i][3*j+k]=(force[2*i+1][j][k]-force[2*i+2][j][k])/disp2;
    }
  }
}
```

First derivative of force by center difference approximation

noa3 = # of atom X 3, numberofatom = # of atom, disp2 = displacement

Sum rules

2. Sum rules in the matrix of force constants

We will be concerned with satisfying two properties of the matrix of force constants [8], $\Phi_{i\alpha,j\beta}$ (where i and j label the atoms and α and β label Cartesian directions) which are difficult to impose simultaneously in *ab initio* lattice dynamics. Firstly, it should be symmetric because partial differentiation is commutative:

Rule 1 $$\Phi_{i\alpha,j\beta} = \Phi_{j\beta,i\alpha} \tag{2}$$

although from equation (1) we see that this explicit symmetry is missing when the element is calculated from the force. Secondly, it should obey the following sum rule which follows from Newton's third law:

Rule 2 $$\Phi_{i\alpha,i\beta} = -\sum_{j\neq i} \Phi_{i\alpha,j\beta}. \tag{3}$$

It follows from these two rules that:

Rule 3 $$\sum_{j\neq i} \Phi_{i\alpha,j\beta} = \sum_{j\neq i} \Phi_{i\beta,j\alpha}. \tag{4}$$

These three rules are true regardless of the actual symmetry of the system under consideration. If the force calculation is exact, then the rules above are automatically

Acoustic sum rule (ASR)

```
// apply the rule 1 and rule 2 to fc[noa3][noa3]
// rule 1
  for (i=0;i<noa3;i++)
    for (j=i+1;j<noa3;j++){
      double tmp=(fc[i][j]+fc[j][i])/2;
      fc[j][i]=tmp;
      fc[i][j]=tmp;
    }

// rule 2 : the acoustic sum rule
  for (k=0;k<3;k++)
    for (o=0;o<3;o++){
      for (i=0;i<numberofatom;i++){
        double tmp=0.0;
        for (j=0;j<numberofatom;j++){
          if (i!=j) tmp+=fc[3*i+k][3*j+o];
        }
        fc[3*i+k][3*i+o]=-tmp;
      }
    }
```

$$\Phi_{i\alpha,j\beta} = \Phi_{j\beta,i\alpha}$$

Both off-diagonal terms are averaged.

k=α

o=β

$$\Phi_{i\alpha,i\beta} = -\sum_{j\neq i} \Phi_{i\alpha,j\beta}$$

Unit = cm^{-1}

Results with ASR

For example 1: Graphene (1x1x1), cutoff 150 Ry, Gamma point

No rules applied

-3.883152 19.082851 43.459675 912.271754 1580.463273 1585.862521

Rule 1

19.083004 21.090209 37.816403 912.271750 1580.083579 1586.240450

Rule 1 and rule 2

-0.000018 -0.000008 0.000001 912.072138 1579.865328 1585.866813

For example 2: Graphene (3x3x1), cutoff 150 Ry, Gamma point

Rule 1 and rule 2

-0.130588 -0.000015 0.049880 912.282112 1588.279770 1591.485822

For example 3: Graphene (5x5x1), cutoff 150 Ry, Gamma point

Rule 1 and rule 2

-0.153711 0.054393 0.354314 912.275948 1585.839309 1588.701312

Calculate dynamical matrix

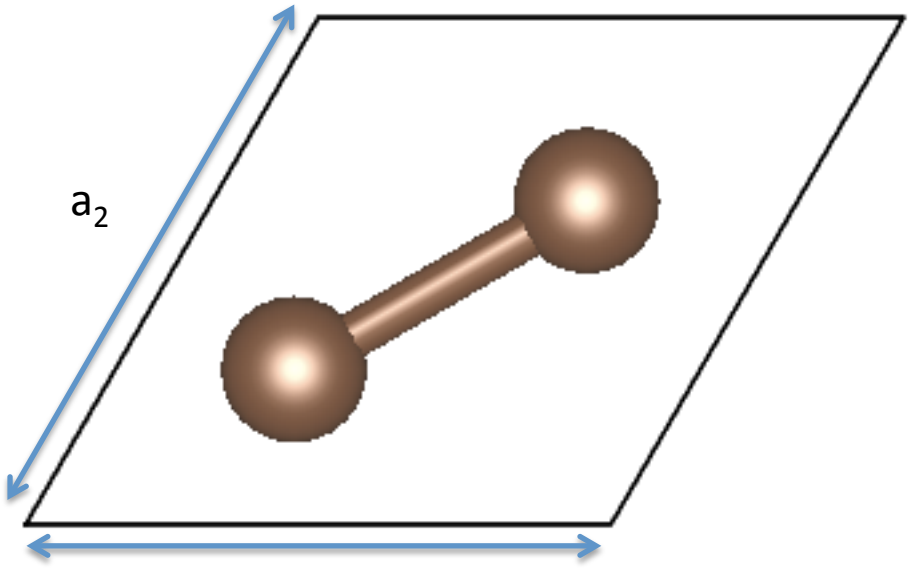
```
// ### start to calculate dynamical matrix ###
int aa=4;
double Dre[fc_numberofkgrids][l*3][l*3],Dim[fc_numberofkgrids][l*3][l*3]; // Dre,Dim
for (t=0;t<fc_numberofkgrids;t++){ // Dynamical matrix [t][i][j]
  for (i=0;i<3*l;i++){     i = l x 3 + α
    for (j=0;j<3*l;j++){     j = J x 3 + β
      double sumbre=0,sumbim=0,pf;
      for (o=0;o<ll;o++){ // unit cell R'
        int ii,jj;
        double uv[3][3],rlvt[3][3];

        // (1) R'-R and (2) dot product between q and (R'-R)
        for (ii=0;ii<3;ii++)
          for (jj=0;jj<3;jj++){
            uv[ii][jj]=unitvectors_ori[o][ii][jj]-unitvectors_ori[aa][ii][jj]; // (1)
            rlvt[jj][ii]=q[t][jj]*rlv[jj][ii];
          }

        pf=two_lattices_product(uv[0],uv[1],uv[2],rlvt[0],rlvt[1],rlvt[2]); // (2)
        sumbre+=fcmatrix[aa][o][i][j]*cos(pf); // sum over R'
        sumbim+=fcmatrix[aa][o][i][j]*sin(pf);
      }

      sqrt_mimj=sqrt(Gxyz[(i/3)+1][20]*Gxyz[(j/3)+1][20]);   Sqrt ( I-th mass X J-th mass)
      Dre[t][i][j]=sumbre/sqrt_mimj;
      Dim[t][i][j]=sumbim/sqrt_mimj;
    }
  }
}
```

$$\widetilde{D}_{I\alpha J\beta}(\vec{q}) = \frac{1}{\sqrt{m_I m_J}} \sum_{\vec{R},\vec{R}'} K_{I\alpha J\beta}\left(\vec{R}' - \vec{R}\right) e^{i\vec{q}\cdot(\vec{R}'-\vec{R})}$$

Optimization of graphene

2 carbon atoms

$a_1 = a_2 = 2.46$ angstrom
$a_3 = 15.00$ angstrom



Energy Cutoff = **150 Ry**
K-points = **20 X 20** X 1
SCF Criterion = 10^{-9} hartree
MD type = BFGS
MD.Opt.Criterion = 10^{-7} hartree/Bohr

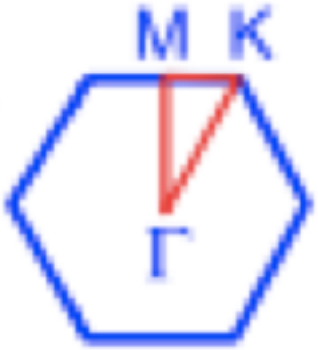
$$\vec{a}_1 = (a_0, 0, 0) ,$$

$$\vec{a}_2 = (a_0/2, a_0\sqrt{3}/2, 0)$$

$$\vec{a}_3 = (0, 0, c_0)$$

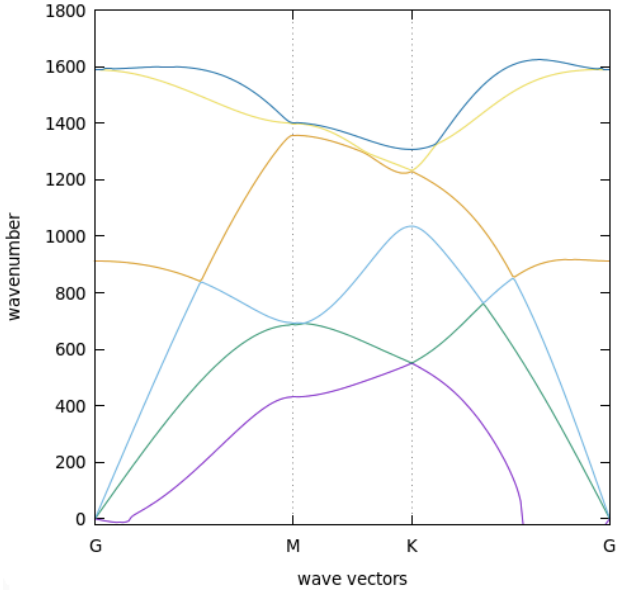
Input file

```
#
# MD or Geometry Optimization
#
MD.Initial.MaxStep 0.002
MD.Type FC # Nomd|Opt|DIIS|NVE|NVT_VS|NVT_NH
MD.Opt.DIIS.History 7 # default=7
MD.Opt.StartDIIS 10 # default=5
MD.maxIter 200 # default=1
MD.Opt.criterion 1.0e-7 # default=1.0e-4 (Hartree/bohr)
MD.FC.Displacement 0.05 # default=0.01
MD.FC.Supercell.grid 7 7 1 # default = 3 3 3
```

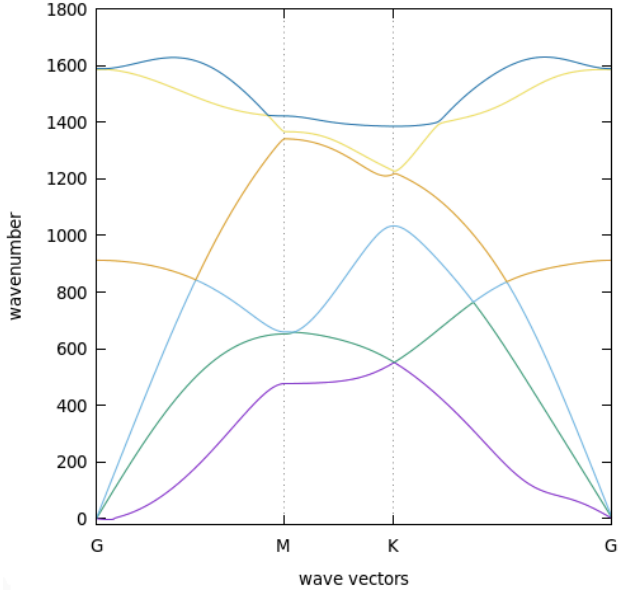



```
Phonon.Nkpath   3
<Phonon.kpath
 173   0.000000 0.000000 0.000000    0.000000 0.500000 0.000000   G M
 100   0.000000 0.500000 0.000000    0.333333 0.666666 0.000000   M K
 200   0.333333 0.666666 0.000000    0.000000 0.000000 0.000000   K G
Phonon.kpath>
```

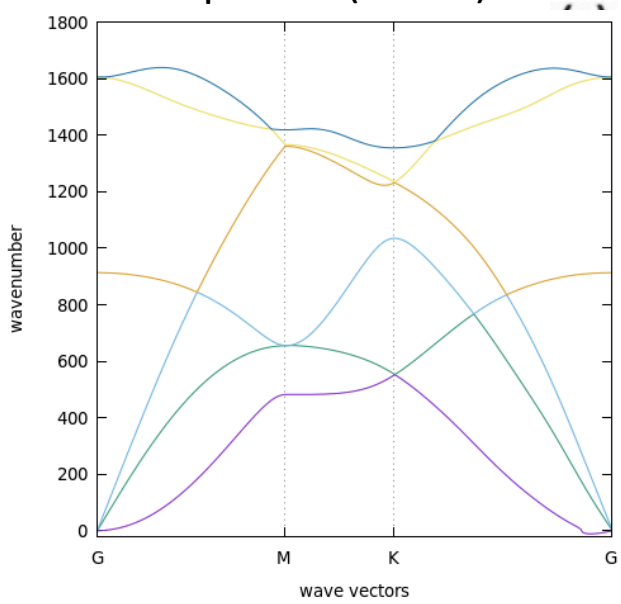
Supercell (3x3x1)

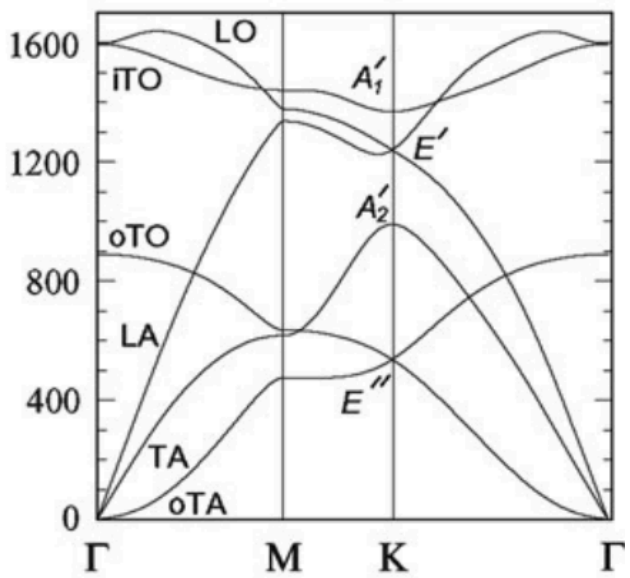


Supercell (5x5x1)



Supercell (7x7x1)





Displacement =0.05 Ang.

Phys. Chem. Chem. Phys., 2007, **9**, 1276–1291 | 1277

References

- *Scientific Reports* **3** (2013): 2999.
- *Phys. Rev. B* **55** (1997) 10355.
- *J. Phys: Condens. Matter* **9** (1997) 7861.
- *J. Phys: Condens. Matter* **25** (2013) 144201.
- N. W. Ashroft, N. D. Mermin, *Solid state physics*

Thanks for your attention.