Linear algebra libraries

(線形幾何学・行列計算ライブラリ)

Fortran, C, C++, etc

- LAPACK (Linear Algebra PACKage)
- ScaLAPACK (Scalable LAPACK)
- Intel Math Kernel Library (MKL)

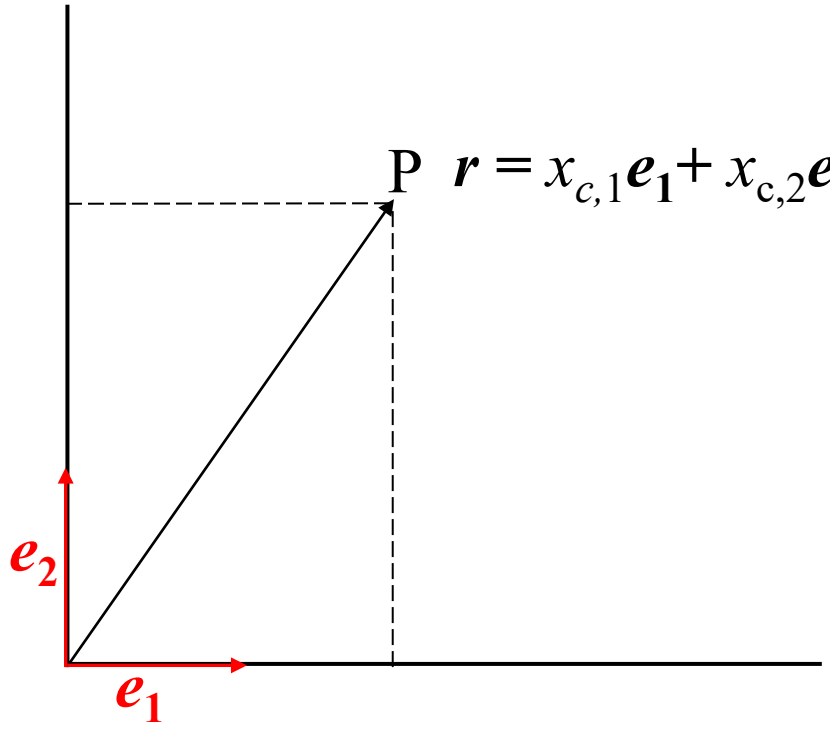
Python: numpy.linalg, scipy.linalg

matrix.py

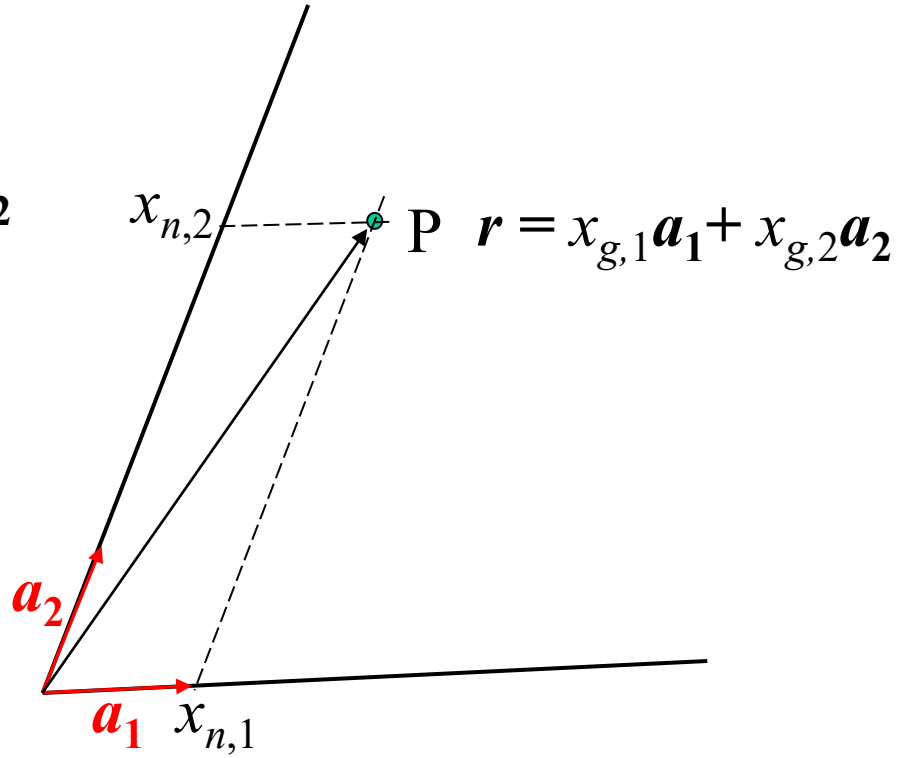
Product of matrixes	**AB**	: C	= A @ B
Inner product	**V1・V2**	: inner	= numpy.dot(V1, V2)
		inner	= numpy.inner(V1, V2)
Outer product	**V1 × V2**	: V3	= numpy.cross(V1, V2)
Inverse matrix		: Ai	= numpy.linalg.inv(A)
Determinant		: det	= numpy.linalg.det(A)
Eigen values/vectors		: lA, vA	= numpy.linalg.eig(A)
Solve simul. linear eqs.	**AX = B**	: X	= numpy.linalg.solve(A, B)
LU decomposition		: P, L, U	= numpy.linalg.lu(A)
Cholesky decomposition	**$A=LL^T$**	: L	= numpy.linalg.cholesky(A)
QR decomposition	**A=QR**	: Q, R	= scypy.linalg.qr(A)

一般座標系 (general coordinate system)

直交座標系 (Orthogonal)
デカルト座標系 (Cartesian)



一般座標/非直交系 (Non-Cartesian)



正規直交系 (orthonormal system)

$$e_i \cdot e_j = \delta_{ij}$$
$$|e_i| = 1$$

一般座標系 (general coordinate system)

$$a_i \cdot a_j \neq \delta_{ij}$$

e_i, a_i: 基底ベクトル (base vecor)

Cartesian – general coord. Conversion

(直交系 ― 一般座標系変換)

$$\boldsymbol{r} = x_{c,1}\boldsymbol{e_1} + x_{c,2}\boldsymbol{e_2} = x_{g,1}\boldsymbol{a_1} + x_{g,2}\boldsymbol{a_2}$$

$$x_{c,1} = x_{g,1}\,\boldsymbol{a_1}\cdot\boldsymbol{e_1} + x_{g,2}\,\boldsymbol{a_2}\cdot\boldsymbol{e_1}$$
$$x_{c,2} = x_{g,1}\,\boldsymbol{a_1}\cdot\boldsymbol{e_2} + x_{g,2}\,\boldsymbol{a_2}\cdot\boldsymbol{e_2}$$

If $\boldsymbol{a_1} = a_{11}\boldsymbol{e_1} + a_{12}\boldsymbol{e_2}$
$\boldsymbol{a_2} = a_{21}\boldsymbol{e_1} + a_{22}\boldsymbol{e_2}$
are given,

$$\begin{pmatrix}\boldsymbol{a_1}\\ \boldsymbol{a_2}\end{pmatrix} = \begin{pmatrix}a_{11} & a_{12}\\ a_{21} & a_{22}\end{pmatrix}\begin{pmatrix}\boldsymbol{e_1}\\ \boldsymbol{e_2}\end{pmatrix}$$

$$x_{c,1} = x_{g,1}a_{11} + x_{g,2}a_{21}$$
$$x_{c,2} = x_{g,1}a_{12} + x_{g,2}a_{22}$$

$$\begin{pmatrix}x_{c,1}\\ x_{c,2}\end{pmatrix} = \begin{pmatrix}a_{11} & a_{21}\\ a_{12} & a_{22}\end{pmatrix}\begin{pmatrix}x_{g,1}\\ x_{g,2}\end{pmatrix}$$

Fractional coordinates in crystal

(結晶の内部座標)

Lattice parameters: $a, b, c\ (= a_1, a_2, a_3), \alpha, \beta, \gamma (= \alpha_{23}, \alpha_{13}, \alpha_{12})$

Lattice vectors: $\boldsymbol{a_1}, \boldsymbol{a_2}, \boldsymbol{a_3} = \boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$

$$\boldsymbol{r} = x_{f,1}\boldsymbol{a_1} + x_{f,2}\boldsymbol{a_2} + x_{f,3}\boldsymbol{a_3} = x_{c,1}\boldsymbol{e_1} + x_{c,2}\boldsymbol{e_2} + x_{c,3}\boldsymbol{e_3}$$

$(x_{f,1}, x_{f,1}, x_{f,3})$: Fractional coordinate (部分座標)

Internal coordinate (内部座標)

$$|\boldsymbol{a_i}| = a_i$$

$$\boldsymbol{a_i} \cdot \boldsymbol{a_i} = a_i a_i \cos\alpha_{ij} \quad (i \neq j)$$

$$\begin{pmatrix} \boldsymbol{a_1} \\ \boldsymbol{a_2} \\ \boldsymbol{a_3} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} \boldsymbol{e_1} \\ \boldsymbol{e_2} \\ \boldsymbol{e_3} \end{pmatrix}$$

Fractional coordinate to Cartesian coordinate

$$\begin{pmatrix} x_{c,1} \\ x_{c,2} \\ x_{c,3} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} \begin{pmatrix} x_{f,1} \\ x_{f,2} \\ x_{f,3} \end{pmatrix}$$

Conversion matrix

$$\begin{pmatrix} \boldsymbol{a_1} \\ \boldsymbol{a_2} \\ \boldsymbol{a_3} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} \boldsymbol{e_1} \\ \boldsymbol{e_2} \\ \boldsymbol{e_3} \end{pmatrix}$$

$|\boldsymbol{a_i}| = a_i$

$\boldsymbol{a_i} \cdot \boldsymbol{a_j} = \cos\alpha_{ij} \ \ (i \neq j)$

$a, b, c \ \ (= a_1, a_2, a_3)$

$\alpha, \beta, \gamma \ (= \alpha_{23}, \alpha_{13}, \alpha_{12})$

tkcrystalbase.py

cal_lattice_vectors()

$$\begin{pmatrix} \boldsymbol{a_1} \\ \boldsymbol{a_2} \\ \boldsymbol{a_3} \end{pmatrix} = \begin{pmatrix} a & 0 & 0 \\ b\cos\gamma & b\sin\gamma & 0 \\ c\cos\beta & c\cos\beta - c\cos\beta\cos\gamma & a_{33} \end{pmatrix} \begin{pmatrix} \boldsymbol{e_1} \\ \boldsymbol{e_2} \\ \boldsymbol{e_3} \end{pmatrix}$$

$$a_{33} = \sqrt{c^2 - {a_{31}}^2 - {a_{32}}^2}$$

Lattice properties

Unit cell volume

$V = \boldsymbol{a_1} \cdot (\boldsymbol{a_2} \times \boldsymbol{a_3})$ tkcrystalbase.cal_volume ()

Distance $r_{kl} = r_k - r_l$ tkcrystalbase.distance2() / .distance()

$$r_{kl}{}^2 = |\boldsymbol{r_{kl}}|^2 = \sum_{i=0}^{2} \sum_{j=0}^{2} \boldsymbol{a_i} \cdot \boldsymbol{a_j} x_{kl,i} x_{kl,j} = \sum_{i,j} g_{ij} x_{kl,i} x_{kl,j}$$

$g_{ij} = \boldsymbol{a_i} \cdot \boldsymbol{a_j}$: Metric tensor (計量テンソル)

tkcrystalbase.cal_metrics()

Reciprocal lattice vectors tkcrystalbase.cal_reciprocal_lattice_vectors()

$$\boldsymbol{a^*}_1 = \boldsymbol{a_2} \times \boldsymbol{a_3}/\mathrm{V}$$
$$\boldsymbol{a^*}_2 = \boldsymbol{a_3} \times \boldsymbol{a_1}/\mathrm{V}$$
$$\boldsymbol{a^*}_3 = \boldsymbol{a_1} \times \boldsymbol{a_2}/\mathrm{V}$$

Reciprocal vector at $(h\ k\ l)$

$$\boldsymbol{G_{hkl}} = h\boldsymbol{a^*}_1 + k\boldsymbol{a^*}_2 + l\boldsymbol{a^*}_3$$

Lattice space

$$d_{hkl}{}^{-2} = |\boldsymbol{G_{hkl}}|^2 = \sum_{i=0}^{3} \sum_{j=0}^{3} \boldsymbol{a^*}_i \cdot \boldsymbol{a^*}_j h_i h_j = \sum_{i,j} R g_{ij} h_i h_j$$

Bragg angle

$2d_{hkl} \sin\theta = \lambda$

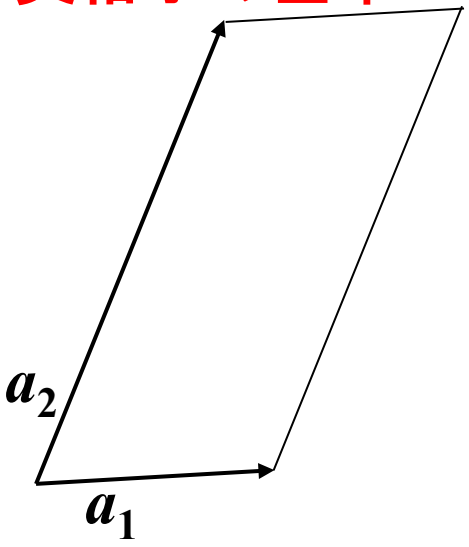
$h, k, l\ (= h_1, h_2, h_3)$

$Rg_{ij} = \boldsymbol{a^*}_i \cdot \boldsymbol{a^*}_j$

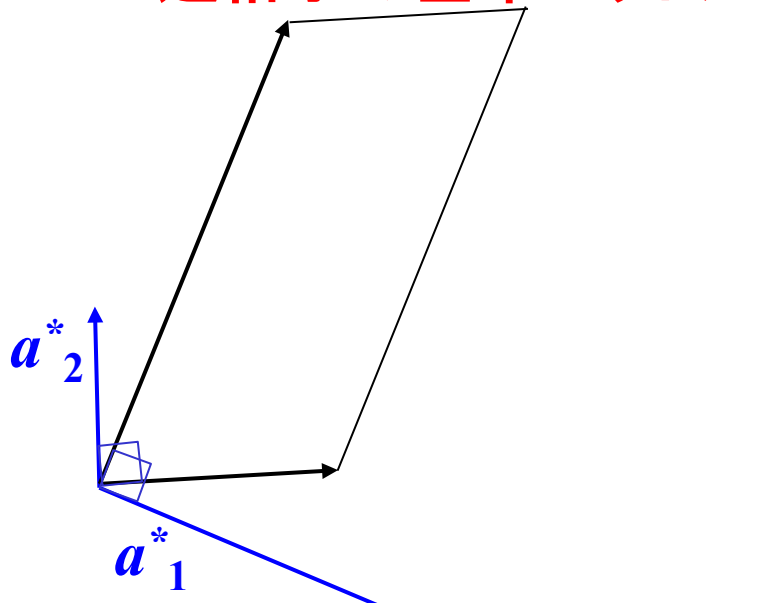
どうやって逆格子を描くか

- 実格子のフーリエ変換
  逆格子の長さ: 実格子の逆数
  角度: $\alpha^* = 180^o - \alpha$
- 逆格子の基本ベクトルは実格子の基本ベクトルに直交する
- ブラベー格子の消滅側を考える
  (基本格子の基本ベクトルを考えるのと同じ結果が得られる)

実格子の基本ベクトル



逆格子の基本ベクトル

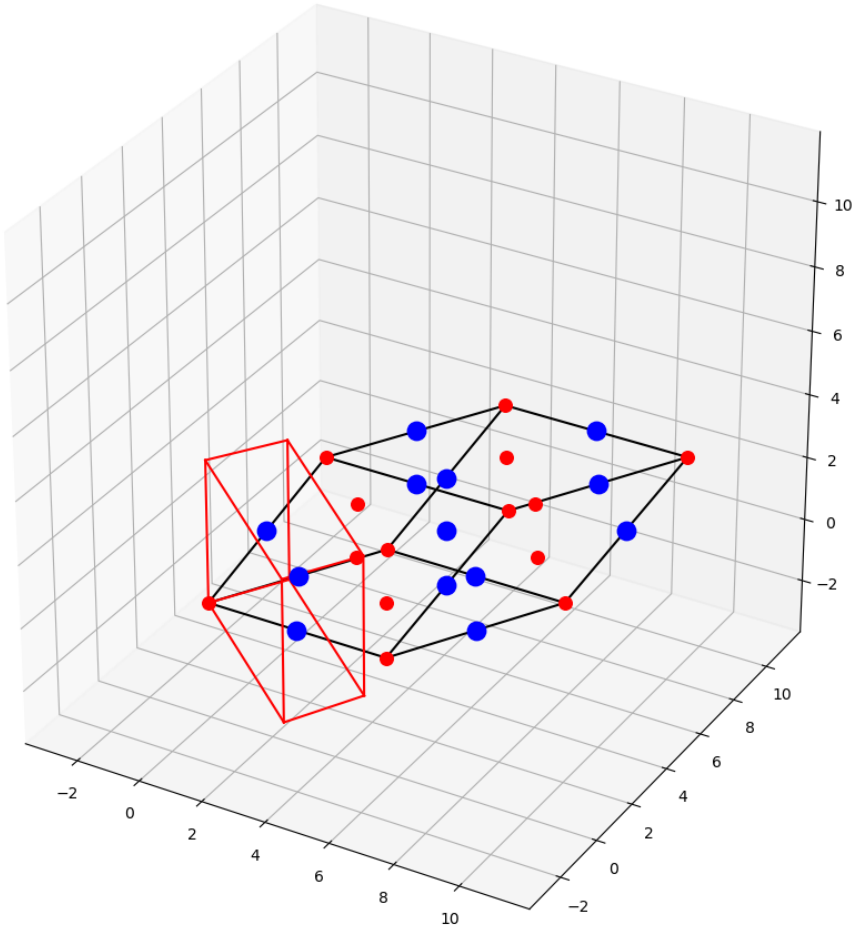


$$\mathbf{a}^*_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_\perp}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_\perp)}$$

Fractional – Cartesian conversion

python crystal_draw_cell.py

Rhombohedral cell
and reciprocal unit cell



Inter-atomic distances

crystal_distance.py

NaCl

Source code:

```
# Lattice parameters (angstrom and degree)
lattice_parameters = [ 5.62, 5.62, 5.62, 90.0, 90.0, 90.0]

# Site information (atom name, site label, atomic number, atomic mass, charge, radius, color, position)
sites = [
#                          原子量          電荷     描画条件          内部座標
       ['Na', 'Na1', 11, 22.98997, +1.0,    0.7, 'red',    np.array([0.0, 0.0, 0.0])]
      ,['Na', 'Na2', 11, 22.98997, +1.0,    0.7, 'red',    np.array([0.0, 0.5, 0.5])]
      ,['Na', 'Na3', 11, 22.98997, +1.0,    0.7, 'red',    np.array([0.5, 0.0, 0.5])]
      ,['Na', 'Na4', 11, 22.98997, +1.0,    0.7, 'red',    np.array([0.5, 0.5, 0.0])]
      ,['Cl',  'Cl1', 17, 35.4527,   -1.0,    1.4, 'blue',   np.array([0.5, 0.0, 0.0])]
      ,['Cl',  'Cl2', 17, 35.4527,   -1.0,    1.4, 'blue',   np.array([0.5, 0.5, 0.5])]
      ,['Cl',  'Cl3', 17, 35.4527,   -1.0,    1.4, 'blue',   np.array([0.0, 0.0, 0.5])]
      ,['Cl',  'Cl4', 17, 35.4527,   -1.0,    1.4, 'blue',   np.array([0.0, 0.5, 0.0])]
       ]

# Distance range
rmin = 0.1  # angstrom.  原子間距離がrmin未満の場合、同一の原子とみなす
rmax = 4.5  # angstrom. rmaxまでの原子間距離を計算
```

Inter-atomic distances

python crystal_distance.py

NaCl

OUTPUT

```
Lattice parameters: [5.62, 5.62, 5.62, 90.0, 90.0, 90.0]
Lattice vectors:
  ax: (      5.62,         0,         0) A
  ay: ( 2.546e-10,      5.62,         0) A
  az: ( 2.546e-10,         0,      5.62) A
Metric tensor:
  gij: (     31.58,  1.431e-09,  1.431e-09) A
       ( 1.431e-09,     31.58,   6.48e-20) A
       ( 1.431e-09,   6.48e-20,      31.58) A
Volume:        177.5 A^3
Unit cell volume:        177.5 A^3
Reciprocal lattice parameters: [0.17793594306049823, 0.17793594306049823, 0.17793594306049823, 90.00000000257246,
90.00000000516778, 90.00000000516778]
Reciprocal lattice vectors:
  Rax: (    0.1779,  -8.06e-12,  -8.06e-12) A^-1
  Ray: (         0,     0.1779,         0) A^-1
  Raz: (         0,         0,     0.1779) A^-1
Reciprocal lattice metric tensor:
  Rgij: (   0.03166, -1.422e-12, -1.422e-12) A^-1
        (-1.422e-12,    0.03166,  6.382e-23) A^-1
        (-1.422e-12,  6.382e-23,    0.03166) A^-1
Reciprocal unit cell volume:     0.005634 A^-3

nmax: 1 1 1

Interatomic distances:
  Cl1  (     0.5,       0,       0) - Na4  (     0.5,     0.5,       0) + ( 0, -1,  0): dis =      2.81 A
(cut)
  Na4  (     0.5,     0.5,       0) - Na1  (       0,       0,       0) + ( 0,  1,  0): dis =     3.974 A
  Na4  (     0.5,     0.5,       0) - Na2  (       0,     0.5,     0.5) + ( 1,  0, -1): dis =     3.974 A
  Na4  (     0.5,     0.5,       0) - Na1  (       0,       0,       0) + ( 1,  0,  0): dis =     3.974 A
```

三斜晶の面間隔 d_{hkl}

$$d_{hkl}^{-2} = \left|\mathbf{G}_{hkl}\right|^2 = \left|h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\right|^2$$

$$\frac{1}{d^2} = \frac{1}{V^2}\left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{31}lh\right)$$

$$S_{11} = b^2c^2\sin^2\alpha$$

$$S_{22} = c^2a^2\sin^2\beta$$

$$S_{33} = c^2a^2\sin^2\gamma$$

$$S_{12} = abc^2\left(\cos\alpha\cos\beta - \cos\gamma\right)$$

$$S_{23} = a^2bc\left(\cos\beta\cos\gamma - \cos\alpha\right)$$

$$S_{31} = ab^2c\left(\cos\gamma\cos\alpha - \cos\beta\right)$$

$$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

Bragg angles

NaCl

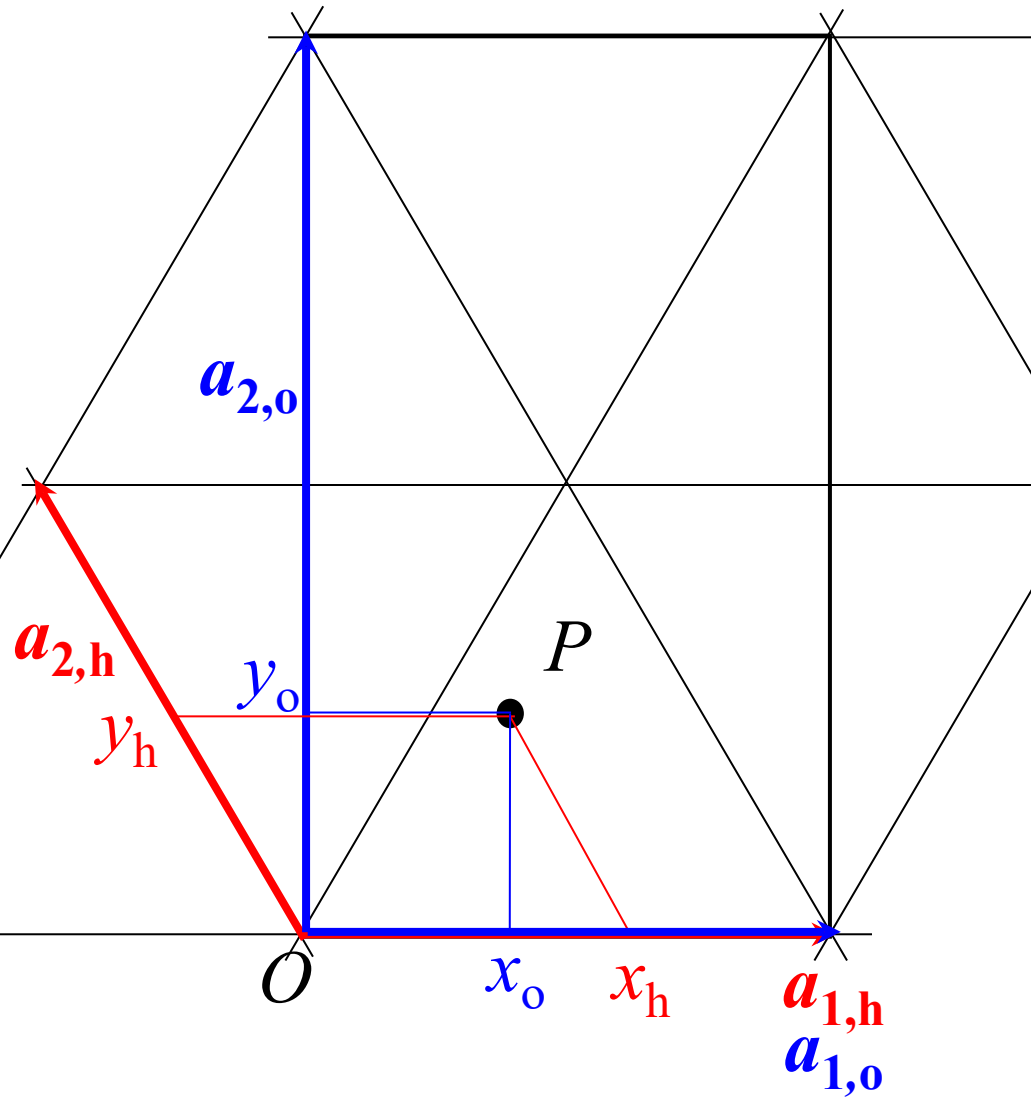
python crystal_xrd.py

OUTPUT

```
Lattice parameters: [5.62, 5.62, 5.62, 90.0, 90.0, 90.0]
Lattice vectors:
  ax: (      5.62,          0,          0) A
  ay: ( 2.546e-10,       5.62,          0) A
  az: ( 2.546e-10,          0,       5.62) A
Metric tensor:
  gij: (     31.58,  1.431e-09,  1.431e-09) A
       ( 1.431e-09,      31.58,   6.48e-20) A
       ( 1.431e-09,   6.48e-20,      31.58) A
Volume:        177.5 A^3
Unit cell volume:        177.5 A^3
Reciprocal lattice parameters: [0.17793594306049823, 0.17793594306049823, 0.17793594306049823, 90.00000000257246,
90.00000000516778, 90.00000000516778]
Reciprocal lattice vectors:
  Rax: (    0.1779,  -8.06e-12,  -8.06e-12) A^-1
  Ray: (         0,     0.1779,          0) A^-1
  Raz: (         0,          0,     0.1779) A^-1
Reciprocal lattice metric tensor:
  Rgij: (   0.03166, -1.422e-12, -1.422e-12) A^-1
        (-1.422e-12,    0.03166,  6.382e-23) A^-1
        (-1.422e-12,  6.382e-23,    0.03166) A^-1
Reciprocal unit cell volume:     0.005634 A^-3
hkl range: 7 7 7

Diffraction angle, d, h, k, l:
  2Q=      15.75  d=       5.62  ( -1   0   0)
  2Q=      15.75  d=       5.62  (  0  -1   0)
(cut)
  2Q=      22.35  d=    3.97394  ( -1  -1   0)
  2Q=      22.35  d=    3.97394  ( -1   0  -1)
  2Q=      22.35  d=    3.97394  (  1   0   1)
```

六方/三方格子 ― 底心斜方格子変換



$\boldsymbol{a'}_i = \Sigma_j (t_{ij}\, \boldsymbol{a}_j)$ $(\mathbf{A'} = \mathrm{TA})$

$$\begin{pmatrix} \boldsymbol{a}_{1,o} \\ \boldsymbol{a}_{2,o} \\ \boldsymbol{a}_{3,o} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \boldsymbol{a}_{1,h} \\ \boldsymbol{a}_{2,h} \\ \boldsymbol{a}_{3,h} \end{pmatrix}$$

$\mathbf{R} = \Sigma_i (x_i\, \boldsymbol{a}_i) = \Sigma_i (x'_i\, \boldsymbol{a'}_i) = \Sigma_{i,j} (x'_i\, t_{ij}\, \boldsymbol{a}_j)$ から、

$x_i = \Sigma_j (x'_j\, t_{ji})$ $(\mathbf{X} = {}^t\mathrm{T}\mathbf{X'})$

$$\begin{pmatrix} x_{1,h} \\ x_{2,h} \\ x_{3,h} \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{1,o} \\ x_{2,o} \\ x_{3,o} \end{pmatrix}$$

$x'_i = \Sigma_j x'_j\, (t_{ji})^{-1}$ $(\mathbf{X'} = {}^t\mathrm{T}^{-1}\mathbf{X})$

$$\begin{pmatrix} x_{1,o} \\ x_{2,o} \\ x_{3,o} \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}^{-1} \begin{pmatrix} x_{1,h} \\ x_{2,h} \\ x_{3,h} \end{pmatrix}$$

格子変換と行列

実格子空間のベクトルの変換: $(\boldsymbol{a}_i) \Rightarrow (\boldsymbol{a}'_i)$　　変換行列: (t_{ij})

$$\boldsymbol{a}'_i = \Sigma_j (t_{ij}\, \boldsymbol{a}_j) \qquad (\mathbf{A}' = \mathrm{T}\mathbf{A})$$

$\mathbf{R} = \Sigma_i (x_i\, \boldsymbol{a}_i) = \Sigma_i (x'_i\, \boldsymbol{a}'_i) = \Sigma_{i,j} (x'_i\, t_{ij}\, \boldsymbol{a}_j)$ から、

$$x_i = \Sigma_{,j} (x'_j\, t_{ji}) \qquad (\mathbf{X} = {}^{t}\mathrm{T}\mathbf{X}')$$

$$x'_i = \Sigma_{,j} x'_j\, (t_{ji})^{-1} \qquad (\mathbf{X}' = {}^{t}\mathrm{T}^{-1}\mathbf{X})$$

$\mathbf{R}\cdot\mathbf{G}_{hkl} = hx + ky + lz$ はスカラー: $\mathbf{R}\cdot\mathbf{G}_{hkl} = \mathbf{R}'\cdot\mathbf{G}'_{h'k'l'}$

$$\Sigma_i (h_i x_i) = \Sigma_i (h'_i x'_i) = \Sigma_{i,j} (h_i\, x'_j\, t_{ji})$$

$$h'_j = \Sigma_i (h_i\, t_{ji}) \qquad (\mathbf{H}' = \mathrm{T}\mathbf{H})$$

$\mathbf{G}_{hkl} = \mathbf{G}'_{h'k'l'}$ より、

$$\Sigma_i (h'_i \boldsymbol{a}^{*\prime}_i) = \Sigma_i (h_i \boldsymbol{a}^*_i) = \Sigma_{i,j} (h_i\, t_{ji}\, \boldsymbol{a}^{*\prime}_i)$$

$$\boldsymbol{a}^*_i = \Sigma_{i,j} (t_{ji}\, \boldsymbol{a}^{*\prime}_j) \qquad (\mathbf{A}^* = {}^{t}\mathrm{T}\mathbf{A}^{*\prime})$$

$$\boldsymbol{a}^{*\prime}_i = \Sigma_{i,j} ((t_{ji})^{-1}\, \boldsymbol{a}^*_j) \qquad (\mathbf{A}^{*\prime} = {}^{t}\mathrm{T}^{-1}\mathbf{A}^*)$$

単位格子(ブラベー格子) と 基本格子

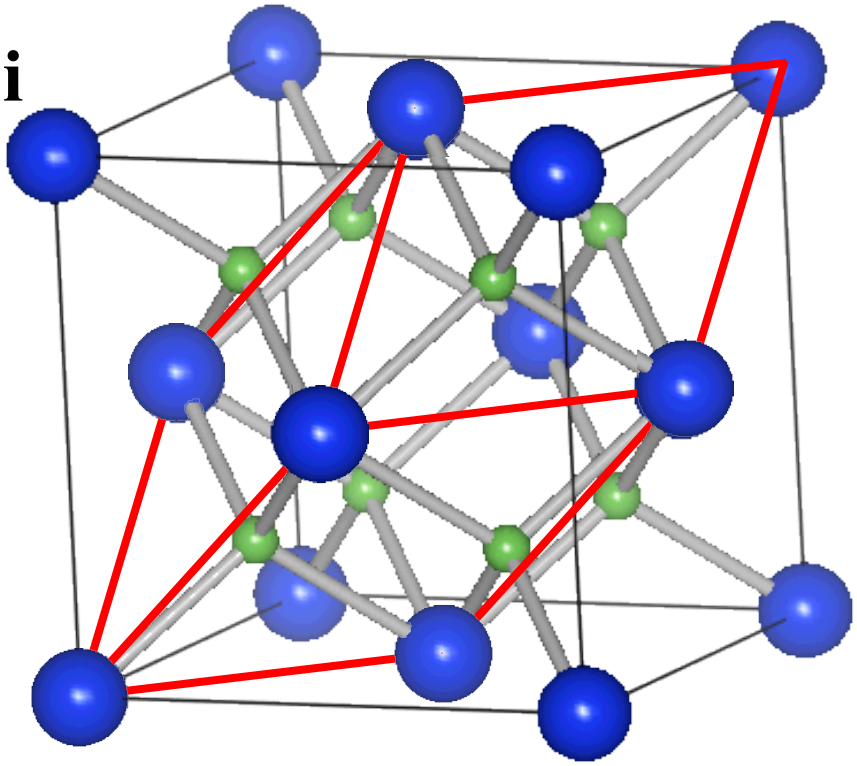
Siの構造 (室温)

空間群　*Fd3m*, No. 227 (立方晶系, ダイヤモンド構造)

ブラベー格子　　**基本格子**

$a_C = 0.5431$ nm　　$a_R = 0.3840$ nm　$\alpha = 60^o$

Si



$\boldsymbol{a'}_i = \Sigma_j (t_{ij}\, \boldsymbol{a}_j)$　　$(\mathbf{A'} = \mathrm{TA})$

$$\begin{pmatrix} \boldsymbol{a}_{1,p} \\ \boldsymbol{a}_{2,p} \\ \boldsymbol{a}_{3,p} \end{pmatrix} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ 1/2 & 0 & 1/2 \\ 0 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} \boldsymbol{a}_{1,FCC} \\ \boldsymbol{a}_{2,FCC} \\ \boldsymbol{a}_{3,FCC} \end{pmatrix}$$

$\mathbf{R} = \Sigma_i (x_i\, \boldsymbol{a}_i) = \Sigma_i (x'_i\, \boldsymbol{a'}_i) = \Sigma_{i,j} (x'_i\, t_{ij}\, \boldsymbol{a}_j)$ から、

$x_i = \Sigma_{,j} (x'_j\, t_{ji})$　　$(\mathbf{X} = {}^t\mathrm{T}\mathbf{X'})$

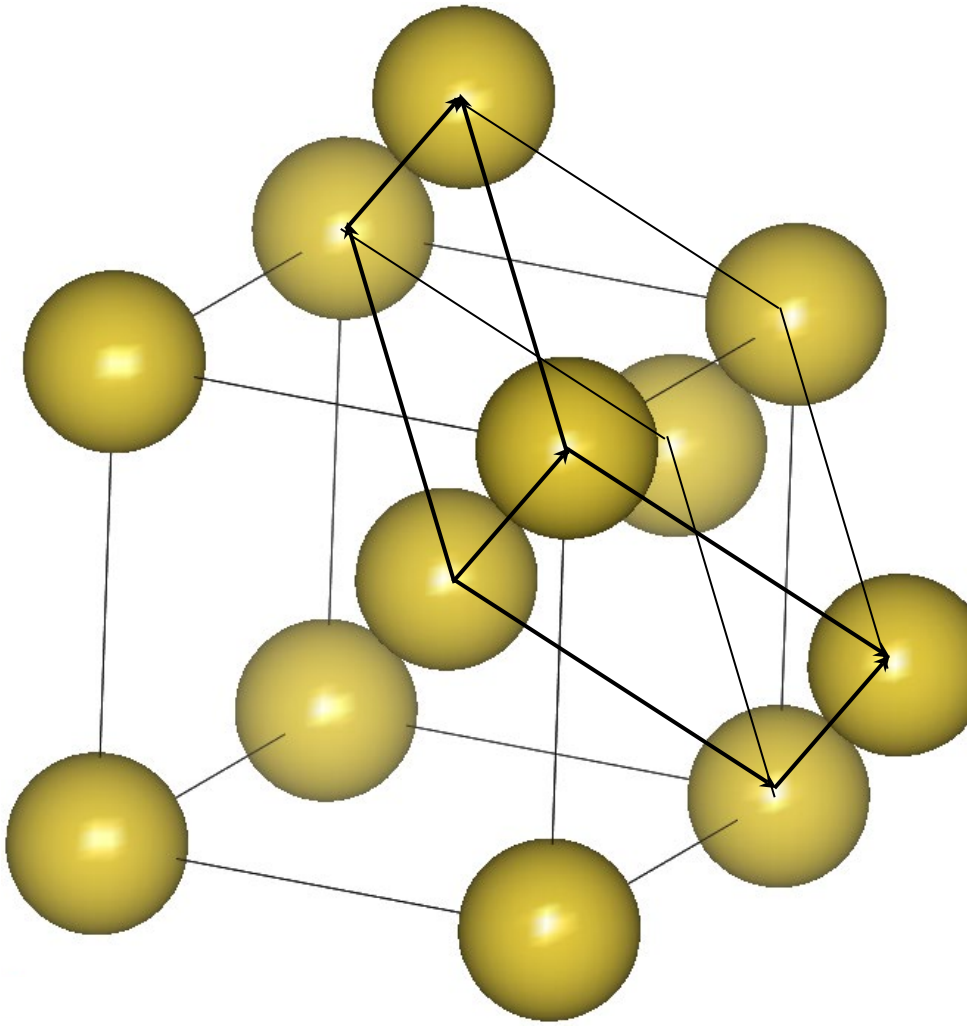
$$\begin{pmatrix} x_{1,FCC} \\ x_{2,FCC} \\ x_{3,FCC} \end{pmatrix} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ 1/2 & 0 & 1/2 \\ 0 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} x_{1,p} \\ x_{2,p} \\ x_{3,p} \end{pmatrix}$$

$x'_i = \Sigma_{,j}\, x'_j\, (t_{ji})^{-1}$　　$(\mathbf{X'} = {}^t\mathrm{T}^{-1}\mathbf{X})$

$$\begin{pmatrix} x_{1,p} \\ x_{2,p} \\ x_{3,p} \end{pmatrix} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ 1/2 & 0 & 1/2 \\ 0 & 1/2 & 1/2 \end{pmatrix}^{-1} \begin{pmatrix} x_{1,FCC} \\ x_{2,FCC} \\ x_{3,FCC} \end{pmatrix}$$

単位格子(ブラベー格子) と 基本格子

体心立方格子



$$\boldsymbol{a'}_{\mathbf{i}} = \Sigma_j \, (t_{ij} \, \boldsymbol{a}_{\mathbf{j}}) \qquad (\mathbf{A'} = \mathrm{T}\mathbf{A})$$

$$\begin{pmatrix} \boldsymbol{a}_{\mathbf{1,o}} \\ \boldsymbol{a}_{\mathbf{2,o}} \\ \boldsymbol{a}_{\mathbf{3,o}} \end{pmatrix} = \begin{pmatrix} -1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & 1/2 \\ -1 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} \boldsymbol{a}_{\mathbf{1,BCC}} \\ \boldsymbol{a}_{\mathbf{2,BCC}} \\ \boldsymbol{a}_{\mathbf{3,BCC}} \end{pmatrix}$$

$\mathbf{R} = \Sigma_i \, (x_i \, \boldsymbol{a}_{\mathbf{i}}) = \Sigma_i \, (x'_i \, \boldsymbol{a'}_{\mathbf{i}}) = \Sigma_{i,j} \, (x'_i \, t_{ij} \, \boldsymbol{a}_{\mathbf{j}})$ から、

$$x_i = \Sigma_{,j} \, (x'_j \, t_{ji}) \qquad (\mathbf{X} = {}^{t}\mathrm{T}\mathbf{X'})$$

$$\begin{pmatrix} x_{1,\mathrm{BCC}} \\ x_{2,\mathrm{BCC}} \\ x_{3,\mathrm{BCC}} \end{pmatrix} = \begin{pmatrix} -1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & 1/2 \\ -1 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} x_{1,\mathrm{p}} \\ x_{2,\mathrm{p}} \\ x_{3,\mathrm{p}} \end{pmatrix}$$

$$x'_i = \Sigma_{,j} \, x'_j \, (t_{ji})^{-1} \qquad (\mathbf{X'} = {}^{t}\mathrm{T}^{-1}\mathbf{X})$$

$$\begin{pmatrix} x_{1,\mathrm{p}} \\ x_{2,\mathrm{p}} \\ x_{3,\mathrm{p}} \end{pmatrix} = \begin{pmatrix} -1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & 1/2 \\ -1 & 1/2 & 1/2 \end{pmatrix}^{-1} \begin{pmatrix} x_{1,\mathrm{BCC}} \\ x_{2,\mathrm{BCC}} \\ x_{3,\mathrm{BCC}} \end{pmatrix}$$

六方格子－三方格子変換

菱面体晶: 六方格子軸と三方格子軸のどちらも取れる。

六方格子軸の基本ベクトル: $\mathbf{a}_1(H)$, $\mathbf{a}_2(H)$, $\mathbf{a}_3(H)$
三方格子軸の基本ベクトル: $\mathbf{a}_1(R)$, $\mathbf{a}_2(R)$, $\mathbf{a}_3(R)$

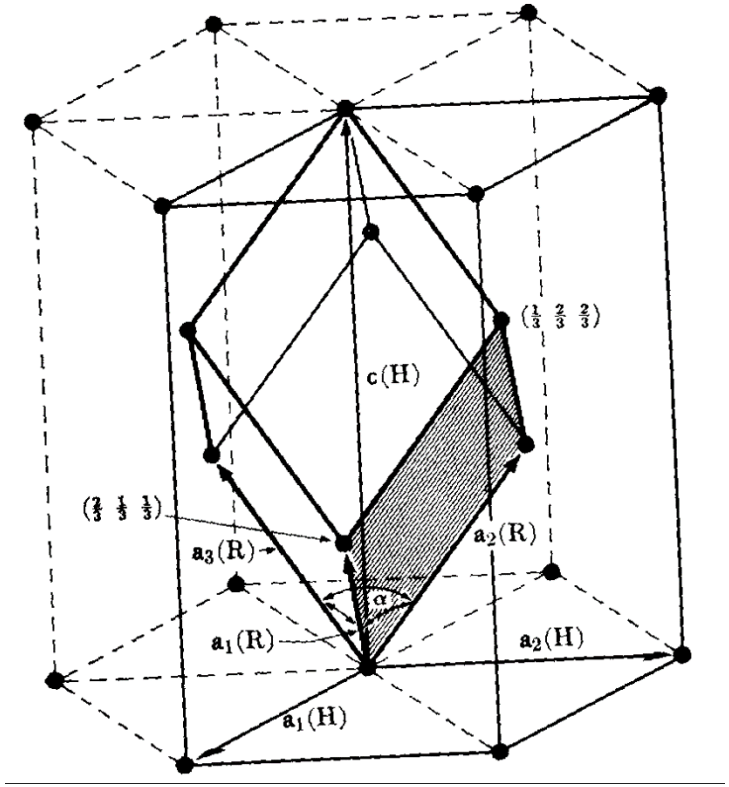
$$\mathbf{a}_1(R) = (2\mathbf{a}_1(H) + \mathbf{a}_2(H) + \mathbf{a}_3(H)) / 3$$
$$\mathbf{a}_2(R) = (-\mathbf{a}_1(H) + \mathbf{a}_2(H) + \mathbf{a}_3(H)) / 3$$
$$\mathbf{a}_3(R) = (-\mathbf{a}_2(H) - 2\mathbf{a}_2(H) + \mathbf{a}_3(H)) /3$$

三方格子軸での逆格子座標 h k l
六方格子軸での逆格子座標 H K L

$$h = (2H + K + L) / 3$$
$$k = (-H + K + L) / 3$$
$$l = (-H - 2K + L) /3$$
$$H = h - k$$
$$K = k - l$$
$$L = h + k + l$$

格子定数の関係

$$a_R = \sqrt{(3a_H^2 + c^2)}$$
$$\sin(\alpha/2) = 3/2 / \sqrt{(3 + (c/a_H)^2)}$$



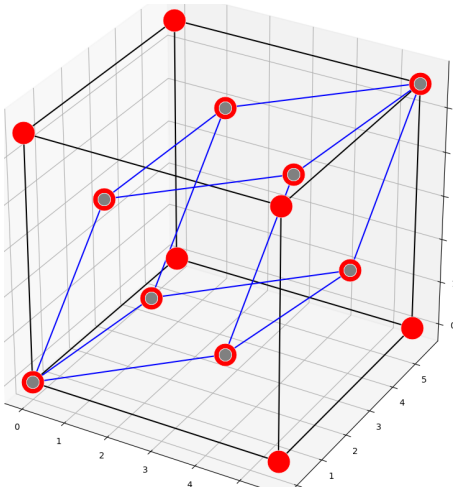
$$\boldsymbol{a'}_i = \Sigma_j (t_{ij}\, \boldsymbol{a}_j) \qquad (\mathbf{A'} = \mathrm{T}\mathbf{A})$$

$$\begin{pmatrix} \boldsymbol{a}_{1,h} \\ \boldsymbol{a}_{2,h} \\ \boldsymbol{a}_{3,h} \end{pmatrix} = \begin{pmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \boldsymbol{a}_{1,r} \\ \boldsymbol{a}_{2,r} \\ \boldsymbol{a}_{3,r} \end{pmatrix}$$

Program: crystal_convert_cell.py

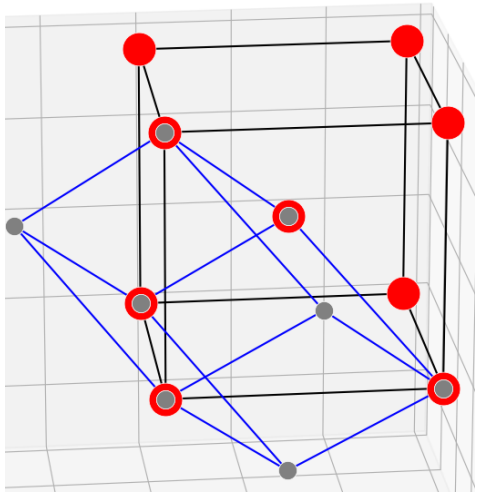
立方面心 => 基本格子变换

python crystal_convert_cell.py FCC FCCPrim



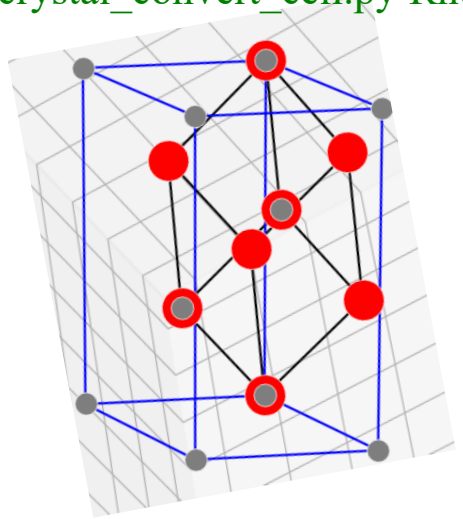
立方体心 => 基本格子变换

python crystal_convert_cell.py BCC BCCPrim



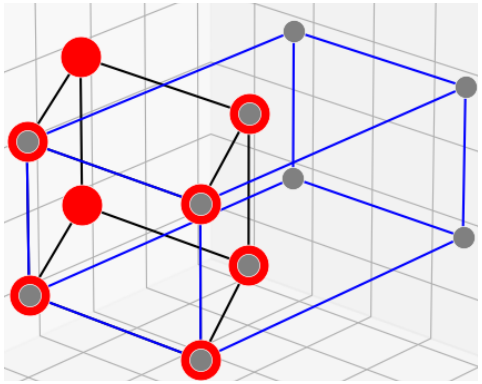
三方 => 六方格子变换

python crystal_convert_cell.py Rhomb RhombHex



六方 => 直方格子变换

python crystal_convert_cell.py Hex HexOrtho



Madelung potential

Sum of Coulomb potential in 3D is very slowly converging

Potential is proportional to r^{-1}

Polarization potential due to +/- ions is to r^{-2}

Number of ions on the sphere surface at radius r is to r^2

=> Contribution of ions from a surface region at r to Coulomb sum is almost constant, independent of r

$$U_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\varepsilon_0}\frac{1}{r_{ij}} + U_{Rij}(r_{ij})$$

$$U = \frac{1}{2}\sum_{i\neq j} U_{ij} = -A_M N_A \frac{Z^2 e^2}{4\pi\varepsilon_0 R} + U_R$$

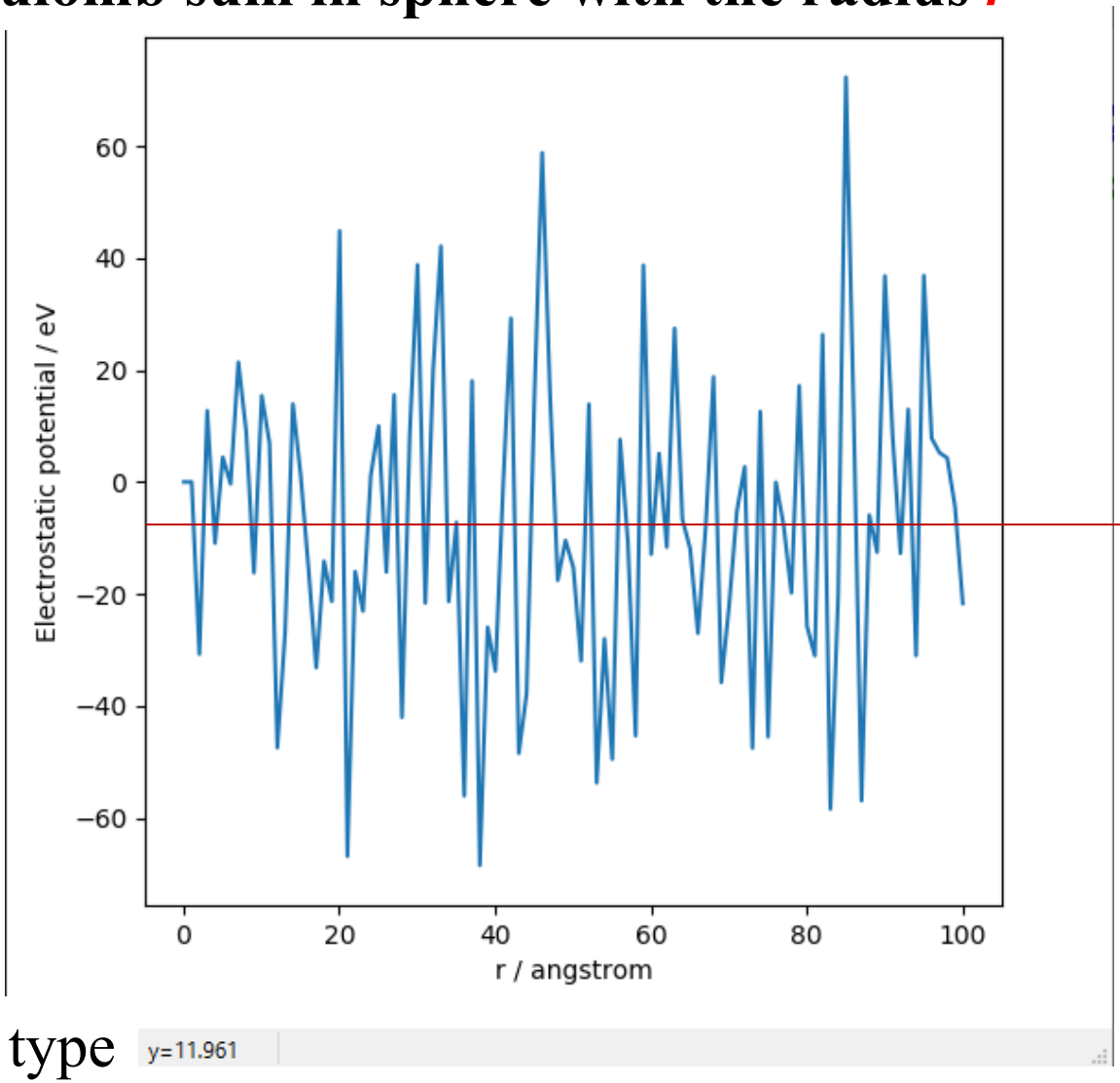
Crystal structure	A_r
Rock salt type(NaCl)	1.7476
CsCl type(CsCl)	1.7627
Zinc blend (CuCl)	1.6380
Wurzite(ZnO)	1.6413
Cu_2O type	4.116
Fluorite type (CaF_2)	2.520

$$A_M = \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}/R}$$ **Madelung constant**

Madelung potential: Simple sum

python crystal_MP_simple.py

Coulomb sum in sphere with the radius *r*



Exact: -8.9 eV

Rock salt type

Efficient Coulomb sum: Evjen method

Sum up Coulomb potential in units with zero net charge

Ion charges: Z_i

On boundary plane : $1/2Z_i$

On boundary edge : $1/4Z_i$

On boundary corner : $1/8Z_i$

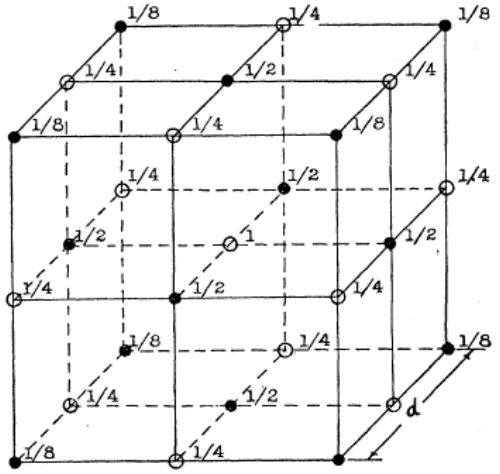


Fig. 1. Elementary cell of the NaCl-type.

Madelung constant of Rock salt type structure

$$A_M = -\frac{1}{2} \sum_{n_x,n_y,n_z=-\infty,\neq(0,0,0)}^{\infty} (-1)^{n_x+n_y+n_z} \frac{1}{\sqrt{n_x^{\,2}+n_y^{\,2}+n_z^{\,2}}}$$

$$A_M = 6\times\frac{1}{2}\times\frac{1}{\sqrt{1}} - 12\times\frac{1}{4}\times\frac{1}{\sqrt{1+1}} + 8\times\frac{1}{8}\times\frac{1}{\sqrt{1+1+1}} = 1.456$$

Madelung potential: Evjen method

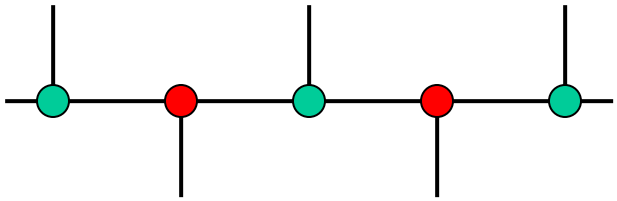
Usage: python crystal_MP_Evjen.py n_{cell}

n_{cell}	MP	Madelung constant
1	-8.9766	1.7517691
2	-8.95586	1.7477211
3	-8.95521	1.7475955
4	-8.9511	1.7475744
5	-8.95508	1.7475686
6	-8.95507	1.7475665
8	-8.95506	1.7475652
10	-8.95506	1.747564 8
Exact (精確値)		1.74756

Rock salt type

3D sum of Coulomb potential: Ewald method

Periodic calculation can be enhanced by FT?



Periodic positions of charge

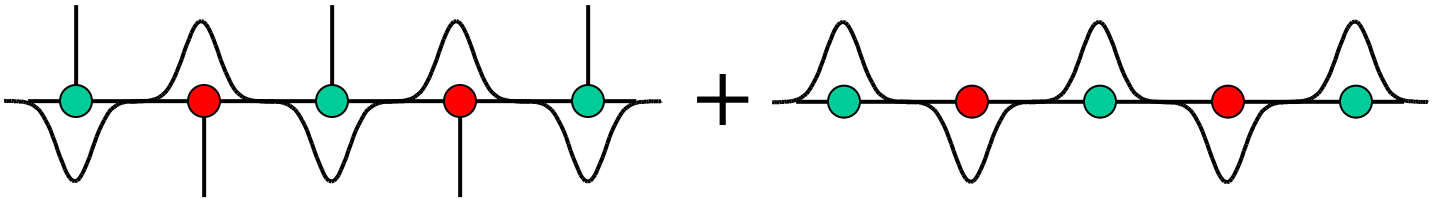
=> converted to the origin of FT data

But the charges are point charges

=> converted to infinite in FT space

=> Calculate for charges with finite width

(拡がりのある電荷の周期配列として計算する)



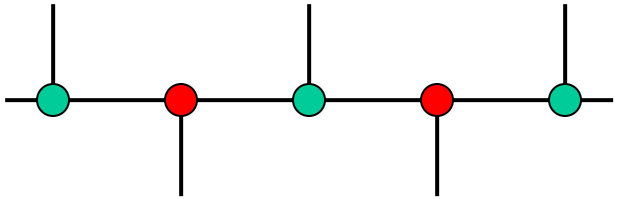
3D sum of Coulomb potential: Ewald method

The finite width charge distributions are converted by FT

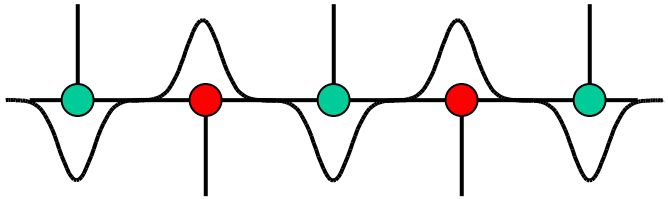
=> Take faster calculation parts in the real space and the reciprocal space

拡がった電荷のフーリエ変換を利用し、実空間和と逆空間和の計算の速い部分をとる

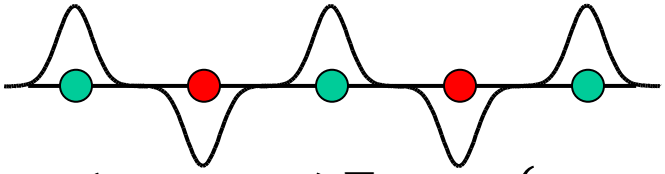
$$\Phi_i = K_C Z_i \sum_j \frac{Z_j}{r_{ij}} \qquad \left(K_C = \frac{e^2}{4\pi\varepsilon_0}\right)$$



$$\Phi_i^I = K_C Z_i \sum_j Z_j \frac{\mathrm{erfc}(\alpha|r_{ij}|)}{|r_{ij}|}$$



$$\Phi_i^{II} = K_C \frac{Z_i}{\pi V} \sum_{h,k,l} \frac{1}{|\mathbf{G}_{hkl}|^2} \exp\left(-\frac{\pi^2 |\mathbf{G}_{hkl}|^2}{\alpha^2}\right)$$



$$\times \left\{\cos(2\pi \mathbf{G}_{hkl}\cdot\mathbf{r}_i)\sum_j Z_j \cos\left(2\pi \mathbf{G}_{hkl}\cdot\mathbf{r}_j\right) + \sin(2\pi \mathbf{G}_{hkl}\cdot\mathbf{r}_i)\sum_j Z_j \sin\left(2\pi \mathbf{G}_{hkl}\cdot\mathbf{r}_j\right)\right\}$$

$$\boldsymbol{G}_{hkl}\cdot\boldsymbol{r}_i = hx_i + ky_i + lz_i$$

$$\Phi_i^{III} = K_C Z_i \frac{2\alpha Z_i}{\sqrt{\pi}}$$

$$\Phi_i = \Phi_i^I + \Phi_i^{II} - \Phi_i^{III}$$

Madelung potential: Ewald method

Usage: python crystal_MP_Ewald.py alpha prec

Alpha	Precision	MP	Madelung constant	Range		Time (s)	
0.3	10^{-3}	-8.95558	1.7476663	10.1/222	0.063 /222	0.016/0	/0.016
0.3	**10^{-5}**	**-8.95506**	**1.7475646**	11.9/333	0.105 /222	0.031/0	/0.031
0.3	**10^{-7}**	**-8.95506**	**1.7475646**	13.6/333	0.147 /333	0.047/0	/0.047
0.2	10^{-3}	-8.95506	1.7475646	15.2/333	0.028 /111	0.042/0	/0.042
0.6	10^{-3}	-8.95607	1.7477629	5.1/111	0.25 /333	0	/0.016 /0.016
0.8	10^{-3}	-8.95584	1.747718	3.8/111	0.45 /444	0	/0.016 /0.016
0.2	**10^{-10}**	**-8.95506**	**1.7475646**	24.3/555	0.093/222	0.16/0	/0.16
0.4	**10^{-10}**	**-8.95506**	**1.7475646**	12.1/333	0.373/444	0.036/0.016/0.052	
0.5	**10^{-10}**	**-8.95506**	**1.7475646**	9.7/222	0.58 /555	0.016/0.016/0.031	
0.6	**10^{-10}**	**-8.95506**	**1.7475646**	8.1/222	0.84 /666	0.016/0.031/0.047	
Exact (精確値)			**1.74756**				

Range: R_{max} [Å]/$n_{xmax}n_{ymax}n_{zmax}$ G_{max} [Å^{-1}]/$h_{max}k_{max}l_{max}$
Time: Real space sum / Reciprocal space sum / Total [s]

Rock salt type

Comparison: Evjen method

Rock salt type $$A_M = -\frac{1}{2} \sum_{n_x,n_y,n_z=-\infty,\neq(0,0,0)}^{\infty} (-1)^{n_x+n_y+n_z} \frac{1}{\sqrt{{n_x}^2+{n_y}^2+{n_z}^2}}$$

nx	ny	nz	r	m	Z	S(mZ/r)	f	S(mZf/r)
0	0	1	1	6	−1	−6	0.5	−3
0	1	1	1.4142	12	1	8.48528	0.25	2.12132034
1	1	1	1.7321	8	−1	−4.6188	0.13	−0.5773503
						−2.13		−1.456

nx	ny	nz	r	m	Z	S(mZ/r)	f	S(mZf/r)
0	0	1	1	6	−1	−6	1	−6
0	1	1	1.4142	12	1	8.48528	1	8.48528137
1	1	1	1.7321	8	−1	−4.6188	1	−4.6188022
0	0	2	2	6	1	3	0.5	1.5
0	1	2	2.2361	24	−1	−10.733	0.5	−5.3665631
0	2	2	2.8284	12	1	4.24264	0.25	1.06066017
1	1	2	2.4495	24	1	9.79796	0.5	4.89897949
1	2	2	3	24	−1	−8	0.25	−2
2	2	2	3.4641	8	1	2.3094	0.13	0.28867513
						−1.52		−1.7518

nx	ny	nz	r	m	Z	S(mZ/r)	f	S(mZf/r)
0	0	1	1	6	−1	−6	1	−6
0	1	1	1.4142	12	1	8.48528	1	8.485281374
1	1	1	1.7321	8	−1	−4.6188	1	−4.61880215
0	0	2	2	6	1	3	1	3
0	1	2	2.2361	24	−1	−10.733	1	−10.7331263
0	2	2	2.8284	12	1	4.24264	1	4.242640687
1	1	2	2.4495	24	1	9.79796	1	9.797958971
1	2	2	3	24	−1	−8	1	−8
2	2	2	3.4641	8	1	2.3094	1	2.309401077
0	0	3	3	6	−1	−2	0.5	−1
0	1	3	3.1623	24	1	7.58947	0.5	3.794733192
0	2	3	3.6056	24	−1	−6.6564	0.5	−3.32820118
0	3	3	4.2426	12	1	2.82843	0.25	0.707106781
1	1	3	3.3166	24	−1	−7.2363	0.5	−3.61813613
1	2	3	3.7417	48	1	12.8285	0.5	6.414269806
1	3	3	4.3589	24	−1	−5.506	0.25	−1.3764944
2	2	3	4.1231	24	−1	−5.8209	0.5	−2.9104275
2	3	3	4.6904	24	1	5.11682	0.25	1.279204298
3	3	3	5.1962	8	−1	−1.5396	0.13	−0.19245009
						−1.91		−1.7470

Exact value = 1.7476