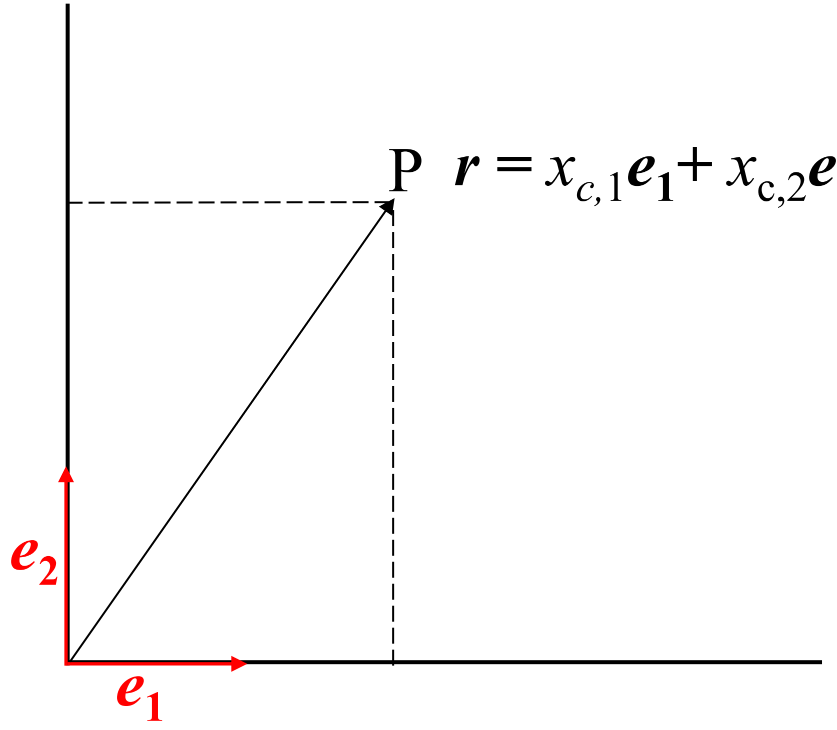
Applications of Numerical Analysis in Materials Science

応用

General coordinate system (一般座標系)

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

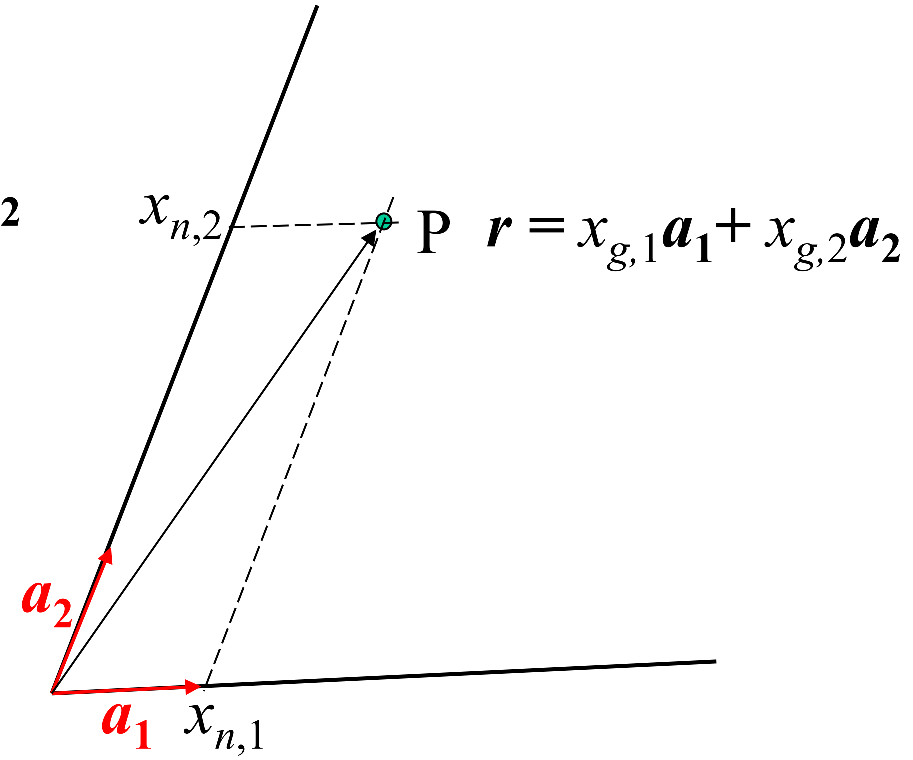


Normalized orthonormal system (正規直交系)

$$\boldsymbol{e}_i \cdot \boldsymbol{e}_j = \delta_{ij}$$

$$|\boldsymbol{e}_i| = 1$$

Non-Cartesian coordinate (一般座標/非直交系)



Normalized general coordinate system (一般座標系)

$$\boldsymbol{a}_i \cdot \boldsymbol{a}_j \neq \delta_{ij}$$

$\boldsymbol{e}_i$, $\boldsymbol{a}_i$: **basis vectors (基底ベクトル)**

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

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

$(x_{f,1}, x_{f,2}, x_{f,3})$: Fractional coordinate (部分座標)

Internal coordinate (内部座標)

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

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

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

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.cal_lattice_vectors()

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

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

Lattice properties

Unit cell volume

$$V = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$$

tkcrystalbase.cal_volume()

Distance $\boldsymbol{r}_{kl} = \boldsymbol{r}_k - \boldsymbol{r}_l$

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 $(h\ k\ l)$

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

Lattice space

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

Bragg angle

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

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

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

Inter-atomic distances

python crystal_distance.py

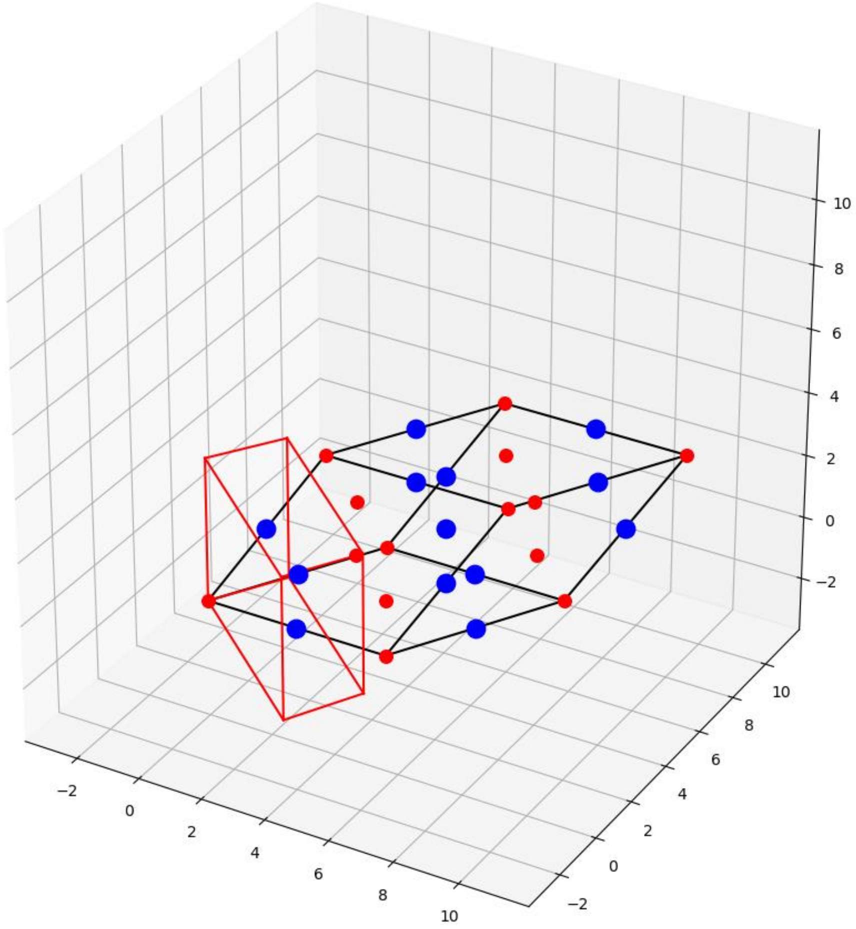
NaCl

```
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
```

Fractional – Cartesian conversion

python crystal_draw_cell.py

Rhombohedral cell
and reciprocal unit cell



Bragg angles

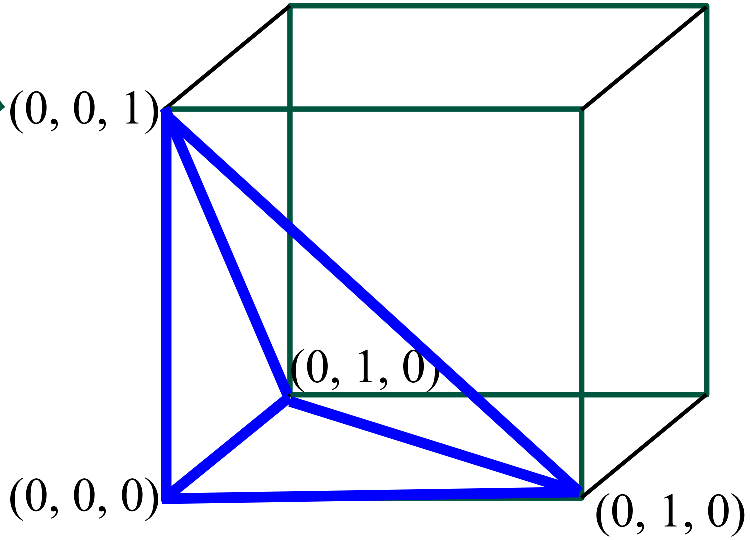
NaCl

```
python crystal_xrd.py
```

```
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)
¥
```

3D integration: Tetrahedron method

1. Divide the first Brillouin zone to tetrahedrons
2. Choose one tetrahedron with the vertexes $(x_0, y_0, z_0), (x_1, y_1, z_1), (x_2, y_2, z_2), (x_3, y_3, z_3)$, normalize the vertexes to



3. Interpolate by

$$E(\boldsymbol{k}) = E_{000} + (E_{100} - E_{000})x + (E_{010} - E_{000})y + (E_{001} - E_{000})z$$

, where E_{ijk} is $E(x, y, z)$ at a vertex (i, j, k)

4. Integrate $E(x, y, z)$ in the tetrahedron

$$0 \leq x, y, z \leq 1 \text{ and } 0 \leq x + y + z \leq 1$$

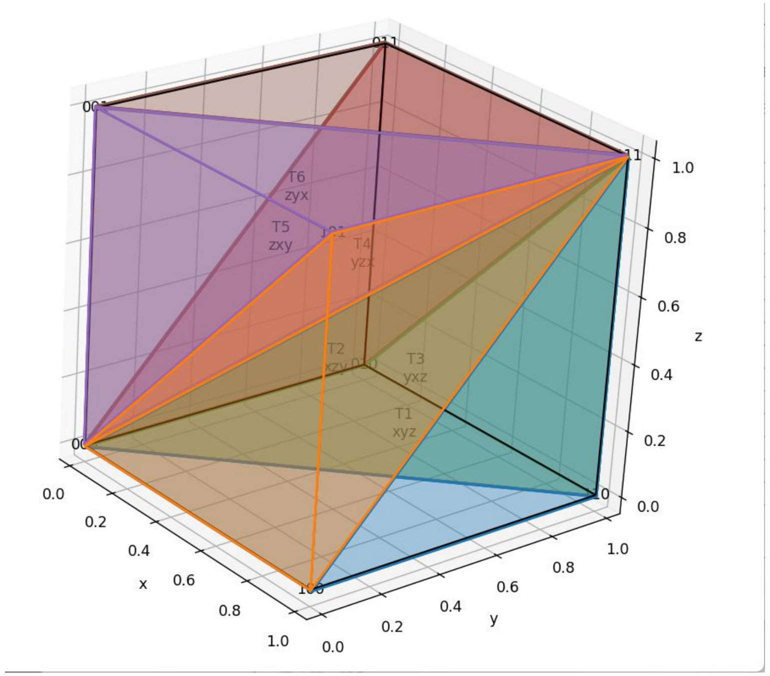
3D integration: Tetrahedron method

First Brillouin Zone integration for band calculations

- A method for 3D numerical integration for function $E(x, y, z)$
- Divide 3D space to parallelepipeds (平行六面体)
- Divide a parallelepiped to two triangular prisms (三角柱)
- Divide a triangular prisms to three tetrahedrons
- Normalize the vertexes to x, y and z to be in [0, 1]
- Liner interpolation by $E(x, y, z) = E_{000} + (E_{100} - E_{000})x + (E_{010} - E_{000})y + (E_{001} - E_{000})z$

  A general method for multi-dimensional numerical integration (Finite Element Method etc)
- Integrate $E(x, y, z)$ in the tetrahedron

tetrahedron.py:
How to divide to tetrahedrons



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

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

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

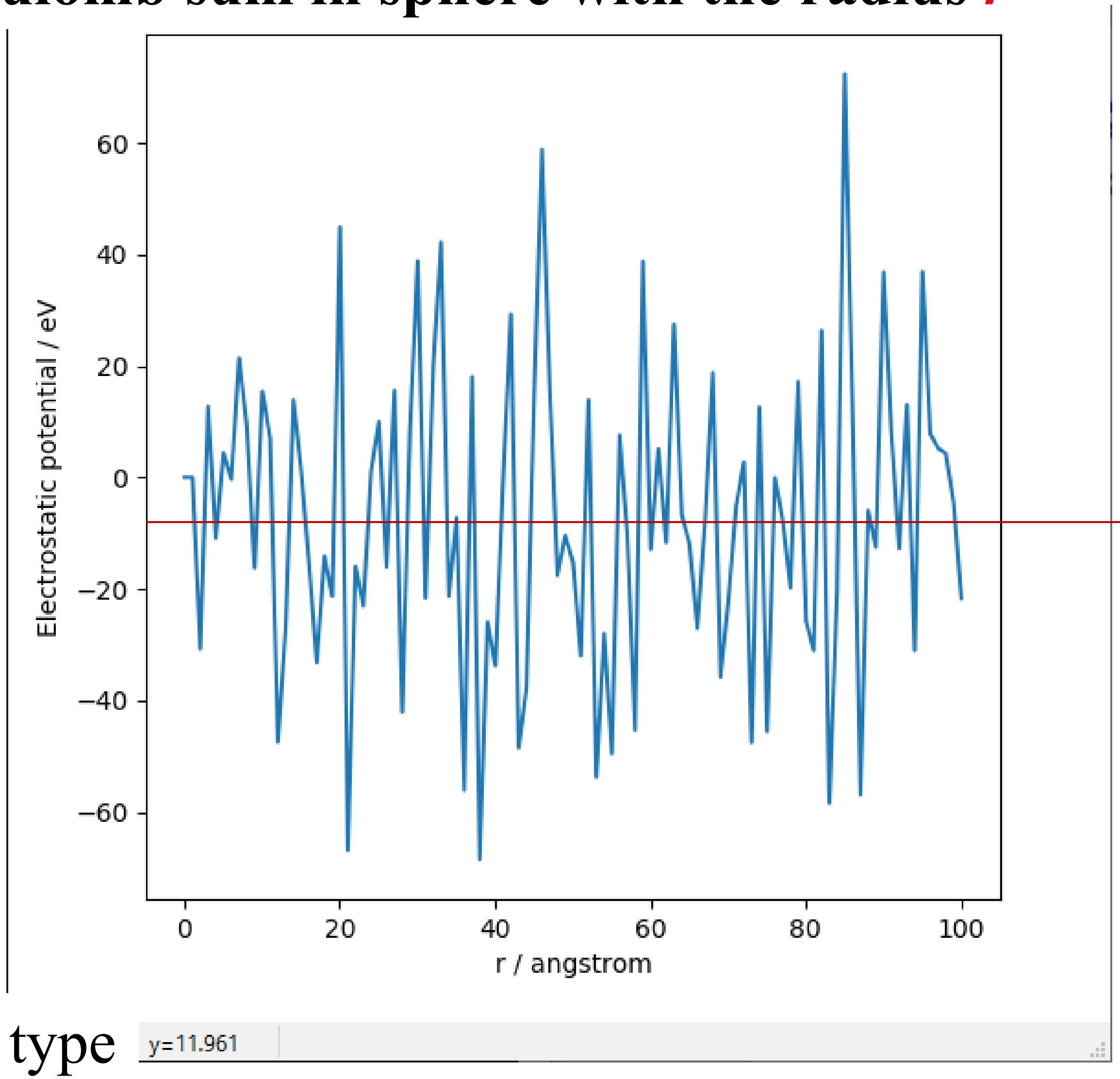
Crystal structure	A_r
Rock salt type (NaCl)	1.7476
CsCl type (CsCl)	1.7627
Zinc blend (CuCl)	1.6380
Wurzite (ZnO)	1.6413
Cu_2O type	4.116
Fluorite type (CaF_2)	2.520

$$A_M = \frac{1}{2}\sum_{i\neq j} \frac{1}{r_{ij}/R}$$ **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 : $1/2Z_\mathrm{i}$
On boundary edge : $1/4Z_\mathrm{i}$
On boundary corner : $1/8Z_\mathrm{i}$

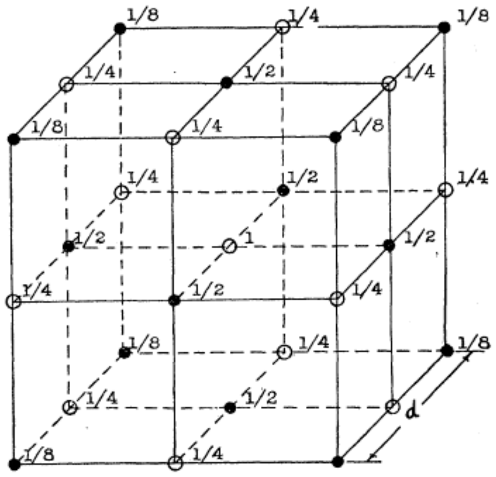


Fig. 1. Elementary cell of the NaCl-type.

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**	**1.7475648**
Exact (精確値)		**1.74756**

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**

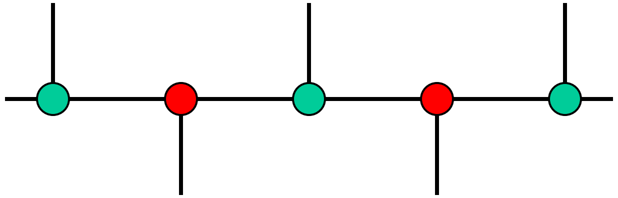
nx	ny	nz	r	m	Z	S(mZ/r)	f	S(mZf/r)
0	0	1	1	6	−1	−6	1	−6
0	1	1	1.4142	12	1	8.48528	1	8.48528137
1	1	1	1.7321	8	−1	−4.6188	1	−4.6188022
0	0	2	2	6	1	3	0.5	1.5
0	1	2	2.2361	24	−1	−10.733	0.5	−5.3665631
0	2	2	2.8284	12	1	4.24264	0.25	1.06066017
1	1	2	2.4495	24	1	9.79796	0.5	4.89897949
1	2	2	3	24	−1	−8	0.25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

3D sum of Coulomb potential: Ewald method

Periodic calculation can be enhanced by FT?



Periodic positions of charge

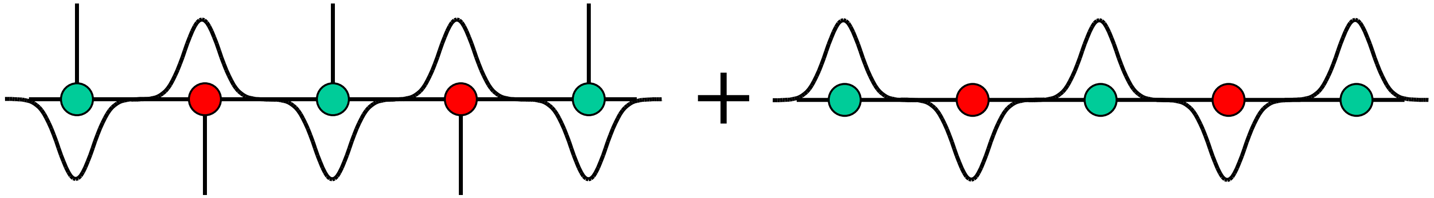
=> converted to the origin of FT data

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)



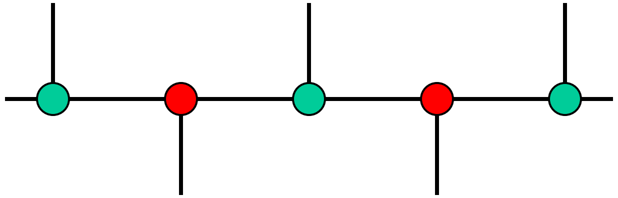
3D sum of Coulomb potential: Ewald method

The finite width charge distributions are converted by FT

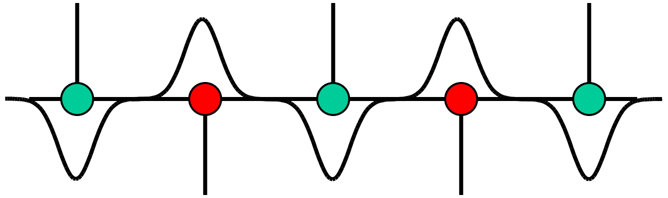
=> Take faster calculation parts in the real space and the reciprocal space

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

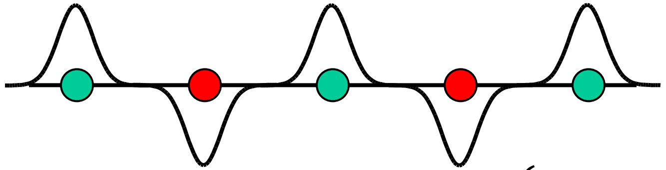
$$\Phi_i = K_C Z_i \sum_j \frac{Z_j}{r_{ij}} \qquad \left(K_C = \frac{e^2}{4\pi\varepsilon_0}\right)$$



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



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



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

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

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

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

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