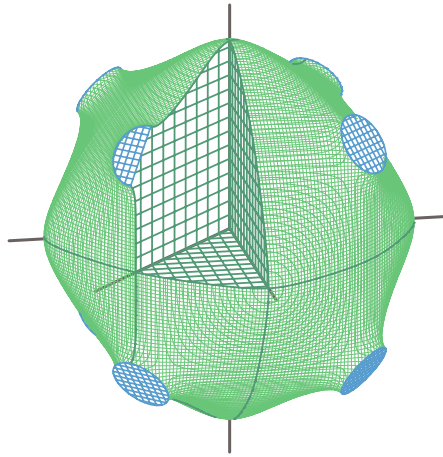




Symmetry of Crystals and Electronic States



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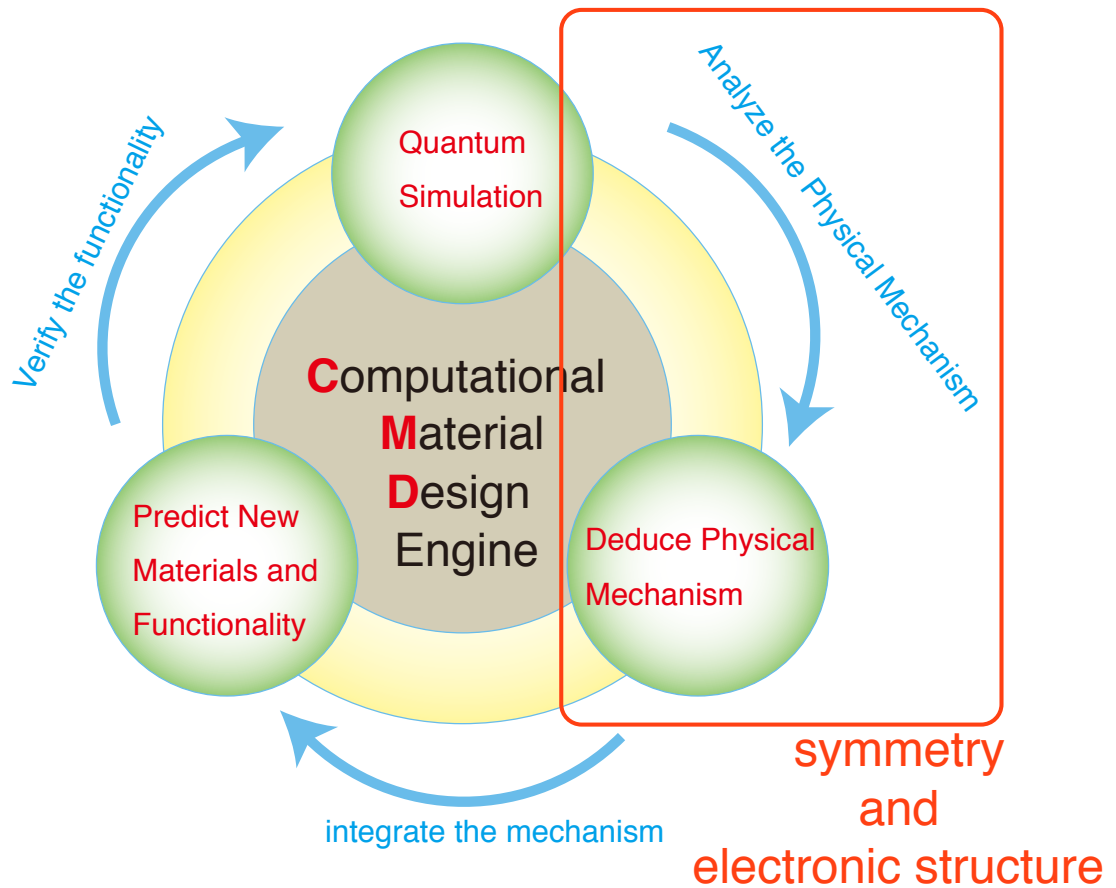
Email: funa@crystal.kobe-u.ac.jp

“The laws of nature should be expressed in beautiful equation.”

“If there is a God, he’s great mathematician”



- P. A. M. Dirac -



Kohn-Sham Equations

$$\mathcal{H}\psi_j(\vec{r}) = \left\{ -\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\vec{r}) \right\} \psi_j(\vec{r}) = \varepsilon_j \psi_j(\vec{r})$$

$$n(\vec{r}) = \sum_j |\psi_j(\vec{r})|^2$$

$$v_{\text{eff}} = v_{\text{ext}}(\vec{r}) + e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{\text{xc}}[n(\vec{r})]$$



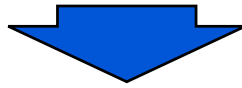
what kind of influence do crystalline potentials have?

Crystals have symmetry.

Translational Symmetry

Rotational Symmetry

Symmetry of Crystals



Mathematical Tool

Space Group



e.g. TSPACE99

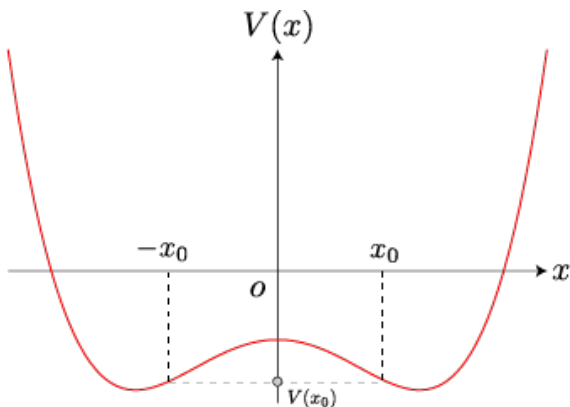
Symmetry and Quantum Mechanics

From the beginning, we consider low dimensional systems.

1Dim: Symmetric potential

Schrödinger Equation in 1dim system.

$$-\frac{\hbar^2}{2m} \frac{d^2 u(x)}{dx^2} + V(x)u(x) = \underbrace{E}_{\text{Eigenvalue}} \underbrace{u(x)}_{\text{Eigenfunction}}$$



We assume the symmetric potential

$$V(x) = V(-x)$$

$$x \rightarrow -x$$

$$-\frac{\hbar^2}{2m} \frac{d^2 u(-x)}{dx^2} + V(-x)u(-x) = E u(-x)$$

$$\Leftrightarrow -\frac{\hbar^2}{2m} \frac{d^2 u(-x)}{dx^2} + V(x)u(-x) = E u(-x)$$

$$\Leftrightarrow \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\} u(-x) = \underbrace{E}_{\text{Eigenvalue}} \underbrace{u(-x)}_{\text{Eigenfunction}}$$

same eigenvalue



- degenerated case
- non-degenerated case

1Dim: Free Electron in periodic potential

We consider the free electron in periodic potential as the simplified example at previous section.

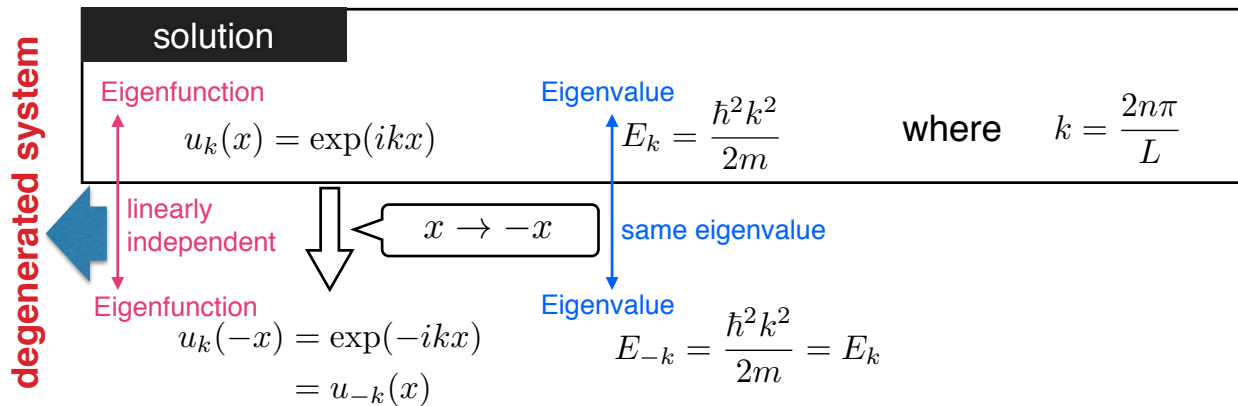
Schrödinger Equation

$$-\frac{\hbar^2}{2m} \frac{d^2 u(x)}{dx^2} = E u(x)$$

Under the periodic condition,

$$u(x + L) = u(x)$$

we can solve this differential equation



According to the linear combination between $u_k(x)$ and $u_{-k}(x)$,

we can re-generate different basis set for eigenfunction in degenerated system

$$\cos(kx) = \frac{1}{2} \{ \exp(ikx) + \exp(-ikx) \} \quad \text{(even function)}$$

$$\sin(kx) = \frac{1}{2i} \{ \exp(ikx) - \exp(-ikx) \} \quad \text{(odd function)}$$

Background:

degeneracy between k and $-k$ **(Time Reversal Symmetry)**

Schrödinger Equation is not invariant when we take the complex conjugate for it.

$$-\frac{\hbar^2}{2m} \frac{d^2 u(x)}{dx^2} + V(x)u(x) = E u(x)$$

$u(x)$ and $u^*(x)$ are degenerate

2Dim: reflective symmetries at x-axis and y-axis(C_{2v})

If Hamiltonian is invariant for the replacement for the sign of x and that of y, eigenvalues is the odd function or even function for x and y. Thus number of basis set is 4.

1. (even function for x) and (even function for y)

$$\left\{ \begin{array}{l} x \rightarrow -x \\ \text{and} \\ y \rightarrow -y \end{array} \right. \begin{array}{c} \text{operate} \\ \text{simultaneously} \end{array} \text{invariant} \quad 1 \times 1 = 1$$

2. (odd function for x) and (odd function for y)

$$\left\{ \begin{array}{l} x \rightarrow -x \\ \text{and} \\ y \rightarrow -y \end{array} \right. \begin{array}{c} \text{operate} \\ \text{simultaneously} \end{array} \text{invariant} \quad (-1) \times (-1) = 1$$

3. and 4. (odd function for x) and (even function for y)
(even function for x) and (odd function for y)

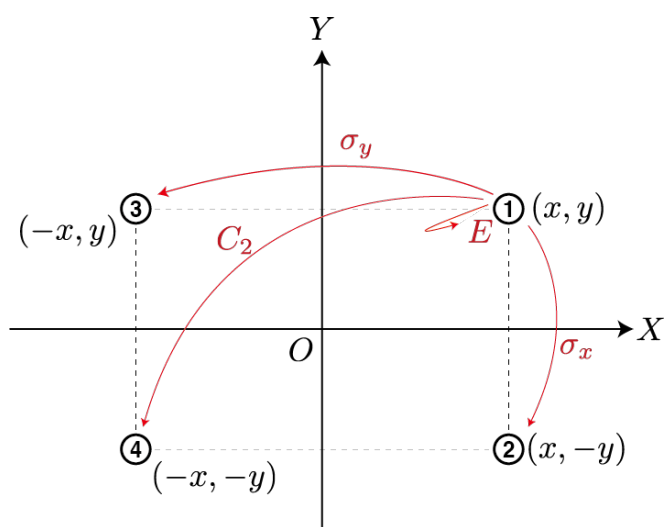
$$\left\{ \begin{array}{l} x \rightarrow -x \\ \text{and} \\ y \rightarrow -y \end{array} \right. \begin{array}{c} \text{operate} \\ \text{simultaneously} \end{array} \text{change of sign of function}$$

$$1 \times (-1) = -1$$

$$(-1) \times 1 = -1$$

In this case, there are 4 symmetry operations,

1. identity operation (E)
2. reflection at x-axis (σ_x)
3. reflection at y-axis (σ_y)
4. combination reflection at x-axis and that at y-axis (C_2)



	E	σ_x	σ_y	C_2
E	E	σ_x	σ_y	C_2
σ_x	σ_x	E	C_2	σ_y
σ_y	σ_y	C_2	E	σ_x
C_2	C_2	σ_y	σ_x	E

multiples among symmetry operations

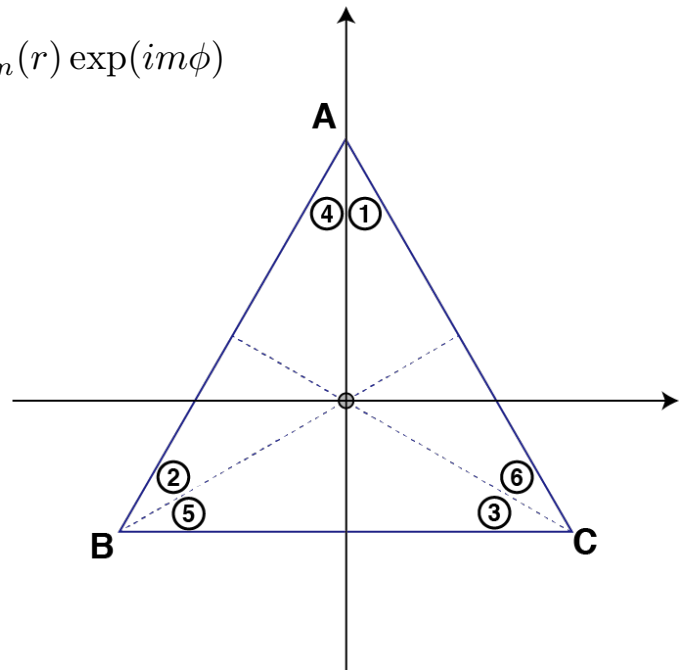
2Dim: Equilateral Triangular Symmetry (C_{3v})

We introduce the equilateral triangular symmetry system as the more complex case in 2dim. In polar coordinate, a wave function is written as Fourier series

$$\Psi(r, \phi) = \sum_m R_m(r) \exp(im\phi)$$

6 symmetry operations

1. identity operation (E)
2. $2\pi/3$ rotation (C_3) ① \rightarrow ②
3. $-2\pi/3$ rotation (C_3^{-1}) ① \rightarrow ③
4. reflection at A-axis (σ_A) ① \rightarrow ④
5. reflection at B-axis (σ_B) ② \rightarrow ⑤
6. reflection at C-axis (σ_C) ③ \rightarrow ⑥



Rotational effect for wave function (C_3^\pm)

At first, we operate $2\pi/3$ rotation for wave function,

$$O(C_3) \xleftrightarrow{\text{equivalent}} \phi \rightarrow \phi - 2\pi/3$$

$$\begin{aligned} \Psi\left(r, \phi - \frac{2}{3}\pi\right) &= \sum_m R_m(r) \exp\left\{im\left(\phi - \frac{2}{3}\pi\right)\right\} \\ &= \sum_m \underbrace{\exp\left(-i\frac{2}{3}m\pi\right)}_{\text{phase factor}} R_m(r) \exp(im\phi) \end{aligned}$$

We can classify 3 types for m

$$m = \begin{cases} 3n \\ 3n + 1 \\ 3n + 2 \end{cases}$$

$$\Psi\left(r, \phi - \frac{2}{3}\pi\right) = \sum_m \exp\left(-i\frac{2}{3}m\pi\right) R_m(r) \exp(im\phi)$$

$$= \begin{cases} \sum_m R_m(r) \exp(im\phi) = \Psi(r, \phi) & m = 3n \\ \exp\left(-i\frac{2}{3}\pi\right) \sum_m R_m(r) \exp(im\phi) = \exp\left(-i\frac{2}{3}\pi\right) \Psi(r, \phi) & m = 3n + 1 \\ \exp\left(i\frac{2}{3}\pi\right) \sum_m R_m(r) \exp(im\phi) = \exp\left(i\frac{2}{3}\pi\right) \Psi(r, \phi) & m = 3n + 2 \end{cases}$$

Similarly, for $-2\pi/3$ rotation,

$$\Psi\left(r, \phi + \frac{2}{3}\pi\right) = \sum_m \exp\left(i\frac{2}{3}m\pi\right) R_m(r) \exp(im\phi)$$

$$= \begin{cases} \sum_m R_m(r) \exp(im\phi) = \Psi(r, \phi) & m = 3n \\ \exp\left(i\frac{2}{3}\pi\right) \sum_m R_m(r) \exp(im\phi) = \exp\left(i\frac{2}{3}\pi\right) \Psi(r, \phi) & m = 3n + 1 \\ \exp\left(-i\frac{2}{3}\pi\right) \sum_m R_m(r) \exp(im\phi) = \exp\left(-i\frac{2}{3}\pi\right) \Psi(r, \phi) & m = 3n + 2 \end{cases}$$

Reflectional effect for wave function ($\sigma_A, \sigma_B, \sigma_C$)

Definition for the angle ϕ

$$\mathcal{O}(\sigma_A) \xleftrightarrow{\text{equivalent}} \phi \rightarrow -\phi \quad \text{change the sign of } \phi$$

Then reflectional operations are equivalents these operations,

$$\left\{ \begin{array}{l} \sigma_A : \phi \rightarrow -\phi \\ \sigma_B : \phi \rightarrow -\phi + \frac{2}{3}\pi \\ \sigma_C : \phi \rightarrow -\phi - \frac{2}{3}\pi \end{array} \right. \xleftrightarrow{\text{equivalent}} \left\{ \begin{array}{l} \sigma_B = \sigma_A \cdot C_3^{-1} \\ \sigma_C = \sigma_A \cdot C_3 \end{array} \right.$$

These operations are represented as the combination with reflection σ_A and rotation

Relationship between the classification for m and characters of WFs

$$m = 3n$$

For rotational operation (C_3^\pm)

$$\begin{aligned} \Psi\left(r, \phi \pm \frac{2}{3}\pi\right) &= \sum_m \exp\left(\pm i\frac{2}{3}m\pi\right) R_m(r) \exp(im\phi) \\ &= \sum_m R_m(r) \exp(im\phi) = \Psi(r, \phi) \end{aligned} \quad \text{invariant}$$

For reflectional operation ($\sigma_A, \sigma_B, \sigma_C$)

The angular component of wave function, $\exp(im\phi)$ is variant for $\mathcal{O}(\sigma_A)$,
in other word, $\phi \rightarrow -\phi$

$$\exp(3n\phi i) \rightarrow \exp(-3n\phi i)$$

Using the linear combination with $\exp(3n\phi i)$ and $\exp(-3n\phi i)$,
we can re-generate different basis set for eigenfunction

$$\begin{aligned} \cos(3n\phi) &= \frac{1}{2} \{\exp(3n\phi i) + \exp(-3n\phi i)\} \quad \phi \rightarrow -\phi \quad \text{invariant} \\ \sin(3n\phi) &= \frac{1}{2i} \{\exp(3n\phi i) - \exp(-3n\phi i)\} \quad \text{---} \sin(3n\phi) \end{aligned}$$

$$m = 3n + 1, 3n + 2$$

For reflectional operation σ_A , $\phi \rightarrow -\phi$

$$\begin{aligned} m(-\phi) &= (3n + 1)(-\phi) \\ m\phi = (3n + 1)\phi &\rightarrow = -(3n + 1)\phi \\ &= \{3(-n - 1) + 2\} \phi \\ &\quad \text{element in } m=3m+2 \text{ group} \\ \\ m(-\phi) &= (3n + 2)(-\phi) \\ m\phi = (3n + 2)\phi &\rightarrow = -(3n + 2)\phi \\ &= \{3(-n - 1) + 1\} \phi \\ &\quad \text{element in } m=3m+1 \text{ group} \end{aligned} \quad \text{2-fold degeneracy}$$

Summary for equilateral triangular symmetry

There are 3 types eigenfunctions.

1. Invariant for all symmetry operations ($C_3^\pm, \sigma_A, \sigma_B, \sigma_C$) \rightarrow $\cos(3n\phi)$ type
2. Invariant for rotational operation and odd function for the reflectional operations ($\sigma_A, \sigma_B, \sigma_C$) \rightarrow $\sin(3n\phi)$ type
3. 2-fold degenerated states

Space Group

periodicity: **14 Bravais Lattice**
point symmetry: **32 point group**

point group
rotation (including reflection)
+
translational group

space group

7 crystal systems

Cubic
Tetragonal
Orthorhombic
Hexagonal

Trigonal
Monoclinic
Triclinic

P, F, I
P, I
P, F, I, C
P

R
P, C
P

Point Group

O_h, O, T_d, T_h, T
 $D_{4h}, D_4, D_{2d}, C_{4v}, C_{4h}, S_4, C_4$
 D_{2h}, D_2, C_{2v}
 $D_{6h}, D_6, D_{3h}, C_{6v}, C_{6h}, C_{3h}, C_6$
 $D_{3d}, D_3, C_{3v}, S_6, C_3$
 $D_{3d}, D_3, C_{3v}, S_6, C_3$
 C_{2h}, C_s, C_2
 C_i, C_1

Subgroup
of
 O_h / D_{6h}

symmetry Operation

$$(\alpha | \vec{t} + \vec{u}_\alpha) = \alpha \vec{u} + \vec{t} + \vec{u}_\alpha$$

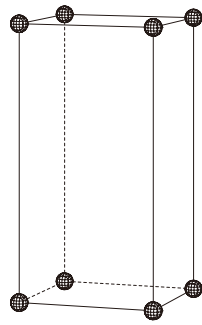
$$(\alpha | \vec{a}) (\beta | \vec{b}) = (\alpha\beta | \alpha \vec{b} + \vec{a})$$

$$(\alpha | \vec{b})^{-1} = (\alpha^{-1} | -\alpha^{-1} \vec{b})$$

P... simple
F... Face Centered
I ... Body Centered
C... Base Centered
R... Rhombohedral

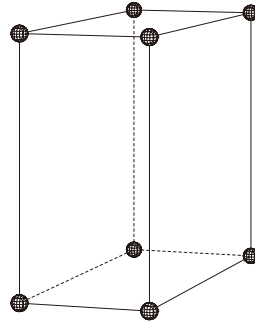
7 crystal systems

(simple lattice)



tetragonal

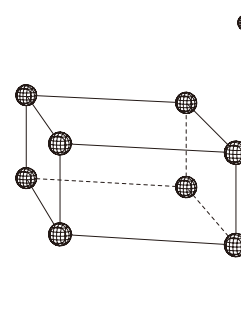
$$a = b \neq c$$



orthorhombic

$$a \neq b \neq c$$

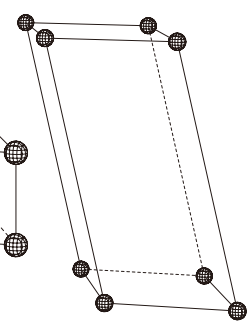
$$\alpha = \beta = \gamma = \frac{\pi}{2}$$



monoclinic

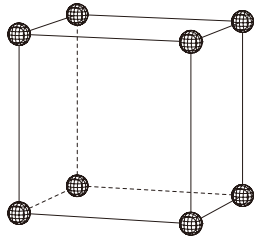
$$a \neq b \neq c \text{ (not necessary condition)}$$

$$\alpha = \beta = \frac{\pi}{2} \neq \gamma$$



triclinic

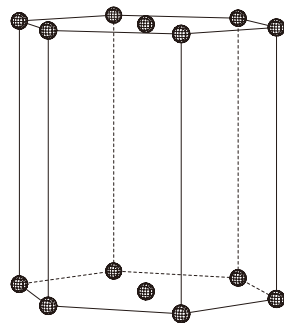
$$\alpha \neq \beta \neq \gamma \neq \frac{\pi}{2}$$



cubic

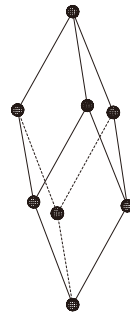
$$a = b = c$$

$$\alpha = \beta = \gamma = \frac{\pi}{2}$$



hexagonal

$$a = b \neq c$$

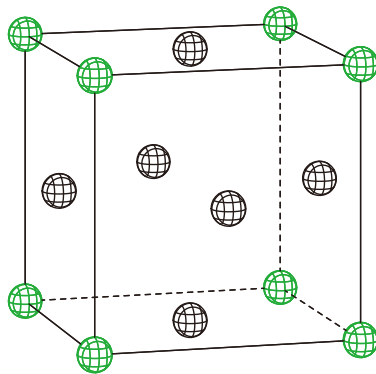


trigonal (rhombohedral)

$$a = b = c$$

$$\alpha = \beta = \gamma$$

Example (Cubic and Tetragonal)



add lattice point

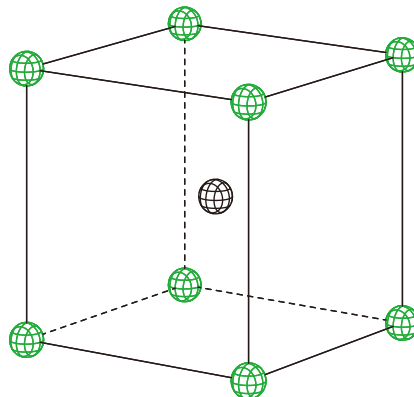
$$(0, 1/2, 1/2)$$

$$(1/2, 0, 1/2)$$

$$(1/2, 1/2, 0)$$

(F)

Face Centered Lattice

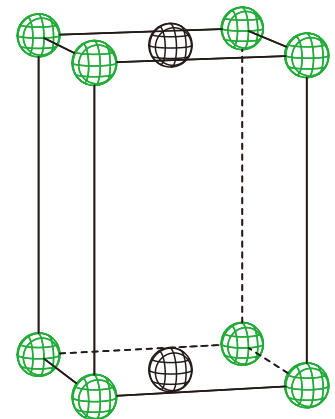


add lattice point

$$(1/2, 1/2, 1/2)$$

(I)

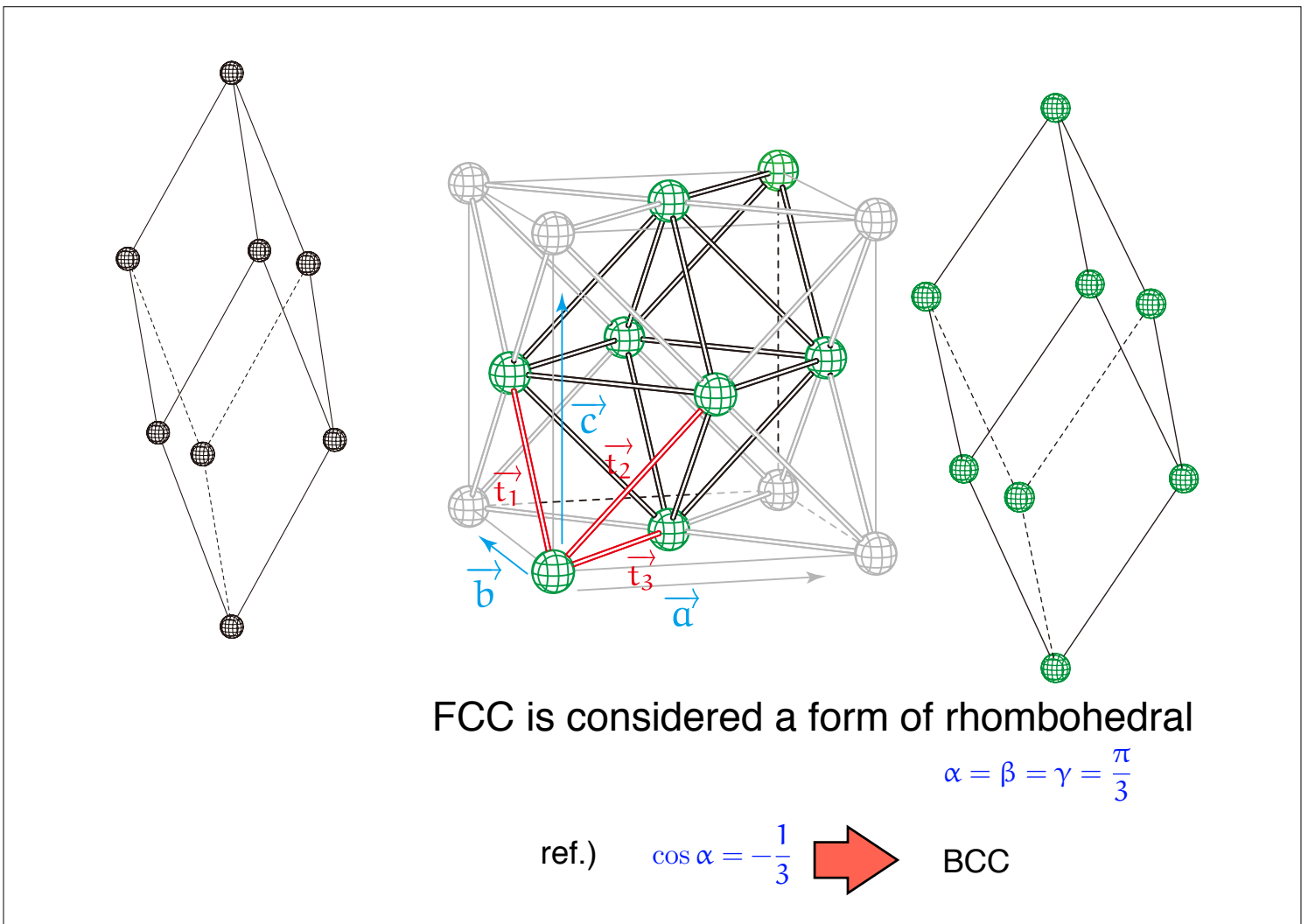
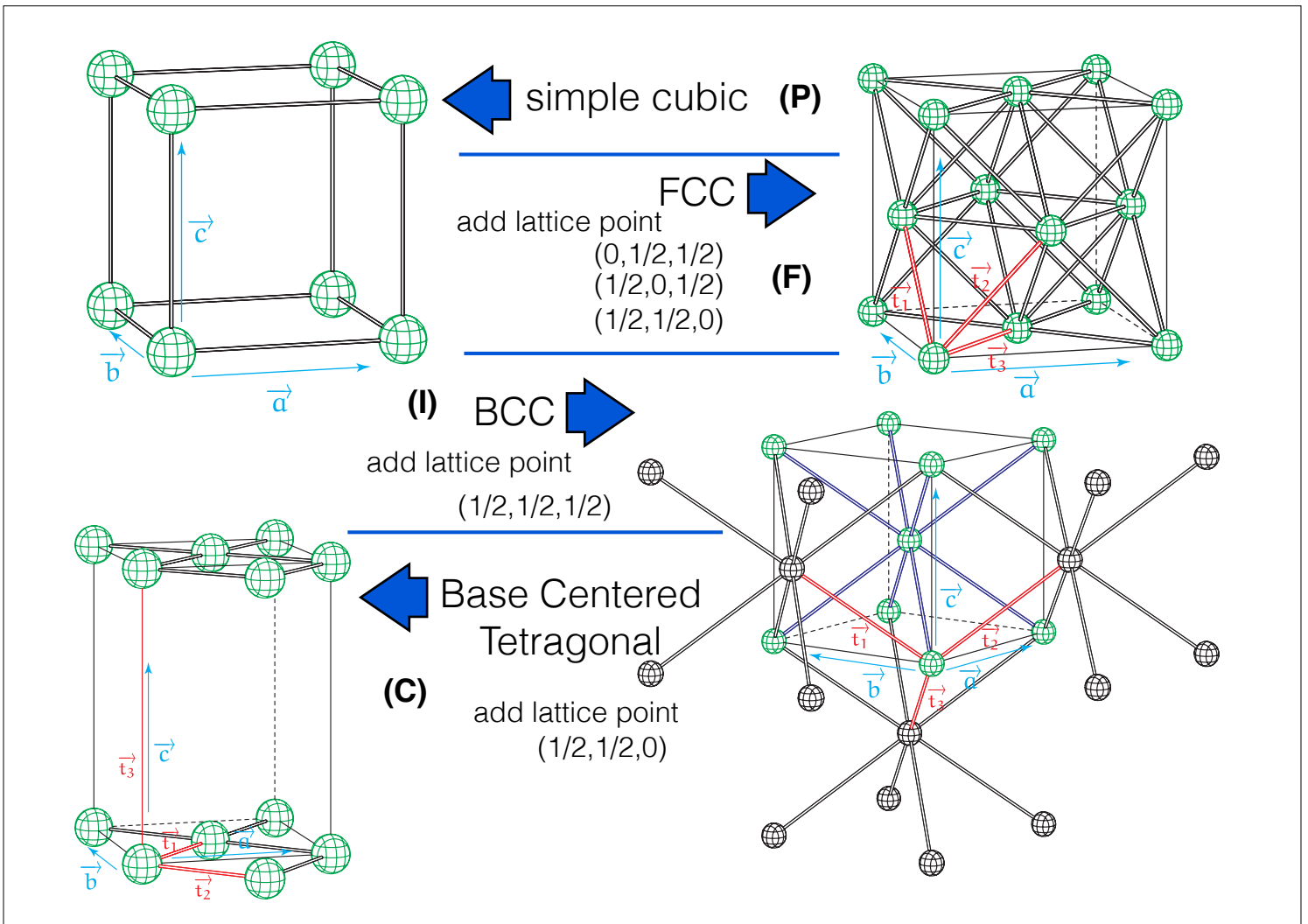
Body Centered Lattice



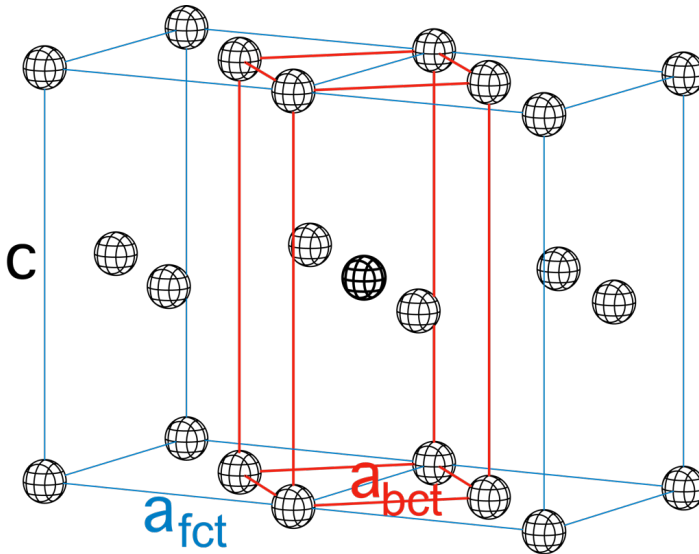
(C)

add lattice point
 $(1/2, 1/2, 0)$

Base Centered Lattice
(c-centered)



duplicate case in crystal system

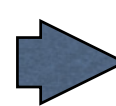


Body centered tetragonal(BCT) is equivalent to
face centered tetragonal(FCT)

Space Group

periodicity: **14 Bravais Lattice**
point symmetry: **32 point group**

point group
rotation(including reflection)
+
translational group



space group

7 crystal systems

Cubic
Tetragonal
Orthorhombic
Hexagonal

Trigonal
Monoclinic
Triclinic

P,F,I
P,I
P,F,I,C
P

R
P,C
P

Point Group

O_h, O, T_d, T_h, T
 $D_{4h}, D_4, D_{2d}, C_{4v}, C_{4h}, S_4, C_4$
 D_{2h}, D_2, C_{2v}
 $D_{6h}, D_6, D_{3h}, C_{6v}, C_{6h}, C_{3h}, C_6$
 $D_{3d}, D_3, C_{3v}, S_6, C_3$
 $D_{3d}, D_3, C_{3v}, S_6, C_3$
 C_{2h}, C_s, C_2
 C_i, C_1

Subgroup
of
 O_h / D_{6h}

symmetry Operation

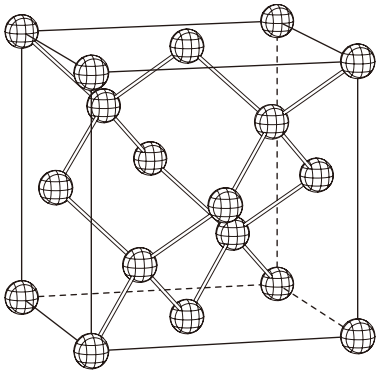
$$(\alpha | \vec{t} + \vec{u}_\alpha) = \alpha \vec{u} + \vec{t} + \vec{u}_\alpha$$

$$(\alpha | \vec{a}) (\beta | \vec{b}) = (\alpha\beta | \alpha \vec{b} + \vec{a})$$

$$(\alpha | \vec{b})^{-1} = (\alpha^{-1} | -\alpha^{-1} \vec{b})$$

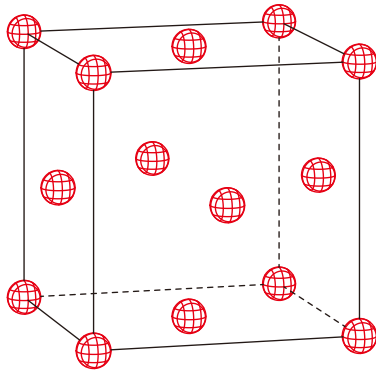
P... simple
F... Face Centered
I ... Body Centered
C... Base Centered
R... Rhombohedral

symmetry Operation

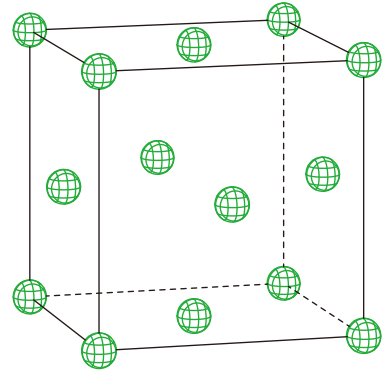


Diamond Structure

=



+



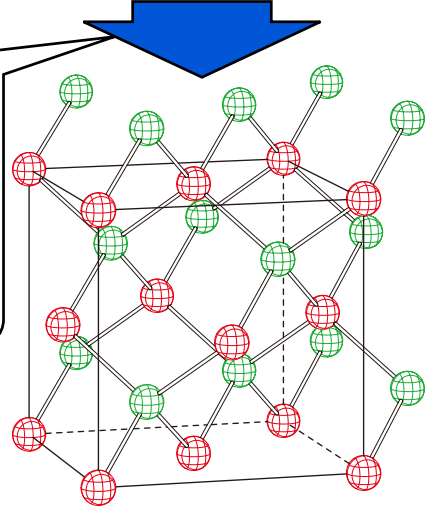
Symmetry operation: (Seitz Notation)



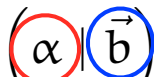
rotation
(include inversion, reflection)

translation

$\frac{\pi}{2}$ rotation
+
 $\begin{bmatrix} 1/4 \\ 1/4 \\ 1/4 \end{bmatrix}$ translation



Symmetry operation: (Seitz Notation)



rotation
(include inversion, reflection)

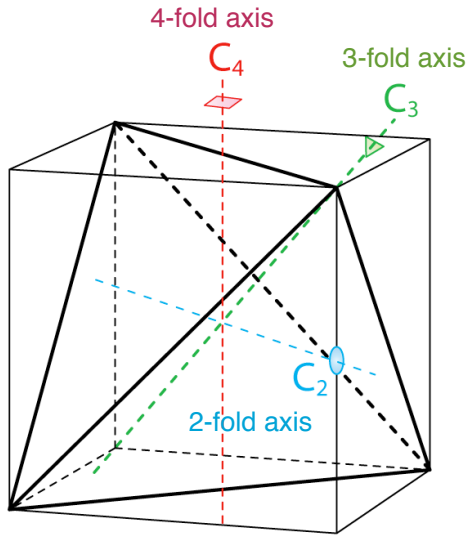
translation

$$(\alpha | \vec{t} + \vec{u}_\alpha) = \alpha \vec{u} + \vec{t} + \vec{u}_\alpha$$

$$(\alpha | \vec{a}) (\beta | \vec{b}) = (\alpha\beta | \alpha \vec{b} + \vec{a})$$

$$(\alpha | \vec{b})^{-1} = (\alpha^{-1} | -\alpha^{-1} \vec{b})$$

Point Group: O_h



Cubic Symmetry O_h

$E \dots\dots 1$ identity operation

$C_4 \dots\dots 6$ $\pm\pi/2$
 $C_4^2 \dots\dots 3$

$C_2 \dots\dots 6$ $\pm\pi$

$C_3 \dots\dots 8$ $\pm 2\pi/3$

24 rotational operation

+ inversion, rotation inversion,
reflection and rotational reflection



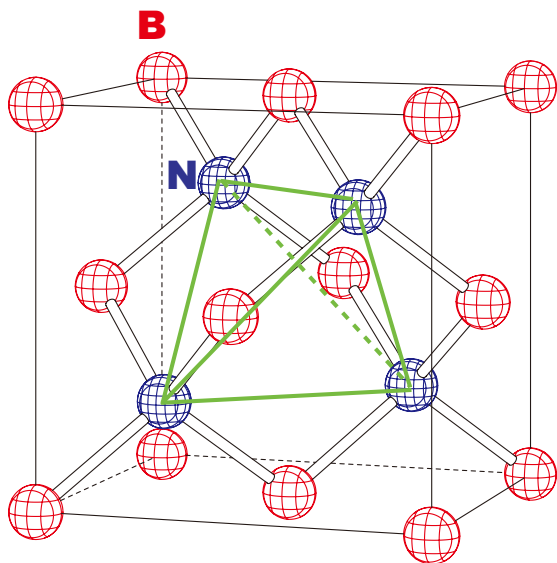
48 symmetry Operation

subgroup of O_h

example

Tetrahedral Symmetry $\rightarrow T_d$

$$T_d \otimes C_4 = O_h$$



zincblende Structure

Lattice type: Face Centered

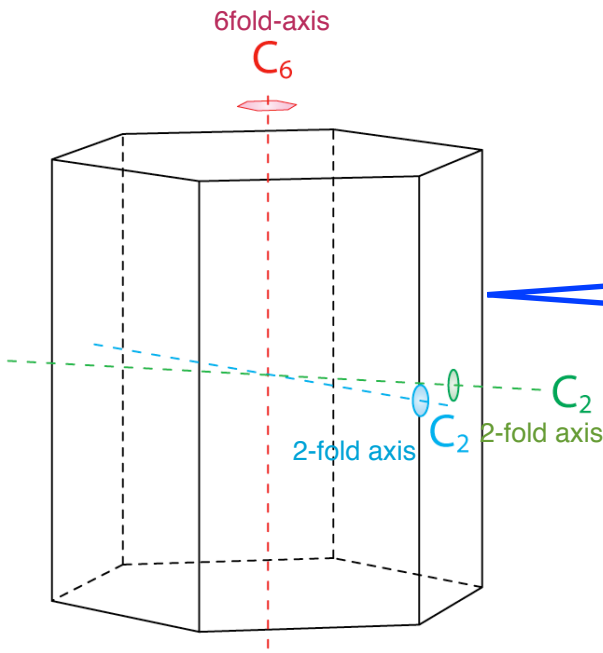
There is not 4-fold axis

Tetrahedral Symmetry $\rightarrow T_d$

Subgroup of O_h

tetrahedron in zincblende Structure

Point Group: D_{6h}



Hexagonal Symmetry D_{6h}

$E \dots\dots 1$ identity operation

$C_6 \dots\dots 2$	$\pm\pi/3$
$C_6^2 \dots\dots 2$	$\pm 2\pi/3$
$C_6^3 \dots\dots 1$	$\pm\pi$
$C_2' \dots\dots 3$	$\pm\pi$
$C_2'' \dots\dots 3$	$\pm\pi$

12 rotational operation
+ inversion, rotation inversion,
reflection and rotational reflection

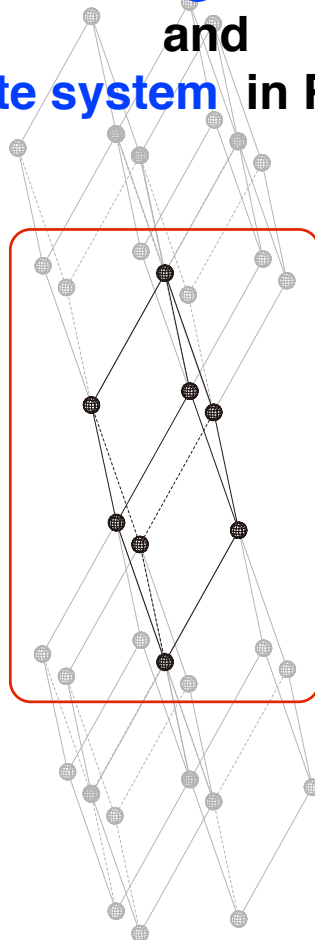


24 symmetry operation

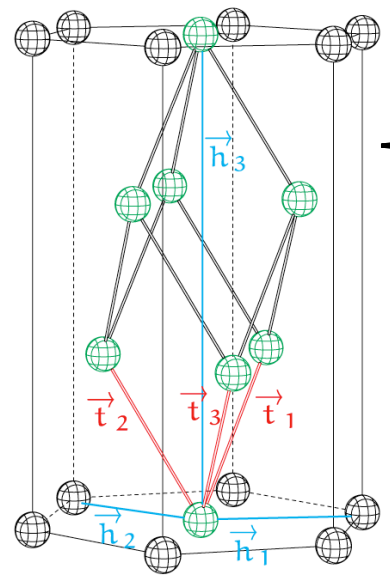
subgroup of D_{6h}

Rhombohedral $D_{3d}, C_{3v}, C_3, \dots$

Relation between Hexagonal coordinate system and Trigonal coordinate system in Rhombohedral Crystal



Relation between Hexagonal coordinate system and Trigonal coordinate system in Rhombohedral Crystal



transformation basis

$$\vec{t}_1 = \frac{2}{3}\vec{h}_1 + \frac{1}{3}\vec{h}_2 + \frac{1}{3}\vec{h}_3$$

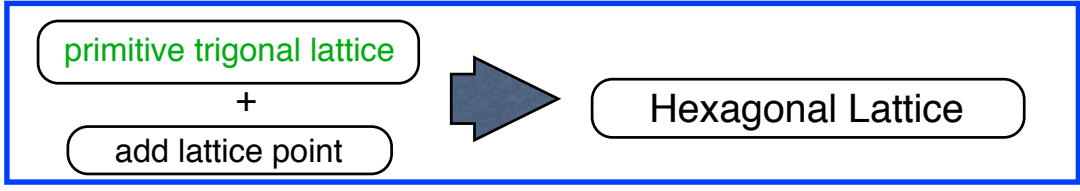
$$\vec{t}_2 = -\frac{1}{3}\vec{h}_1 + \frac{1}{3}\vec{h}_2 + \frac{1}{3}\vec{h}_3$$

$$\vec{t}_3 = -\frac{1}{3}\vec{h}_1 - \frac{2}{3}\vec{h}_2 + \frac{1}{3}\vec{h}_3$$

$$\vec{h}_1 = \vec{t}_1 - \vec{t}_2$$

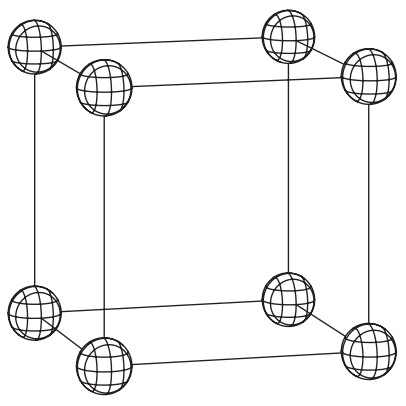
$$\vec{h}_2 = \vec{t}_2 - \vec{t}_3$$

$$\vec{h}_3 = \vec{t}_1 + \vec{t}_2 + \vec{t}_3$$



Magnetic case

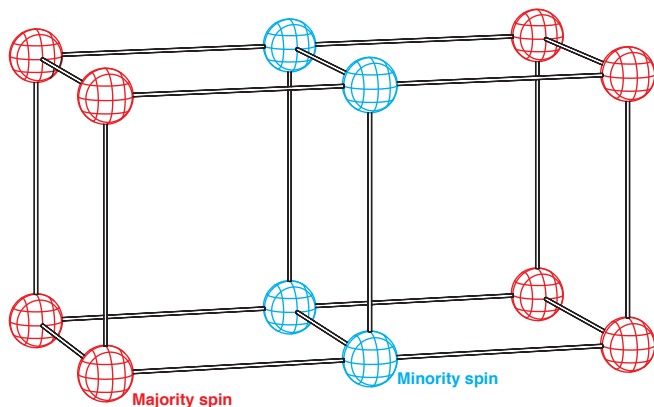
Simple Cubic Lattice (Ferromagnetic)



antiferromagnetic case...?

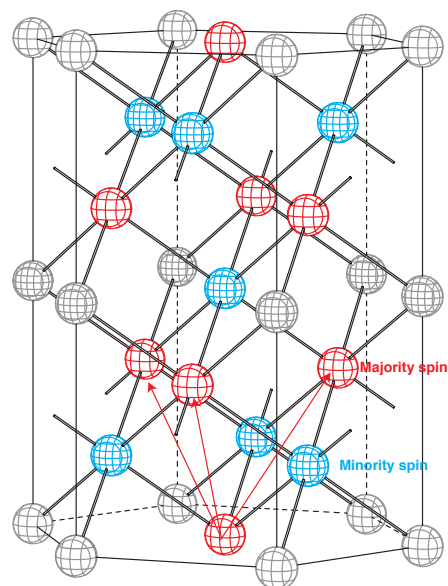
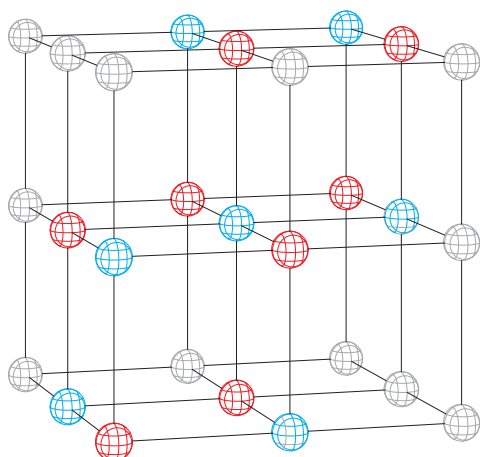
Cubic Lattice

Antiferromagnetic(type1)



Anti-Ferro magnetics (type1)

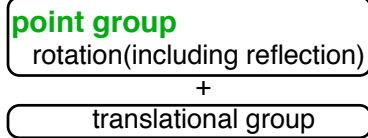
Tetragonal Lattice



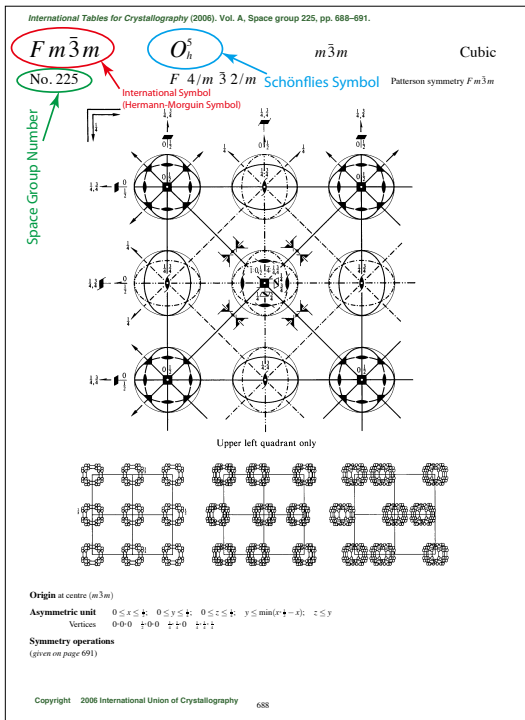
Anti-Ferro magnetics (type2)

rhombohedral Lattice

Space Group



space group



International Table of Crystallography

How many kinds of space group are there?



only **230** space group



3 ways to classify

- Schönflies Symbol
- International Symbol (Hermann Mauguin Symbol)
- Space Group Number (1 ~ 230)

The symmetry groups of the crystal



Space Group

Mathematically, it is defined as the group which has an invariant subgroup of the translational group

symmetry operation of space group

The operations of the space group can be given as

$$\left(\alpha \mid \vec{b} \right) r = \alpha \vec{r} + \vec{b}$$

rotational operator translation vector

The simple translation is given by

$$\left(\epsilon \mid \vec{t} \right) \vec{r} = \vec{r} + \vec{t}$$

identical operation

$$(\alpha | \vec{b})r = \alpha \vec{r} + \vec{b} \quad \leftarrow \text{lattice invariant}$$

rotational operator translation vector

$$(\alpha | \vec{b}) = (\alpha | \vec{R}_n + \vec{b}') = (\epsilon | \vec{R}_n) (\alpha | \vec{b}')$$

general vector of the Bravais lattice zero vector or not primitive translation vector

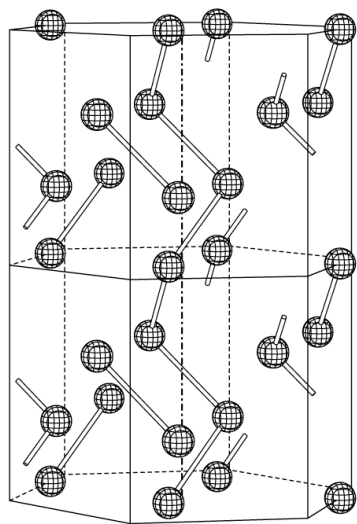
With a suitable choice of origin...

Do we find all the element of the symmetry operation in the form

$$(\alpha | \vec{b}) = (\alpha | \vec{R}_n) = (\epsilon | \vec{R}_n) (\alpha | \vec{0}) \quad ?$$

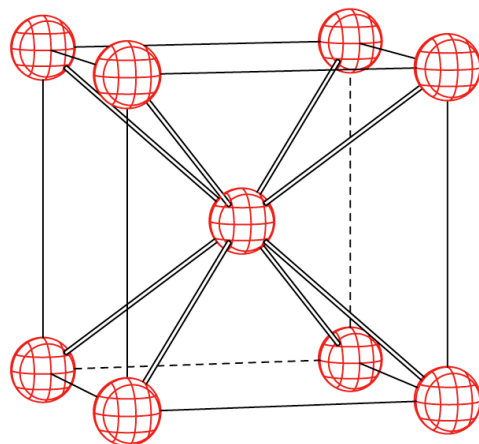
Yes \Rightarrow **symmorphic(共型)**

No \Rightarrow **non-symmorphic(非共型)**



non-symmorphic(非共型)

157(screw:らせん and glide:映進 + 2)



symmorphic(共型)

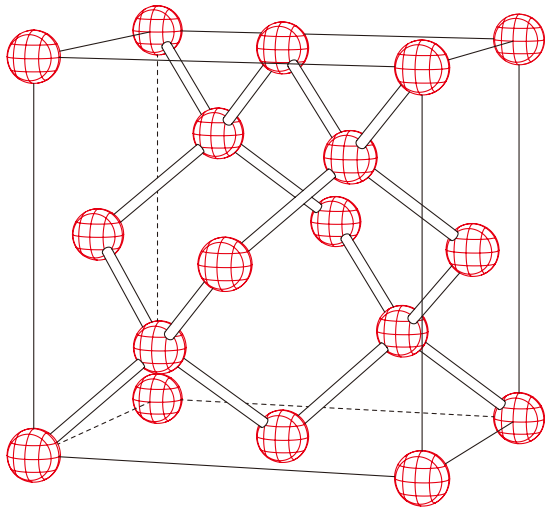
73 space group

In symmorphic case, most of $(\alpha | \vec{b}')$

are screw operation or glide operation

Example : non-symmorphic

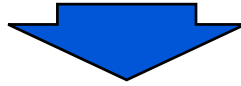
In this case(diamond structure), one of the operations :



$$(\alpha | \vec{b}')$$

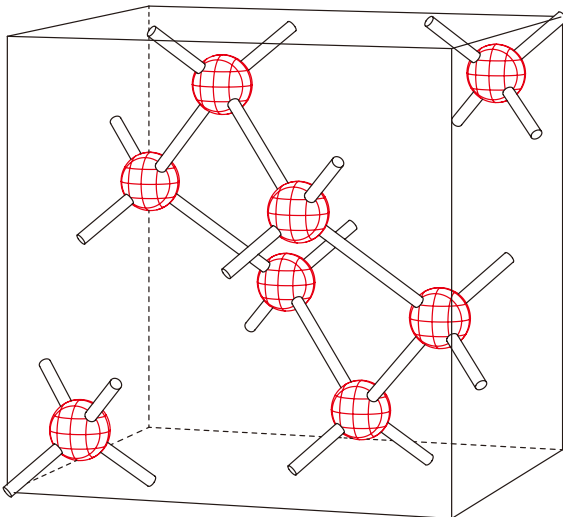
$$\alpha : \frac{\pi}{2} \text{ rotation}$$

$$\beta = \begin{bmatrix} 1/4 \\ 1/4 \\ 1/4 \end{bmatrix}$$



Hmm...let's challenge other choice of the origin...

In this case(diamond structure), one of the operations :



$$(\alpha | \vec{b}')$$

$$\alpha : \frac{\pi}{2} \text{ rotation}(x\text{-axis})$$

$$\beta = \begin{bmatrix} 1/4 \\ 0 \\ 1/4 \end{bmatrix}$$



Diamond structure is non-symmorphic.

How do you define the origin of Nonsymmorphic Crystal?

How do you define the origin of Nonsymmorphic Crystal?



In general, nonsymmorphic crystal has **some choices**

➡ There is no guideline to define the origin.

How many number of choices each for space group?

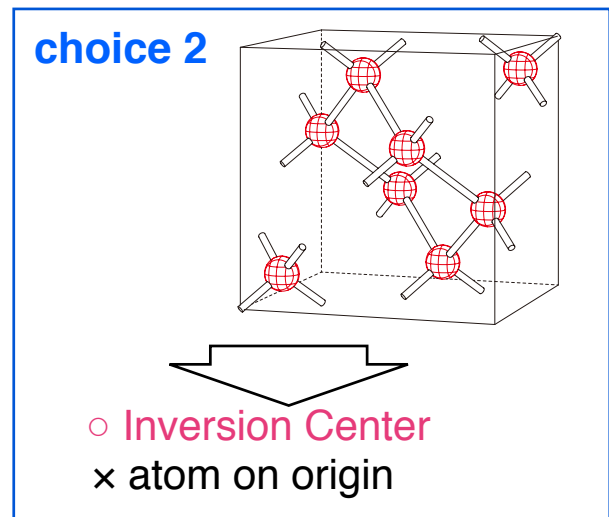
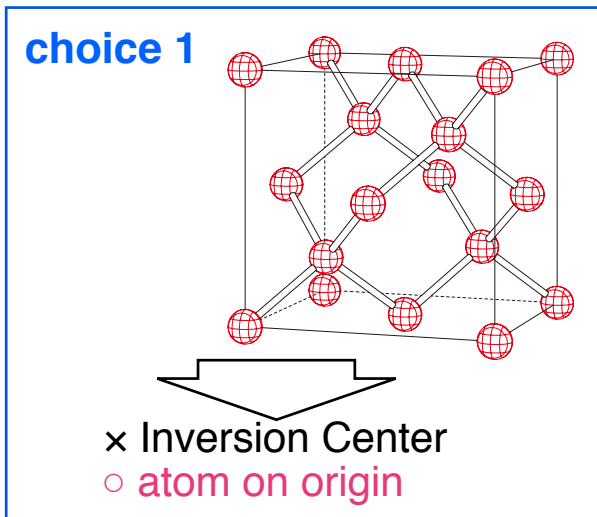
Diamond Structure : O_h^7 2	Si, C, ...
C_{2h}^3 3	αO , βPu , ...
Cs^2 6	unknown

(International Table of Crystallography)

How do you define the origin of Nonsymmorphic Crystal?

Example: diamond structure

$Fd\bar{3}m(O_h^7)$



	atomic position	inversion center
choice 1	(0,0,0) and (1/4, 1/4, 1/4)	No
choice 2	(±1/8, ±1/8, ±1/8)	Yes

which is better?

Translational Symmetry

Bloch State, Bloch function

1-electron Schrödinger Equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r})$$

Born - von Karman condition

Periodicity of Potential

$$V(\vec{r} - \vec{t}_n) = V(\vec{r})$$

$$\vec{t}_n = n_1 \vec{t}_1 + n_2 \vec{t}_2 + n_3 \vec{t}_3$$



effect?

eigenstate

Operator and Operation

$$\underbrace{O_\xi}_{\text{operator}} \psi(\vec{r}) \equiv \psi(\underbrace{\xi^{-1} \vec{r}}_{\text{operation}})$$

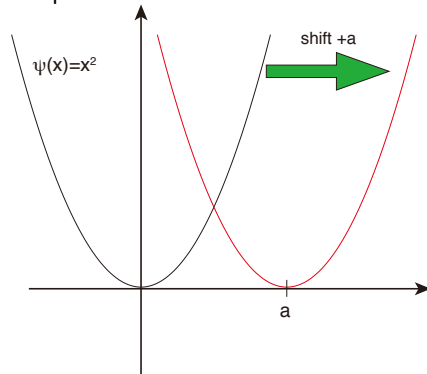
multiplication

$$\begin{aligned} O_\xi O_\eta \psi(\vec{r}) &= O_\xi \psi(\eta^{-1} \vec{r}) = \psi(\eta^{-1} \xi^{-1} \vec{r}) \\ &= \psi((\xi\eta)^{-1} \vec{r}) = O_{\xi\eta} \psi(\vec{r}) \end{aligned}$$



$$O_\xi O_\eta = O_{\xi\eta}$$

example



$$\psi(x) \rightarrow O_\xi \psi(\vec{r}) = \{x + (-a)\}^2$$

1-electron Schrödinger Equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E \psi(\vec{r})$$

Hamiltonian Operator
Eigenfunction
Eigenvalue
 $O(\epsilon|\vec{t}_n)$

$$O_\xi \psi(\vec{r}) \equiv \psi(\xi^{-1} \vec{r})$$

Born - von Karman condition

Periodicity of Potential

$$V(\vec{r} - \vec{t}_n) = V(\vec{r})$$

$$\vec{t}_n = n_1 \vec{t}_1 + n_2 \vec{t}_2 + n_3 \vec{t}_3$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r} - \vec{t}_n) = E \psi(\vec{r} - \vec{t}_n)$$

Hamiltonian Operator
Eigenfunction
Eigenvalue
same eigenvalue

$O(\epsilon|\vec{t}_n)$ ($= \psi(\vec{r} - \vec{t}_n)$) also is Eigenfunction whose eigenvalue is E

If Schrödinger Equation has p -fold degeneracy

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_i(\vec{r}) = E \psi_i(\vec{r}) \quad (i = 1, 2, \dots, p)$$

Eigenfunction

linear combination

$$O_{(\epsilon|\vec{t}_n)} \psi_j(\vec{r}) = \psi_j(\vec{r} - \vec{t}_n) = \sum_{i=1}^p T_{i,j}(\vec{t}_n) \psi_i(\vec{r})$$

coefficient Eigenfunction

$$\begin{bmatrix} O_{(\epsilon|\vec{t}_n)} \psi_1(\vec{r}) \\ O_{(\epsilon|\vec{t}_n)} \psi_2(\vec{r}) \\ \vdots \\ O_{(\epsilon|\vec{t}_n)} \psi_p(\vec{r}) \end{bmatrix} = T(\vec{t}_n) \begin{bmatrix} \psi_1(\vec{r}) \\ \psi_2(\vec{r}) \\ \vdots \\ \psi_p(\vec{r}) \end{bmatrix}$$

representation matrix of $O_{(\epsilon|\vec{t}_n)}$

Here, Matrix T is given as

$$T(\vec{t}_n) = \{ T_{i,j}(\vec{t}_n) \}$$

Matrix T is unitary matrix ← norm conservation

$$\begin{cases} \mathcal{H} |\phi_j\rangle = \varepsilon |\phi_j\rangle \\ \mathcal{H} |\phi_i\rangle = \varepsilon |\phi_i\rangle \end{cases} \quad \Rightarrow \quad \begin{aligned} \mathcal{H}(a_i |\phi_i\rangle + a_j |\phi_j\rangle) &= a_i \mathcal{H} |\phi_i\rangle + a_j \mathcal{H} |\phi_j\rangle \\ &= a_i \varepsilon |\phi_i\rangle + a_j \varepsilon |\phi_j\rangle \\ &= \varepsilon (a_i |\phi_i\rangle + a_j |\phi_j\rangle) \end{aligned}$$

$$O_{(\varepsilon|\vec{t}_n)} \psi_j(\vec{r}) = \psi_j(\vec{r} - \vec{t}_n) = \sum_{i=1}^p \underbrace{T_{i,j}(\vec{t}_n)}_{\text{coefficient}} \underbrace{\psi_i(\vec{r})}_{\text{Eignefunction}}$$

If Schrödinger Equation has p -fold degeneracy

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \underbrace{\psi_i(\vec{r})}_{\text{Eignefunction}} = E \underbrace{\psi_i(\vec{r})}_{\text{Eignefunction}} \quad (i = 1, 2, \dots, p)$$

 linear combination

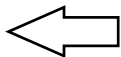
$$O_{(\varepsilon|\vec{t}_n)} \psi_j(\vec{r}) = \psi_j(\vec{r} - \vec{t}_n) = \sum_{i=1}^p \underbrace{T_{i,j}(\vec{t}_n)}_{\text{coefficient}} \underbrace{\psi_i(\vec{r})}_{\text{Eignefunction}}$$

$$\begin{bmatrix} O_{(\varepsilon|\vec{t}_n)} \psi_1(\vec{r}) \\ O_{(\varepsilon|\vec{t}_n)} \psi_2(\vec{r}) \\ \vdots \\ O_{(\varepsilon|\vec{t}_n)} \psi_p(\vec{r}) \end{bmatrix} = T(\vec{t}_n) \begin{bmatrix} \psi_1(\vec{r}) \\ \psi_2(\vec{r}) \\ \vdots \\ \psi_n(\vec{r}) \end{bmatrix}$$

representation matrix
of
 $O_{(\varepsilon|\vec{t}_n)}$

Here, Matrix T is given as

$$T(\vec{t}_n) = \{T_{i,j}(\vec{t}_n)\}$$

Matrix T is unitary matrix  norm conservation

Translation operators are commutable:

$$\begin{aligned} \mathcal{O}_{(\epsilon|\vec{t}_n)} \left\{ \mathcal{O}_{(\epsilon|\vec{t}_m)} \psi(\vec{r}') \right\} &= \mathcal{O}_{(\epsilon|\vec{t}_m)} \left\{ \mathcal{O}_{(\epsilon|\vec{t}_n)} \phi(\vec{r}') \right\} = \mathcal{O}_{(\epsilon|\vec{t}_n + \vec{t}_m)} \phi(\vec{r}') \\ &= \psi \left(\vec{r}' - (\vec{t}_n + \vec{t}_m) \right) \end{aligned}$$

therefore

$$\underline{T(\vec{t}_n)T(\vec{t}_m)} = \underline{T(\vec{t}_m)T(\vec{t}_n)} = T(\vec{t}_n + \vec{t}_m)$$

Commutable

simultaneous to diagonal form

and

Matrix T is unitary matrix

$$\Rightarrow S^{-1}T(\vec{t}_n)S = \begin{bmatrix} e^{-i\vec{k}_1 \cdot \vec{t}_n} & 0 & \dots & 0 \\ 0 & e^{-i\vec{k}_2 \cdot \vec{t}_n} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & e^{-i\vec{k}_p \cdot \vec{t}_n} \end{bmatrix}$$

(absolute value of eigenvalue for unitary matrix = 1)

Diagonalization

$$S^{-1}T(\vec{t}_n)S = \begin{bmatrix} e^{-i\vec{k}_1 \cdot \vec{t}_n} & 0 & \dots & 0 \\ 0 & e^{-i\vec{k}_2 \cdot \vec{t}_n} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & e^{-i\vec{k}_p \cdot \vec{t}_n} \end{bmatrix}$$

Eigenvalue of $T(\vec{t}_n)$

therefore

Bloch Theorem

phase factor

$$\mathcal{O}_{(\epsilon|\vec{t}_n)} \psi_{\vec{k}}(\vec{r}) = e^{-i\vec{k} \cdot \vec{t}_n} \psi_{\vec{k}}(\vec{r}) \quad \text{Bloch condition}$$

$$\psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \underline{u_{\vec{k}}(\vec{r})} \quad \text{Bloch function}$$

$$\text{periodic function } u_{\vec{k}}(\vec{r} - \vec{t}_n) = u_{\vec{k}}(\vec{r})$$

Bloch state is characterized by \vec{k}

Next Theme: k-space and reciprocal lattice

Bloch function and basis set

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

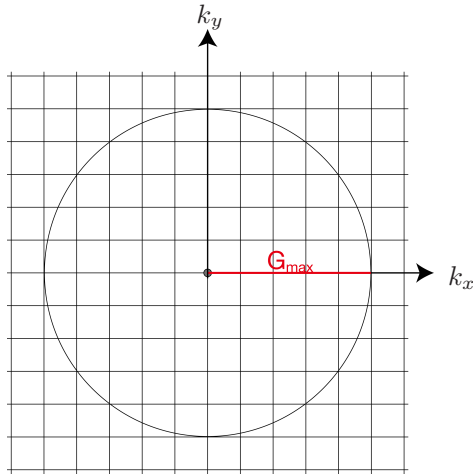
How do we represent the periodic function?

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum \phi(\vec{r})$$

basis set

e.g., planewave basis set

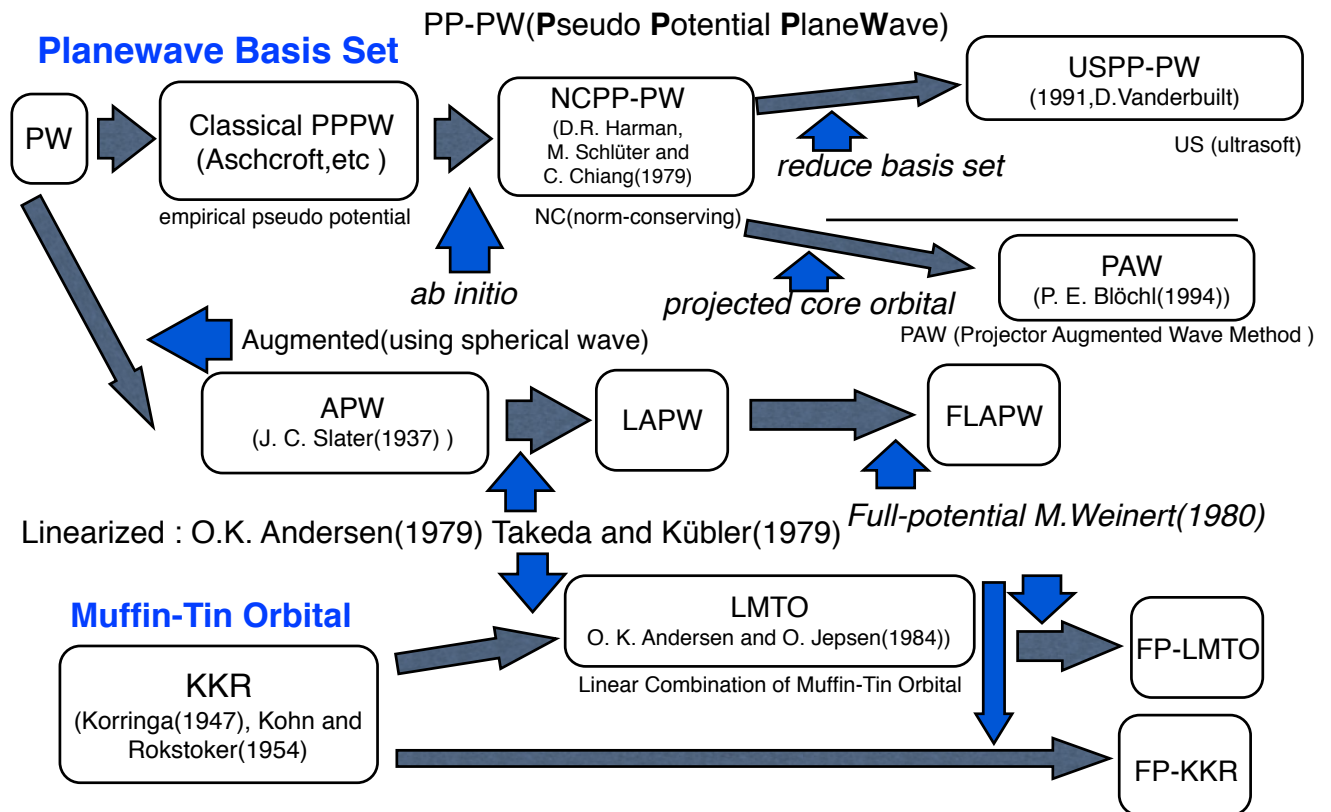
$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$



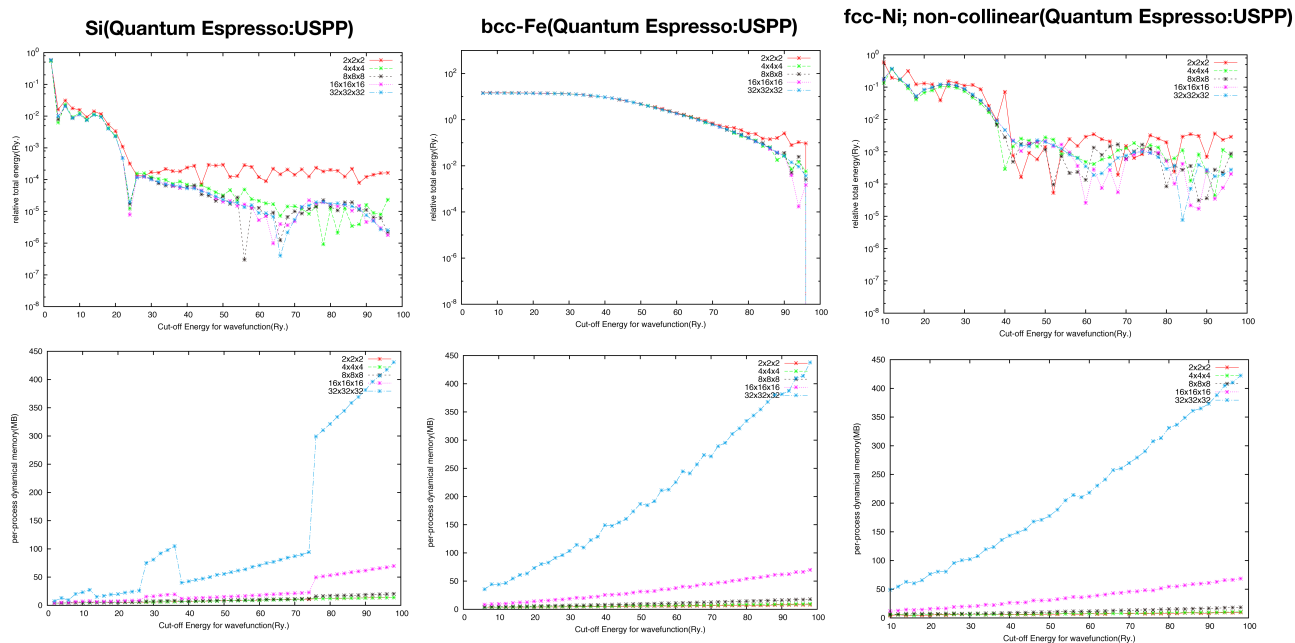
cut-off energy is defined as

$$E_{\text{cut-off}} = \frac{\hbar^2 G_{\text{max}}^2}{2m_e}$$

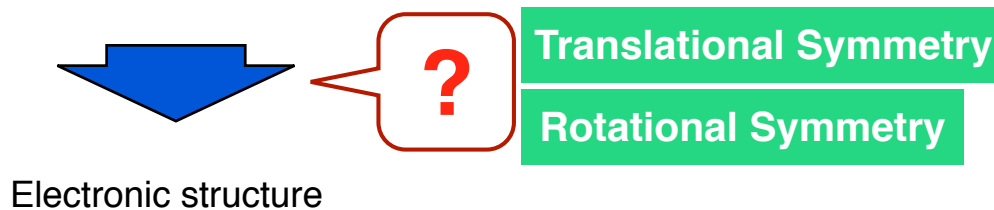
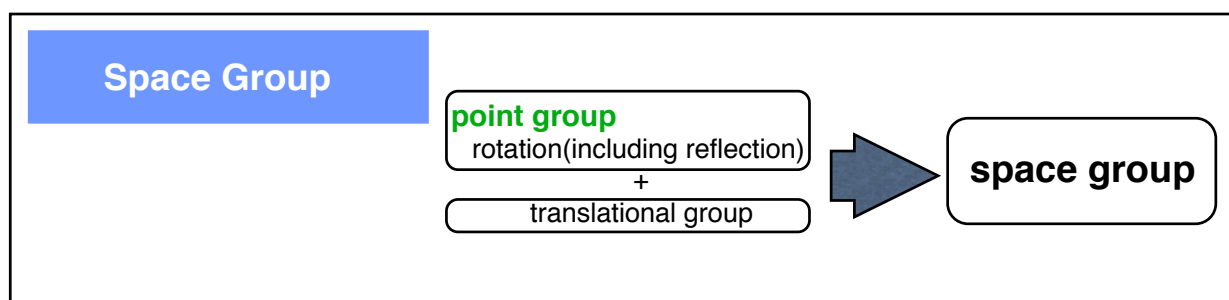
genealogy of DFT calculation



Accuracy, cut-off energy, number of k-points in B.Z. and computational resources



Next theme



Reciprocal Lattice and k-space

At Bloch state, phase factor is given as $e^{i\vec{k}\cdot\vec{r}}$

$e^{i\vec{k}\cdot\vec{r}}$  dimensionless quantity  \vec{k} has dimension of reciprocal length


k-space (reciprocal space)

Someone said

Is k-space “*virtual space*”?



No. \vec{k} represents “*wave nature of electron*”.



It is natural idea that electrons are in k-space

translational lattice vector in real space

$$\vec{t}_n = n_1 \vec{t}_1 + n_2 \vec{t}_2 + n_3 \vec{t}_3$$

$\vec{t}_1, \vec{t}_2, \vec{t}_3$: primitive translational lattice vector

primitive reciprocal vector

$$\begin{aligned} \vec{g}_1 &= \frac{2\pi(\vec{t}_2 \times \vec{t}_3)}{\vec{t}_1(\vec{t}_2 \times \vec{t}_3)} \\ \vec{g}_2 &= \frac{2\pi(\vec{t}_3 \times \vec{t}_1)}{\vec{t}_2(\vec{t}_3 \times \vec{t}_1)} \\ \vec{g}_3 &= \frac{2\pi(\vec{t}_1 \times \vec{t}_2)}{\vec{t}_3(\vec{t}_1 \times \vec{t}_2)} \end{aligned}$$



reciprocal lattice

$$\vec{g}_l = l_1 \vec{g}_1 + l_2 \vec{g}_2 + l_3 \vec{g}_3$$

orthogonality

$$\vec{g}_i \cdot \vec{t}_j = 2\pi\delta_{i,j}$$



$$e^{i\vec{g}_l \cdot \vec{t}_n} = e^{2\pi n i} = 1 \quad (n:\text{integer})$$

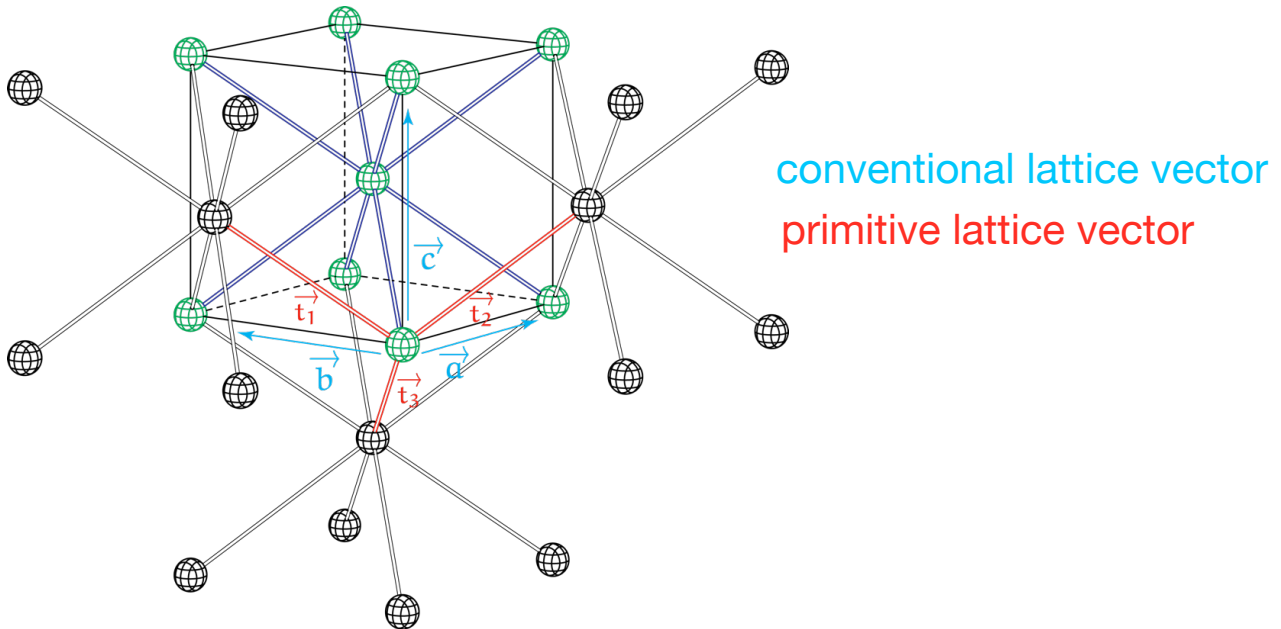


$$e^{-i(\vec{k} + \vec{g}_l) \cdot \vec{t}_n} = e^{-i\vec{k} \cdot \vec{t}_n}$$

(periodicity in k-space)

the condition of [hkl] in crystal

For example, we think about face centered cubic(BCC) lattice,



therefore, basis set of primitive vector is written as

$$\begin{cases} \vec{t}_1 = \frac{1}{2}(-\vec{a} + \vec{b} + \vec{c}) \\ \vec{t}_2 = \frac{1}{2}(\vec{a} - \vec{b} + \vec{c}) \\ \vec{t}_3 = \frac{1}{2}(\vec{a} + \vec{b} - \vec{c}) \end{cases}$$

Here, it satisfies the following condition

$$\begin{cases} \vec{a} \cdot \vec{b} = \vec{b} \cdot \vec{c} = \vec{c} \cdot \vec{a} = 0 \\ |\vec{a}|^2 = |\vec{b}|^2 = |\vec{c}|^2 = a^2 \end{cases}$$

“Primitive reciprocal lattice vector” is defined as

$$\begin{cases} \mathbf{g}_1 = \frac{2\pi}{\Omega} (\mathbf{t}_2 \times \mathbf{t}_3) \\ \mathbf{g}_2 = \frac{2\pi}{\Omega} (\mathbf{t}_3 \times \mathbf{t}_1) \\ \mathbf{g}_3 = \frac{2\pi}{\Omega} (\mathbf{t}_1 \times \mathbf{t}_2) \end{cases}$$

where Ω is

$$\Omega = \mathbf{t}_1 \cdot (\mathbf{t}_2 \times \mathbf{t}_3) = \frac{1}{2}a^3$$

In particular,

$$\begin{aligned} \mathbf{g}_1 &= \frac{2\pi}{\Omega} (\mathbf{t}_2 \times \mathbf{t}_3) \\ &= \frac{2\pi}{\Omega} \left\{ \frac{1}{2} (\mathbf{a} - \mathbf{b} + \mathbf{c}) \times \frac{1}{2} (\mathbf{a} + \mathbf{b} - \mathbf{c}) \right\} \\ &= \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{b} + \mathbf{c}) \end{aligned}$$

Primitive reciprocal lattice vector

$$\begin{cases} \mathbf{g}_1 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{b} + \mathbf{c}) \\ \mathbf{g}_2 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{c} + \mathbf{a}) \\ \mathbf{g}_3 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{a} + \mathbf{b}) \end{cases}$$

from similar calculation...

Reciprocal lattice point is defined as

$$\mathbf{g}_l = l_1 \mathbf{g}_1 + l_2 \mathbf{g}_2 + l_3 \mathbf{g}_3 \quad (l_1, l_2, l_3 : \text{integer})$$

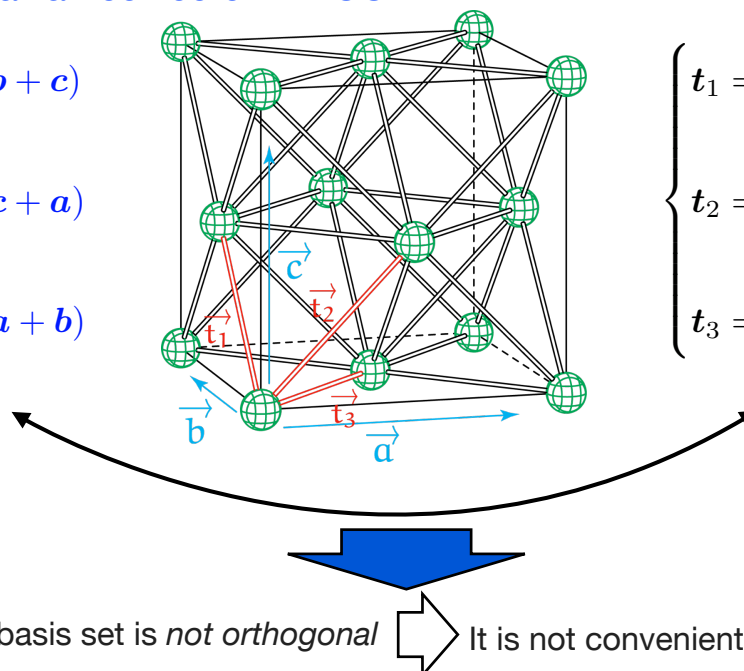
Primitive reciprocal vectors of BCC is similar as the primitive lattice vector of the face-centered cubic(FCC) lattice.

Primitive reciprocal lattice vector in BCC

$$\begin{cases} \mathbf{g}_1 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{b} + \mathbf{c}) \\ \mathbf{g}_2 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{c} + \mathbf{a}) \\ \mathbf{g}_3 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{a} + \mathbf{b}) \end{cases}$$

Primitive lattice vector in FCC

$$\begin{cases} \mathbf{t}_1 = \frac{1}{2} (\mathbf{b} + \mathbf{c}) \\ \mathbf{t}_2 = \frac{1}{2} (\mathbf{c} + \mathbf{a}) \\ \mathbf{t}_3 = \frac{1}{2} (\mathbf{a} + \mathbf{b}) \end{cases}$$



For convenience, we introduce "Conventional reciprocal vector"

$$\begin{cases} \mathbf{a}^* = \frac{1}{\Omega_c} (\mathbf{b} \times \mathbf{c}) = \frac{1}{\Omega} \frac{1}{2} \mathbf{a} \\ \mathbf{b}^* = \frac{1}{\Omega_c} (\mathbf{c} \times \mathbf{a}) = \frac{1}{\Omega} \frac{1}{2} \mathbf{b} \\ \mathbf{c}^* = \frac{1}{\Omega_c} (\mathbf{a} \times \mathbf{b}) = \frac{1}{\Omega} \frac{1}{2} \mathbf{c} \end{cases}$$

where Ω_c is

$$\Omega_c = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = a^3 = 2\Omega$$

This basis set satisfies the orthogonality obviously.
We try to express the reciprocal lattice point

$$\mathbf{g}_l = 2\pi (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$

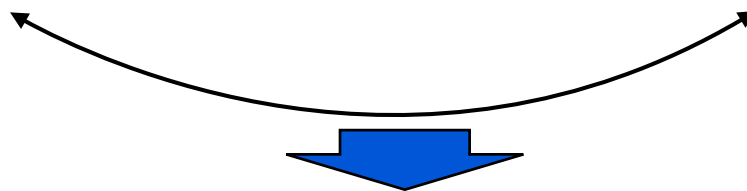
using conventional reciprocal vector. What is the constraint condition for h, k, l?

Primitive reciprocal lattice vector

$$\begin{cases} \mathbf{g}_1 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{b} + \mathbf{c}) \\ \mathbf{g}_2 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{c} + \mathbf{a}) \\ \mathbf{g}_3 = \frac{2\pi}{\Omega} \frac{1}{2} (\mathbf{a} + \mathbf{b}) \end{cases}$$

conventional reciprocal lattice vector

$$\begin{cases} \mathbf{a}^* = \frac{1}{\Omega} \frac{1}{2} \mathbf{a} \\ \mathbf{b}^* = \frac{1}{\Omega} \frac{1}{2} \mathbf{b} \\ \mathbf{c}^* = \frac{1}{\Omega} \frac{1}{2} \mathbf{c} \end{cases}$$



$$\begin{cases} \mathbf{g}_1 = 2\pi (\mathbf{b}^* + \mathbf{c}^*) \\ \mathbf{g}_2 = 2\pi (\mathbf{c}^* + \mathbf{a}^*) \\ \mathbf{g}_3 = 2\pi (\mathbf{a}^* + \mathbf{b}^*) \end{cases}$$

substitute

Reciprocal lattice point is defined as

$$\mathbf{g}_l = l_1\mathbf{g}_1 + l_2\mathbf{g}_2 + l_3\mathbf{g}_3 \quad (l_1, l_2, l_3 : \text{integer})$$

$$\begin{aligned}
\mathbf{g}_l &= l_1 \mathbf{g}_1 + l_2 \mathbf{g}_2 + l_3 \mathbf{g}_3 \\
&= 2\pi l_1 (\mathbf{b}^* + \mathbf{c}^*) + 2\pi l_2 (\mathbf{c}^* + \mathbf{a}^*) + 2\pi l_3 (\mathbf{a}^* + \mathbf{b}^*) \\
&= 2\pi \{ (l_2 + l_3) \mathbf{a}^* + (l_3 + l_1) \mathbf{b}^* + (l_1 + l_2) \mathbf{c}^* \}
\end{aligned}$$

On the other hand, we try to write....

$$\mathbf{g}_l = 2\pi (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$

$$\begin{cases} h = l_2 + l_3 \\ k = l_3 + l_1 \\ l = l_1 + l_2 \end{cases} \Leftrightarrow \begin{cases} l_1 = \frac{1}{2}(-h + k + l) \\ l_2 = \frac{1}{2}(h - k + l) \\ l_3 = \frac{1}{2}(h + k - l) \end{cases}$$

Here the constrain condition for $l_i^{\forall i}$ is that $l_i^{\forall i}$ are integer. From above formula,

$$l_1 + l_2 + l_3 = \frac{1}{2}(h + k + l)$$

$$h + k + l = 2(l_1 + l_2 + l_3) = 2m \quad (m \equiv l_1 + l_2 + l_3)$$

In other word, $h + k + l$ MUST BE EVEN.

Conversely, if $h + k + l$ is even,

$$\begin{cases} l_1 = \frac{1}{2}(-h + k + l) = \frac{1}{2}(2m - 2h) = m - h \\ l_2 = \frac{1}{2}(h - k + l) = \frac{1}{2}(2m - 2k) = m - k \\ l_3 = \frac{1}{2}(h + k - l) = \frac{1}{2}(2m - 2l) = m - l \end{cases}$$

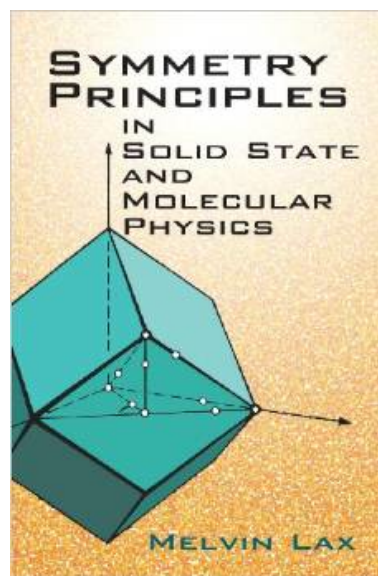
l_1, l_2 and l_3 are integer.

“ $h + k + l$ is even” is necessary and sufficient condition for “ l_1, l_2 and l_3 are integer”

Selection rule for Reciprocal Lattice

$$\vec{g}_l = l_1 \vec{g}_1 + l_2 \vec{g}_2 + l_3 \vec{g}_3 \quad (l_1, l_2, l_3 : \text{integer} \quad)$$

Simple:	all
Hexagonal:	all
Trigonal:	$-l_1 + l_2 + l_3 = 3m \quad (m:\text{integer})$
Face Centered:	$l_i = 2m \text{ for } \forall i \text{ or } l_i = 2m + 1 \text{ for } \forall i \quad (i = 1, 2, 3)$
Body Centered:	$l_1 + l_2 + l_3 = 2m \quad (m:\text{integer})$
Base Centered:	$l_1 + l_2 = 2m \quad (m:\text{integer})$



Rotational Symmetry

symmetry operator and operation are represented as: $O_{\xi}\psi(\vec{r}) \equiv \psi(\xi^{-1}\vec{r})$

Now we suppose that potential is invariant for operation $(\alpha|\vec{v})$

$$V(\vec{r}) = V(\underbrace{\alpha^{-1}(\vec{r} - \vec{v})}_{\text{rotation translation}}) \quad \text{rotational symmetry}$$

Schrödinger Equation in crystal:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \underbrace{\exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r})}_{\text{Eigenfunction}} = \underbrace{E_{\vec{k}}}_{\text{Eigenvalue}} \exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r})$$

operate
 $O_{(\alpha|\vec{v})}$

$$\begin{aligned} O_{(\alpha|\vec{v})} \exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r}) &= \exp\{i\vec{k} \cdot \alpha^{-1}(\vec{r} - \vec{v})\} u_{\vec{k}}(\alpha^{-1}(\vec{r} - \vec{v})) \\ &= \exp(i\alpha\vec{k} \cdot \vec{r}) \underbrace{\exp(-i\alpha\vec{k} \cdot \vec{v})}_{\equiv u_{\alpha\vec{k}}(\vec{r})} u_{\vec{k}}(\alpha^{-1}(\vec{r} - \vec{v})) \end{aligned}$$

same eigenvalue

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \underbrace{\exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r})}_{\text{Eigenfunction}} = \underbrace{E_{\vec{k}}}_{\text{Eigenvalue}} \exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r})$$

$\Rightarrow \exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r})$ is also eigenstate

Check periodicity...

Operate $O_{(\epsilon|\vec{t}_n)}$ to $\exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r})$ $u_{\alpha\vec{k}}(\vec{r}) \equiv \exp(-i\alpha\vec{k} \cdot \vec{v})u_{\vec{k}}(\alpha^{-1}(\vec{r} - \vec{v}))$

$$O_{(\epsilon|\vec{t}_n)} \exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r}) = \exp(-i\alpha\vec{k} \cdot \vec{t}_n) \exp(i\alpha\vec{k} \cdot \vec{r}) \exp(-i\alpha\vec{k} \cdot \vec{v}) \times u_{\vec{k}}(\alpha^{-1}(\vec{r} - \vec{v}) - \alpha^{-1}\vec{t}_n)$$

A lattice has crystalline symmetry

vector $\alpha\vec{t}_n$ is a translation vector which has crystalline periodicity.

$$u_{\vec{k}}(\alpha^{-1}(\vec{r} - \vec{v}) - \alpha^{-1}\vec{t}_n) = u_{\vec{k}}(\alpha^{-1}(\vec{r} - \vec{v}))$$

$$O_{(\epsilon|\vec{t}_n)} \exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r}) = \exp(-i\alpha\vec{k} \cdot \vec{t}_n) \exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r})$$

$$\exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r}) = O_{(\alpha|\vec{v})} \exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r})$$

Bloch function

compare \Updownarrow

Bloch Theorem

$$O_{(\epsilon|\vec{t}_n)} \exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r}) = \exp(-i\vec{k} \cdot \vec{t}_n) \exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r})$$

Bloch function

$\vec{k} \rightarrow \alpha\vec{k}$

Summary of Rotational Symmetry

- ① $\exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r}) (= O_{(\alpha|\vec{v})} \exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r}))$ is Bloch function
- ② Eigenvalue of $\exp(i\alpha\vec{k} \cdot \vec{r})u_{\alpha\vec{k}}(\vec{r})$ is equal to that of $\exp(i\vec{k} \cdot \vec{r})u_{\vec{k}}(\vec{r})$



\vec{k} has point group of crystal.

Advanced theme

relativistic effect (spin-orbit coupling)

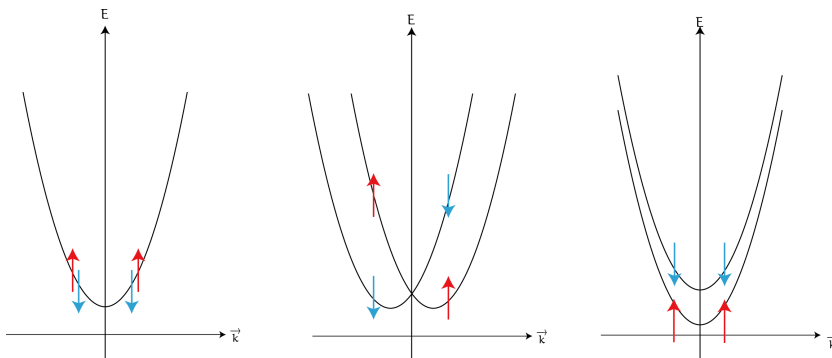
$$H_{SO} = -\frac{\hbar}{4m_0^2c^2} \boldsymbol{\sigma} \cdot \mathbf{p} \times (\nabla V_0)$$

space inverse operation

$$E(\mathbf{k}, \boldsymbol{\sigma}) \longrightarrow E(-\mathbf{k}, \boldsymbol{\sigma})$$

time reversal operation

$$E(\mathbf{k}, \boldsymbol{\sigma}) \longrightarrow E(-\mathbf{k}, -\boldsymbol{\sigma})$$



Atomic Origin view for Spin-Orbit Interaction:

Biot-Savart Law

$$\mathbf{B}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0 c^2} \frac{\mathbf{r} \times (-Zq_e \mathbf{v})}{|\mathbf{r}|^3} = \frac{1}{c^2} \{\mathbf{E}(\mathbf{r}) \times \mathbf{v}\} \quad \left(\mathbf{E}(\mathbf{r}) = \frac{Zq_e}{4\pi\epsilon_0 r^2} \frac{\mathbf{r}}{r} \right)$$

Using Angular Momentum operator,

$$\mathbf{B}(\mathbf{r}) = \frac{Zq_e}{4\pi\epsilon_0 c^2} \frac{\mathbf{r} \times \mathbf{v}}{|\mathbf{r}|^3} = \frac{Zq_e}{4\pi\epsilon_0 c^2 m_e} \frac{\mathbf{L}}{|\mathbf{r}|^3}$$

Thus magnetic interaction field operator is defined as:

$$\begin{aligned} \mathcal{H}_{\text{spin-orbit}} &= -\frac{1}{2} \boldsymbol{\mu}_s \cdot \mathbf{B}(\mathbf{r}) = \frac{1}{2} \left(\frac{g_s}{\hbar} \mathbf{S} \right) \cdot \left(\frac{Zq_e}{4\pi\epsilon_0 c^2 m_e} \frac{\mathbf{L}}{|\mathbf{r}|^3} \right) \quad \text{Spin-Orbit Interaction} \\ &= \frac{Ze^2}{2m_e^2 c^2} \frac{1}{r^3} \mathbf{S} \cdot \mathbf{L} \end{aligned}$$

Thomas precession factor: L. H. Thomas, "The motion of the spinning electron", Nature **117**, 514(1926)

Nonzero-diagonal and off-diagonal elements

$$\langle n, l, m_l, m_s | \mathcal{H}_{\text{spin-orbit}} | n', m', m'_l, m'_s \rangle$$

connecting states with equal / different n, m_l, m_s

$$\mathcal{H}_{\text{spin-orbit}} \simeq \frac{Ze^2}{2m_e^2 c^2} \sum_{n,l} |n, l\rangle \left\langle n, l \left| \frac{1}{r^3} \right| n, l \right\rangle \langle n, l | \mathbf{S} \cdot \mathbf{L}$$

Radial Integral can be evaluated for $l \geq 0$ hydrogenic wave function obtains

$$\xi_{n,l} = \left(\frac{Z}{a} \right)^3 \frac{2}{n^3 l(l+1)(2l+1)} = Z^4 \alpha^2 E_{Ha} \left(\frac{\mu}{m_e} \right)^3 \frac{1}{n^3 l(l+1)(2l+1)}$$

Spin-Orbit Interaction is rewritten as

$$\mathcal{H}_{\text{spin-orbit}} = \sum_{n,l} \xi_{n,l} |n, l\rangle \langle n, l | \frac{\mathbf{S} \cdot \mathbf{L}}{\hbar^2}$$

where

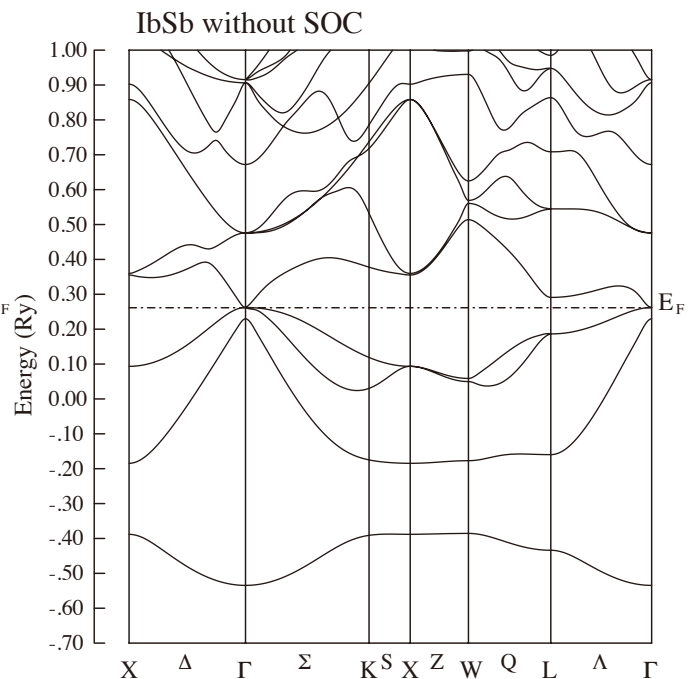
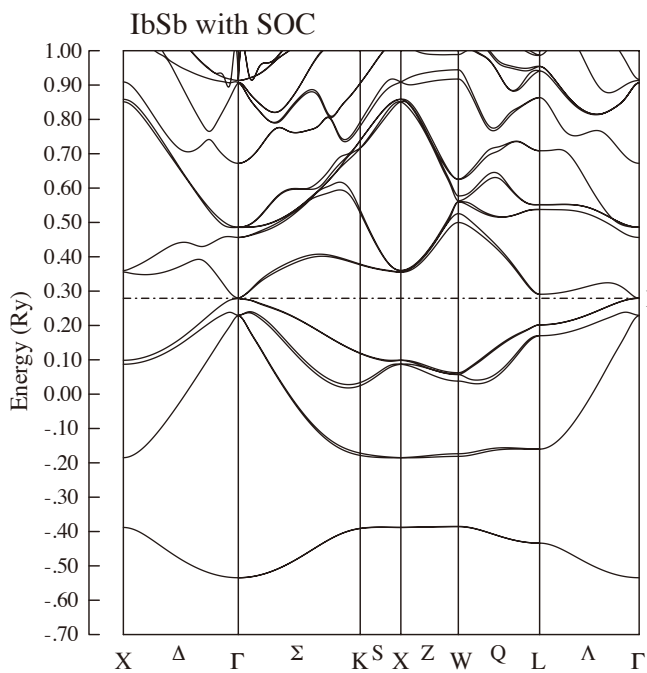
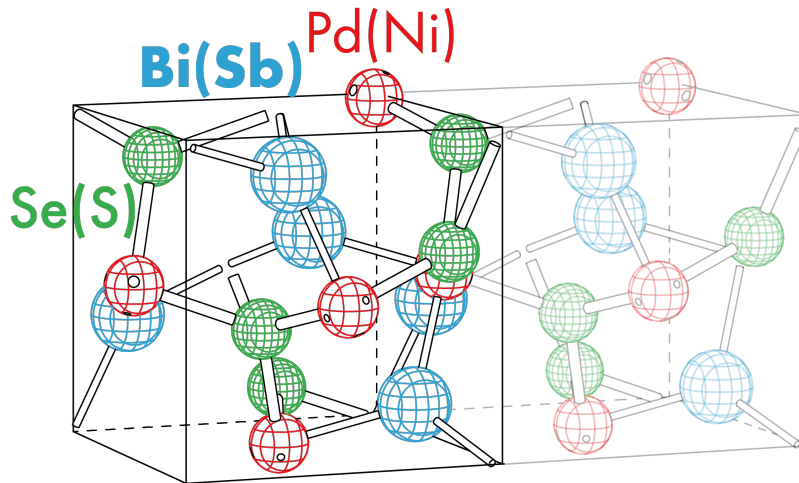
$$\xi_{n,l} = \left(\frac{Z}{a} \right)^3 \frac{2}{n^3 l(l+1)(2l+1)} = Z^4 \alpha^2 E_{Ha} \left(\frac{\mu}{m_e} \right)^3 \frac{1}{n^3 l(l+1)(2l+1)}$$

Crystal Effect Field Origin view for Spin-Orbit Interaction:

➔ Anti-symmetric Spin-Orbit Interaction (ASOI)

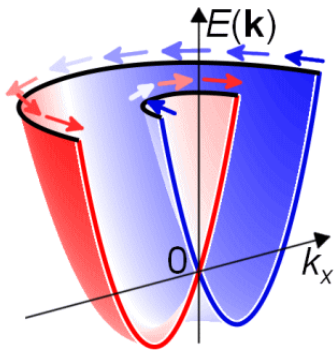
$$\mathcal{H}_{ASOI} = \sum \alpha g(\mathbf{k}) \cdot \mathbf{S}(\mathbf{k})$$

Break down to centrosymmetric in the Crystal

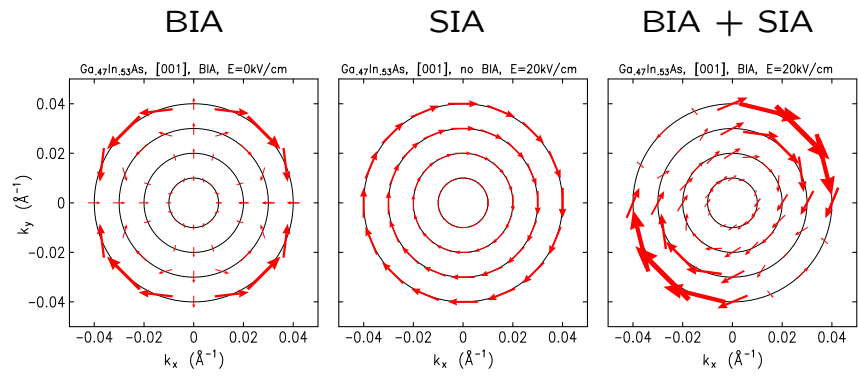


Anti-Symmetric Spin-Orbit Interaction(ASOI)

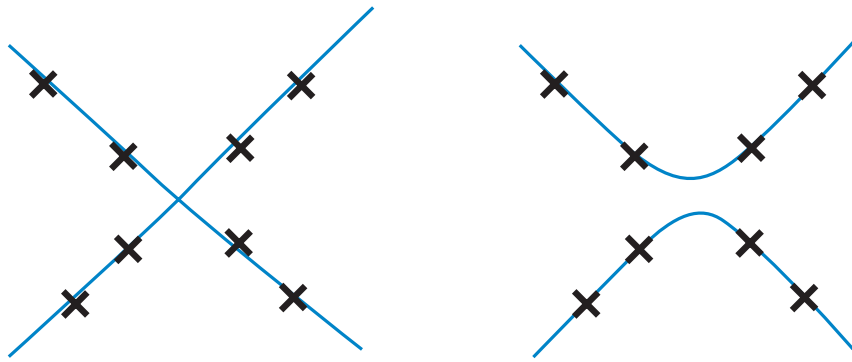
$$\mathcal{H}_{ASOI} = \sum \alpha \mathbf{g}(\mathbf{k}) \cdot \mathbf{S}(\mathbf{k})$$



Rashba-Type

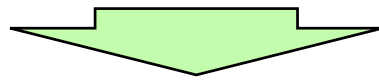


Free electron model
and
Alkali / Alkali Earth Metal



Which is correct?

(in rough k-point sampling case...)



Space Group teaches us.

Free electron Model

under Born-von Karman Condition

$$V(\vec{r} - \vec{t}_n) = V(\vec{r}) \quad \vec{t}_n = n_1 \vec{t}_1 + n_2 \vec{t}_2 + n_3 \vec{t}_3$$

(here, $V(\vec{r} - \vec{t}_n) = V(\vec{r}) = 0$)

1-electron Schrödinger Equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = E \psi(\vec{r})$$

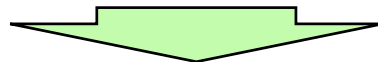


Bloch-Theorem

$$\psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r})$$

where $u_{\vec{k}}(\vec{r})$ is periodic function

$$u_{\vec{k}}(\vec{r} - \vec{t}_n) = u_{\vec{k}}(\vec{r})$$



$u_{\vec{k}}(\vec{r})$ can be represented as Fourier Series

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{g}_i} C_{\vec{g}_i} e^{-i\vec{g}_i \cdot \vec{r}}$$

$$\therefore \psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \sum_{\vec{g}_i} C_{\vec{g}_i} e^{-i\vec{g}_i \cdot \vec{r}} = \sum_{\vec{g}_i} C_{\vec{g}_i} e^{i(\vec{k} - \vec{g}_i) \cdot \vec{r}}$$

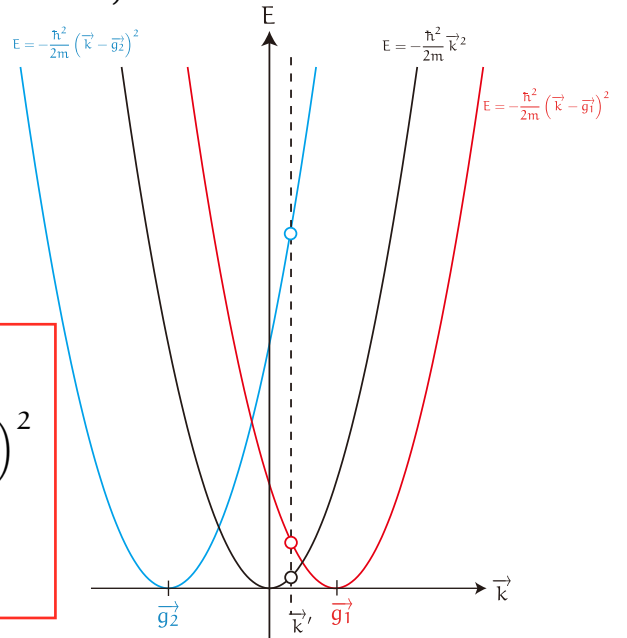
1-electron Schrödinger Equation

$$\begin{aligned}
 &-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = E \psi(\vec{r}) \\
 \Leftrightarrow &-\frac{\hbar^2}{2m} \nabla^2 \left\{ \sum_{\vec{g}_i} C_{\vec{g}_i} e^{i(\vec{k}-\vec{g}_i) \cdot \vec{r}} \right\} = E \left\{ \sum_{\vec{g}_i} C_{\vec{g}_i} e^{i(\vec{k}-\vec{g}_i) \cdot \vec{r}} \right\} \\
 \Leftrightarrow &\sum_{\vec{g}_i} \left\{ \frac{\hbar^2}{2m} (\vec{k}-\vec{g}_i)^2 e^{i(\vec{k}-\vec{g}_i) \cdot \vec{r}} \cdot C_{\vec{g}_i} \right\} = \left\{ \sum_{\vec{g}_i} E_{\vec{k}} C_{\vec{g}_i} e^{i(\vec{k}-\vec{g}_i) \cdot \vec{r}} \right\} \\
 \Leftrightarrow &\sum_{\vec{g}_i} \left[\underbrace{\left\{ \frac{\hbar^2}{2m} (\vec{k}-\vec{g}_i)^2 - E_{\vec{k}} \right\}}_{\equiv E(\vec{k}-\vec{g}_i)} e^{i(\vec{k}-\vec{g}_i) \cdot \vec{r}} \cdot C_{\vec{g}_i} \right] = 0
 \end{aligned}$$

plane wave
(wave number is $\vec{k} - \vec{g}_i$)

↑

Superposition of plane waves



at \vec{k}

Eigenenergy $E(\vec{k} - \vec{g}_i) = \frac{\hbar^2}{2m} (\vec{k} - \vec{g}_i)^2$

Eigenfunction $\psi_{\vec{k}}(\vec{r}) = e^{i(\vec{k}-\vec{g}_i) \cdot \vec{r}}$

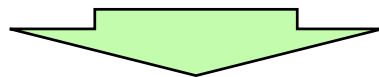
Nearly Free electron model (NFE)

under Born-von Karman Condition (**periodic boundary condition**)

$$V(\vec{r} - \vec{t}_n) = V(\vec{r}) \quad \vec{t}_n = n_1 \vec{t}_1 + n_2 \vec{t}_2 + n_3 \vec{t}_3$$

Potential can be represented as Fourier series

$$V(\vec{r}) = \sum_{\vec{g}_i} \underbrace{V_{\vec{g}_i}}_{\text{Fourier Component of } \vec{g}_i} e^{i\vec{g}_i \cdot \vec{r}} \quad \left(V_{\vec{g}_i} = \frac{1}{\Omega_c} \iiint_{\Omega_c} e^{-i\vec{g}_i \cdot \vec{r}} V(\vec{r}) dV \right)$$



Hamiltonian Matrix element(2-wave approximation)

$$\mathcal{H} = \begin{pmatrix} \epsilon_{\vec{k}} + \langle \vec{k} | V | \vec{k} \rangle & V_{\vec{g}_i} \\ V_{\vec{g}_i}^* & \epsilon_{\vec{k}+\vec{g}_i} + \langle \vec{k} + \vec{g}_i | V | \vec{k} + \vec{g}_i \rangle \end{pmatrix} V_{\vec{g}_i}$$

where

$$\langle \vec{k} | V | \vec{k}' \rangle \equiv \frac{1}{\Omega} \iiint e^{-i(\vec{k}' - \vec{k}) \cdot \vec{r}} V(\vec{r}) dV$$

Here

$$\langle \vec{k} | V | \vec{k} \rangle = \langle \vec{k} + \vec{g}_i | V | \vec{k} + \vec{g}_i \rangle \equiv V_{\vec{k}}$$

Eigenenergy

$$E_{\vec{k}} = \frac{1}{2} (\varepsilon_{\vec{k}} + \varepsilon_{\vec{k} + \vec{g}_i}) + V_{\vec{k}} \pm \sqrt{\left(\frac{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k} + \vec{g}_i}}{2} \right)^2 + |V_{\vec{g}_i}|^2}$$

Free electron Model

Cubic Lattice case

$$\vec{t}_i \cdot \vec{t}_j = a^2 \delta_{i,j}$$

$$\vec{t}_1 \cdot (\vec{t}_2 \times \vec{t}_3) = \Omega_C = a^3$$

$$\vec{t}_i \times \vec{t}_j = \vec{t}_k$$



$$\vec{g}_k = \frac{2\pi}{\Omega_C} (\vec{t}_i \times \vec{t}_j) = \frac{2\pi}{a^3} \vec{t}_k$$

(i, j, k = 1, 2, 3)

Eigenenergy $E(\vec{g}_i) \equiv E(\vec{k} - \vec{g}_i) = \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2 \{ (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_3)^2 \}$

to convenient
Energy unit

→

$$\frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2$$

$$\left(\vec{k} = \frac{2\pi}{a} \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix}, \vec{g}_i = \frac{2\pi}{a} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \right)$$

Eigenenergy

$$E(\vec{g}_i) = E(\vec{k} - \vec{g}_i) = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_3)^2 \quad \left(\vec{k} = \frac{2\pi}{a} \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix}, \vec{g}_i = \frac{2\pi}{a} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \right)$$

Eigenfunction

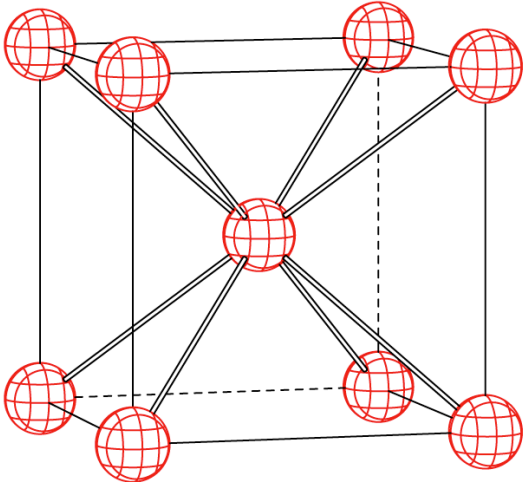
$$\Psi_{\vec{k}}(\vec{r}) = \exp \left\{ \frac{2\pi i}{a} [(\xi - n_1)x + (\eta - n_2)y + (\zeta - n_3)z] \right\}$$

Li ³	bcc
Na ¹¹	bcc
K ¹⁹	bcc
Rb ³⁷	bcc
Cs ⁵⁵	bcc
Fr ⁸⁷	bcc

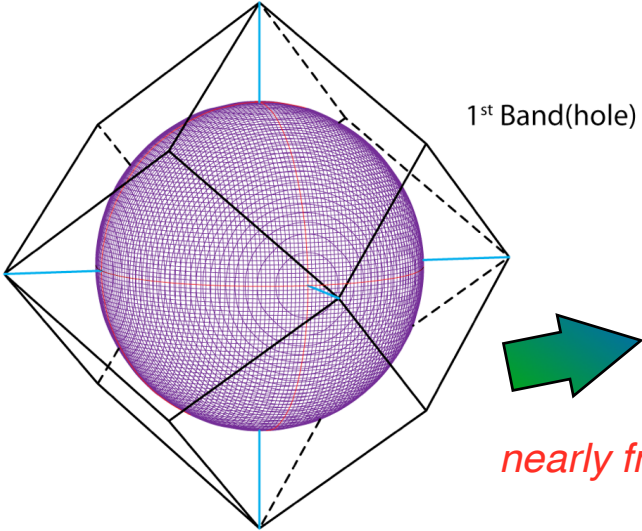
Alkali Metals

the **b**ody **c**entered **c**ubic (**bcc**)

space group
Im $\bar{3}m$ (O_h⁹)



Fermi Surface of Na



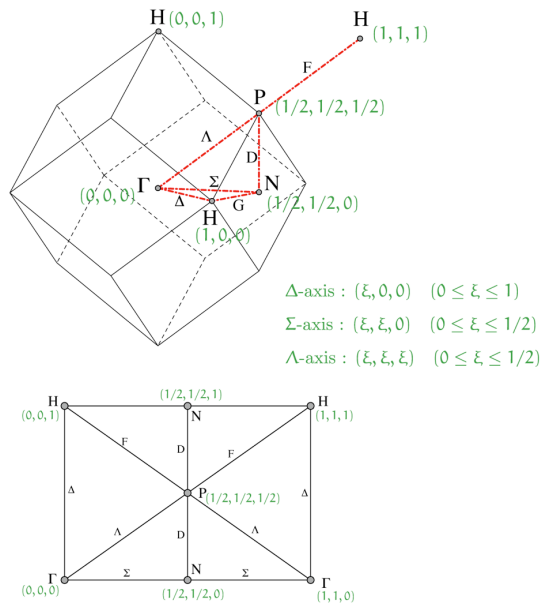
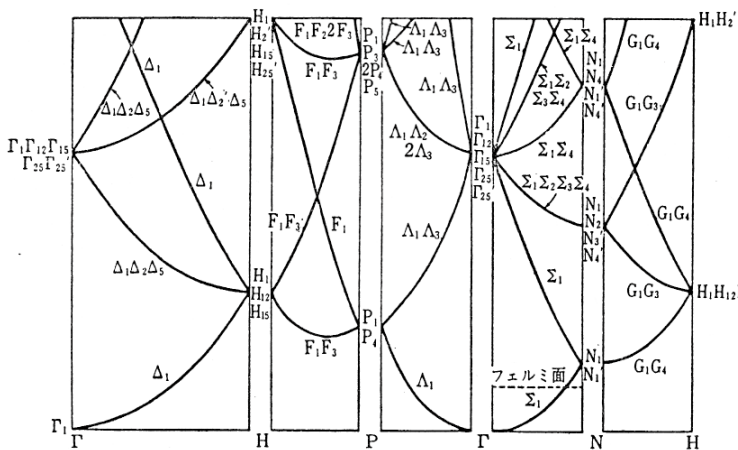
free electron

$$\frac{\hbar^2 k_F^2}{2m} = E_F \Leftrightarrow k_x^2 + k_y^2 + k_z^2 = \frac{2mE_F}{\hbar^2}$$

Fermi surface is "sphere" in shape.
It is called "fermi sphere"

nearly free electron

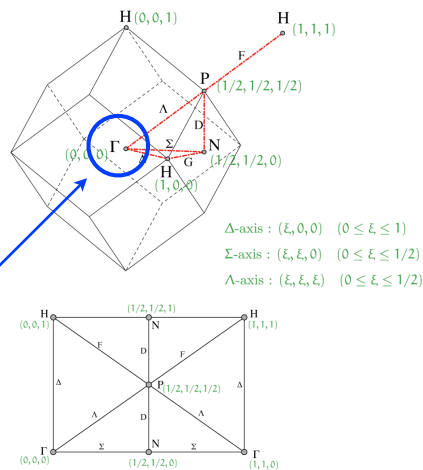
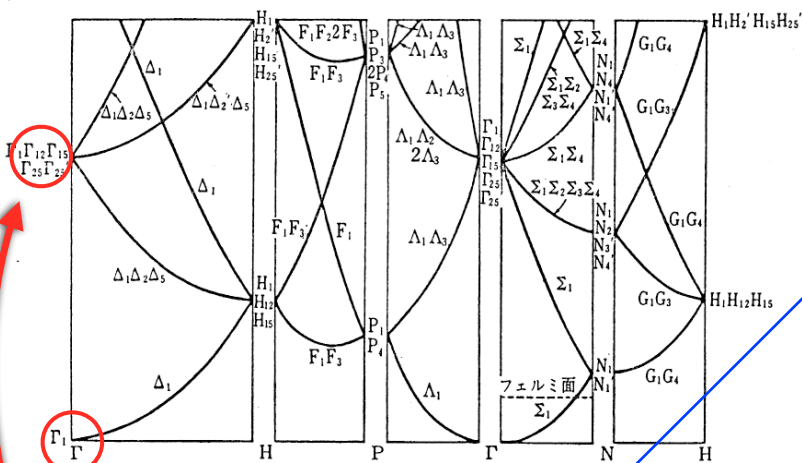
bcc free electron



$$E(\vec{g}_i) = E(\vec{k} - \vec{g}_i) = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_3)^2 \quad \left(\vec{k} = \frac{2\pi}{a} \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix}, \vec{g}_i = \frac{2\pi}{a} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \right)$$

$$\psi_{\vec{k}}(\vec{r}) = \exp \left\{ \frac{2\pi i}{a} [(\xi - n_1)x + (\eta - n_2)y + (\zeta - n_3)z] \right\}$$

bcc free electron

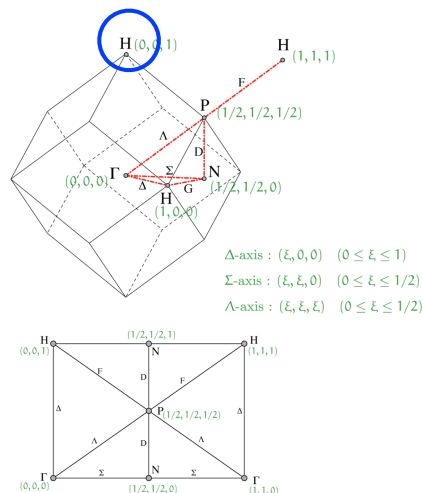
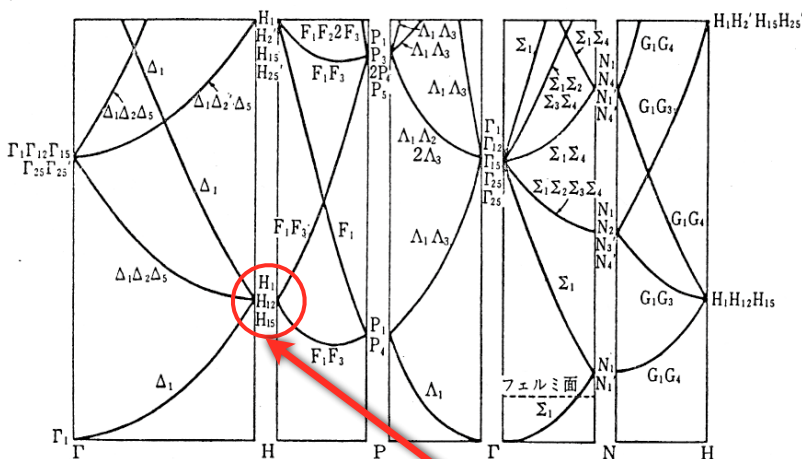


$$E(\vec{g}_i) = E(\vec{k} - \vec{g}_i) = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_1)^2 \quad \left(\vec{k} = \frac{2\pi}{a} \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix}, \vec{g}_i = \frac{2\pi}{a} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \right)$$

$$E = 0; \quad \vec{k} = \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \vec{g}_i = \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

$$E = 2; \quad \vec{k} = \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \vec{g}_i = \left\{ \frac{2\pi}{a} \begin{bmatrix} 0 \\ \pm 1 \\ \pm 1 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} \pm 1 \\ 0 \\ \pm 1 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} \pm 1 \\ \pm 1 \\ 0 \end{bmatrix} \right\}$$

bcc free electron



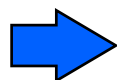
wavefunction is given as

$$E = 1;$$

$$\vec{k}_n = \left\{ \frac{2\pi}{a} \begin{bmatrix} 0 \\ \pm 1 \\ 1 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} \pm 1 \\ 0 \\ 1 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 2 \end{bmatrix} \right\}$$

$$\psi_H(\vec{r}) = \begin{cases} \exp\left(\pm \frac{2\pi}{a} x\right) \\ \exp\left(\pm \frac{2\pi}{a} y\right) \\ \exp\left(\pm \frac{2\pi}{a} z\right) \end{cases}$$

These wavefunction are not convenient to reflect crystal potential which has crystal symmetry



Symmetrization

if $\psi_a(\vec{r}), \psi_b(\vec{r})$ are eigenfunction which have same eigenvalue:

$$\mathcal{H}\psi_a(\vec{r}) = E_j\psi_a(\vec{r})$$

$$\mathcal{H}\psi_b(\vec{r}) = E_j\psi_b(\vec{r})$$

then

$$\frac{1}{\sqrt{2}}(\psi_a(\vec{r}) + \psi_b(\vec{r})) \quad \text{and} \quad \frac{1}{\sqrt{2}}(\psi_a(\vec{r}) - \psi_b(\vec{r})) \quad \text{are also eigenfunction.}$$



In generally, p-fold degenerate states,

$$\{\psi_1(\vec{r}), \psi_2(\vec{r}), \dots, \psi_j(\vec{r}), \dots, \psi_p(\vec{r})\} \rightarrow \{\phi_1(\vec{r}), \phi_2(\vec{r}), \dots, \phi_j(\vec{r}), \dots, \phi_p(\vec{r})\}$$

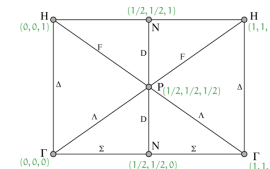
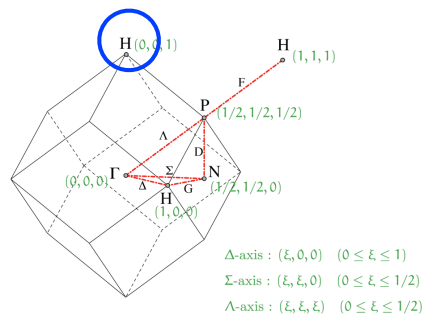
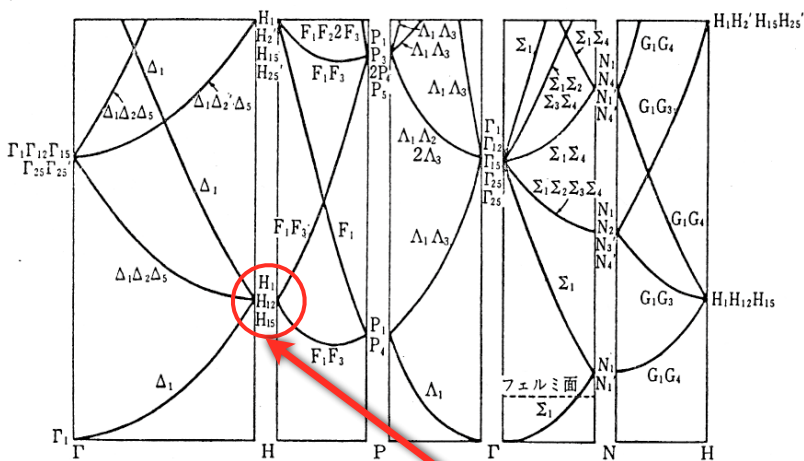
generated by linear combination

$$\psi_1(\vec{r}), \psi_2(\vec{r}), \dots, \psi_j(\vec{r}), \dots, \psi_p(\vec{r})$$

➡ planewave type symmetrization ➡ APW, OPW

➡ linear combination atomic orbital type symmetrization

bcc free electron



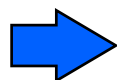
wavefunction is given as

$$E = 1;$$

$$\vec{k}_n = \left\{ \frac{2\pi}{a} \begin{bmatrix} 0 \\ \pm 1 \\ 1 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} \pm 1 \\ 0 \\ 1 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 2 \end{bmatrix} \right\}$$

$$\psi_H(\vec{r}) = \begin{cases} \exp\left(\pm \frac{2\pi}{a} x\right) \\ \exp\left(\pm \frac{2\pi}{a} y\right) \\ \exp\left(\pm \frac{2\pi}{a} z\right) \end{cases}$$

These wavefunction are not convenient to reflect crystal potential which has crystal symmetry



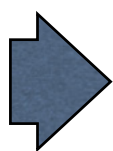
Symmetrization

at H (energy E=1)

$$H_1 = \cos\left(\frac{2\pi}{a} x\right) + \cos\left(\frac{2\pi}{a} y\right) + \cos\left(\frac{2\pi}{a} z\right) \quad (\text{s-type})$$

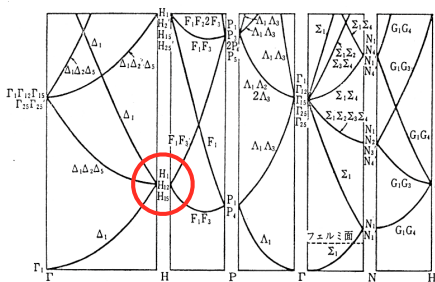
$$\psi_H(\vec{r}) = \begin{cases} \exp\left(\pm \frac{2\pi}{a} x\right) \\ \exp\left(\pm \frac{2\pi}{a} y\right) \\ \exp\left(\pm \frac{2\pi}{a} z\right) \end{cases}$$

change basis set



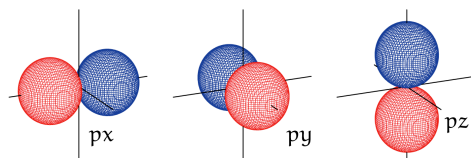
$$H_{12} = \begin{cases} \cos\left(\frac{2\pi}{a}\right) - \frac{1}{2} \left\{ \cos\left(\frac{2\pi}{a} x\right) + \cos\left(\frac{2\pi}{a} y\right) \right\} \\ \cos\left(\frac{2\pi}{a} x\right) - \cos\left(\frac{2\pi}{a} y\right) \end{cases}$$

(dy-type)

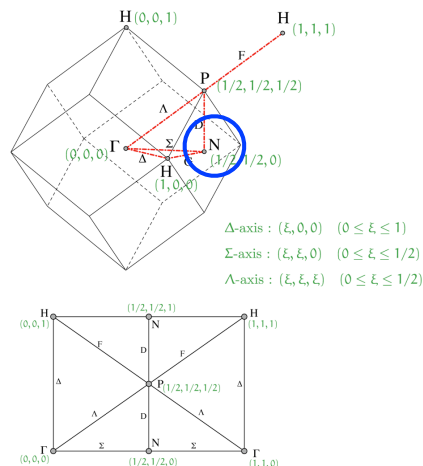
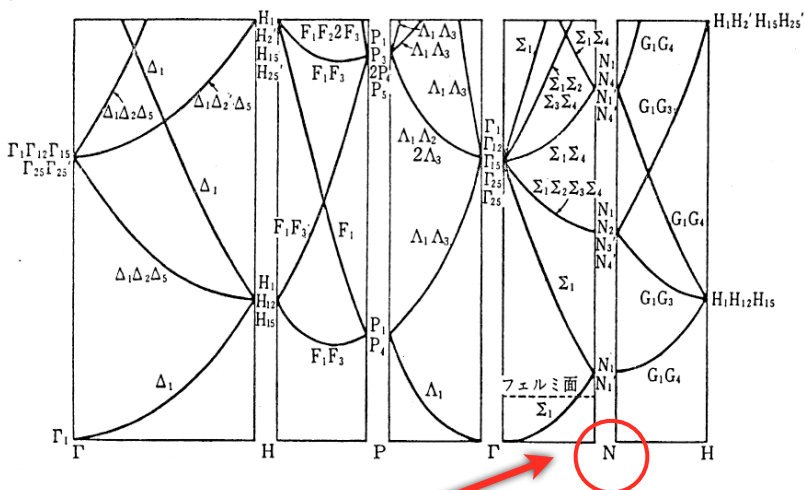


$$H_{15} = \begin{cases} \sin\left(\frac{2\pi}{a} x\right) \\ \sin\left(\frac{2\pi}{a} y\right) \\ \sin\left(\frac{2\pi}{a} z\right) \end{cases}$$

(p-type)



bcc free electron

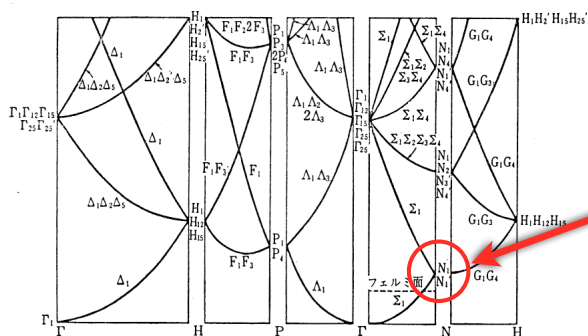


wavefunction is given as

at N, $\xi = \eta = 1/2, \zeta = 0$

therefore

$$\psi_N = \exp \left\{ \frac{\pi i}{a} (x + y) \right\} \times \exp \left\{ -\frac{2\pi i}{a} (n_1 x + n_2 y + n_3 z) \right\}$$



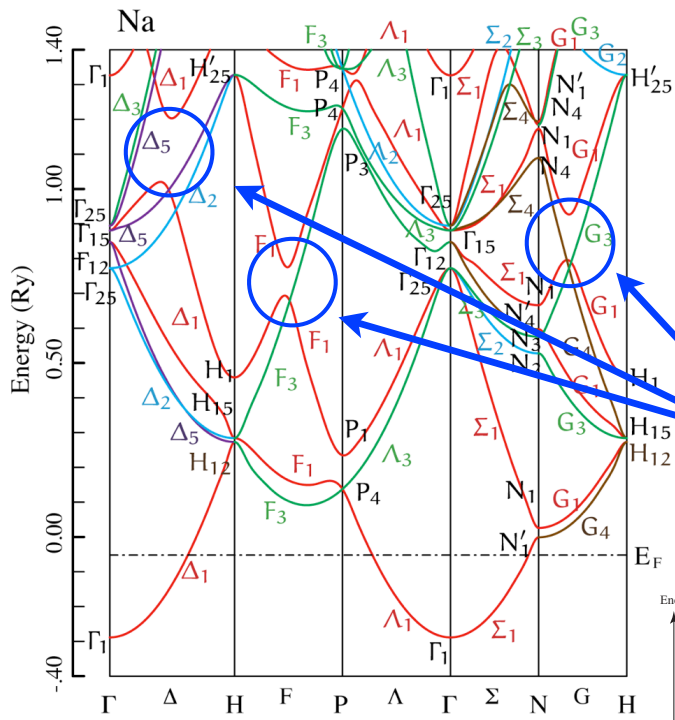
$$E(N) = \left(n_1 - \frac{1}{2} \right)^2 + \left(n_2 - \frac{1}{2} \right)^2 + n_3^2$$

at N (energy $E=1/2$)

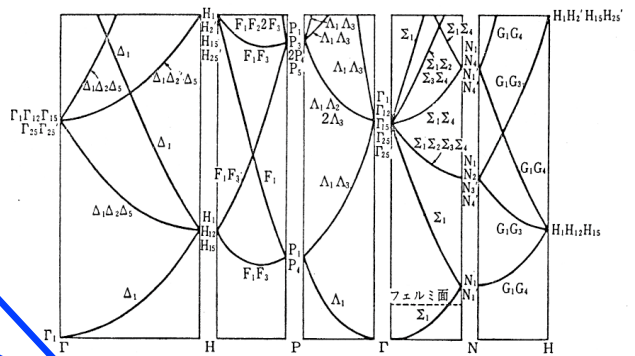
$$\vec{k}_n = \left\{ \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \frac{2\pi}{a} \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix} \right\}$$

change basis set

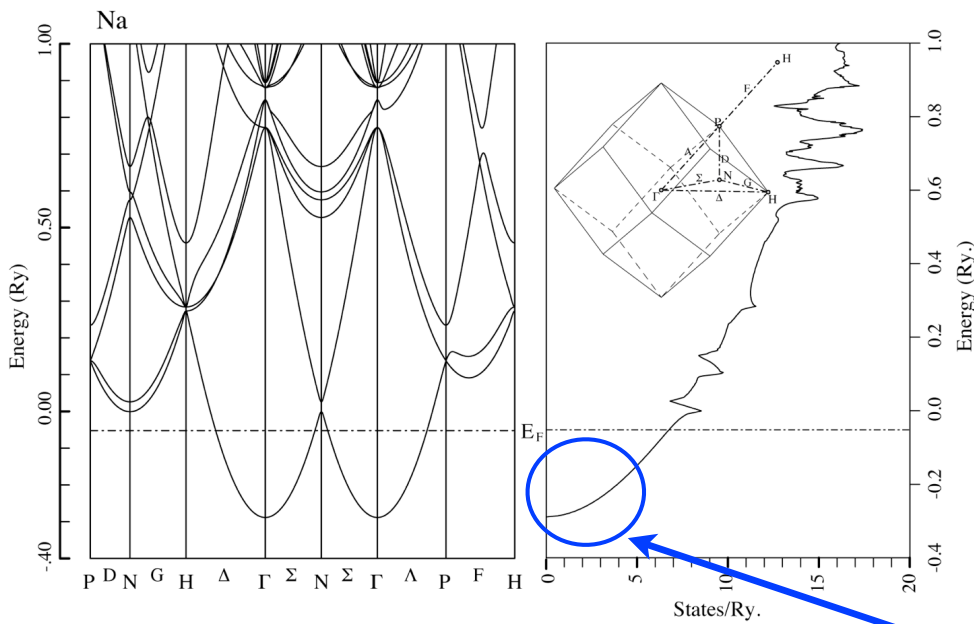
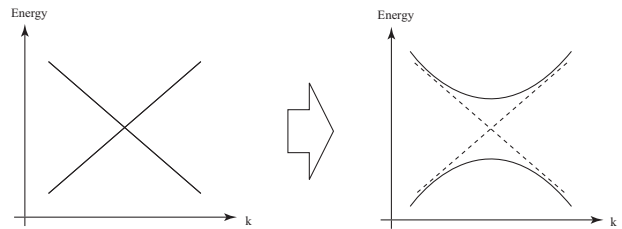
$$\psi_N(\vec{r}) = \exp \left\{ \pm \frac{2\pi i}{a} (x + y) \right\} \rightarrow \begin{cases} N_1 = \cos \left\{ \frac{2\pi i}{a} (x + y) \right\} & \text{(s-type)} \\ N'_1 = \sin \left\{ \frac{2\pi i}{a} (x - y) \right\} & \text{(p-type)} \end{cases}$$



free electron



non-crossing rule



Density of State (free electron)

$$N(\epsilon) = V_0 \frac{(2m)^{3/2}}{4\pi^2 \hbar^3} \sqrt{\epsilon}$$

Free electron Model

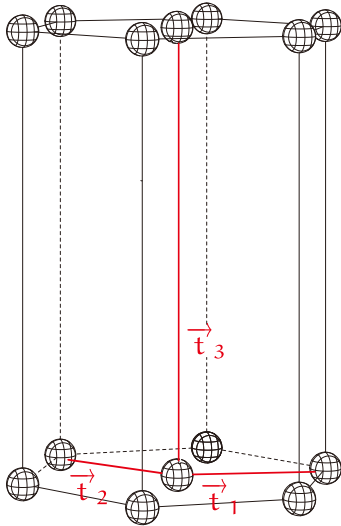
Hexagonal Lattice case

$$|\vec{t}_1| = |\vec{t}_2| = a, \quad |\vec{t}_3| = c$$

$$\vec{t}_1 \cdot \vec{t}_2 = -\frac{a^2}{2} \quad \vec{t}_2 \cdot \vec{t}_3 = \vec{t}_3 \cdot \vec{t}_1 = 0$$

$$\vec{t}_1 \cdot (\vec{t}_2 \times \vec{t}_3) = \Omega_c = \frac{\sqrt{3}}{2} a^2 c$$

$$\vec{g}_k = \frac{2\pi}{\Omega_c} (\vec{t}_i \times \vec{t}_j)$$



Eigenenergy

$$E(\vec{g}_i) \equiv E(\vec{k} - \vec{g}_i) = \frac{\hbar^2}{2m} (\vec{k} - \vec{g}_i)^2$$

Alkaline Earth Metals

hexagonal **closed package (hcp)**

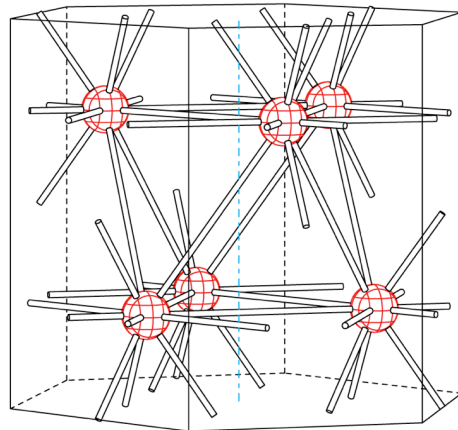
space group

$P6_3/mmc (D_{6h}^4)$

$c/a(\text{Be}) = 1.585$

$c/a(\text{Mg}) = 1.625$

2atom/unit cell

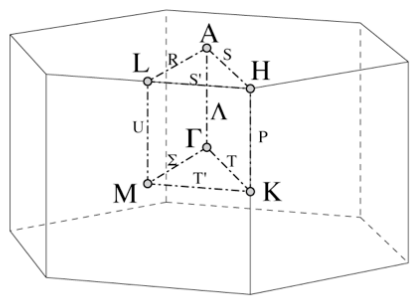
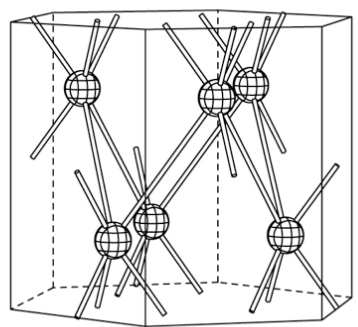
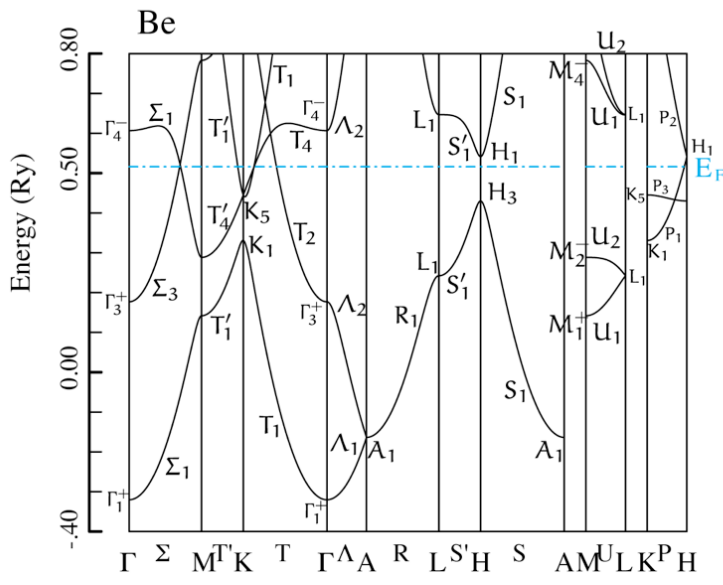


ideal **hcp** lattice

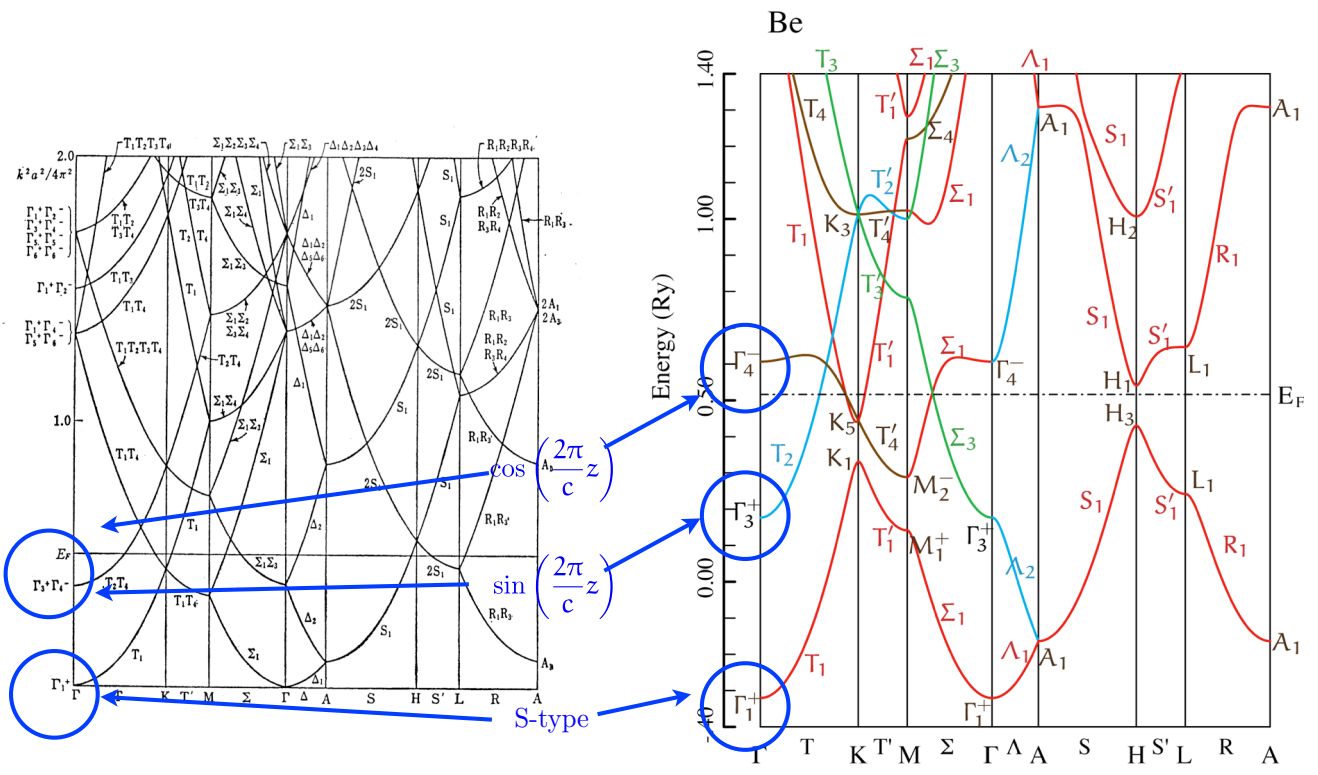
$$c/a = \sqrt{\frac{8}{3}} \approx 1.6330$$

same space group,
but distortional hcp

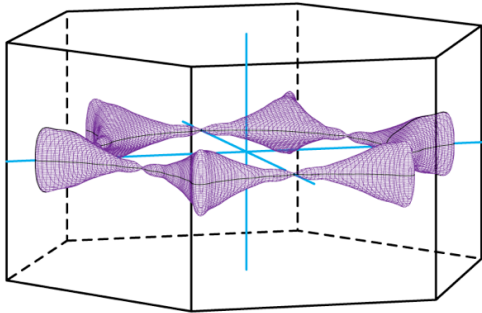
Be ⁴
hex
Mg ¹²
hex
Ca ²⁰
fcc
Sr ³⁸
fcc
Ba ⁵⁶
bcc
Ra ⁸⁸
bcc



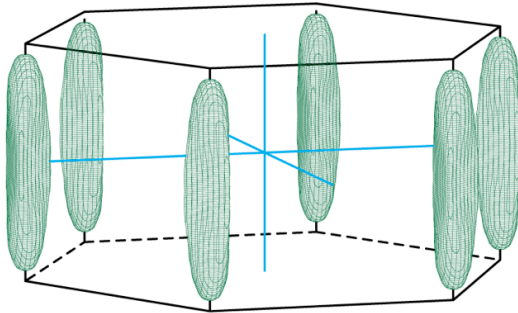
free electron band and Be band



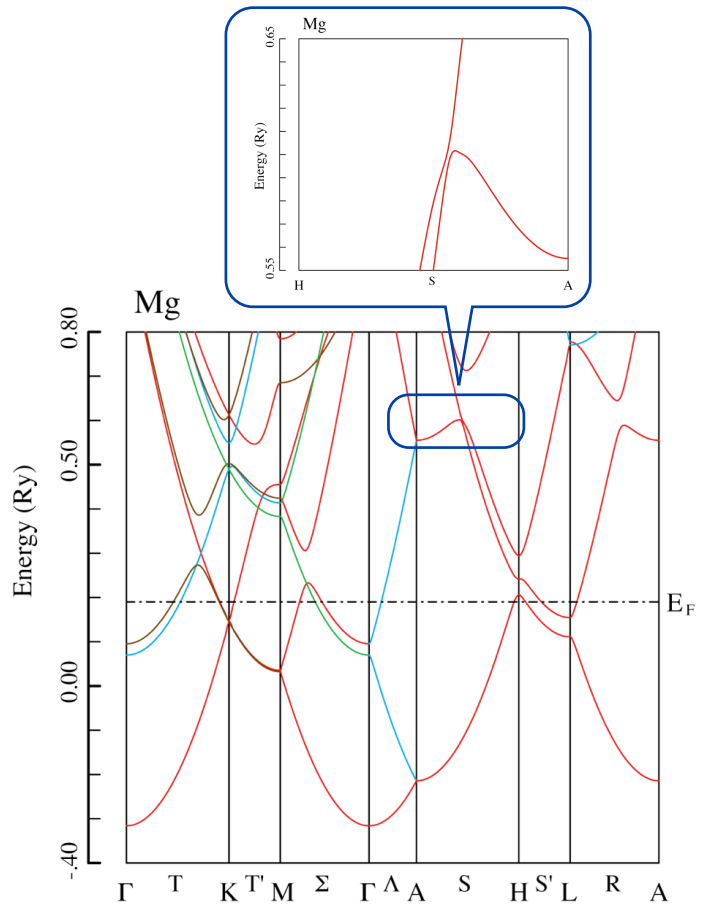
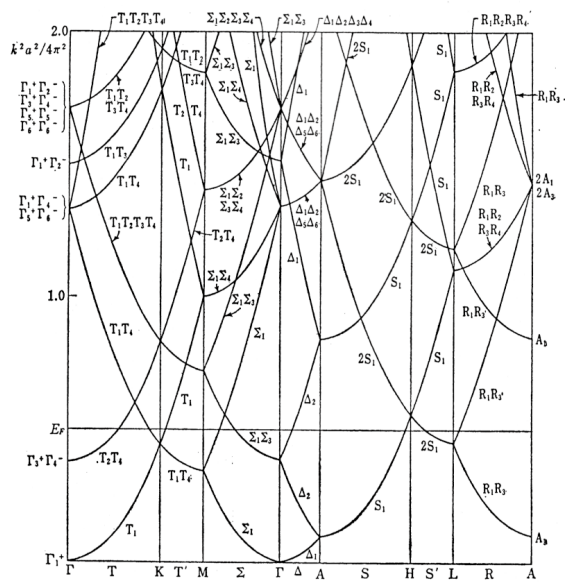
Fermi Surface of Be



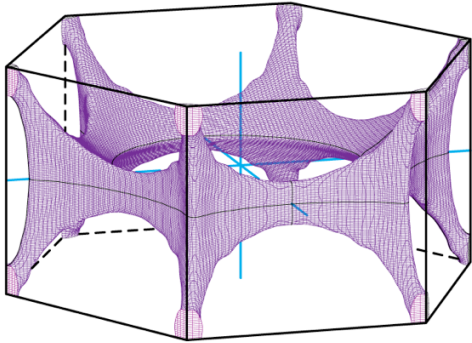
2nd Band(hole)
"Crown"



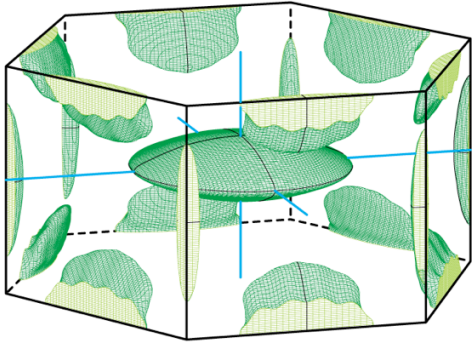
3rd Band(electron)
"Ciger"



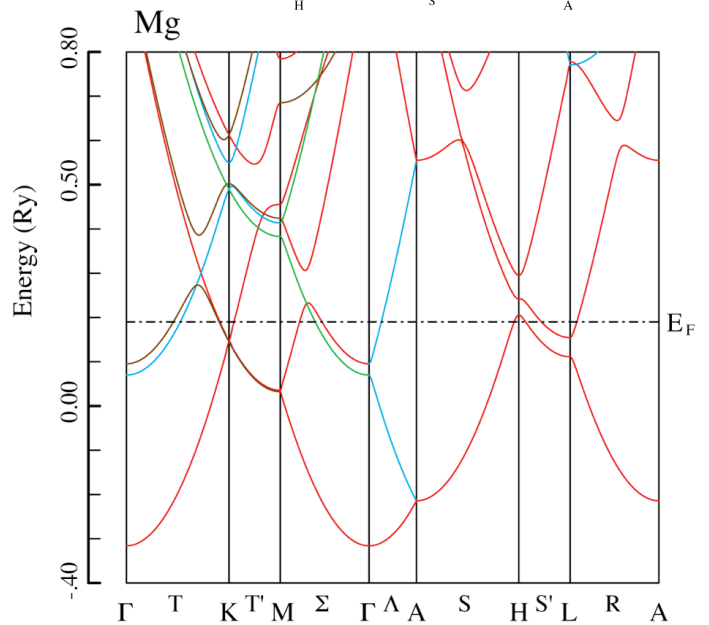
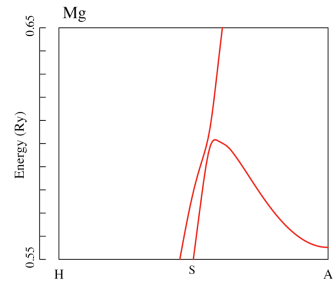
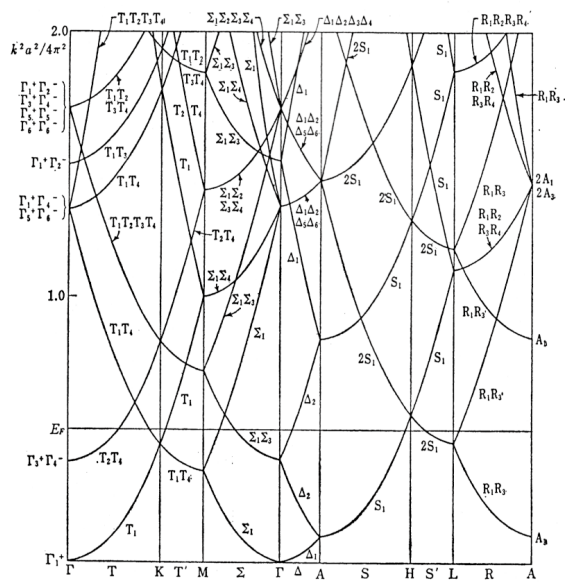
Fermi Surface of Mg



2nd Band(hole)
"Monster"

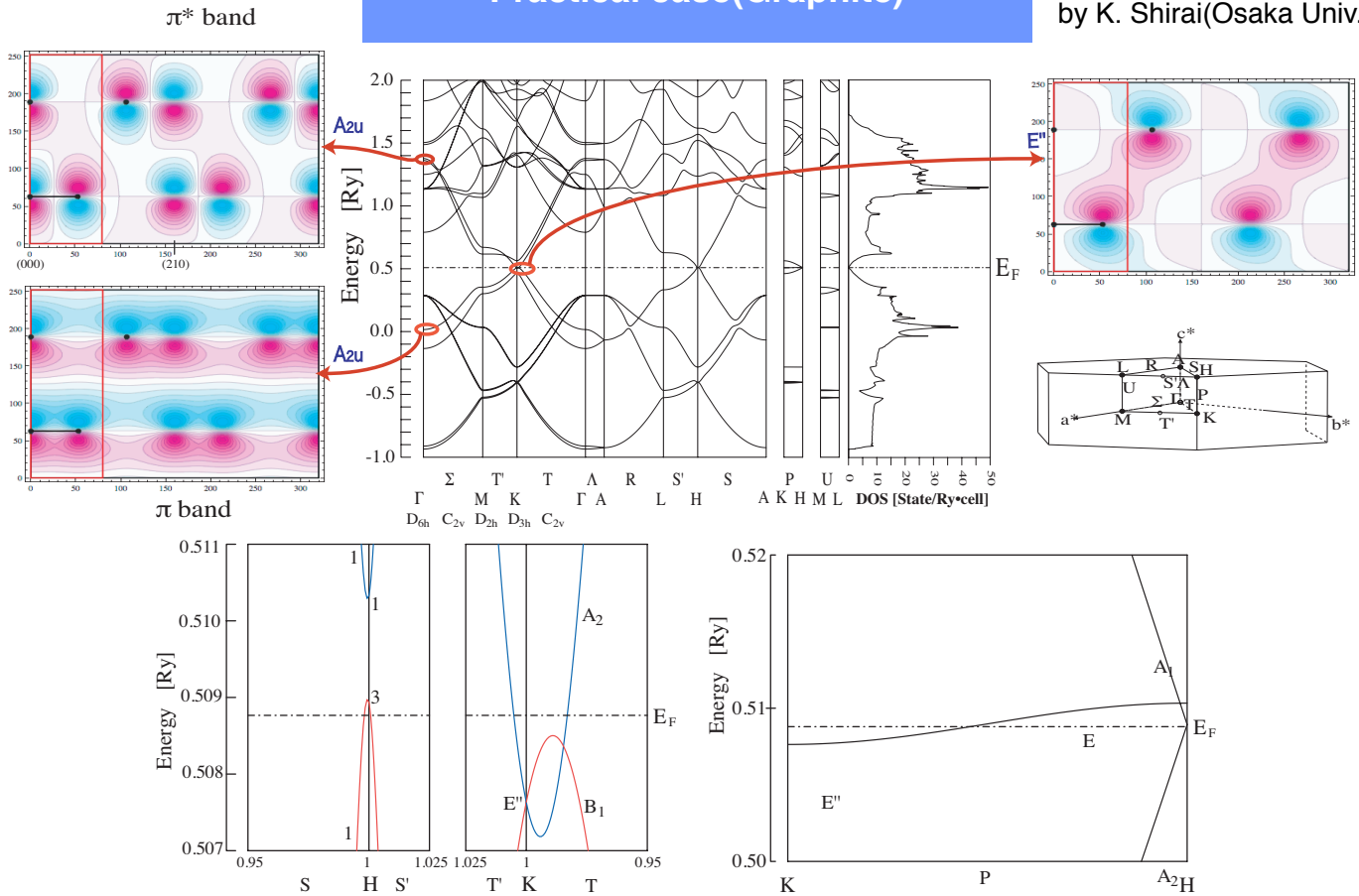


3rd Band(electron)



Practical case(Graphite)

by K. Shirai(Osaka Univ.)



Tight-binding Model

Linear Combination Atomic Orbital(LCAO) Method

(simplified LCAO)

wave function

$$\Psi_{\mathbf{k},n}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_i} \exp(i\mathbf{k} \cdot \mathbf{R}_i) \psi_n(\mathbf{r} - \mathbf{R}_i)$$

Hamiltonian Matrix Element

$$\begin{aligned} H_{n,m} &= \langle \Psi_{\mathbf{k},n}(\mathbf{r}) | \mathcal{H} | \Psi_{\mathbf{k},m}(\mathbf{r}) \rangle = \frac{1}{N} \sum_{\mathbf{R}_i} \sum_{\mathbf{R}_j} \exp\left\{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)\right\} \int \psi_n^*(\mathbf{r} - \mathbf{R}_j) \mathcal{H} \psi_m(\mathbf{r} - \mathbf{R}_i) d\mathbf{r} \\ &= \frac{1}{N} \sum_{\mathbf{R}_i, \mathbf{R}_j} \exp\left\{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)\right\} \int \psi_n^*(\mathbf{r} - \mathbf{R}_j) \mathcal{H} \psi_m(\mathbf{r} - \mathbf{R}_i) d\mathbf{r} \end{aligned}$$

Overlap Matrix Element

$$S_{n,m} = \langle \Psi_{\mathbf{k},n}(\mathbf{r}) | \Psi_{\mathbf{k},m}(\mathbf{r}) \rangle = \frac{1}{N} \sum_{\mathbf{R}_i} \sum_{\mathbf{R}_j} \exp \left\{ i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i) \right\} \int \psi_n^*(\mathbf{r} - \mathbf{R}_j) \psi_m(\mathbf{r} - \mathbf{R}_i) d\mathbf{r}$$

$$= \frac{1}{N} \sum_{\mathbf{R}_i, \mathbf{R}_j} \exp \left\{ i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i) \right\} \int \psi_n^*(\mathbf{r} - \mathbf{R}_j) \psi_m(\mathbf{r} - \mathbf{R}_i) d\mathbf{r}$$

Secular Equation

$$\sum_n \{ \mathcal{H}_{m,n}(\mathbf{k}) - \varepsilon_i S_{m,n}(\mathbf{k}) \} c_{i,n}(\mathbf{k}) = 0$$

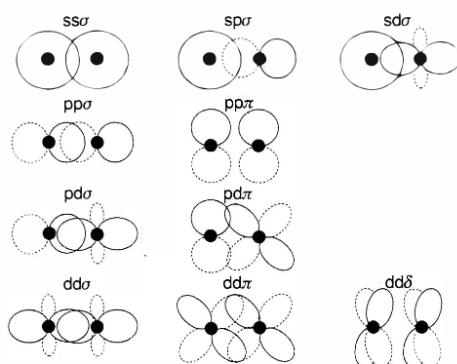
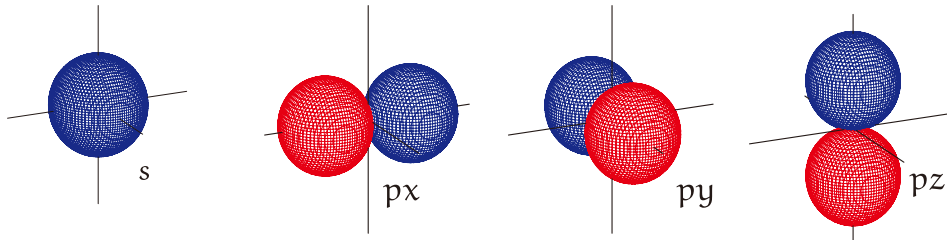
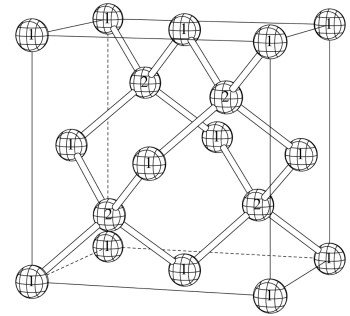


Figure 14.1. Schematic figures of local orbitals indicating all possible overlap and two-center hamiltonian matrix elements for s, p, and d orbitals, which are classified by the angular momentum about the axis with the notation σ ($m = 0$), π ($m = 1$), and δ ($m = 2$). The orbitals shown are the real combinations of the angular momentum eigenstates. Positive and negative lobes are denoted by solid and dashed lines, respectively. Note that the sign of the p orbitals must be fixed by convention; here and in Tab. 14.1 the positive p_x lobe is along the positive x -axis, *etc.*

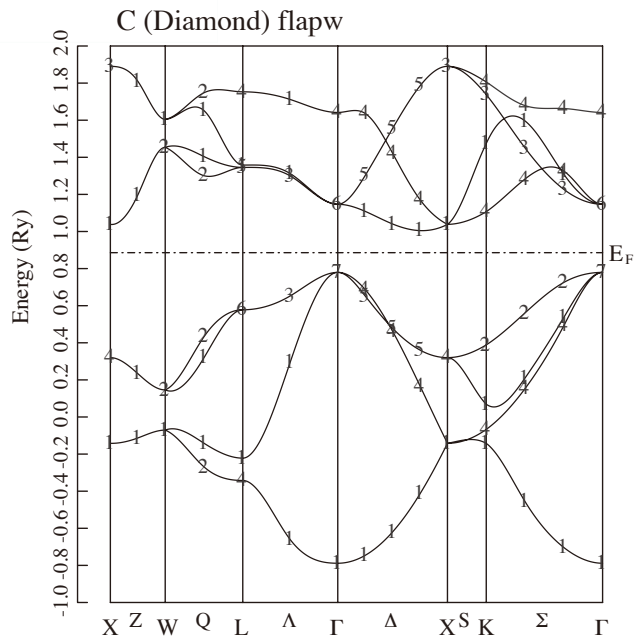
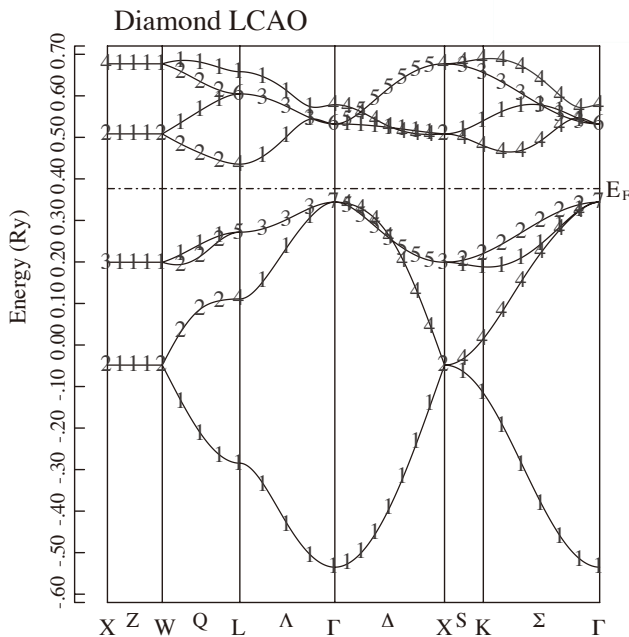
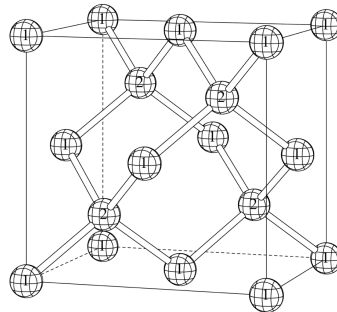
sp³ basis function

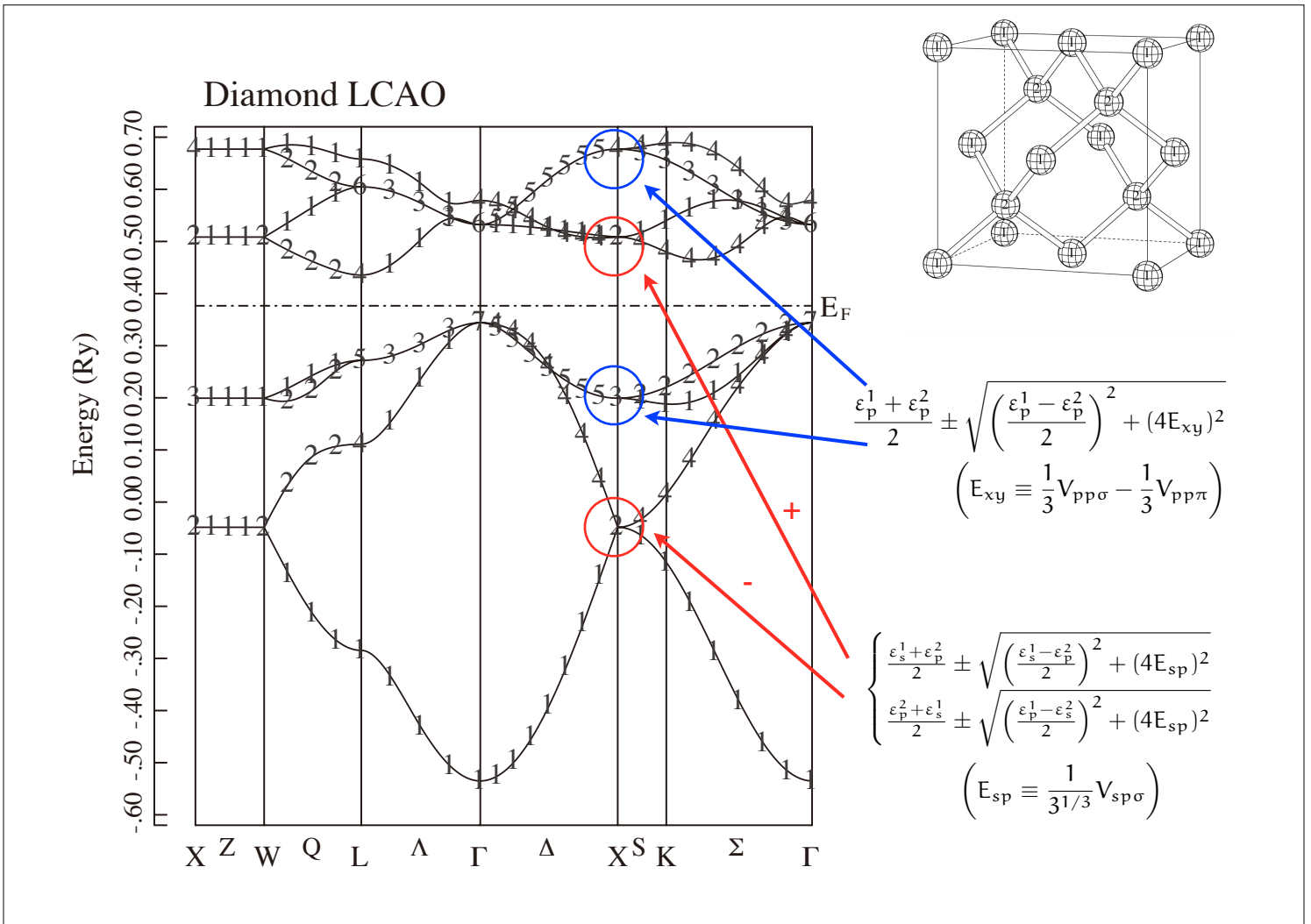
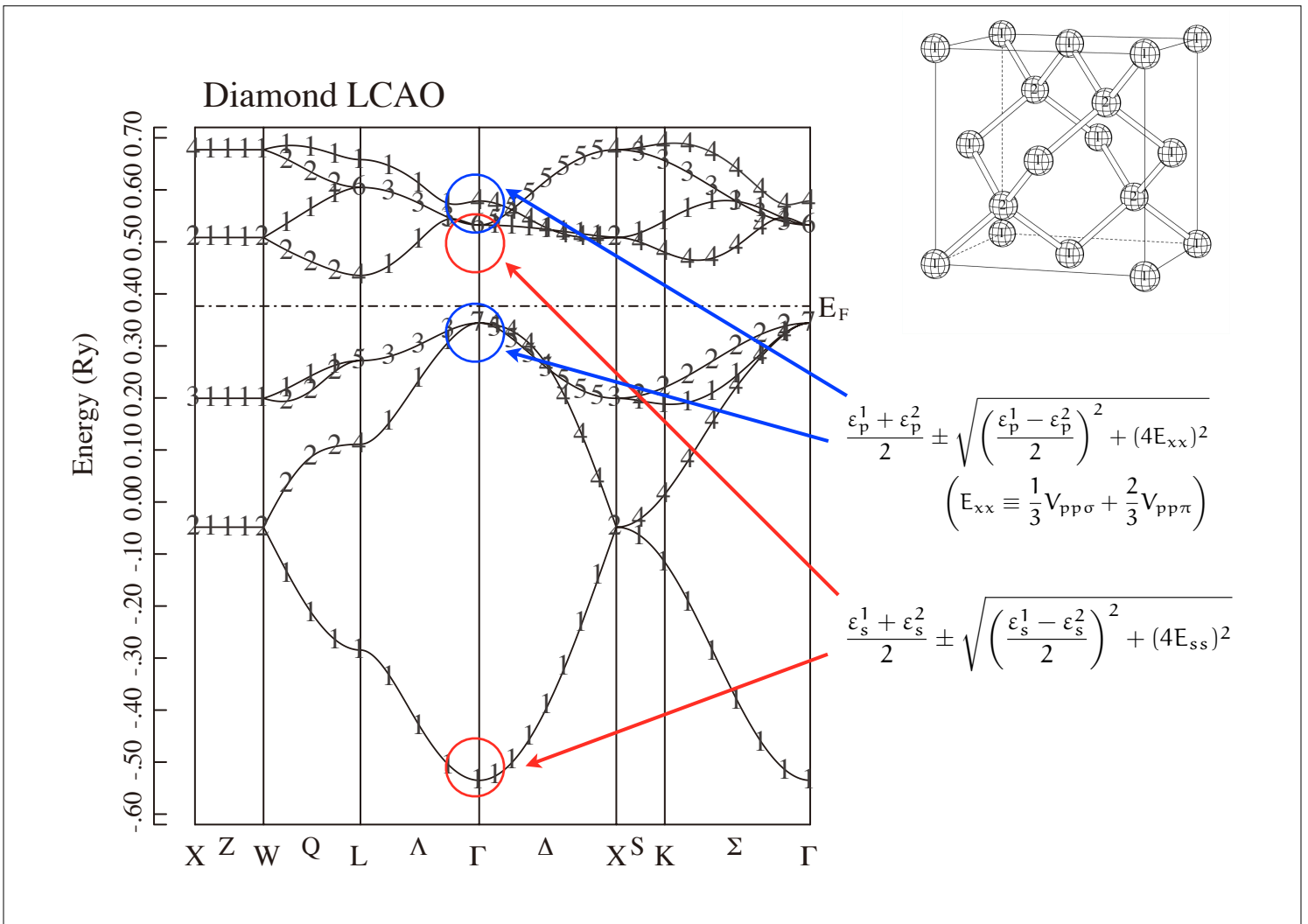


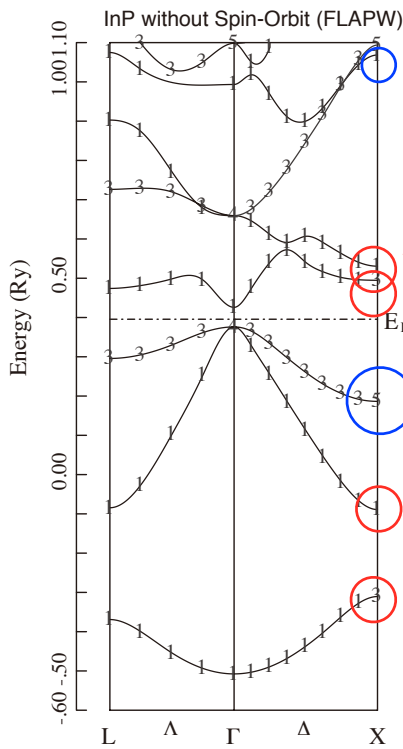
$$\begin{cases} |h_1\rangle = \frac{1}{2} \{ |s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle \} & [111] \\ |h_2\rangle = \frac{1}{2} \{ |s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle \} & [1\bar{1}\bar{1}] \\ |h_3\rangle = \frac{1}{2} \{ |s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle \} & [\bar{1}1\bar{1}] \\ |h_4\rangle = \frac{1}{2} \{ |s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle \} & [\bar{1}\bar{1}1] \end{cases}$$



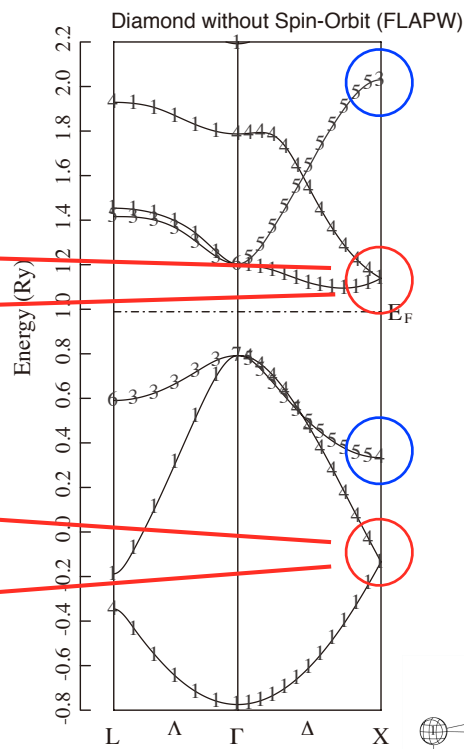
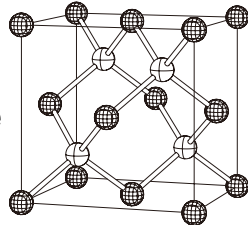
(T_d-Symmetry basis function)



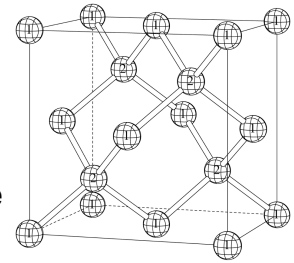




Zinc-Blende Type



Diamond Type



Using package in this lecture

space group

TSPACE99

Ab initio calculation

KANSAI2016

Local **D**ensity **A**pproximation(**LDA**) based on **D**ensity **F**unctional **T**heory(**DFT**)
 Full potential **L**inearized **A**ugmented **P**lanewave(**FLAPW**)
 include **relativistic effect (spin-orbit interaction)**

3D-picture

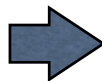
TPERSP AYPLLOT

3-dimensional graphical library ([tperisp](#))

PostScript(PS) drawing library ([ayplot](#))



yahoo!/google



“TSPACE”

Reference

English

- V. Heine ,“Group Theory in Quantum Mechanics” Dover (1964)
- M. Lax, “Symmetry Principles in Solid State and Molecular Physics” John Wiley & Sons Inc.(1974)
- H. Weyl, “The Theory of Groups and Quantum Mechanics”, Dover(1950)
- C. Kittel, “Quantum of Solid” John Wiley & Sons Inc.(1987)
- J.M. Ziman, “Principle of the Theory of Solids” Cambridge(1971)

Thanks for your attention