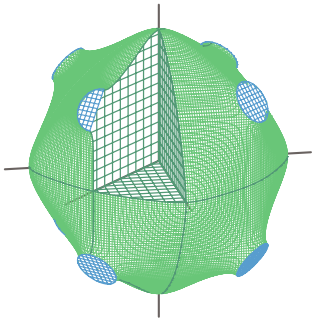
34th CMD Workshop Beginner Course Monday, 18th February 2019

Symmetry of Crystals and Electronic States



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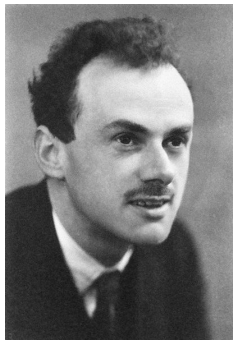
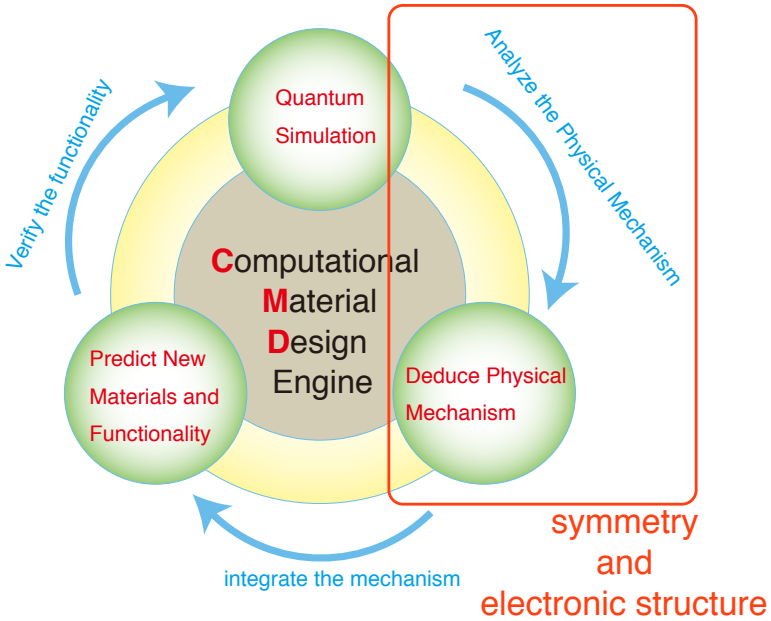
"The laws of nature should be expressed in beautiful equation."

"If there is a God, he's great mathematician"



- P. A. M. Dirac -



Kohn-Sham Equations

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

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

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

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

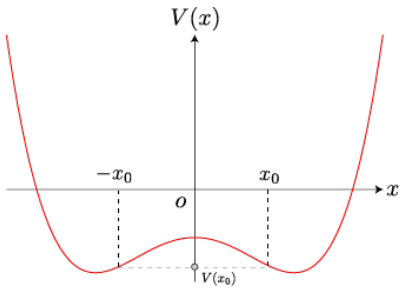
From the beginning, we consider low dimensional systems.

1Dim: Symmetric potential

Schrödinger Equation in 1dim system.

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

Eigenvalue, Eigenfunction, same eigenvalue



We assume the symmetric potential

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

$$x \to -x$$

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

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

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

Eigenvalue, Eigenfunction

- 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

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

Under the periodic condition,

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

we can solve this differential equation

solution

Eigenfunction: $u_k(x)=\exp(ikx)$ — Eigenvalue: $E_k=\frac{\hbar^2k^2}{2m}$ where $k=\frac{2n\pi}{L}$

linearly independent — $x \to -x$ — same eigenvalue

Eigenfunction: $u_k(-x)=\exp(-ikx)=u_{-k}(x)$ — Eigenvalue: $E_{-k}=\frac{\hbar^2k^2}{2m}=E_k$

degenerated system

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

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

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

Background:

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

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

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

$u(x)$ 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)

$$\begin{cases} x \to -x \\ \text{and} \\ y \to -y \end{cases} \xrightarrow[\text{operate simultaneously}]{} \text{invariant} \qquad 1 \times 1 = 1$$

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

$$\begin{cases} x \to -x \\ \text{and} \\ y \to -y \end{cases} \xrightarrow[\text{operate simultaneously}]{} \text{invariant} \qquad (-1) \times (-1) = 1$$

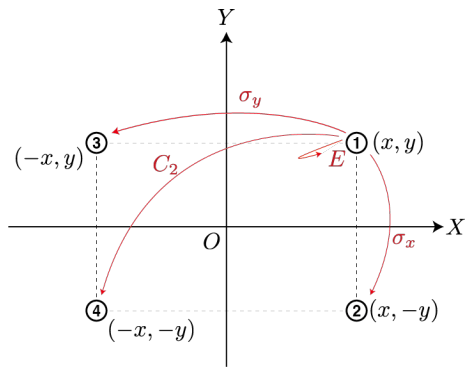
3. and 4. (odd function for x) and (even function for y)
(even function for x) and (odd function for y)

$$\begin{cases} x \to -x \\ \text{and} \\ y \to -y \end{cases} \xrightarrow[\text{operate simultaneously}]{} \text{change of sign of function}$$

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

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

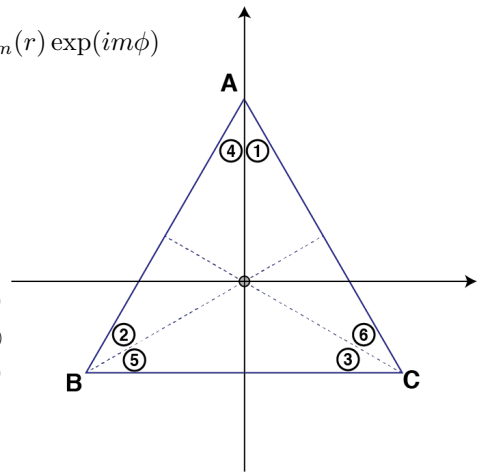
2Dim: Equilateral Triangular Symmetry (C_{3v})

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



Rotational effect for wave function($C_3^{\pm}$)

At first, we operate 2π/3 rotation for wave function,

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

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

We can classify 3 types for m

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

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

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

Similarly, for -2π/3 rotation,

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

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

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

Definition for the angle ϕ

$\mathcal{O}(\sigma_A)$ ⟷ equivalent ⟷ $\phi\to-\phi$ change the sign of ϕ

Then reflectional operations are equivalents these operations,

$$\begin{cases}\sigma_A: & \phi\to-\phi\\ \sigma_B: & \phi\to-\phi+\frac{2}{3}\pi\\ \sigma_C: & \phi\to-\phi-\frac{2}{3}\pi\end{cases}\quad\Longleftrightarrow\quad\begin{cases}\sigma_B=\sigma_A\cdot C_3^{-1}\\ \sigma_C=\sigma_A\cdot C_3\end{cases}$$

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

Relationship between the classification for m and characters of WFs

$\boxed{m=3n}$

For rotational operation($C_3^{\pm}$)

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

$$=\sum_m R_m(r)\exp(im\phi)=\Psi(r,\phi)\Rightarrow \text{invariant}$$

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, $\phi\to-\phi$

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

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

$$\cos(3n\phi)=\frac{1}{2}\{\exp(3n\phi i)+\exp(-3n\phi i)\}\xrightarrow{\phi\to-\phi}\text{invariant}$$

$$\sin(3n\phi)=\frac{1}{2i}\{\exp(3n\phi i)-\exp(-3n\phi i)\}\Rightarrow-\sin(3n\phi)$$

$\boxed{m=3n+1,3n+2}$

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

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

2-fold degeneracy

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

Summary for equilateral triangular symmetry

There are 3 types eigenfunctions.

1. Invariant for all symmetry operations($C_3^{\pm}, \sigma_A, \sigma_B, \sigma_C$) ➡ $\cos(3n\phi)$ type
2. Invariant for rotational operation and odd function for the reflectional operations($\sigma_A, \sigma_B, \sigma_C$) ➡ $\sin(3n\phi)$ 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		Point Group
Cubic	P,F,I	O_h, O, T_d, T_h, T
Tetragonal	P,I	$D_{4h}, D_4, D_{2d}, C_{4v}, C_{4h}, S_4, C_4$
Orthorhombic	P,F,I,C	D_{2h}, D_2, C_{2v}
Hexagonal	P	$D_{6h}, D_6, D_{3h}, C_{6v}, C_{6h}, C_{3h}, C_6$ $D_{3d}, D_3, C_{3v}, S_6, C_3$
Trigonal	R	$D_{3d}, D_3, C_{3v}, S_6, C_3$
Monoclinic	P,C	C_{2h}, C_S, C_2
Triclinic	P	C_i, C_1

➡ Subgroup of O_h / D_{6h}

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

symmetry Operation

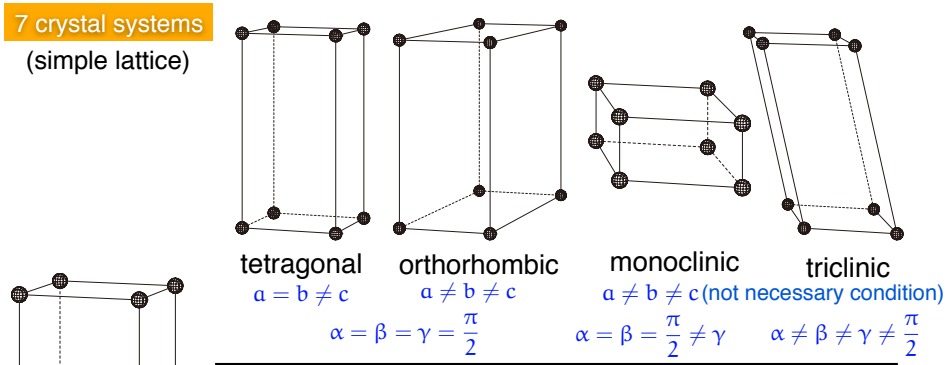
$$\left(\alpha|\vec{t}+\vec{u}_\alpha\right) = \alpha\vec{u}+\vec{t}+\vec{u}_\alpha$$

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

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

7 crystal systems

(simple lattice)



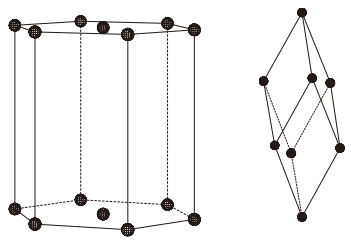
tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = \frac{\pi}{2}$

orthorhombic
$a \neq b \neq c$

monoclinic
$a \neq b \neq c$ (not necessary condition)
$\alpha = \beta = \frac{\pi}{2} \neq \gamma$

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

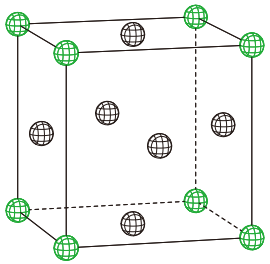
cubic
$a = b = c$
$\alpha = \beta = \gamma = \frac{\pi}{2}$



hexagonal
$a = b \neq c$

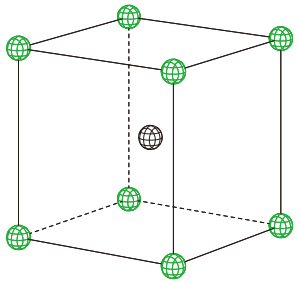
trigonal(rhombohedral)
$a = b = c$
$\alpha = \beta = \gamma$

Example(Cubic and Tetragonal)



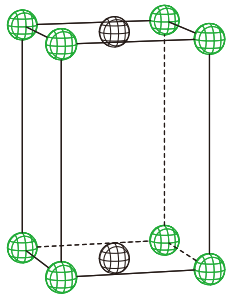
add lattice point
(F) (0,1/2,1/2) (1/2,0,1/2) (1/2,1/2,0)

Face Centered Lattice



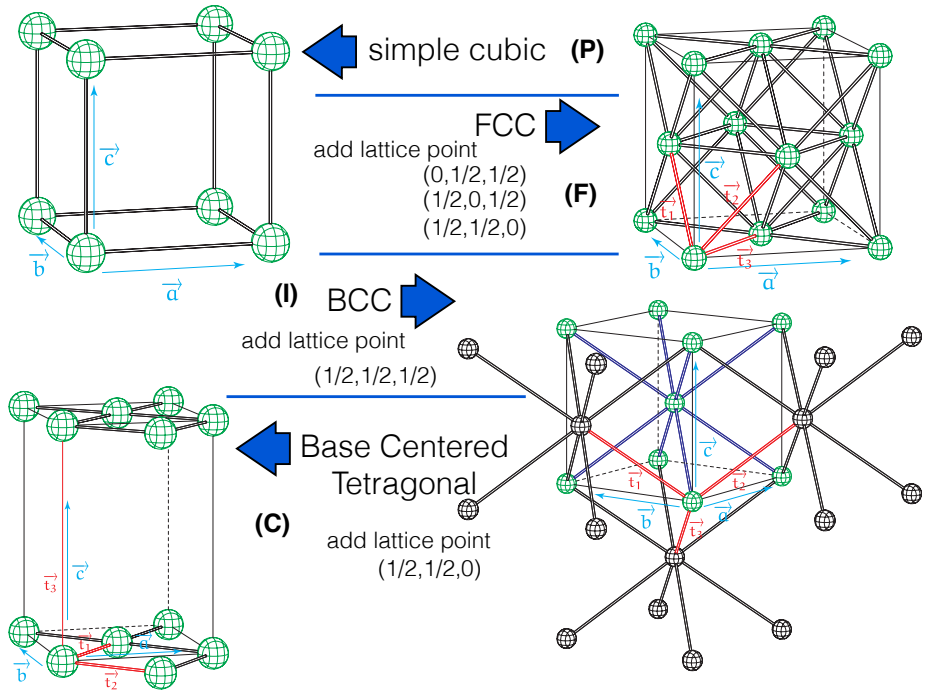
add lattice point
(I) (1/2,1/2,1/2)

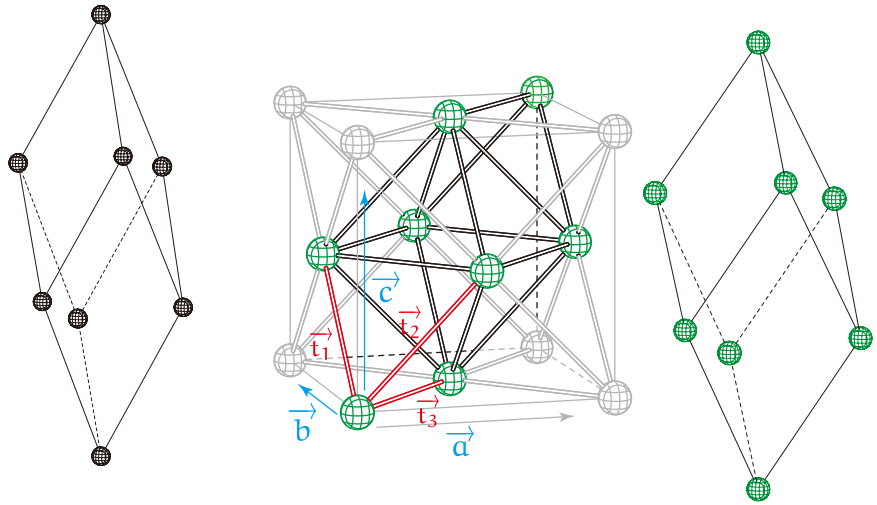
Body Centered Lattice



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

Base Centered Lattice
(c-centered)



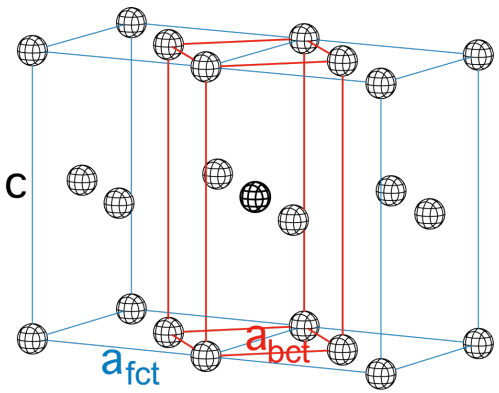


FCC is considered a form of rhombohedral

$\alpha = \beta = \gamma = \frac{\pi}{3}$

ref.) $\cos\alpha = -\frac{1}{3}$ → BCC

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		Point Group
Cubic	P,F,I	O_h, O, T_d, T_h, T
Tetragonal	P,I	$D_{4h}, D_4, D_{2d}, C_{4v}, C_{4h}, S_4, C_4$
Orthorhombic	P,F,I,C	D_{2h}, D_2, C_{2v}
Hexagonal	P	$D_{6h}, D_6, D_{3h}, C_{6v}, C_{6h}, C_{3h}, C_6$ $D_{3d}, D_3, C_{3v}, S_6, C_3$
Trigonal	R	$D_{3d}, D_3, C_{3v}, S_6, C_3$
Monoclinic	P,C	C_{2h}, C_S, C_2
Triclinic	P	C_i, C_1

Subgroup of O_h / D_{6h}

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

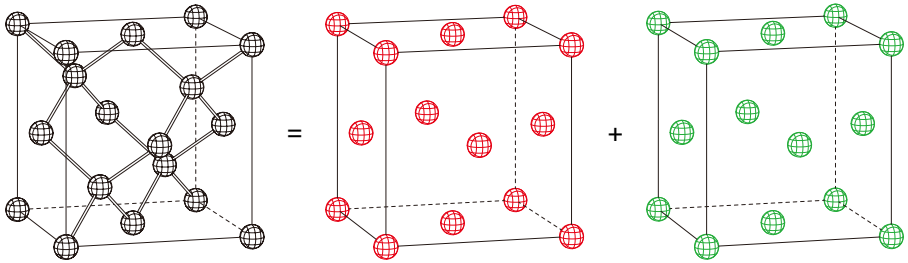
symmetry Operation

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

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

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

symmetry Operation



Diamond Structure

Symmetry operation:
(Seitz Notation)

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

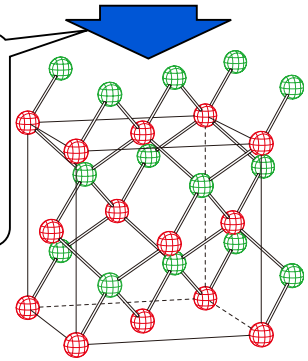
rotation (include inversion,reflection)

translation

$\frac{\pi}{2}$ rotation

+

$\begin{bmatrix}1/4\\1/4\\1/4\end{bmatrix}$ translation



Symmetry operation:
(Seitz Notation)

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

rotation (include inversion,reflection)

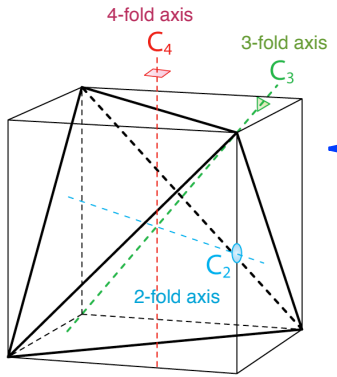
translation

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

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

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

Point Group: O_h



Cubic Symmetry O_h

$E \cdots\cdots 1$ identity operation

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

$C_2 \cdots\cdots 6$ $\pm\pi$

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

24 rotational operation

+ inversion, rotation inversion, reflection and rotational reflection

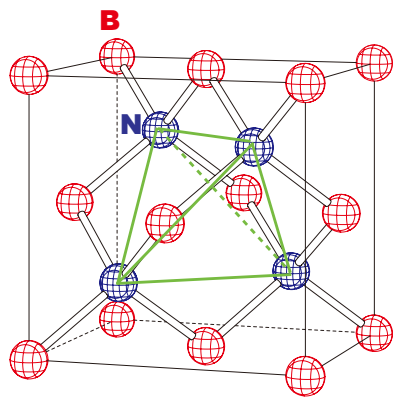
48 symmetry Operation

subgroup of O_h

example

Tetrahedral Symmetry ➡ T_d

$T_d \otimes C_4 = O_h$



tetrahedron in zincblende Structure

zincblende Structure

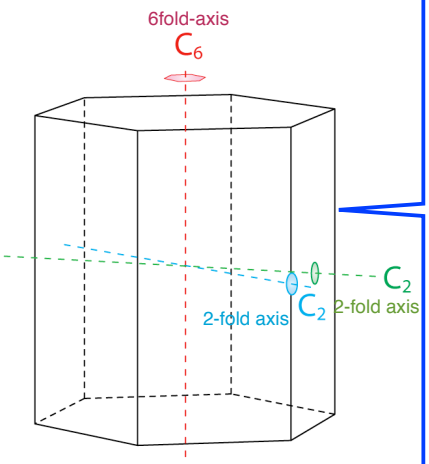
Lattice type: Face Centered

There is not 4-fold axis

Tetrahedral Symmetry ➡ T_d

Subgroup of O_h

Point Group: D_{6h}



Hexagonal Symmetry D_{6h}

$E \cdots\cdots 1$ identity operation

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

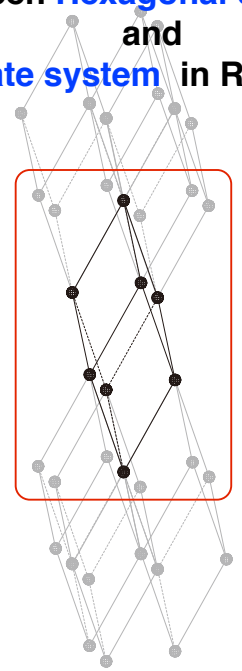
12 rotational operation
+ inversion, rotation inversion, reflection and rotational reflection

24 symmetry operation

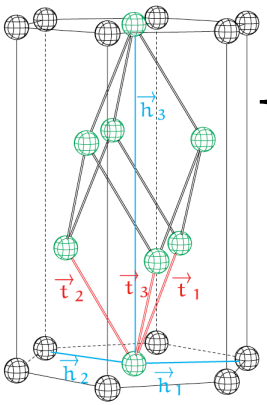
subgroup of D_{6h}

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

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

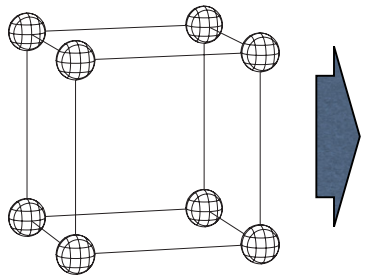
$$\vec{t}_1 = \frac{2}{3}\vec{h}_1 + \frac{1}{3}\vec{h}_2 + \frac{1}{3}\vec{h}_3$$
$$\vec{t}_2 = -\frac{1}{3}\vec{h}_1 + \frac{1}{3}\vec{h}_2 + \frac{1}{3}\vec{h}_3$$
$$\vec{t}_3 = -\frac{1}{3}\vec{h}_1 - \frac{2}{3}\vec{h}_2 + \frac{1}{3}\vec{h}_3$$

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

primitive trigonal lattice
+
add lattice point
→ Hexagonal Lattice

Magnetic case

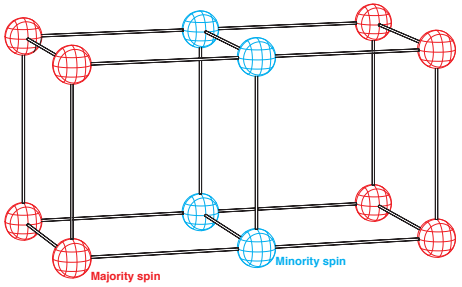
Simple Cubic Lattice (Ferromagnetic)



Cubic Lattice

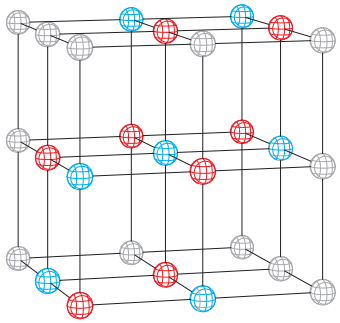
antiferromagnetic case...?

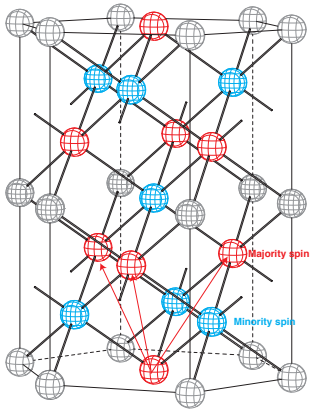
Antiferromagnetic(type1)



Anti-Ferro magnetics (type1)

Tetragonal Lattice





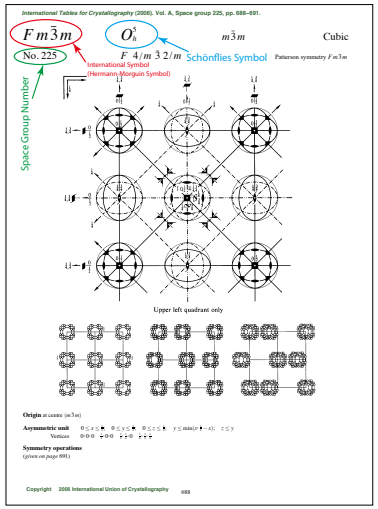
Anti-Ferro magnetics (type2)

rhombohedral Lattice

Space Group

point group
rotation(including reflection)
+
translational group

→ **space group**



International Table of Crystallography

How many kinds of space group are there?

only **230** space group

3ways to classify

- Schöenflies 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 a invariant subgroup of the translational group.

symmetry operation of space group

The operations of the space group can be given as

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

rotational operator — translation vector

The simple translation is given by

$$(\epsilon|\vec{t})\,\vec{r} = \vec{r} + \vec{t}$$

identical operation

$$(\alpha|\vec{b})r = \alpha\vec{r} + \vec{b}$$ ⇐ lattice invariant

rotational operator — translation vector

$$\left(\alpha\middle|\vec{b}\right) = \left(\alpha\middle|\vec{R_n} + \vec{b}'\right) = \left(\epsilon\middle|\vec{R_n}\right)\left(\alpha\middle|\vec{b}'\right)$$

general vector of the Bravais lattice

zero vector or not primitive translation vector

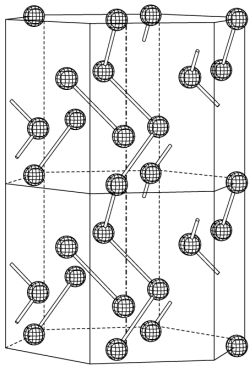
With a suitable choice of origin...

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

$$\left(\alpha\middle|\vec{b}\right) = \left(\alpha\middle|\vec{R_n}\right) = \left(\epsilon\middle|\vec{R_n}\right)\left(\alpha\middle|\vec{0}\right) \quad ?$$

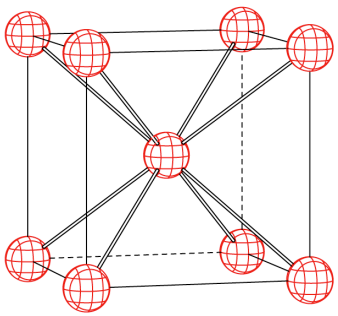
Yes ⇒ **symmorphic(共型)**

No ⇒ **non-symmorphic(非共型)**



non-symmorphic(非共型)

157(screw:らせん and glide:映進 + 2)



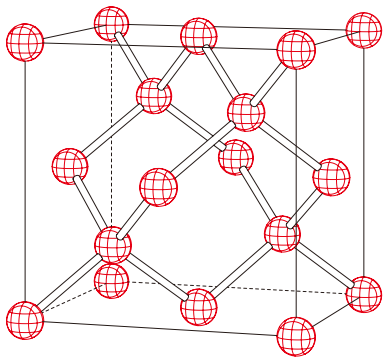
symmorphic(共型)

73 space group

In symmorphic case, most of $\left(\alpha\middle|\vec{b}'\right)$ are screw operation or glide operation

Example : non-symmorphic

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



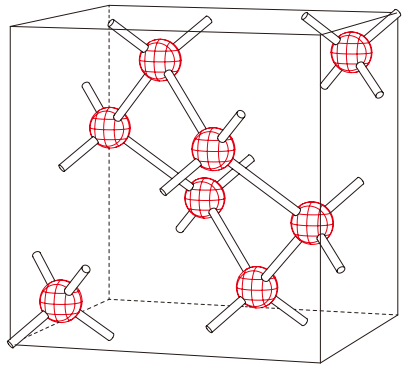
$$\left(\alpha\middle|\vec{b}'\right)$$

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

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

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

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



$$\left(\alpha\middle|\vec{b}'\right)$$

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

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

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,...

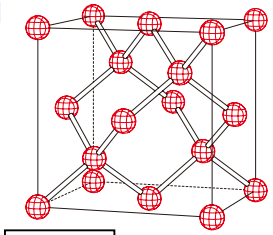
C_s^2.... 6 — unknown

(International Table of Crystallography)

How do you define the origin of Nonsymmorphic Crystal?

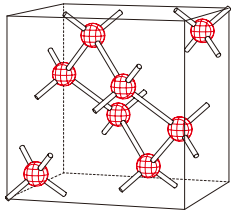
Example: diamond structure $Fd\bar{3}m(O_h^7)$

choice 1



× Inversion Center
○ atom on origin

choice 2



○ Inversion Center
× atom on origin

	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

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

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

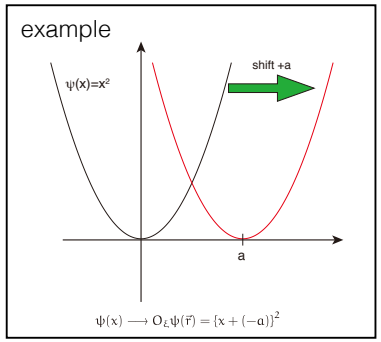
$$\underbrace{O_\xi}_{\text{operator}}\psi(\vec{r}) \equiv \psi(\underbrace{\xi^{-1}}_{\text{operation}}\vec{r})$$

multiplication

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

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

example



1-electron Schrödinger Equation

$$\underbrace{\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]}_{\text{Hamiltonian Operator}} \underbrace{\psi(\vec{r})}_{\text{Eigenfunction}} = \overset{\text{Eigenvalue}}{E}\underbrace{\psi(\vec{r})}_{\text{Eigenfunction}}$$

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

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

Born - von Karman condition

Periodicity of Potential

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

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

$$\underbrace{\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]}_{\text{Hamiltonian Operator}} \underbrace{\psi(\vec{r}-\vec{t}_n)}_{\text{Eigenfunction}} = \overset{\text{Eigenvalue}}{E}\underbrace{\psi(\vec{r}-\vec{t}_n)}_{\text{Eigenfunction}}$$

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

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

linear combination

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

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

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

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

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

If Schrödinger Equation has *p*-fold degeneracy

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

linear combination

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

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

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

Translation operators are commutable:

$$\mathcal{O}_{(\epsilon|\vec{t}_n)}\left\{\mathcal{O}_{(\epsilon|\vec{t}_m)}\psi(\vec{r})\right\} = \mathcal{O}_{(\epsilon|\vec{t}_m)}\left\{\mathcal{O}_{(\epsilon|\vec{t}_n)}\phi(\vec{r})\right\} = \mathcal{O}_{(\epsilon|\vec{t}_n+\vec{t}_m)}\phi(\vec{r})$$
$$= \psi\left(\vec{r} - (\vec{t}_n + \vec{t}_m)\right)$$

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

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

(absolute value of eigenvalue for unitary matrix = 1)

Diagonalization

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

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

therefore

Bloch Theorem

phase factor

$$O_{(\epsilon|\vec{t}_n)}\psi_{\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{t}_n}\psi_{\vec{k}}(\vec{r})$$ Bloch condition

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

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

Bloch state is characterized by $\vec{k}$

Next Theme: k-space and reciprocal lattice

Bloch function and basis set

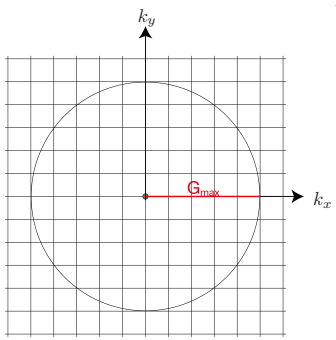
$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$$

How do we represent the periodic function?

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\underbrace{\sum\phi(\vec{r})}_{\text{basis set}}$$

e.g., planewave basis set

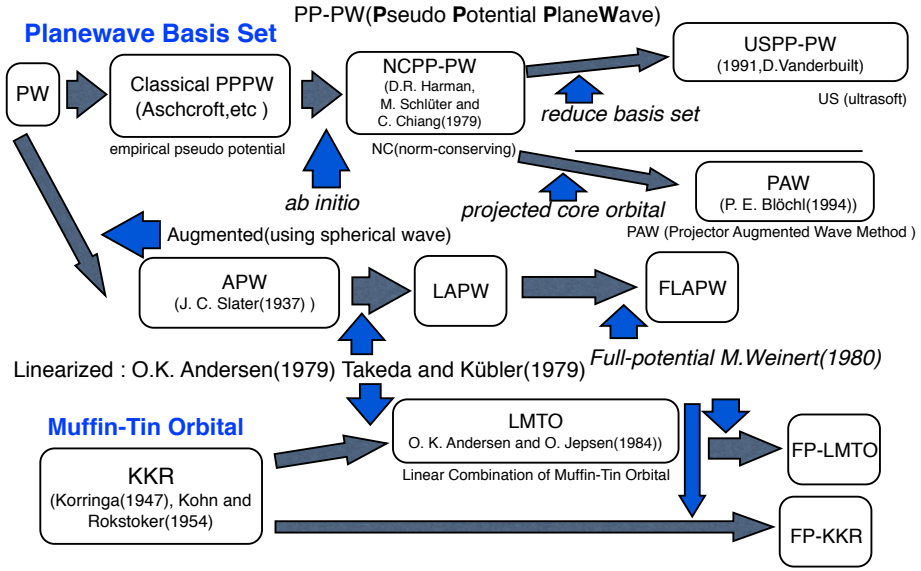
$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\sum_{\vec{G}} C_{\vec{G}}e^{i\vec{G}\cdot\vec{r}}$$



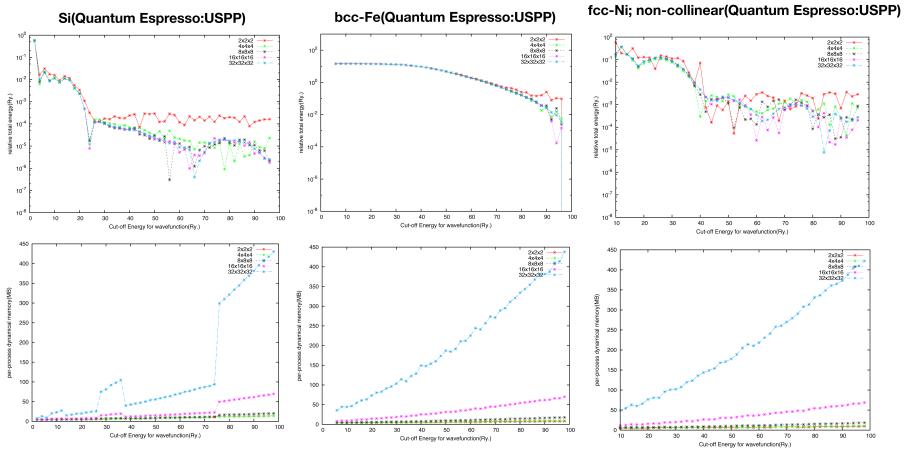
cut-off energy is defined as

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

genealogy of DFT calculation



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



Next theme

Space Group

point group
rotation(including reflection)
+
translational group

→ **space group**

↓ ? **Translational Symmetry**
Rotational Symmetry

Electronic structure

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

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

⇨ **reciprocal lattice**

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

orthogonality

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

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

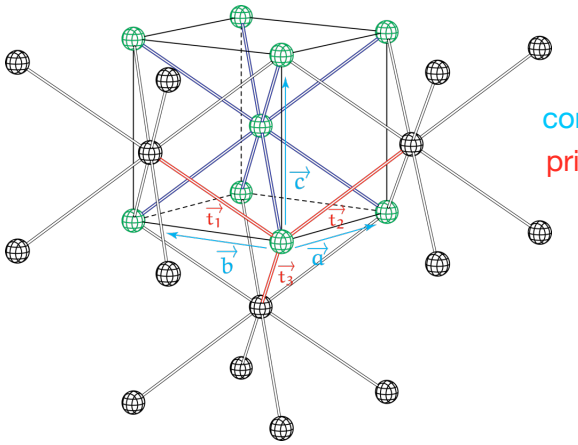
↓

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

(periodicity in k-space)

the condition of [hkl] in crystal

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



conventional lattice vector

primitive lattice vector

therefore, basis set of primitive vector is written as

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

Here, it satisfies the following condition

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

"Primitive reciprocal lattice vector" is defined as

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

where Ω is

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

In particular,

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

from similar calculation...

Primitive reciprocal lattice vector

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

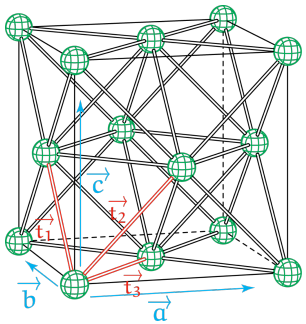
Reciprocal lattice point is defined as

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

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

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



Primitive lattice vector in FCC

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

basis set is *not orthogonal* ⇨ It is not convenient to use.

For convenience, we introduce *"Conventional reciprocal vector"*

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

where Ω_c is

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

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

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

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

Primitive reciprocal lattice vector

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

conventional reciprocal lattice vector

$$\begin{cases} \boldsymbol{a}^* = \dfrac{1}{\Omega}\,\dfrac{1}{2}\boldsymbol{a} \\ \boldsymbol{b}^* = \dfrac{1}{\Omega}\,\dfrac{1}{2}\boldsymbol{b} \\ \boldsymbol{c}^* = \dfrac{1}{\Omega}\,\dfrac{1}{2}\boldsymbol{c} \end{cases}$$

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

substitute

Reciprocal lattice point is defined as

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

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

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

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

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

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,

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

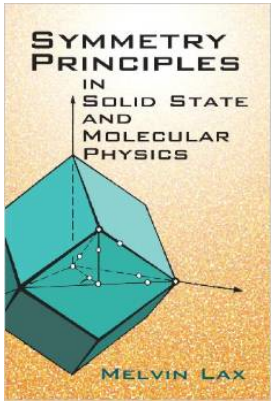
l_1, l_2 and l_3 are integer.

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

Selection rule for Reciprocal Lattice

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

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

$$V(\vec{r}) = V(\alpha^{-1}(\vec{r} - \vec{v})) \qquad \textbf{rotational symmetry}$$

rotation translation

Schrödinger Equation in crystal:

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

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

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

same eigenvalue

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

$\exp(i\alpha\vec{k}\cdot\vec{r})u_{\alpha\vec{k}}(\vec{r})$ 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.

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

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

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

compare

$\vec{k} \to \alpha\vec{k}$

Bloch Theorem

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

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)

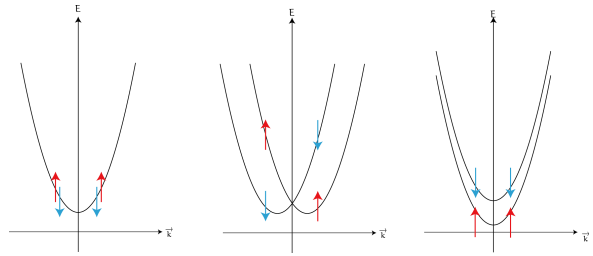
$$H_{SO} = -\frac{\hbar}{4m_0^2c^2}\boldsymbol{\sigma}\cdot\boldsymbol{p}\times(\nabla V_0)$$

space inverse operation

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

time reversal operation

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



Atomic Origin view for Spin-Orbit Interaction:

Biot-Savart Law

$$\boldsymbol{B}(\boldsymbol{r}) = -\frac{1}{4\pi\varepsilon_0c^2}\frac{\boldsymbol{r}\times(-Zq_e\boldsymbol{v})}{|\boldsymbol{r}|^3} = \frac{1}{c^2}\{\boldsymbol{E}(\boldsymbol{r})\times\boldsymbol{v}\} \qquad \left(\boldsymbol{E}(\boldsymbol{r}) = \frac{Zq_e}{4\pi\varepsilon_0r^2}\frac{\boldsymbol{r}}{r}\right)$$

Using Angular Momentum operator,

$$\boldsymbol{B}(\boldsymbol{r}) = \frac{Zq_e}{4\pi\varepsilon_0c^2}\frac{\boldsymbol{r}\times\boldsymbol{v}}{|\boldsymbol{r}|^3} = \frac{Zq_e}{4\pi\varepsilon_0c^2m_e}\frac{\boldsymbol{L}}{|\boldsymbol{r}|^3}$$

Thus magnetic interaction field operator is defined as:

$$\mathcal{H}_{\text{spin-orbit}} = -\frac{1}{2}\boldsymbol{\mu}_s\cdot\boldsymbol{B}(\boldsymbol{r}) = \frac{1}{2}\left(\frac{g_s}{\hbar}\boldsymbol{S}\right)\cdot\left(\frac{Zq_e}{4\pi\varepsilon_0c^2m_e}\frac{\boldsymbol{L}}{|\boldsymbol{r}|^3}\right)$$

Spin-Orbit Interaction

$$= \frac{Ze^2}{2m_e^2c^2}\frac{1}{r^3}\boldsymbol{S}\cdot\boldsymbol{L}$$

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

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

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

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

Spin-Orbit Interaction is rewritten as

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

where

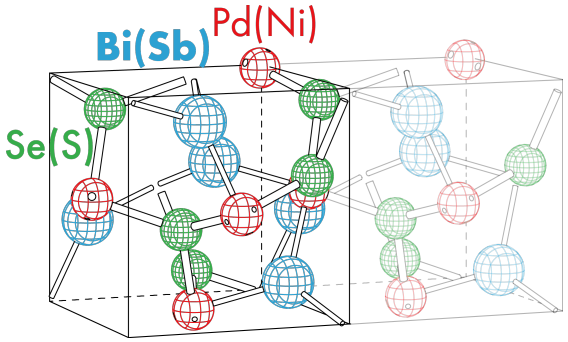
$$\xi_{n,l} = \left(\frac{Z}{a}\right)^3\frac{2}{n^3l(l+1)(2l+1)} = Z^4\alpha^2E_{Ha}\left(\frac{\mu}{m_e}\right)^3\frac{1}{n^3l(l+1)(2l+1)}$$

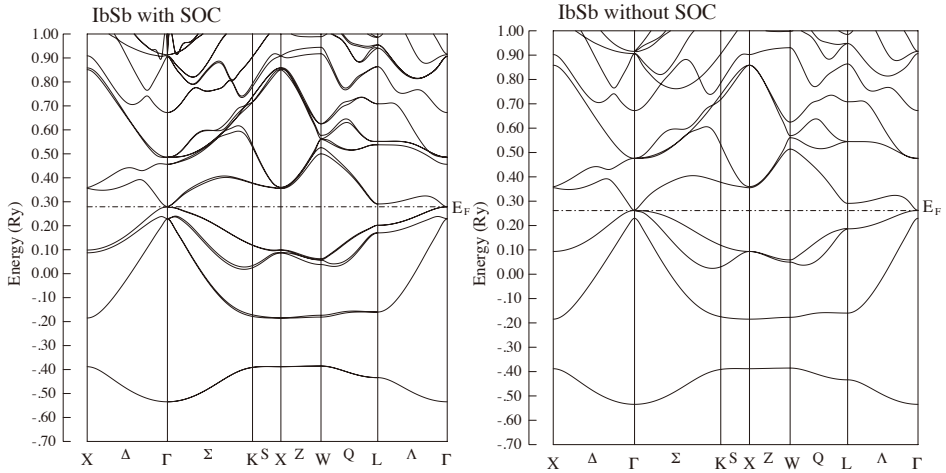
Crystal Effect Field Origin view for Spin-Orbit Interaction:

Anti-symmetric Spin-Orbit Interaction (ASOI)

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

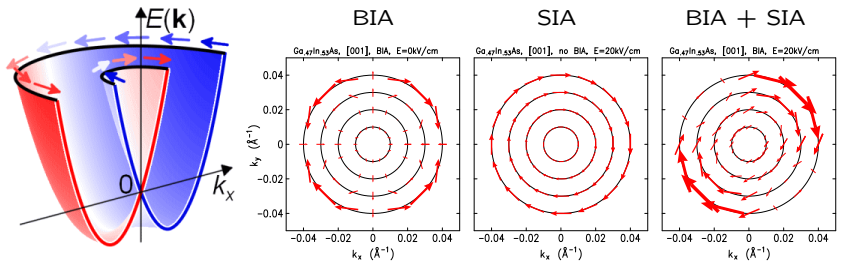
Break down to centrosymmetric in the Crystal





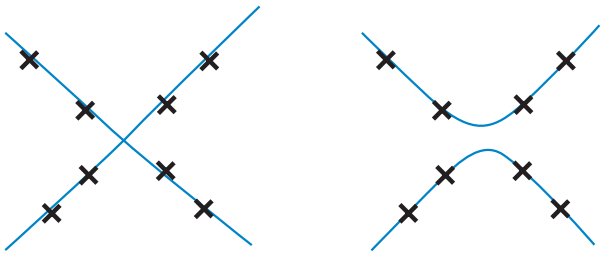
Anti-Symmetric Spin-Orbit Interaction(ASOI)

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



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

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

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

1-electron Schrödinger Equation

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

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

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

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

1-electron Schrödinger Equation

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

$$\Leftrightarrow \quad -\frac{\hbar^2}{2m}\vec{\nabla}^2\left\{\sum_{\vec{g_l}} C_{\vec{g_l}} e^{i(\vec{k}-\vec{g_l})\cdot\vec{r}}\right\} = E\left\{\sum_{\vec{g_l}} C_{\vec{g_l}} e^{i(\vec{k}-\vec{g_l})\cdot\vec{r}}\right\}$$

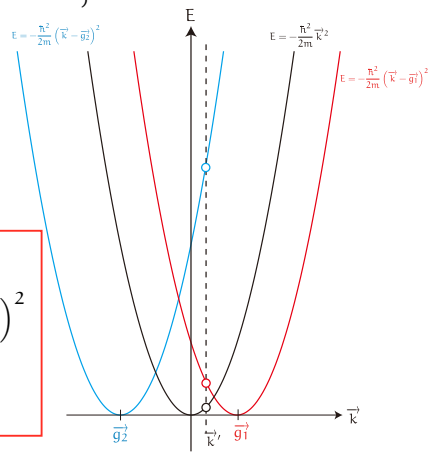
$$\Leftrightarrow \quad \sum_{\vec{g_l}}\left\{\frac{\hbar^2}{2m}(\vec{k}-\vec{g_l})^2 e^{i(\vec{k}-\vec{g_l})\cdot\vec{r}}\cdot C_{\vec{g_l}}\right\} = \left\{\sum_{\vec{g_l}} E_{\vec{k}} C_{\vec{g_l}} e^{i(\vec{k}-\vec{g_l})\cdot\vec{r}}\right\}$$

$$\Leftrightarrow \quad \sum_{\vec{g_l}}\left[\left\{\frac{\hbar^2}{2m}(\vec{k}-\vec{g_l})^2 - E_{\vec{k}}\right\} e^{i(\vec{k}-\vec{g_l})\cdot\vec{r}}\cdot C_{\vec{g_l}}\right] = 0$$

$\equiv E(\vec{k}-\vec{g_l})$

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

Superposition of plane waves



at $\vec{k}$

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

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

Nearly Free electron model (NFE)

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

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

Potential can be represented as Fourier series

$$V(\vec{r}) = \sum_{\vec{g_l}} V_{\vec{g_l}} e^{i\vec{g_l}\cdot\vec{r}} \qquad \left(V_{\vec{g_l}} = \frac{1}{\Omega_c}\iiint_{\Omega_c} e^{-i\vec{g_l}\cdot\vec{r}}V(\vec{r})dV\right)$$

Fourier Component of $\vec{g_l}$

Hamiltonian Matrix element(2-wave approximation)

$$\mathcal{H} = \begin{pmatrix} \varepsilon_{\vec{k}} + \langle\vec{k}|V|\vec{k}\rangle & V_{\vec{g_l}} \\ V^*_{\vec{g_l}} & \varepsilon_{\vec{k}+\vec{g_l}} + \langle\vec{k}+\vec{g_l}|V|\vec{k}+\vec{g_l}\rangle \quad V_{\vec{g_l}} \end{pmatrix}$$

where

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

Here

$$\left\langle \vec{k} \middle| V \middle| \vec{k} \right\rangle = \left\langle \vec{k}+\vec{g_l} \middle| V \middle| \vec{k}+\vec{g_l} \right\rangle \equiv V_{\vec{k}}$$

Eigenenergy

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

Free electron Model

Cubic Lattice case

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

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

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

$$\vec{g_k} = \frac{2\pi}{\Omega_c}\left(\vec{t}_i \times \vec{t}_j\right) = \frac{2\pi}{a^3}\vec{t}_k$$

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

Eigenenergy

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

to convenient Energy unit $\frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2$

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

Eigenenergy

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

Eigenfunction

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

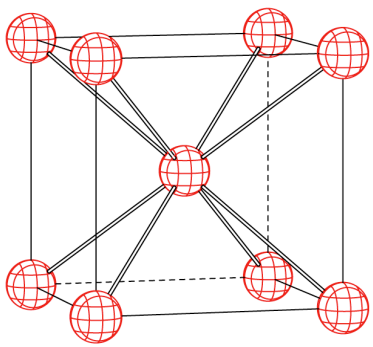
Li^{3} bcc
Na^{11} bcc
K^{19} bcc
Rb^{37} bcc
Cs^{55} bcc
Fr^{87} bcc

Alkali Metals

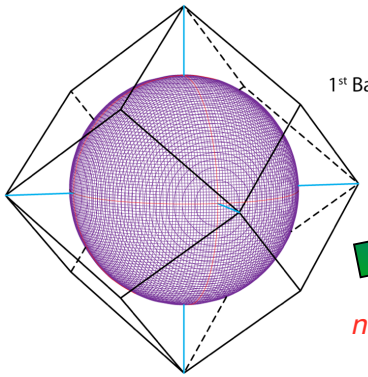
the **b**ody **c**entered **c**ubic (**bcc**)

space group

$Im\bar{3}m$ (O_h^9)



Fermi Surface of Na



1st Band(hole)

nearly free electron

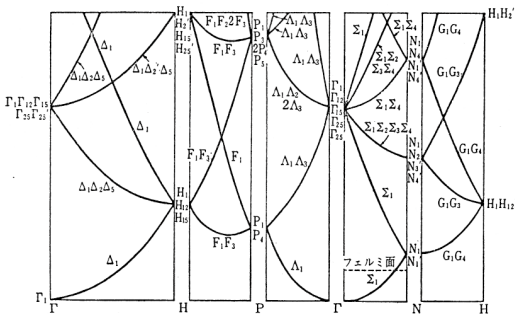
free electron

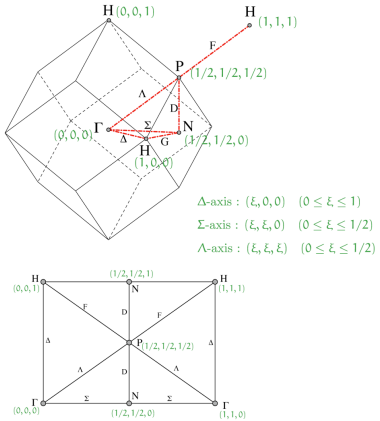
$$\frac{\hbar^2 k_F^2}{2m} = E_F \quad \Leftrightarrow \quad k_x^2 + k_y^2 + k_z^2 = \frac{2mE_F}{\hbar^2}$$

Fermi surface is *"sphere"* in shape.

It is called *"fermi sphere"*

bcc free electron

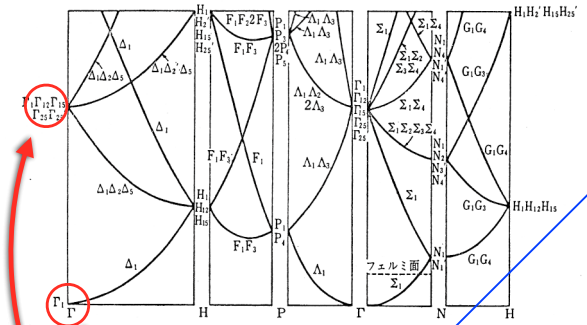


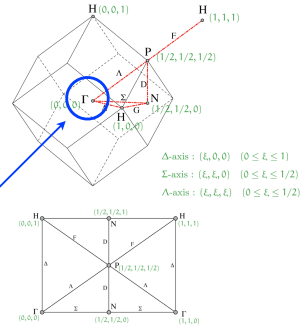


$$E(\vec{g_l}) = E(\vec{k} - \vec{g_l}) = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_3)^2 \qquad \left(\vec{k} = \frac{2\pi}{a}\begin{bmatrix}\xi\\ \eta\\ \zeta\end{bmatrix},\ \vec{g_l} = \frac{2\pi}{a}\begin{bmatrix}n_1\\ n_2\\ n_3\end{bmatrix}\right)$$

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

bcc free electron



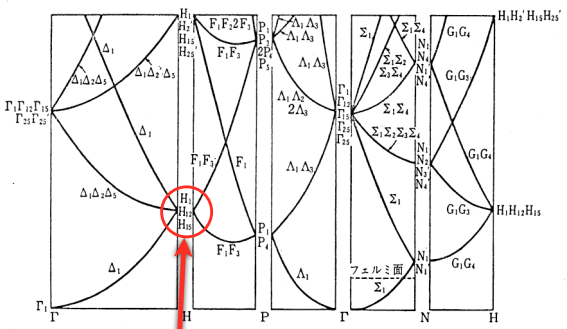


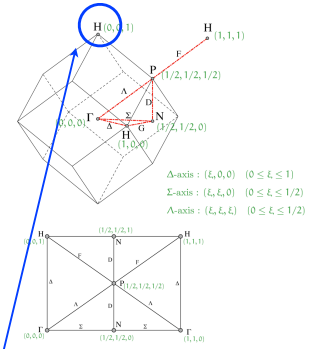
$$E(\vec{g_l}) = E(\vec{k} - \vec{g_l}) = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_1)^2 \qquad \left(\vec{k} = \frac{2\pi}{a}\begin{bmatrix}\xi\\ \eta\\ \zeta\end{bmatrix},\ \vec{g_l} = \frac{2\pi}{a}\begin{bmatrix}n_1\\ n_2\\ n_3\end{bmatrix}\right)$$

$$E = 0; \qquad \vec{k} = \frac{2\pi}{a}\begin{bmatrix}0\\0\\0\end{bmatrix},\ \vec{g_l} = \frac{2\pi}{a}\begin{bmatrix}0\\0\\0\end{bmatrix}$$

$$E = 2; \qquad \vec{k} = \frac{2\pi}{a}\begin{bmatrix}0\\0\\0\end{bmatrix},\ \vec{g_l} = \left\{\frac{2\pi}{a}\begin{bmatrix}0\\ \pm1\\ \pm1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}\pm1\\ 0\\ \pm1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}\pm1\\ \pm1\\ 0\end{bmatrix}\right\}$$

bcc free electron



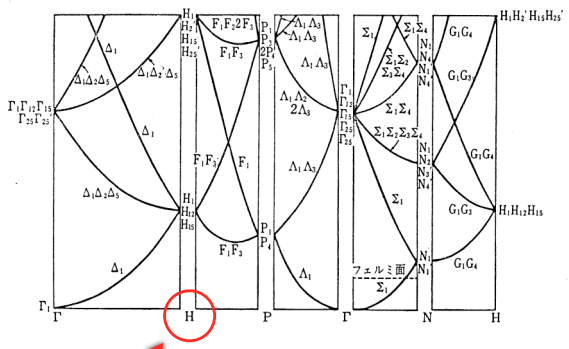


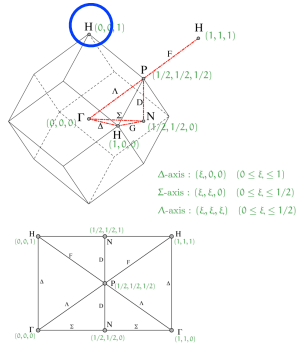
$$E(\vec{g_l}) = E(\vec{k} - \vec{g_l}) = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_3)^2 \qquad \left(\vec{k} = \frac{2\pi}{a}\begin{bmatrix}\xi\\ \eta\\ \zeta\end{bmatrix},\ \vec{g_l} = \frac{2\pi}{a}\begin{bmatrix}n_1\\ n_2\\ n_3\end{bmatrix}\right)$$

$$E(H) = n_1^2 + n_2^2 + (n_3 - 1)^2 \qquad \left(\vec{k} = \frac{2\pi}{a}\begin{bmatrix}0\\0\\1\end{bmatrix}\right)$$

$$E = 1; \qquad \vec{g_l} = \left\{\frac{2\pi}{a}\begin{bmatrix}0\\ \pm1\\ 1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}\pm1\\ 0\\ 1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}0\\0\\0\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}0\\0\\2\end{bmatrix}\right\}$$

bcc free electron





wavefunction is given as

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

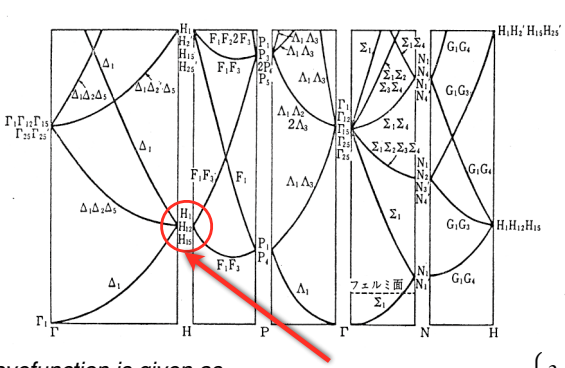
at H,

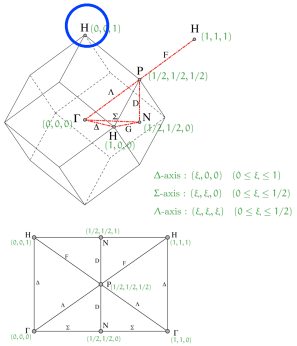
$$\xi = \eta = 0,\ \zeta = 1$$

therefore

$$\psi_H(\vec{r}) = \exp\left(\frac{2\pi i}{a}z\right) \times \exp\left\{-\frac{2\pi i}{a}(n_1 x + n_2 y + n_3 z)\right\} \qquad \left(\vec{K}_n = \frac{2\pi}{a}\begin{bmatrix}n_1\\ n_2\\ n_3\end{bmatrix}\right)$$

bcc free electron





wavefunction is given as

$E = 1;$ $\quad \vec{K}_n = \left\{ \frac{2\pi}{a}\begin{bmatrix}0\\\pm1\\1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}\pm1\\0\\1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}0\\0\\0\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}0\\0\\2\end{bmatrix} \right\}$

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

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

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

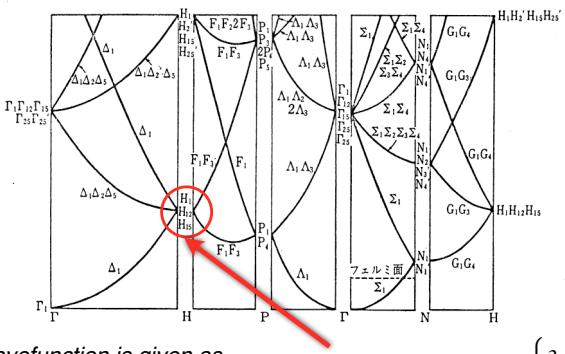
In generally, p-fold degenerate states,

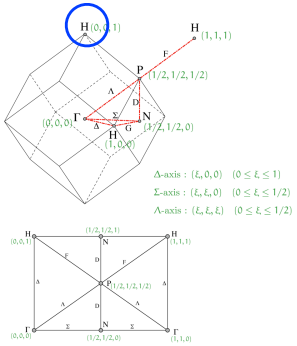
$$\{\psi_1(\vec{r}), \psi_2(\vec{r}), \cdots, \psi_j(\vec{r}), \cdots \psi_p(\vec{r})\} \Rightarrow \underbrace{\{\phi_1(\vec{r}), \phi_2(\vec{r}), \cdots, \phi_j(\vec{r}), \cdots \phi_p(\vec{r})\}}_{\text{generated by linear combination } \psi_1(\vec{r}), \psi_2(\vec{r}), \cdots, \psi_j(\vec{r}), \cdots \psi_p(\vec{r})}$$

→ planewave type symmetrization → APW,OPW

→ linear combination atomic orbital type symmetrization

bcc free electron





wavefunction is given as

$E = 1;$ $\quad \vec{K}_n = \left\{ \frac{2\pi}{a}\begin{bmatrix}0\\\pm1\\1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}\pm1\\0\\1\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}0\\0\\0\end{bmatrix}, \frac{2\pi}{a}\begin{bmatrix}0\\0\\2\end{bmatrix} \right\}$

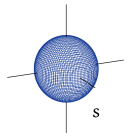
$$\psi_H(\vec{r}) = \begin{cases} \exp\left(\pm\frac{2\pi}{a}x\right) \\ \exp\left(\pm\frac{2\pi}{a}y\right) \\ \exp\left(\pm\frac{2\pi}{a}z\right) \end{cases}$$

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

→ Symmetrization

at H (energy E=1)

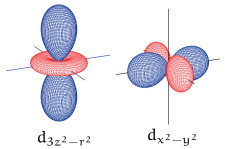
$$H_1 = \cos\left(\frac{2\pi}{a}x\right) + \cos\left(\frac{2\pi}{a}y\right) + \cos\left(\frac{2\pi}{a}z\right) \quad \text{(s-type)}$$

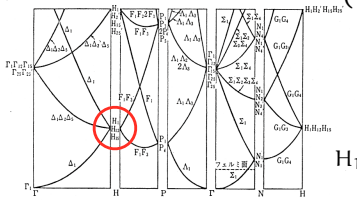


$$\psi_H(\vec{r}) = \begin{cases} \exp\left(\pm\frac{2\pi}{a}x\right) \\ \exp\left(\pm\frac{2\pi}{a}y\right) \\ \exp\left(\pm\frac{2\pi}{a}z\right) \end{cases}$$

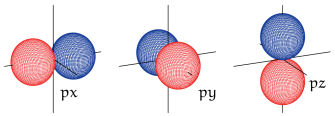
change basis set

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

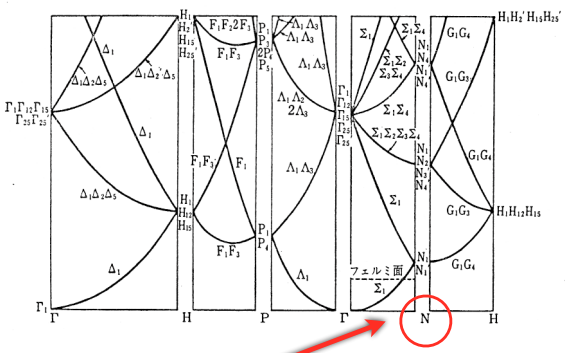


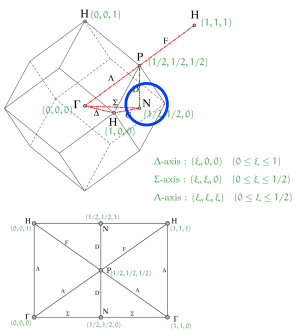


$$H_{15} = \begin{cases} \sin\left(\frac{2\pi}{a}x\right) \\ \sin\left(\frac{2\pi}{a}y\right) \\ \sin\left(\frac{2\pi}{a}z\right) \end{cases} \quad (p-\text{type})$$



bcc free electron



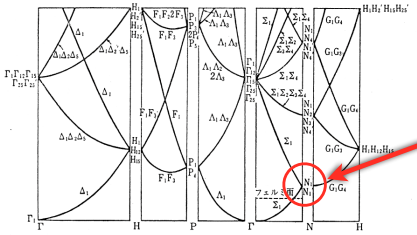


wavefunction is given as

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)

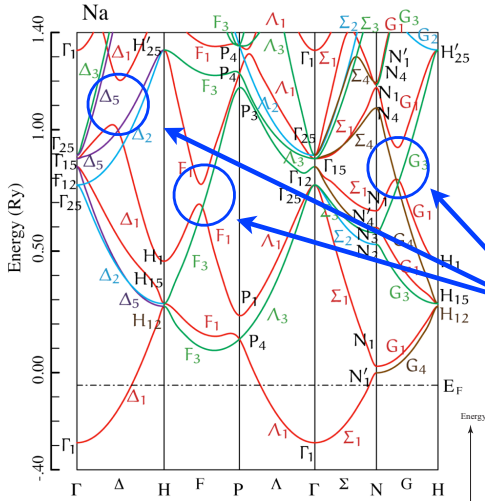
$$\vec{K}_n = \left\{\frac{2\pi}{a}\begin{bmatrix}0\\0\\0\end{bmatrix},\ \frac{2\pi}{a}\begin{bmatrix}1\\1\\0\end{bmatrix}\right\}$$

change basis set

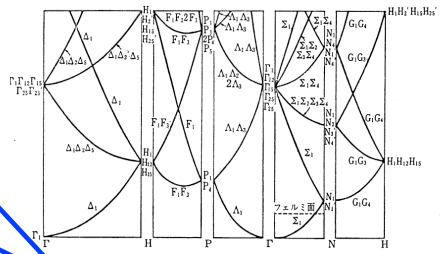
$$\psi_N(\vec{r}) = \exp\left\{\pm\frac{2\pi i}{a}(x+y)\right\}$$

$$N_1 = \cos\left\{\frac{2\pi i}{a}(x+y)\right\} \quad \text{(s-type)}$$

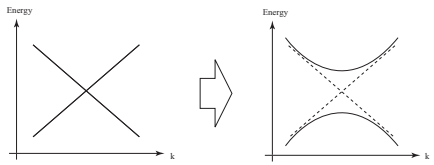
$$N_1' = \sin\left\{\frac{2\pi i}{a}(x-y)\right\} \quad \text{(p-type)}$$

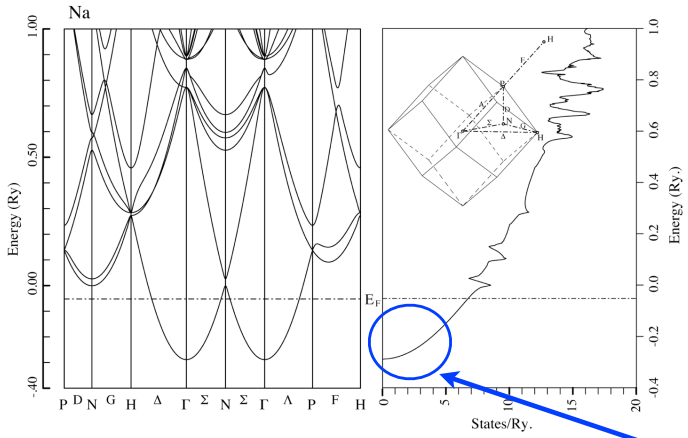


free electron



non-crossing rule





Density of State (free electron)

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

Free electron Model

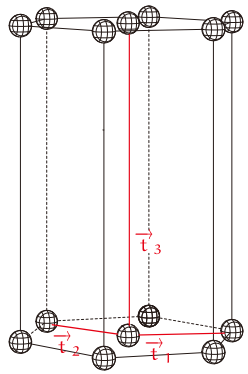
Hexagonal Lattice case

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

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

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

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



Eigenenergy

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

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

Alkaline Earth Metals

hexagonal **c**losed **p**ackage (**hcp**)

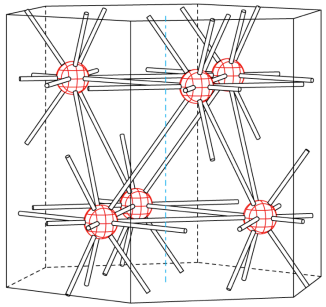
space group

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

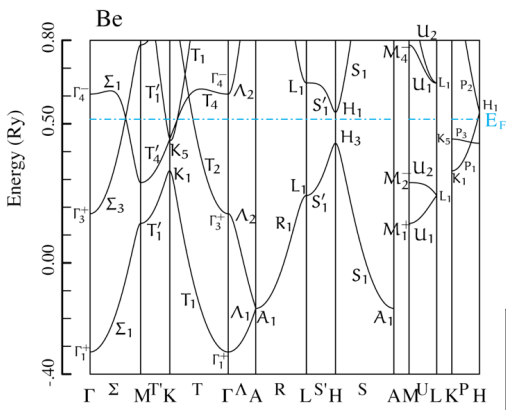
c/a(Be) = 1.585
c/a(Mg) = 1.625

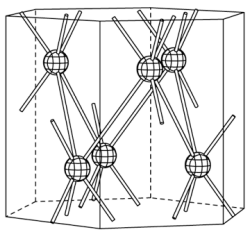
2atom/unit cell

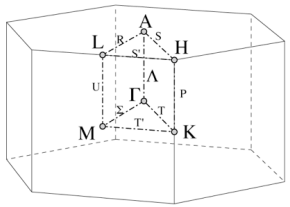
same space group,
but distortional hcp



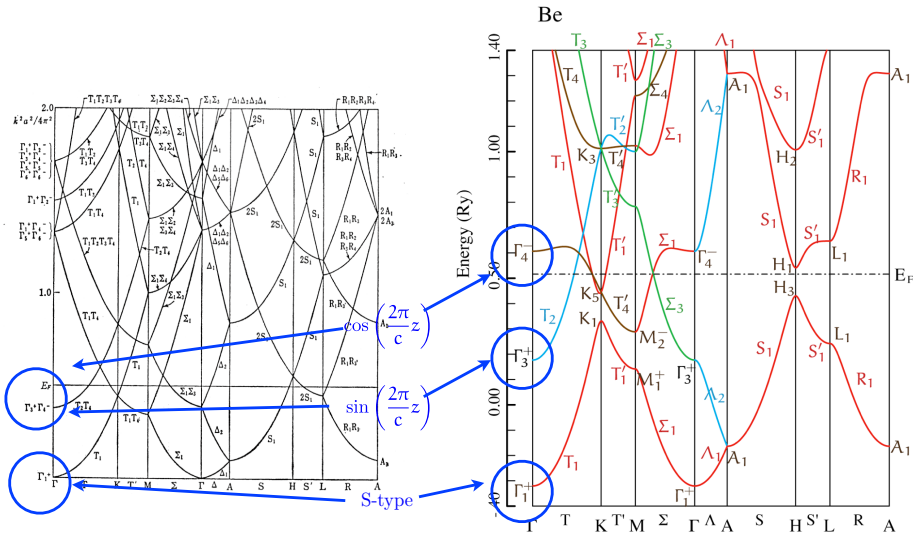
*ideal **hcp** lattice* $c/a = \sqrt{\frac{8}{3}} \simeq 1.6330$



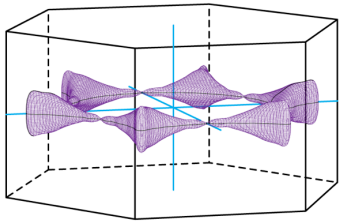




free electron band and Be band

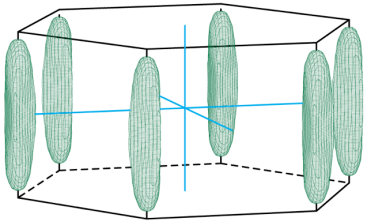


Fermi Surface of Be



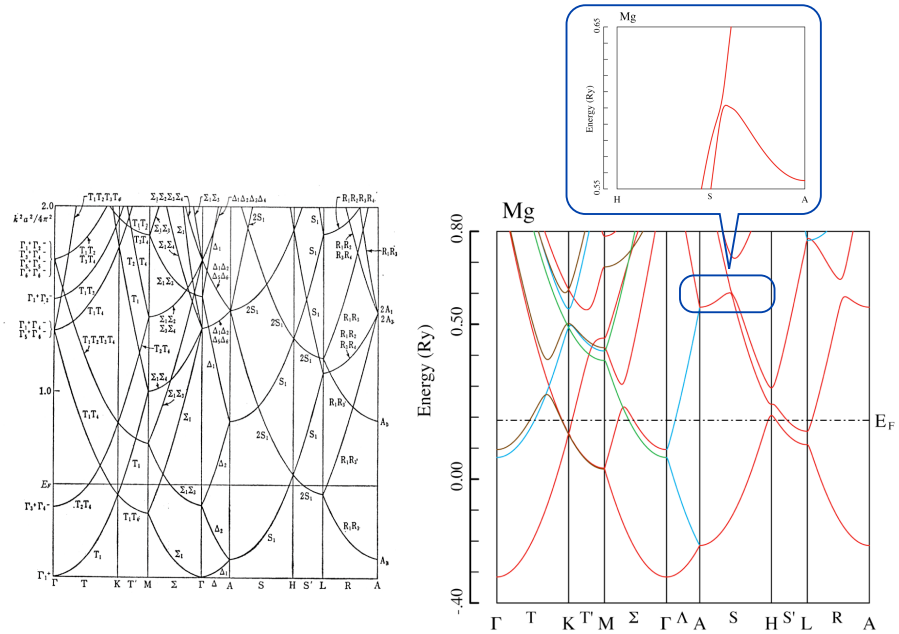
2nd Band(hole)

"Crown"

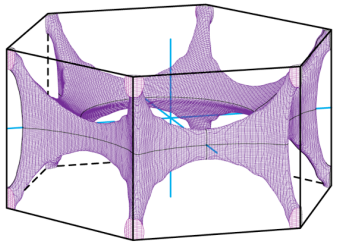


3rd Band(electron)

"Ciger"

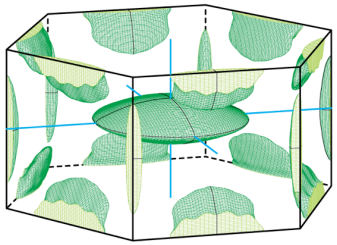


Fermi Surface of Mg

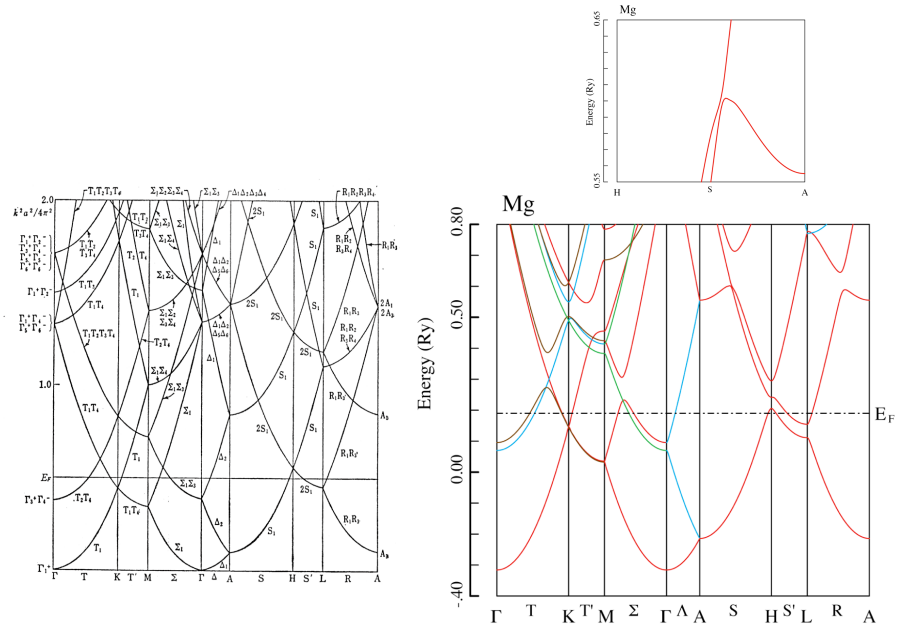


2nd Band(hole)

"Monster"

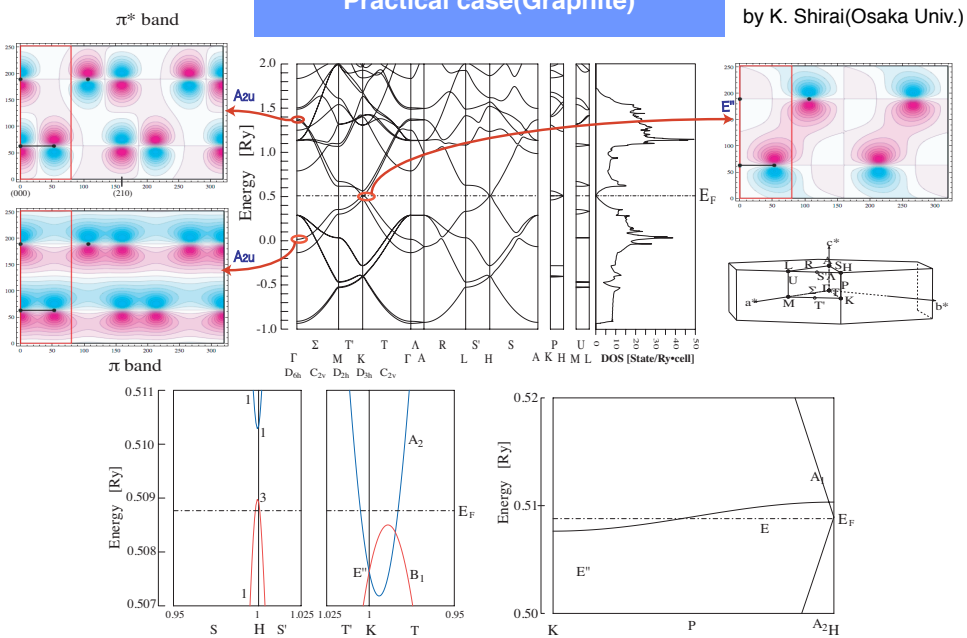


3rd Band(electron)



Practical case(Graphite)

by K. Shirai(Osaka Univ.)



Tight-binding Model

Linear **C**ombination **A**tomic **O**rbital(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

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

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

J. C. Slater and G. F. Koster , Phys. Rev. **94** p.1948(1954)

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

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

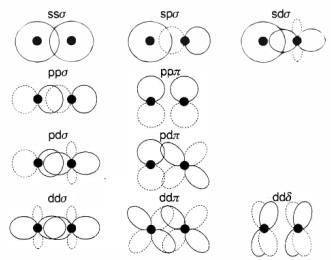
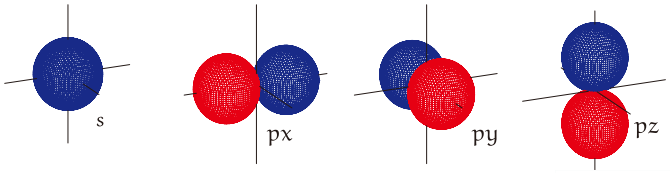
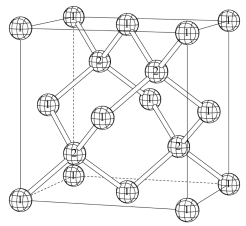


Figure 14.1. Schematic figures of local orbitals indicating all possible overlap and two-center hamiltonian matrix elements for s, p, and d orbitals, which are classified by the angular momentum about the axis with the notation σ ($m = 0$), π ($m = 1$), and δ ($m = 2$). The orbitals shown are the real 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.*

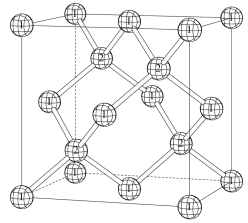
sp³ basis function

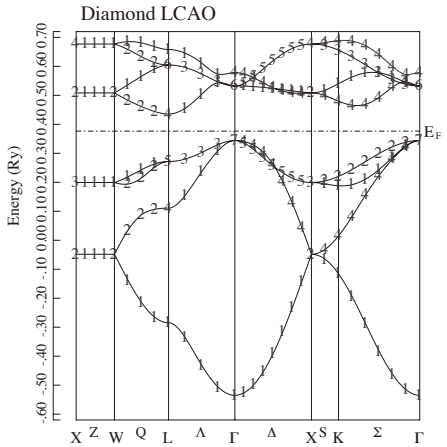


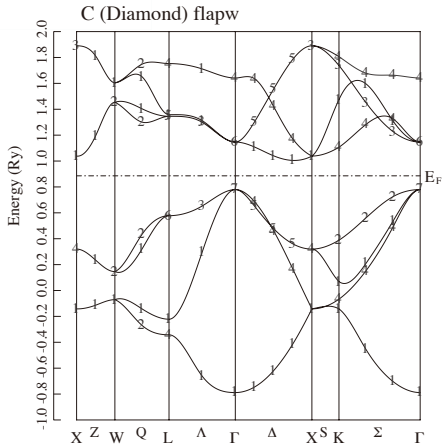
$$\begin{cases} |h_1\rangle = \frac{1}{2}\{|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle\} & [111] \\ |h_2\rangle = \frac{1}{2}\{|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle\} & [1\bar{1}\bar{1}] \\ |h_3\rangle = \frac{1}{2}\{|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle\} & [\bar{1}1\bar{1}]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

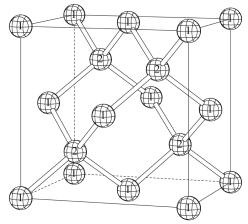


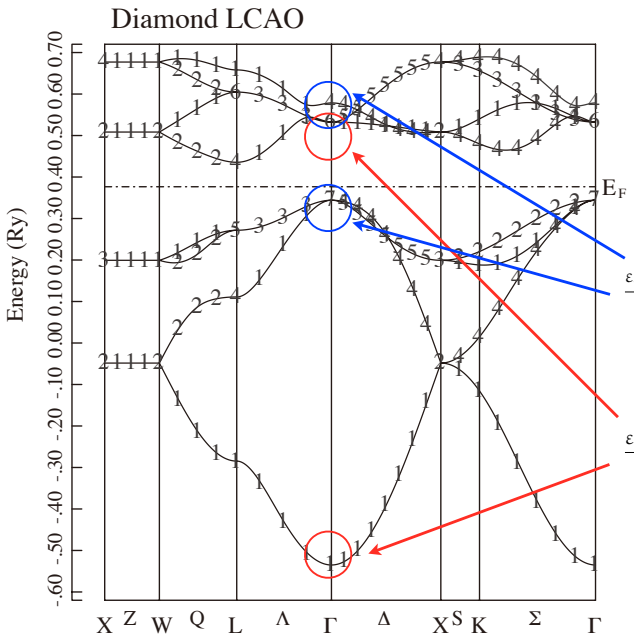
(T_d-Symmetry basis function)







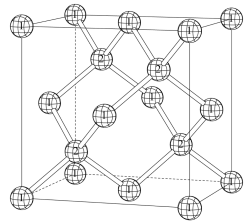


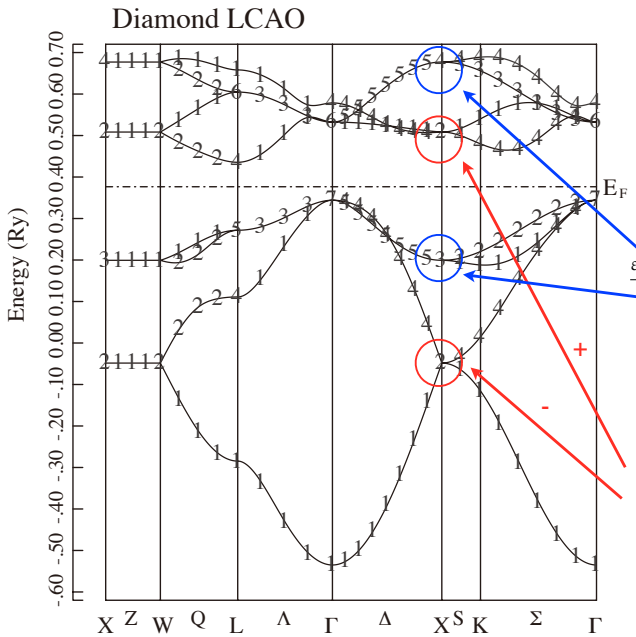


$$\frac{\varepsilon_p^1 + \varepsilon_p^2}{2} \pm \sqrt{\left(\frac{\varepsilon_p^1 - \varepsilon_p^2}{2}\right)^2 + (4E_{xx})^2}$$

$$\left(E_{xx} \equiv \frac{1}{3}V_{pp\sigma} + \frac{2}{3}V_{pp\pi}\right)$$

$$\frac{\varepsilon_s^1 + \varepsilon_s^2}{2} \pm \sqrt{\left(\frac{\varepsilon_s^1 - \varepsilon_s^2}{2}\right)^2 + (4E_{ss})^2}$$



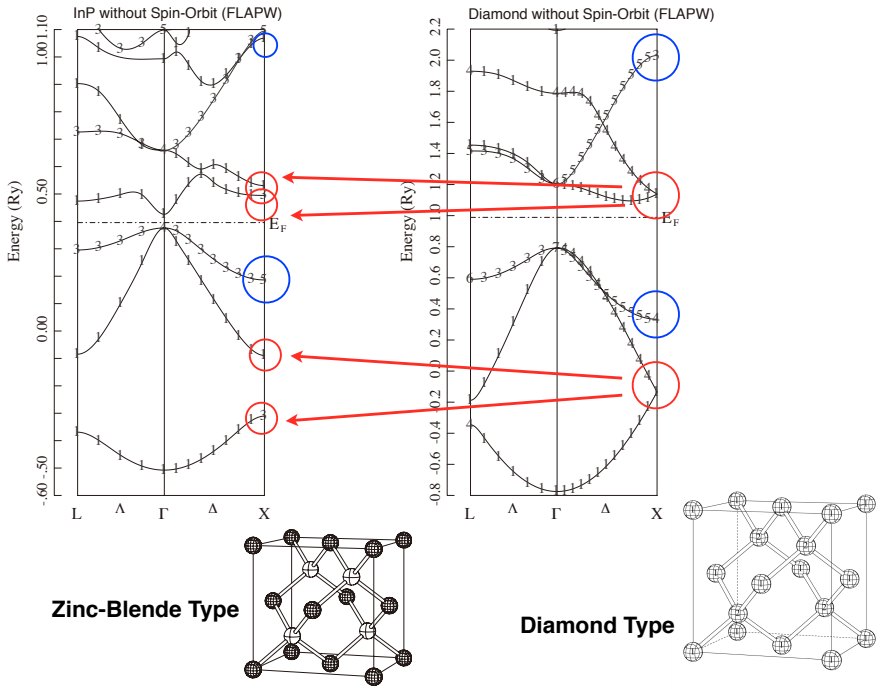


$$\frac{\varepsilon_p^1 + \varepsilon_p^2}{2} \pm \sqrt{\left(\frac{\varepsilon_p^1 - \varepsilon_p^2}{2}\right)^2 + (4E_{xy})^2}$$

$$\left(E_{xy} \equiv \frac{1}{3}V_{pp\sigma} - \frac{1}{3}V_{pp\pi}\right)$$

$$\begin{cases} \frac{\varepsilon_s^1 + \varepsilon_p^2}{2} \pm \sqrt{\left(\frac{\varepsilon_s^1 - \varepsilon_p^2}{2}\right)^2 + (4E_{sp})^2} \\ \frac{\varepsilon_p^2 + \varepsilon_s^1}{2} \pm \sqrt{\left(\frac{\varepsilon_p^1 - \varepsilon_s^2}{2}\right)^2 + (4E_{sp})^2} \end{cases}$$

$$\left(E_{sp} \equiv \frac{1}{3^{1/3}}V_{sp\sigma}\right)$$



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**lane**w**ave(FLAPW)
include **relativistic effect (spin-orbit interaction)**

3D-picture

TPERSP AYPLOT

3-dimensional graphical library (tpersp)
PostScript(PS) drawing library (ayplot)

yahoo!/google → “TSPACE”

Reference

English

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Thanks for your attention