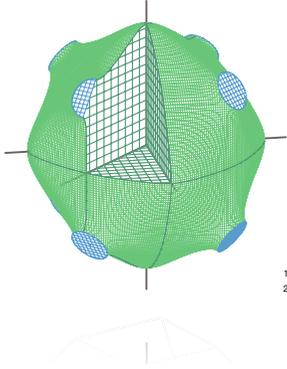


Symmetry of Crystals and Electronic States



Hiroki Funashima¹ and Akira Yanase²

¹Department of Comprehensive Engineering, Kindai University Technical College
²Institute for Industrial and Scientific Research, Osaka University

Email: funashima@kctc.ac.jp (Funashima)

1

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

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



- P. A. M. Dirac -

2

Kohn-Sham Equations

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

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

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



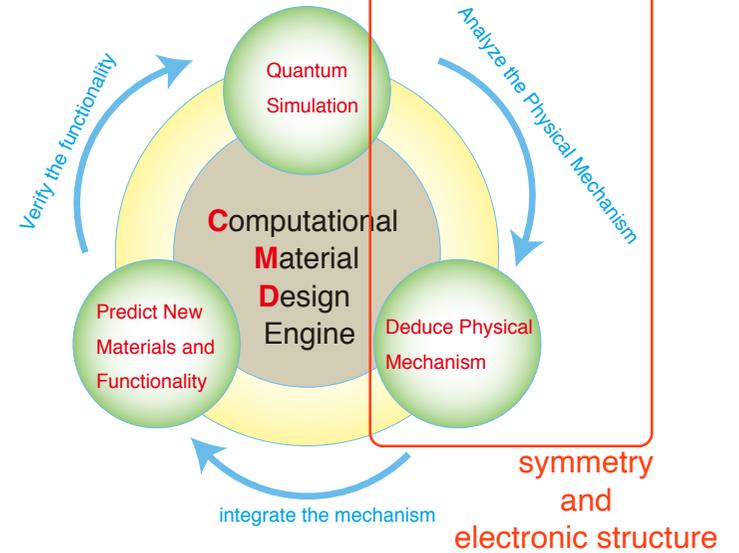
what kind of influence do crystalline potentials have?

Crystals have symmetry.

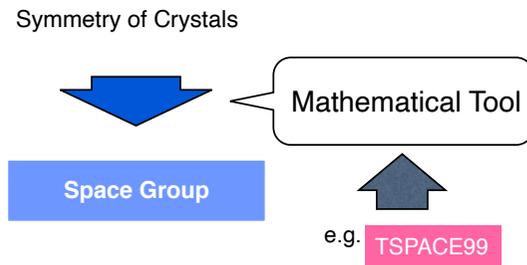
Translational Symmetry

Rotational Symmetry

3



4



1Dim: Free Electron in periodic potential

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

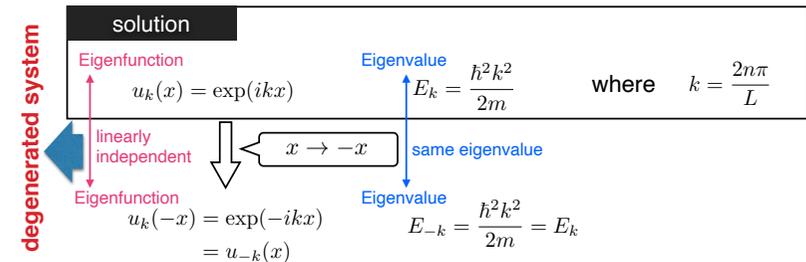
Schrödinger Equation

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

Under the periodic condition,

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

we can solve this differential equation

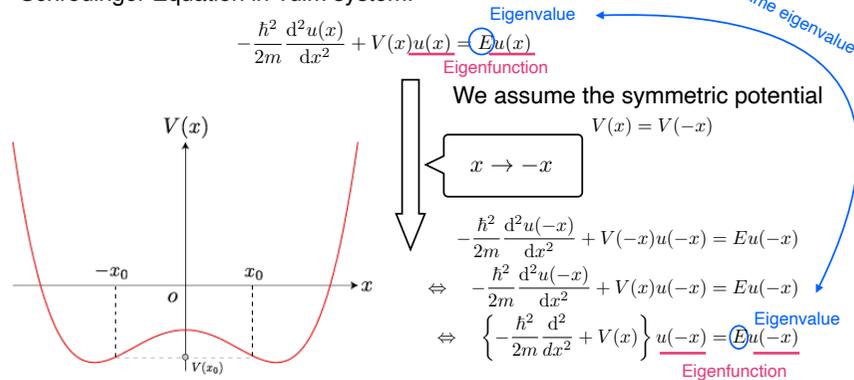


Symmetry and Quantum Mechanics

From the beginning, we consider low dimensional systems.

1Dim: Symmetric potential

Schrödinger Equation in 1dim system.



- degenerated case
- non-degenerated case

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)

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

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

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

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

$$\begin{cases} x \rightarrow -x \\ \text{and} \\ y \rightarrow -y \end{cases} \begin{array}{c} \text{operate} \\ \text{simultaneously} \end{array} \text{change of sign of function} \quad \begin{array}{l} 1 \times (-1) = -1 \\ (-1) \times 1 = -1 \end{array}$$

9

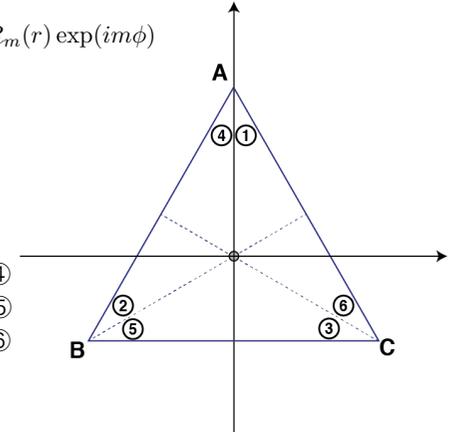
2Dim: Equilateral Triangular Symmetry (C_{3v})

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

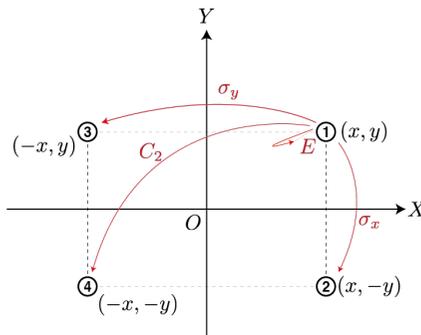
1. identity operation (E)
2. $2\pi/3$ rotation (C_3) ① \rightarrow ②
3. $-2\pi/3$ rotation (C_3^{-1}) ① \rightarrow ③
4. reflection at A-axis (σ_A) ① \rightarrow ④
5. reflection at B-axis (σ_B) ② \rightarrow ⑤
6. reflection at C-axis (σ_C) ③ \rightarrow ⑥



11

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

10

Rotational effect for wave function(C_3^\pm)

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

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

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

We can classify 3 types for m

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

12

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

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

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

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

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

13

Relationship between the classification for m and characters of WFs

$$m = 3n$$

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, $\phi \rightarrow -\phi$

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

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

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

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

15

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 equivalent to these operations,

$$\begin{cases} \sigma_A : \phi \rightarrow -\phi \\ \sigma_B : \phi \rightarrow -\phi + \frac{2}{3}\pi \\ \sigma_C : \phi \rightarrow -\phi - \frac{2}{3}\pi \end{cases} \leftrightarrow \begin{cases} \sigma_B = \sigma_A \cdot C_3^{-1} \\ \sigma_C = \sigma_A \cdot C_3 \end{cases}$$

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

14

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

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

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

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

2-fold degeneracy

16

Summary for equilateral triangular symmetry

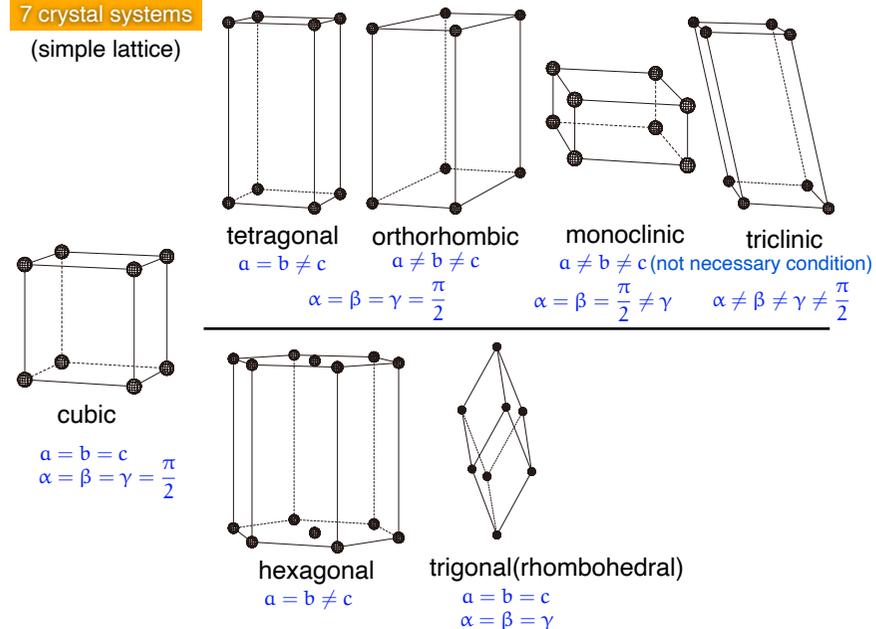
There are 3 types eigenfunctions.

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

17

7 crystal systems

(simple lattice)



19

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

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

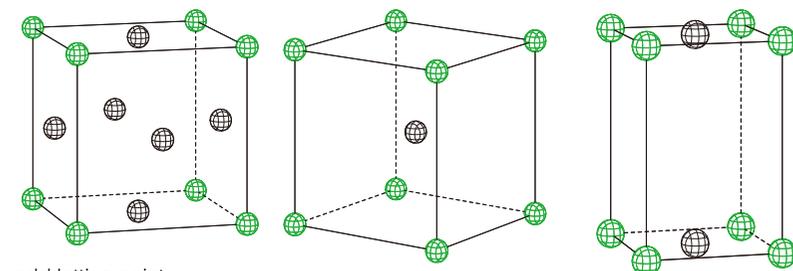
$$(\alpha|\vec{u})(\beta|\vec{v}) = (\alpha\beta|\alpha\vec{v} + \vec{u})$$

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

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

18

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

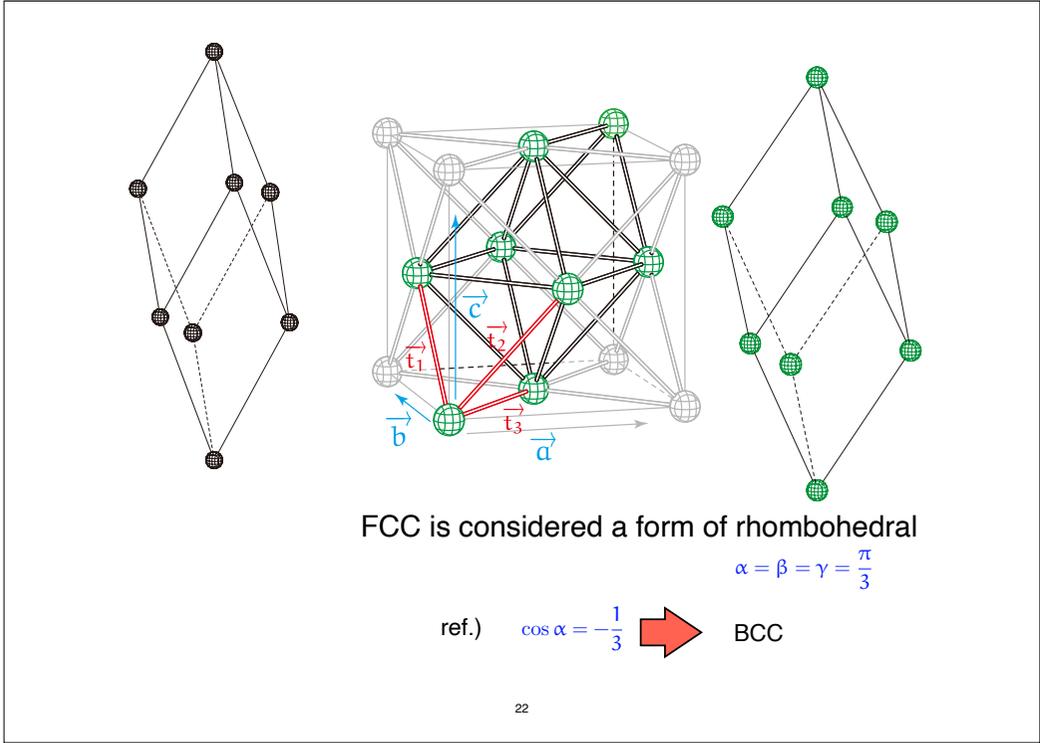
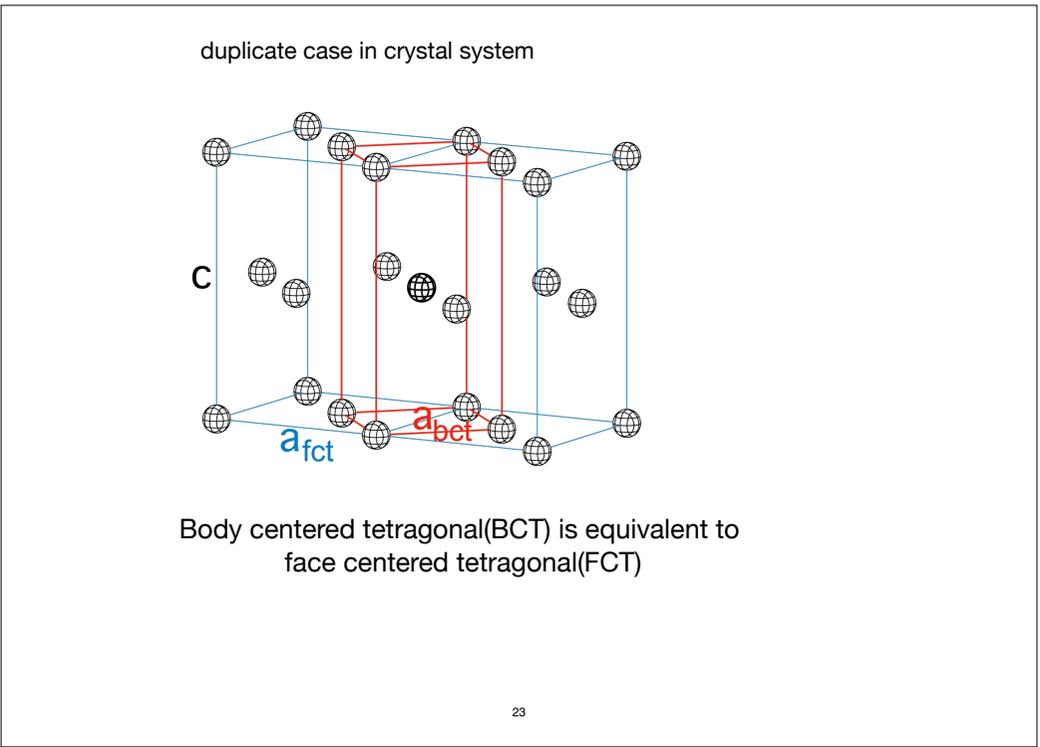
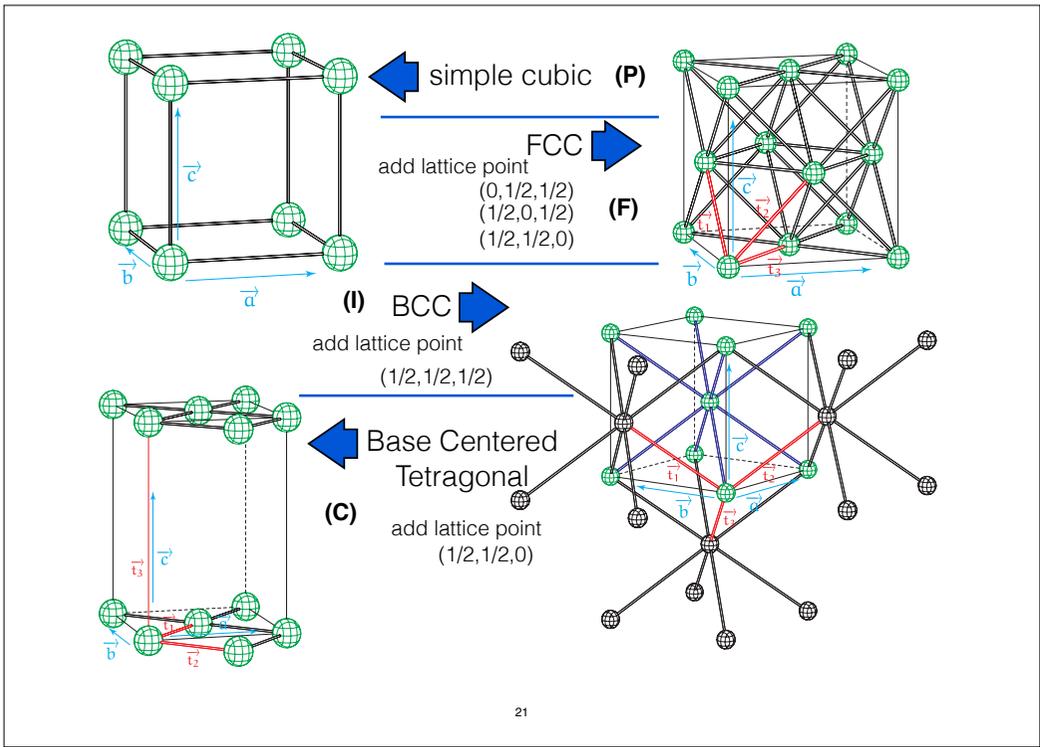
add lattice point
(I) $(1/2, 1/2, 1/2)$

Body Centered Lattice

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

Base Centered Lattice
 (c-centered)

20



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}

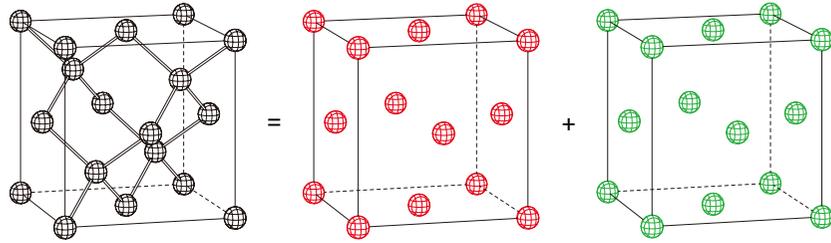
symmetry Operation

$(\alpha|\vec{t} + \vec{u}_\alpha) = \alpha\vec{t} + \vec{t} + \vec{u}_\alpha$
 $(\alpha|\vec{t})(\beta|\vec{t}) = (\alpha\beta|\alpha\vec{t} + \vec{t})$
 $(\alpha|\vec{t})^{-1} = (\alpha^{-1}|\alpha^{-1}\vec{t})$

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

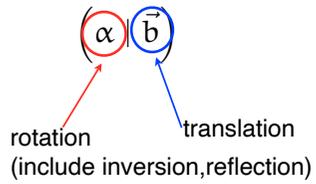
24

symmetry Operation

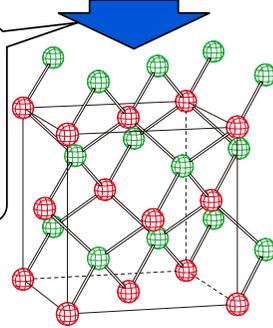


Diamond Structure

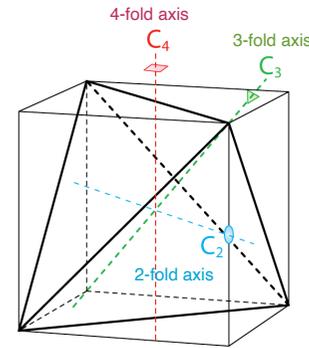
Symmetry operation:
(Seitz Notation)



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



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

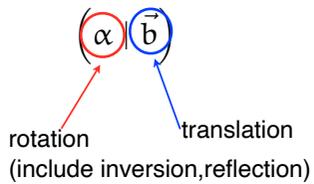
48 symmetry Operation

subgroup of O_h

example
Tetrahedral Symmetry $\rightarrow T_d$

$$T_d \otimes C_4 = O_h$$

Symmetry operation:
(Seitz Notation)



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

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

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

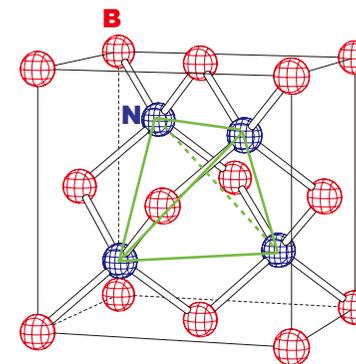
zincblende Structure

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}

6fold-axis C_6

2-fold axis C_2

2-fold axis C_2

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

29

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

31

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

30

Magnetic case

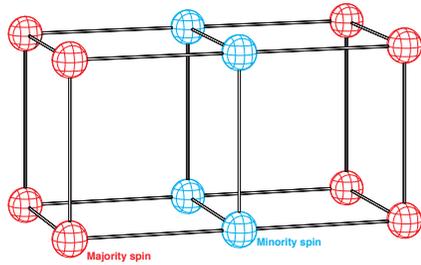
Simple Cubic Lattice (Ferromagnetic)

Cubic Lattice

antiferromagnetic case...?

32

Antiferromagnetic(type1)



Anti-Ferro magnetics (type1)

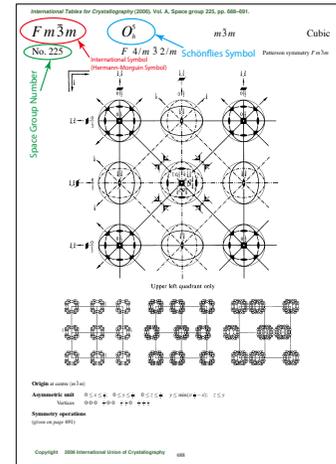
Tetragonal Lattice

Space Group

point group
rotation(including reflection)
+

translational group

space group



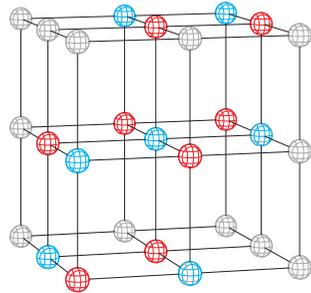
International Table of Crystallography

How many kinds of space group are there?

only **230** space group

3 ways to classify

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



Anti-Ferro magnetics (type2)

rhombohedral Lattice

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

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

rotational operator translation vector

The simple translation is given by

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

identical operation

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

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

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

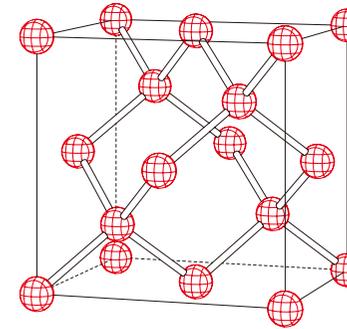
Yes \rightarrow **symmorphic(共型)**

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

37

Example : non-symmorphic

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



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

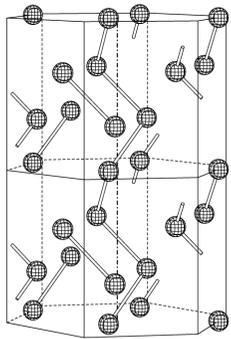
$\alpha : \frac{\pi}{2}$ rotation

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

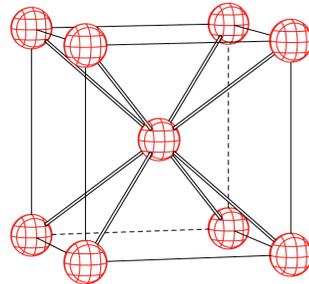


Hmm...let's challenge other choice of the origin...

39



non-symmorphic(非共型)
157(screw:らせん and glide:映進 + 2)



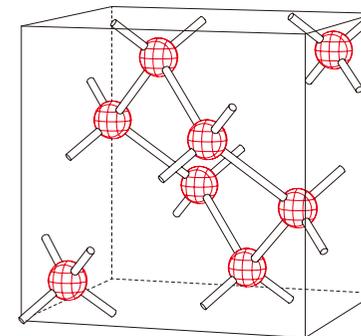
symmorphic(共型)
73 space group

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

are screw operation or glide operation

38

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



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

$\alpha : \frac{\pi}{2}$ 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?

40

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)

41

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

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

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



eigenstate

effect?

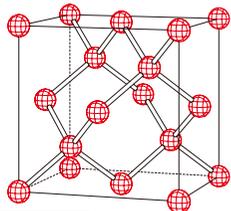
43

How do you define the origin of Nonsymmorphic Crystal?

Example: diamond structure

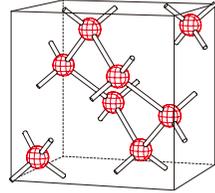
Fd $\bar{3}$ m(O_h⁷)

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?

42

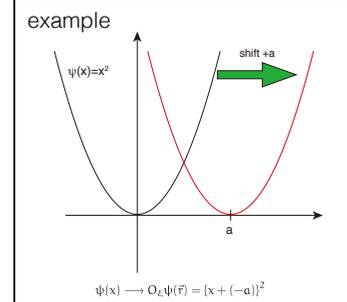
Operator and Operation

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

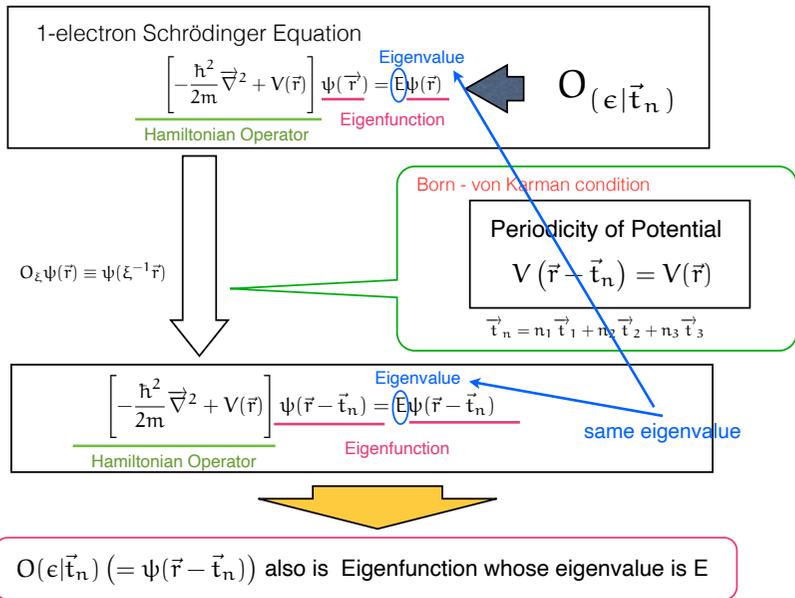
multiplication

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

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



44



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

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

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

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

$$\begin{bmatrix} O_{(\epsilon|\vec{t}_n)}\psi_1(\vec{r}) \\ O_{(\epsilon|\vec{t}_n)}\psi_2(\vec{r}) \\ \vdots \\ O_{(\epsilon|\vec{t}_n)}\psi_p(\vec{r}) \end{bmatrix} = \underbrace{T(\vec{t}_n)}_{\text{representation matrix of } O_{(\epsilon|\vec{t}_n)}} \begin{bmatrix} \psi_1(\vec{r}) \\ \psi_2(\vec{r}) \\ \vdots \\ \psi_p(\vec{r}) \end{bmatrix}$$

Here, Matrix T is given as

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

Matrix T is unitary matrix \leftarrow norm conservation

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

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

$$\begin{bmatrix} O_{(\epsilon|\vec{t}_n)}\psi_1(\vec{r}) \\ O_{(\epsilon|\vec{t}_n)}\psi_2(\vec{r}) \\ \vdots \\ O_{(\epsilon|\vec{t}_n)}\psi_p(\vec{r}) \end{bmatrix} = \underbrace{T(\vec{t}_n)}_{\text{representation matrix of } O_{(\epsilon|\vec{t}_n)}} \begin{bmatrix} \psi_1(\vec{r}) \\ \psi_2(\vec{r}) \\ \vdots \\ \psi_p(\vec{r}) \end{bmatrix}$$

Here, Matrix T is given as

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

Matrix T is unitary matrix \leftarrow norm conservation

Translation operators are commutable:

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

$$= \psi(\vec{r} - (\vec{t}_n + \vec{t}_m))$$

therefore

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

Commutable

simultaneous to diagonal form

and

Matrix T is unitary matrix

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

(absolute value of eigenvalue for unitary matrix = 1)

Bloch function and basis set

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

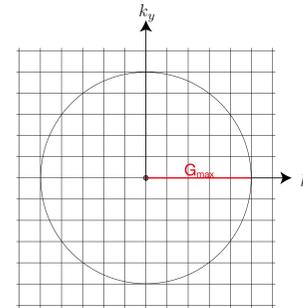
How do we represent the periodic function?

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

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

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

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

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

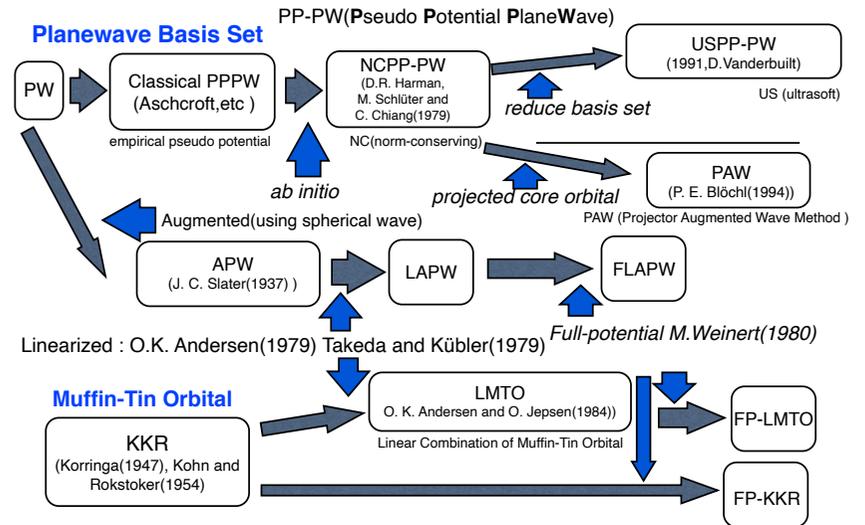
$$\psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{Bloch function}$$

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

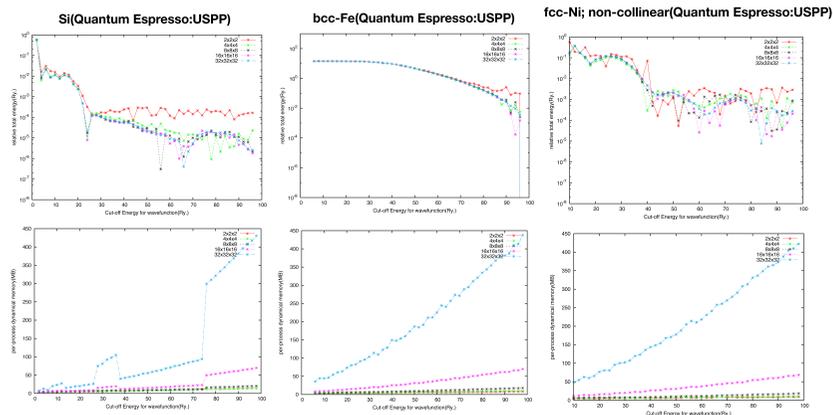
Bloch state is characterized by \vec{k}

Next Theme: k-space and reciprocal lattice

genealogy of DFT calculation



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



53

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

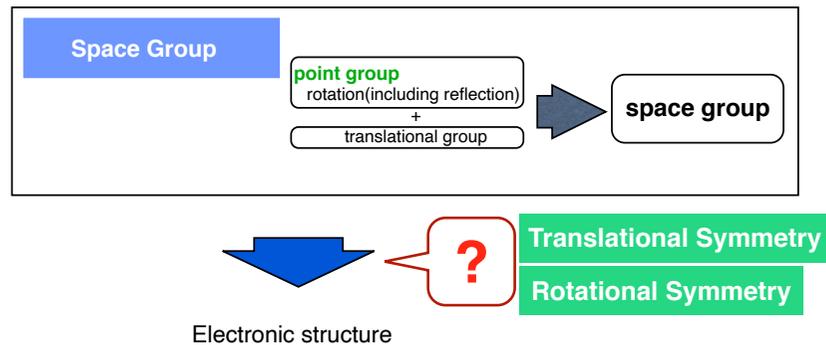
Is k-space “virtual space”?

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

It is natural idea that electrons are in k-space

55

Next theme



54

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

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

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

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

reciprocal lattice

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

orthogonality

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

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

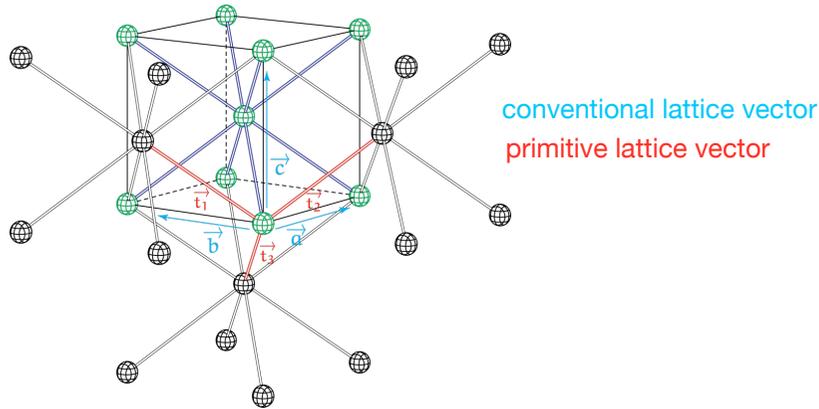
$$e^{-i(\vec{k} + \vec{g}_l) \cdot \vec{t}_n} = e^{-i\vec{k} \cdot \vec{t}_n}$$

(periodicity in k-space)

56

the condition of [hkl] in crystal

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



57

“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...

59

therefore, basis set of primitive vector is written as

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

Here, it satisfies the following condition

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

58

Reciprocal lattice point is defined as

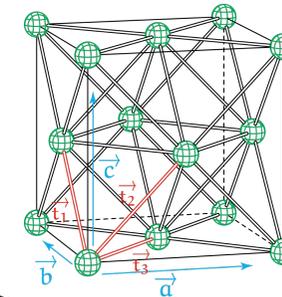
$$\mathbf{g}_l = l_1 \mathbf{g}_1 + l_2 \mathbf{g}_2 + l_3 \mathbf{g}_3 \quad (l_1, l_2, l_3 : \text{integer})$$

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

Primitive lattice vector in FCC

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



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

basis set is *not orthogonal* \Rightarrow It is not convenient to use.

60

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?

61

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

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,

$$\begin{aligned} l_1 + l_2 + l_3 &= \frac{1}{2}(h + k + l) \\ h + k + l &= 2(l_1 + l_2 + l_3) = 2m \quad (m \equiv l_1 + l_2 + l_3) \end{aligned}$$

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

63

Primitive reciprocal lattice vector

conventional reciprocal lattice vector

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

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

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

substitute

Reciprocal lattice point is defined as

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

62

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"

64

Selection rule for Reciprocal Lattice

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

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

65

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

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

rotation translation

Schrödinger Equation in crystal:

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

Eigenvalue Eigenfunction

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

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

$$= \exp(i\alpha\vec{k} \cdot \vec{r}) \exp(-i\alpha\vec{k} \cdot \vec{v}) u_{\vec{k}}(\alpha^{-1}(\vec{r} - \vec{v})) \equiv u_{\alpha\vec{k}}(\vec{r})$$

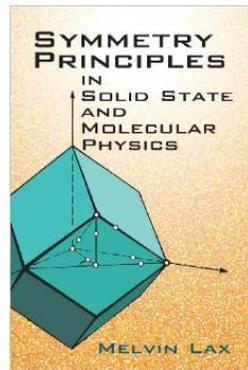
same eigenvalue

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

Eigenvalue Eigenfunction

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

67



66

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

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

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 \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

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

68

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.

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:

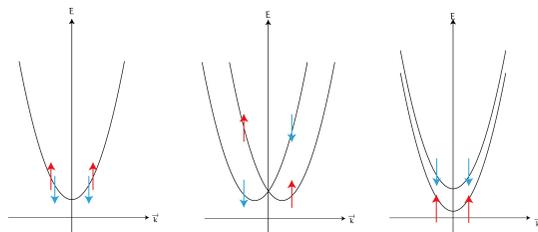
$$\begin{aligned} \mathcal{H}_{\text{spin-orbit}} &= -\frac{1}{2} \mu_s \cdot \mathbf{B}(\mathbf{r}) = \frac{1}{2} \left(\frac{g_s}{\hbar} \mathbf{S} \right) \cdot \left(\frac{Zq_e}{4\pi\epsilon_0 c^2 m_e} \frac{\mathbf{L}}{|\mathbf{r}|^3} \right) \quad \text{Spin-Orbit Interaction} \\ &= \frac{Ze^2}{2m_e^2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

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

Advanced theme

relativistic effect (spin-orbit coupling)

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



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

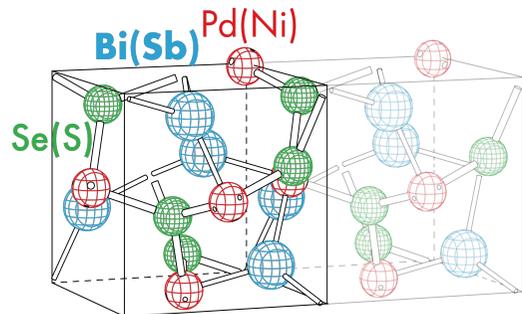
$$\xi_{n,l} = \left(\frac{Z}{a} \right)^3 \frac{2}{n^3 l(l+1)(2l+1)} = Z^4 \alpha^2 E_{Ha} \left(\frac{\mu}{m_e} \right)^3 \frac{1}{n^3 l(l+1)(2l+1)}$$

Crystal Effect Field Origin view for Spin-Orbit Interaction:

➡ Anti-symmetric Spin-Orbit Interaction (ASOI)

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

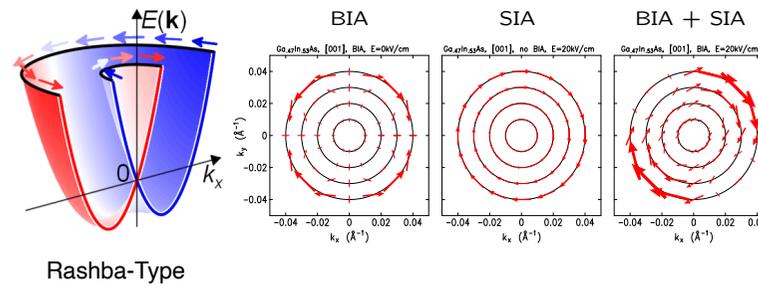
Break down to centrosymmetric in the Crystal



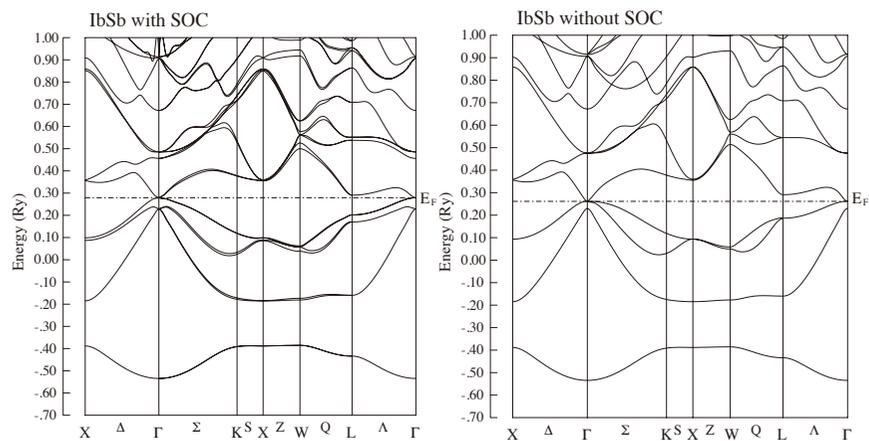
73

Anti-Symmetric Spin-Orbit Interaction(ASOI)

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



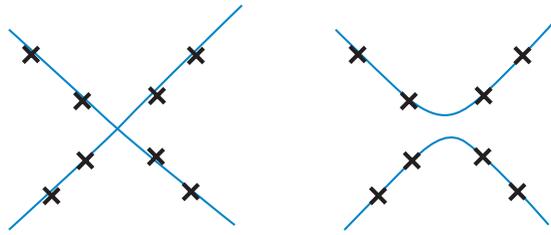
75



74

Free electron model
and
Alkali / Alkali Earth Metal

76



Which is correct?

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



Space Group teaches us.

1-electron Schrödinger Equation

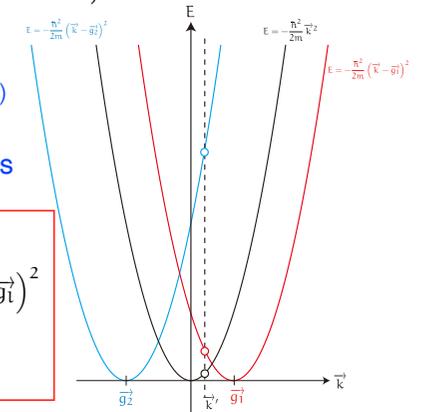
$$\begin{aligned}
 &-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\psi(\vec{r}) \\
 \Leftrightarrow &-\frac{\hbar^2}{2m}\nabla^2\left\{\sum_{\vec{g}_i} C_{\vec{g}_i} e^{i(\vec{k}-\vec{g}_i)\cdot\vec{r}}\right\} = E\left\{\sum_{\vec{g}_i} C_{\vec{g}_i} e^{i(\vec{k}-\vec{g}_i)\cdot\vec{r}}\right\} \\
 \Leftrightarrow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

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



Free electron Model

under Born-von Karman Condition

$$\begin{aligned}
 V(\vec{r}-\vec{t}_n) &= V(\vec{r}) \quad \vec{t}_n = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3 \\
 &\text{(here, } V(\vec{r}-\vec{t}_n) = V(\vec{r}) = 0)
 \end{aligned}$$

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

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

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

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

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

Fourier Component of \vec{g}_i

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

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

Eigenenergy

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

81

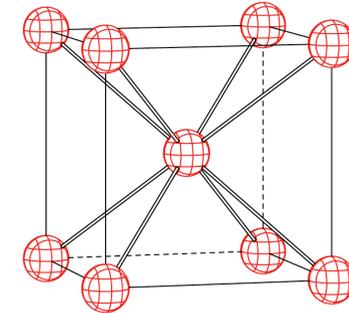
Li ³	bcc
Na ¹¹	bcc
K ¹⁹	bcc
Rb ³⁷	bcc
Cs ⁵⁵	bcc
Fr ⁸⁷	bcc

Alkali Metals

the **body centered cubic (bcc)**

space group

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



83

Free electron Model

Cubic Lattice case

$$\begin{aligned} \vec{t}_i \cdot \vec{t}_j &= a^2 \delta_{i,j} \\ \vec{t}_1 \cdot (\vec{t}_2 \times \vec{t}_3) &= \Omega_c = a^3 \\ \vec{t}_i \times \vec{t}_j &= \vec{t}_k \end{aligned} \quad \Rightarrow \quad \vec{g}_k = \frac{2\pi}{\Omega_c} (\vec{t}_i \times \vec{t}_j) = \frac{2\pi}{a^3} \vec{t}_k \quad (i, j, k = 1, 2, 3)$$

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

to convenient Energy unit $\Rightarrow \frac{\hbar^2}{2m} \left(\frac{2\pi}{a}\right)^2 \left(\vec{k} = \frac{2\pi}{a} \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix}, \vec{g}_l = \frac{2\pi}{a} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \right)$

Eigenenergy

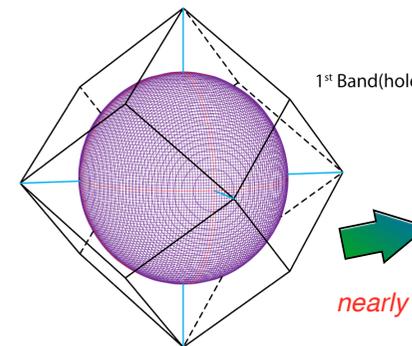
$$E(\vec{g}_l) = E(\vec{k} - \vec{g}_l) = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_3)^2 \quad \left(\vec{k} = \frac{2\pi}{a} \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix}, \vec{g}_l = \frac{2\pi}{a} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \right)$$

Eigenfunction

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

82

Fermi Surface of Na



1st Band(hole)

nearly free electron

free electron

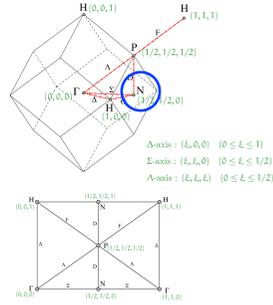
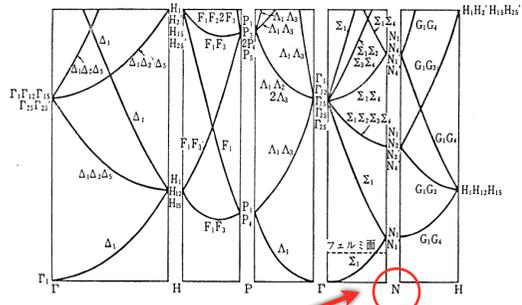
$$\frac{\hbar^2 k_F^2}{2m} = E_F \Leftrightarrow k_x^2 + k_y^2 + k_z^2 = \frac{2mE_F}{\hbar^2}$$

Fermi surface is "sphere" in shape.

It is called "fermi sphere"

84

bcc free electron



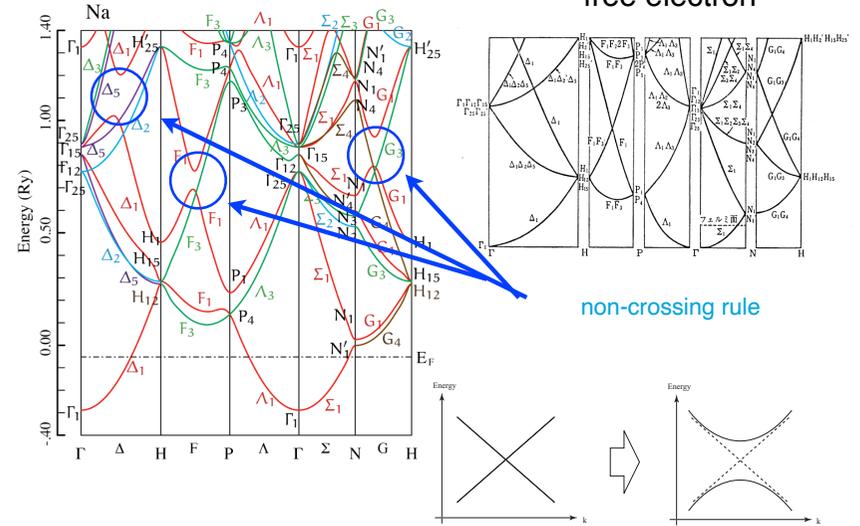
wavefunction is given as

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

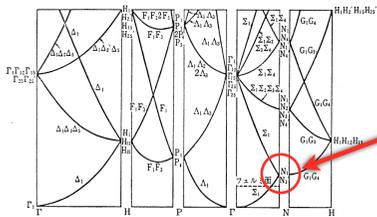
therefore

$$\psi_N = \exp\left\{\frac{\pi i}{a}(x+y)\right\} \times \exp\left\{-\frac{2\pi i}{a}(n_1x + n_2y + n_3z)\right\}$$

free electron



non-crossing rule



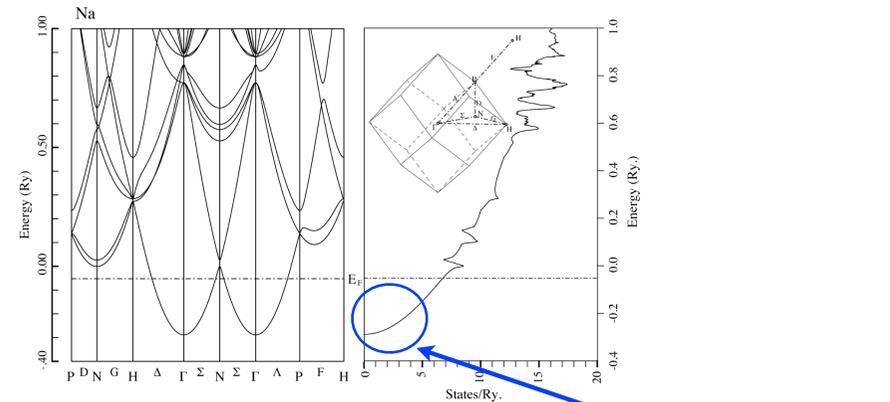
$$E(N) = \left(n_1 - \frac{1}{2}\right)^2 + \left(n_2 - \frac{1}{2}\right)^2 + n_3^2$$

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

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



Density of State (free electron)

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

Free electron Model

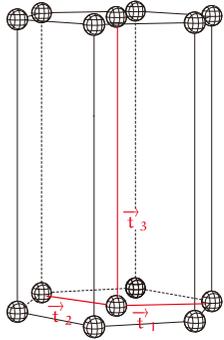
Hexagonal Lattice case

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

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

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

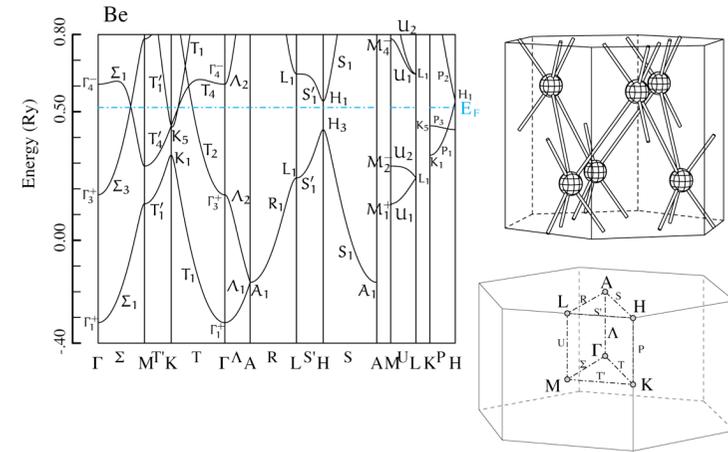
$$\vec{g}_k = \frac{2\pi}{\Omega_c} (\vec{t}_i \times \vec{t}_j)$$



Eigenenergy

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

97



99

Be⁴

hex

Mg¹²

hex

Ca²⁰

fcc

Sr³⁸

fcc

Ba⁵⁶

bcc

Ra⁸⁸

bcc

Alkaline Earth Metals

hexagonal closed package (hcp)

space group

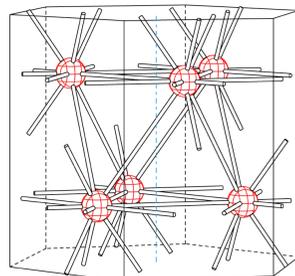
$P6_3/mmc (D_{6h}^4)$

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

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

2atom/unit cell

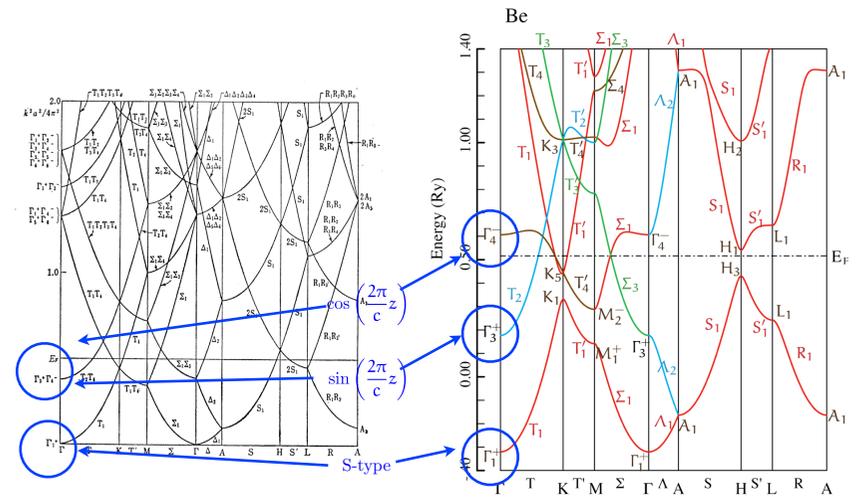
same space group,
but distortional hcp



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

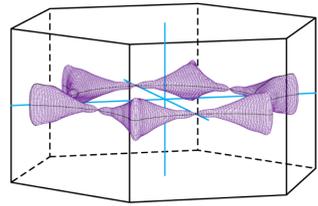
98

free electron band and Be band

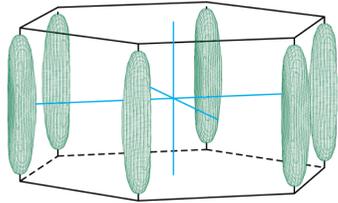


100

Fermi Surface of Be



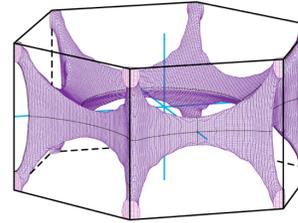
2nd Band(hole)
"Crown"



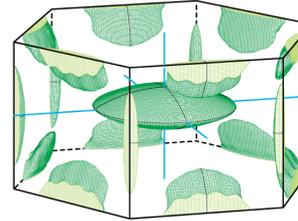
3rd Band(electron)
"Ciger"

101

Fermi Surface of Mg

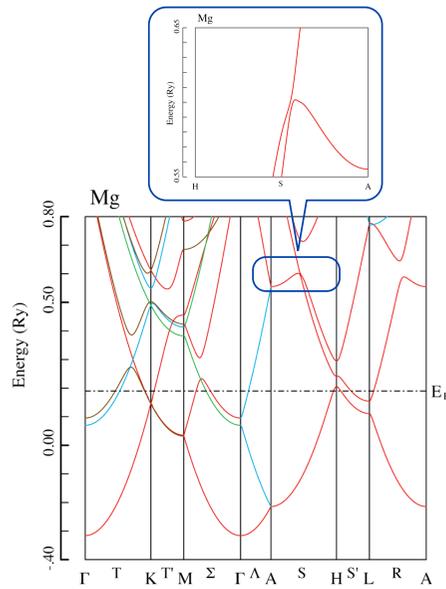
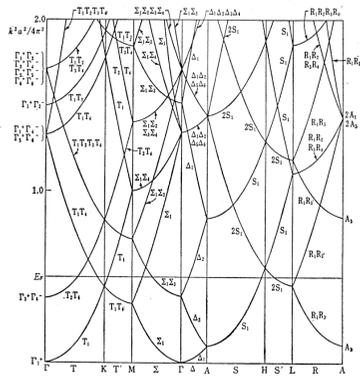


2nd Band(hole)
"Monster"

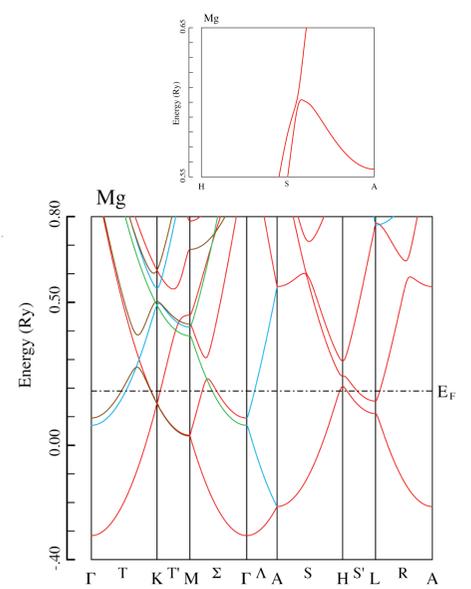
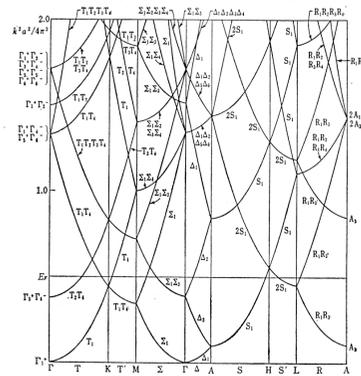


3rd Band(electron)

103



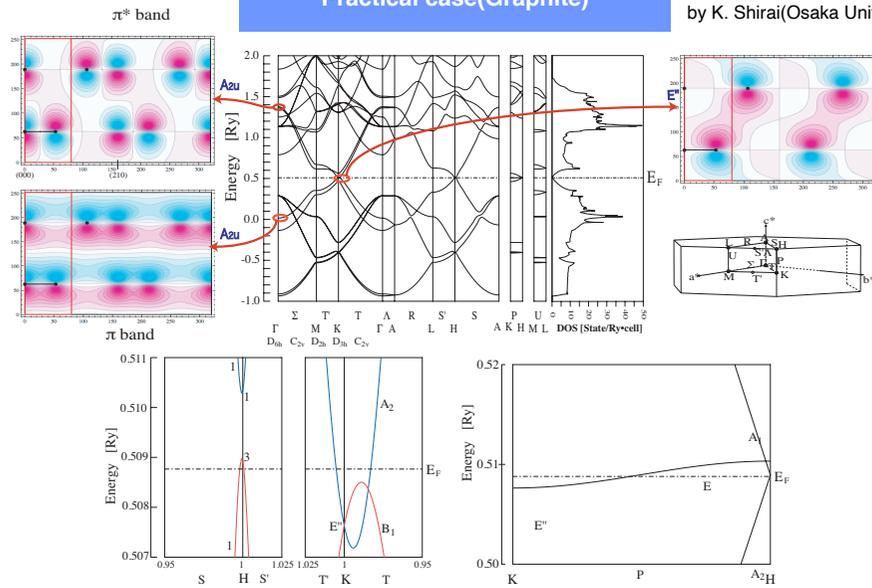
102



104

Practical case(Graphite)

by K. Shirai(Osaka Univ.)



105

Overlap Matrix Element

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

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

Secular Equation

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

107

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

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

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

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

106

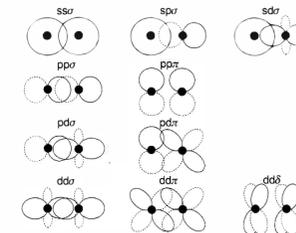
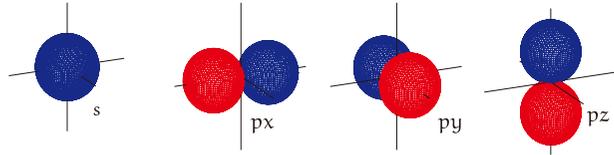


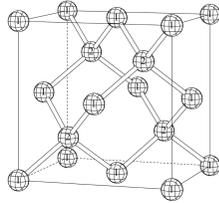
Figure 14.1. Schematic figures of local orbitals indicating all possible overlap and two-center hamiltonian matrix elements for s, p, and d orbitals, which are classified by the angular momentum about the axis with the notation σ ($m = 0$), π ($m = 1$), and δ ($m = 2$). The orbitals shown are the real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

108

sp³ basis function

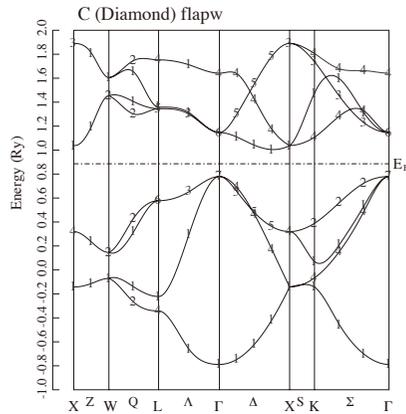
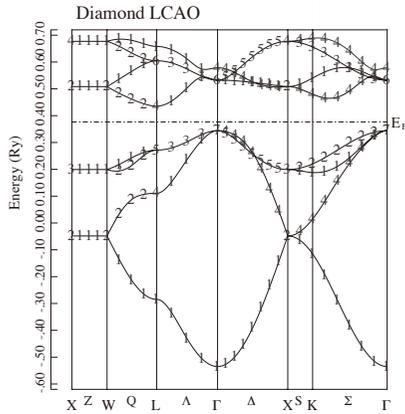
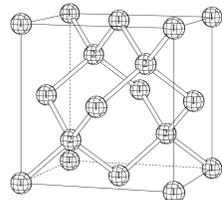
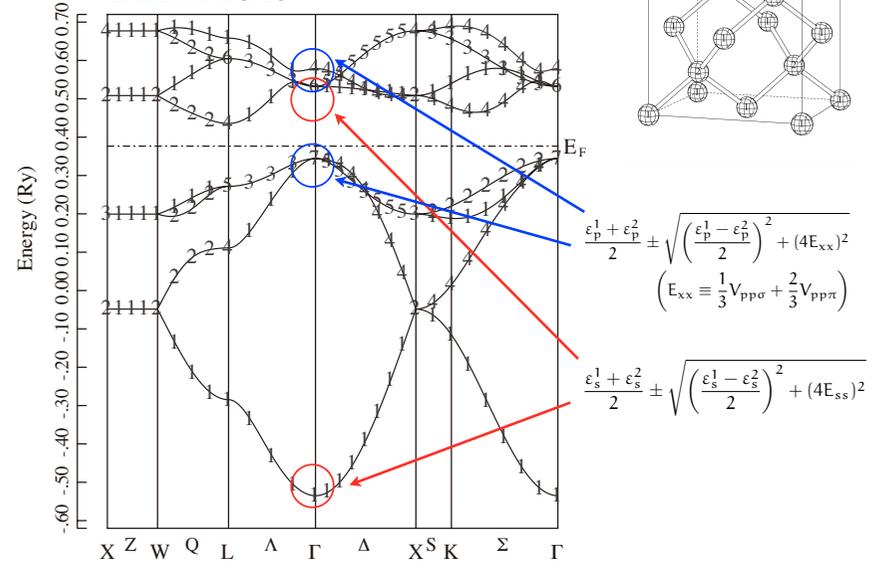


$$\begin{cases} |h_1\rangle = \frac{1}{2} \{ |s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle \} & [111] \\ |h_2\rangle = \frac{1}{2} \{ |s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle \} & [\bar{1}\bar{1}\bar{1}] \\ |h_3\rangle = \frac{1}{2} \{ |s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle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

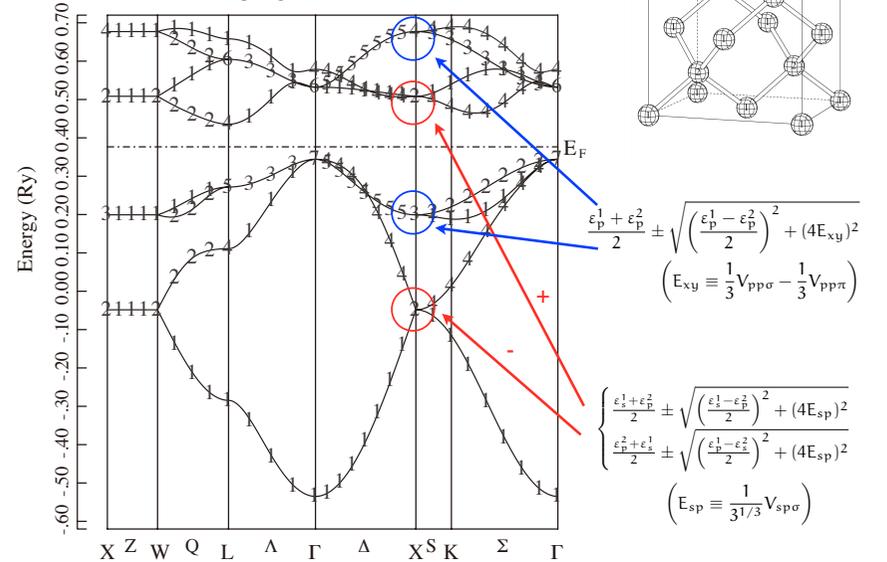


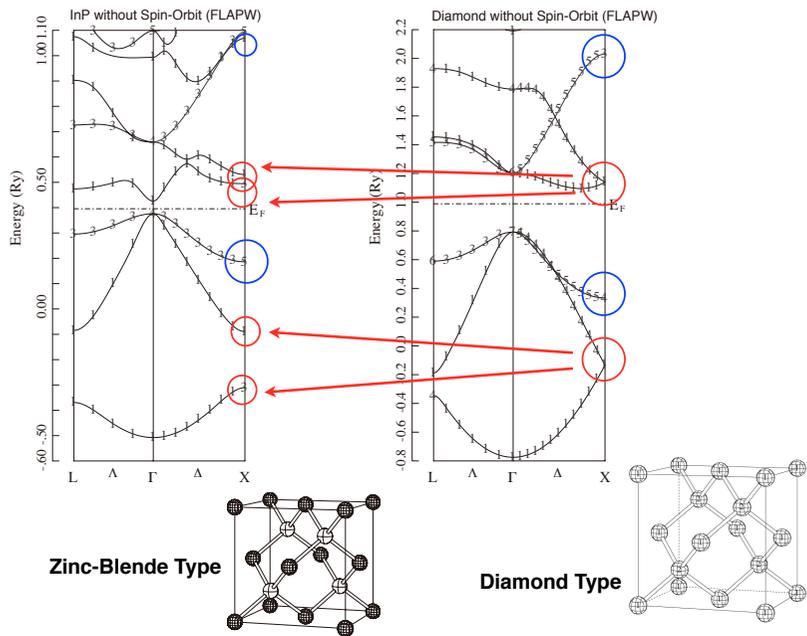
(T_d-Symmetry basis function)

Diamond LCAO



Diamond LCAO





yahoo!/google



"TSPACE"

Using package in this lecture

space group

TSPACE99

Ab initio calculation

KANSAI2016

Local Density Approximation (LDA) based on Density Functional Theory (DFT)
 Full potential Linearized Augmented Planewave (FLAPW)
 include relativistic effect (spin-orbit interaction)

3D-picture

TPERSP AYPLOT

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

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