

(10) Correspondence to the free electron model

$E = \alpha + 2\beta \cos ka$

Free electron model is the bottom parabola of the cos function.

Approximated by  $E = \frac{\hbar^2 k^2}{2m}$

$m$  is different from the value for a real electron. (Effective mass)

$4\beta$  large  $\rightarrow m$  small  $\rightarrow$  mobile

$4\beta$  small  $\rightarrow m$  large  $\rightarrow$  not mobile

Upper half of the band is approximated by free electron with  $m < 0$ .  
Opposite response to electric field,  
 $\rightarrow$  Hole with + charge

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(11) Electron band

Electron band

Hole band

More than half-filled band is a hole band.

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(12) 2-Dimensional Square Lattice

$\phi = \sum_n \sum_m e^{inka} e^{imka} \chi_{nm}$

$E \propto \sum_n \sum_m \sum_p \sum_q e^{i(n-m)ka} e^{i(p-q)ka} \int \chi_m^* H \chi_n d\tau$

$E = e^{ika} \beta + \alpha + e^{-ika} \beta + e^{ika} \beta + e^{-ika} \beta$

$E = \alpha + 2\beta \cos k_x a + 2\beta \cos k_y a$

$\alpha + 4\beta$

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(12) 2-Dimensional Square Lattice

$E = \alpha + 2\beta \cos k_x a + 2\beta \cos k_y a$

Bandwidth:  $8\beta$

(In general, bandwidth is  $2z\beta$ , where  $z$  is the coordination number (the number of the nearby sites.))

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(12) 2-Dimensional Square Lattice

$E = \alpha + 2\beta\cos k_x a + 2\beta\cos k_y a$

Electron-like Fermi surface equi-energy surface for  $E = \alpha$ .

Hole-like Fermi surface

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(12) 2-Dimensional Square Lattice

Copper oxide high-temperature superconductor  $(La_{1-x}Sr_x)_2CuO_4$

Occupied

Fermi surface of the hole-doped superconductor,  $(La_{1-x}Sr_x)_2CuO_4$

Fermi surface of the parent  $La_2CuO_4$  (antiferromagnetic insulator)

$La_2Cu^{2+}O_4 \rightarrow Cu : d^9 \square d_{x^2-y^2}$  band has one electron (Half-filled)

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(13) Tight-binding method for more than two atoms in a cell

LCAO-MO  $\phi = \sum_i c_i \chi_i$

For 2 atoms,  $i=1, 2$

Bloch function is made from  $\chi_i$  for the whole crystal.

$\chi_i \rightarrow \sum_n e^{ink_a} \chi_i(n)$

Crystal orbital is constructed instead of molecular orbital as,

$\phi = \sum_i \sum_n c_i e^{ink_a} \chi_i(n)$

Calculate  $E = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau}$  from this, and similarly to the usual Mo theory,

$\frac{\partial E}{\partial c_i} = 0$  leads to simultaneous equations of  $c_i$ , and the secular equation is

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$$\begin{vmatrix} \alpha_{11}(k) - E & \beta_{12}(k) & \dots \\ \beta_{21}(k) & \alpha_{22}(k) - E & \dots \end{vmatrix} = 0$$

Since  $\chi_i$  is Bloch function, the matrix elements,  $\alpha$  and  $\beta$  are functions of  $k$ :

$\alpha_{ii}(k) = \int (\sum_m e^{-imka} \chi_i^*(m)) H (\sum_n e^{ink_a} \chi_i(n)) d\tau$

$= \alpha_i + \sum_n \beta_{ii}(n) e^{ink_a} \quad \beta_{ii}(n) = \int \chi_i^*(0) H \chi_i(n) d\tau$  (Nearby atoms)

$\beta_{ij}(k) = \int (\sum_m e^{-imka} \chi_i^*(m)) H (\sum_n e^{ink_a} \chi_j(n)) d\tau$

$= \sum_n \beta_{ij}(n) e^{ink_a}$  When interaction  $\beta$  exists in the  $r$  direction, add a term  $\beta e^{ikr}$ .

$\beta_{ij}(n) = \int \chi_i^*(0) H \chi_j(n) d\tau$  (Nearby atoms)

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### Energy band for a system with many atomic orbitals

LCAO-MO from all atomic orbitals in a cell  
( $N$ , each atom may have more than one.)

$$\phi = \sum_i c_i \chi_i$$

Make the Bloch function of each  $\chi$

$$\chi_i \rightarrow \sum_n e^{inka} \chi_i(n)$$

leading to an  $N \times N$  secular equation

$$\begin{vmatrix} \alpha_{11}(k) - E & \beta_{12}(k) & \dots \\ \beta_{21}(k) & \alpha_{22}(k) - E & \dots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0$$

Since each element is a function of  $k$ , this secular equation is solved at each  $k$ , to give  $N$  energy levels. These energy levels for different  $k$  are connected to afford continuous energy bands (right).

### Energy band of Ge

Ge atom orbitals:  $4s$ ,  $4p$ ,  $\sigma$ ,  $\sigma^*$

Energy band of Ge: Conduction band, Energy gap (0.66 eV), Valence band

High symmetry points:  $L$ ,  $\Gamma$ ,  $U$

### Forgetting $k$

Energy gap (Band gap)

C	5.47 eV
Si	1.12 eV
Ge	0.66 eV

Energy band of Ge

Semiconductor

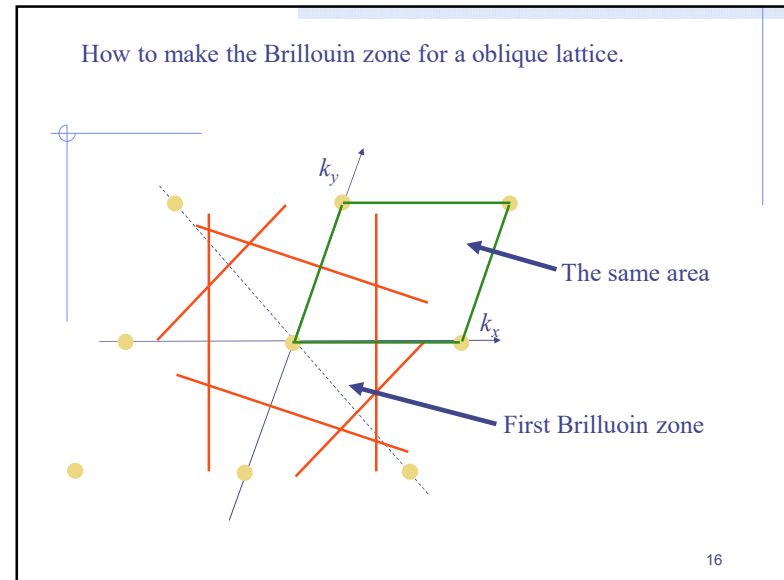
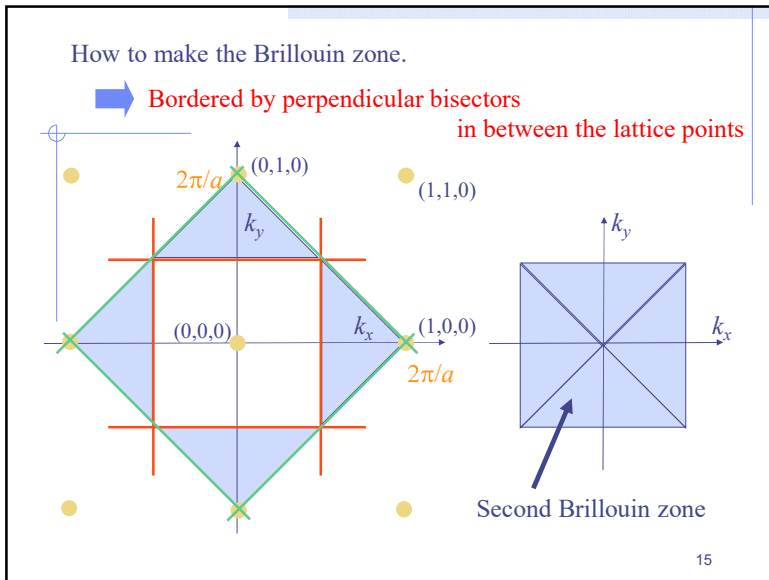
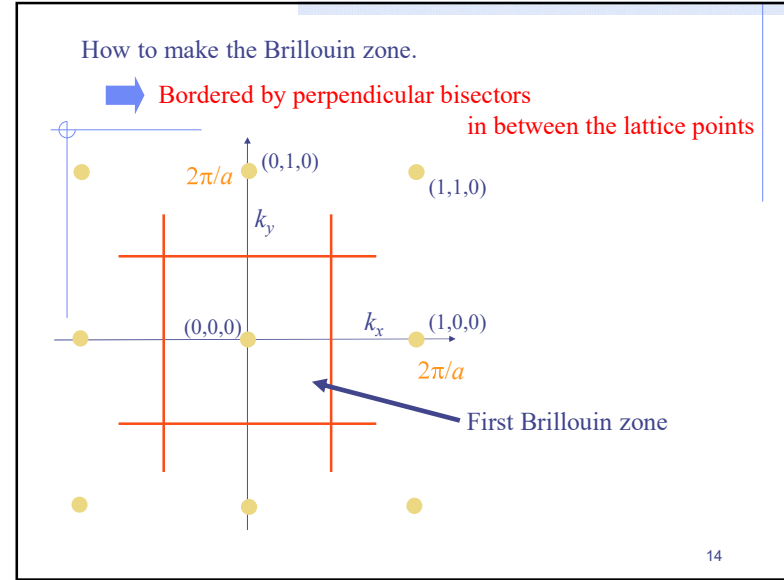
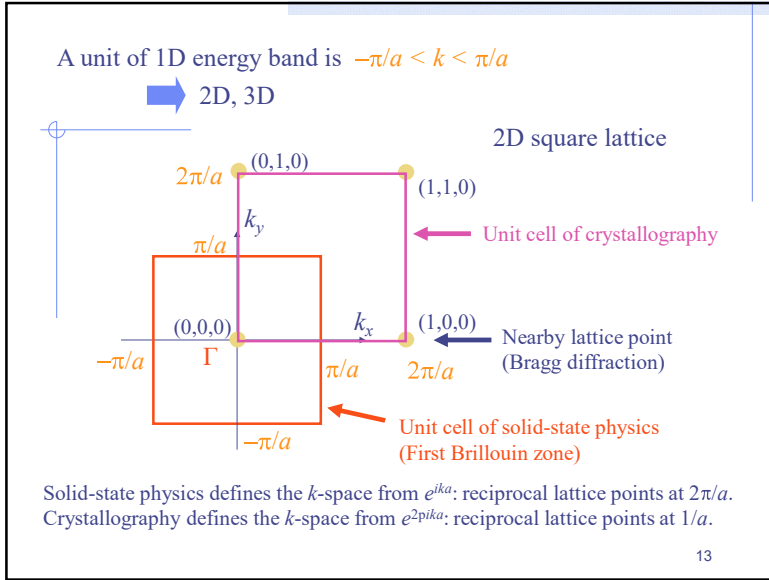
### Energy bands of solids

Conduction band

Valence band

- Insulator: Completely Filled
- Metal: Partially Filled
- Semimetal: Bands overlap partially. Graphite

Conducts electricity



Brillouin zone and the Bravais lattices

Reciprocal of centered is centered

(a) 基本単位ベクトル (b) Wigner-Seitzセル (c) プリムアソン

(1) 三斜晶系 (Triclinic)  $P$   $Monocli: C = \sqrt{a} \sqrt{b}$

(2) 単斜晶系 (Monoclinic)  $P$

(3) 単斜晶系 (Monoclinic)  $C$

(4) 斜方晶系 (Orthorhombic)  $P$

(5) 斜方晶系 (Orthorhombic)  $C$

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Brillouin zone and the Bravais lattices

Reciprocal of face centered is body centered

Reciprocal of body centered is face centered

(6) 斜方晶系 (Orthorhombic)  $I$

(7) 斜方晶系 (Orthorhombic)  $F$

(8) 正方晶系 (Tetragonal)  $P$

(9) 正方晶系 (Tetragonal)  $I$

(10) 三方晶系 (Trigonal, Rhombohedral)  $R$

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Brillouin zone and the Bravais lattices

体心立方格子  
bcc  
body centered  
cubic

面心立方格子  
fcc  
face centered  
cubic

11) 六方晶系 (Hexagonal)  $P$

12) 立方晶系 (Cubic)  $P$

13) 立方晶系 (Cubic)  $I$

14) 立方晶系 (Cubic)  $F$

Fermi surface of metals

(1) Alkali metals Li, Na, K

Fermi surface  $\Leftrightarrow$  trajectory of  $k_F \Leftrightarrow$  Surface at  $E=E_F = \text{const.}$

Assuming free electron

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \text{const.}$$

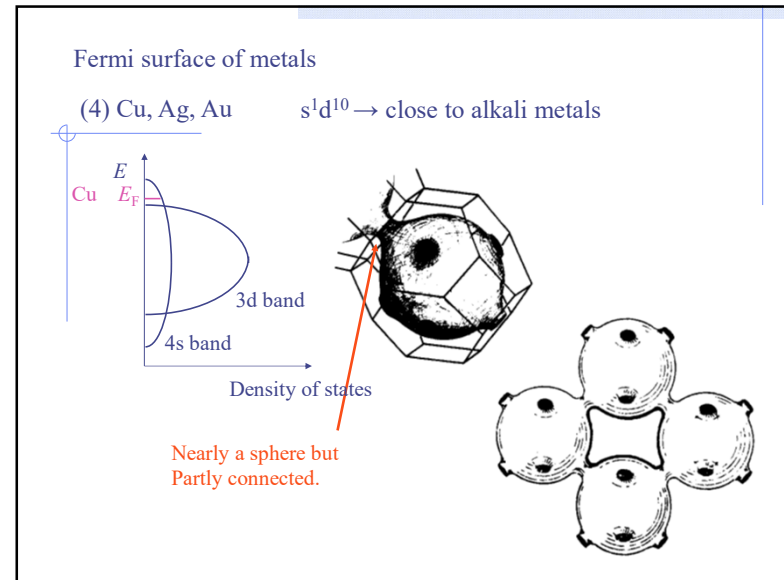
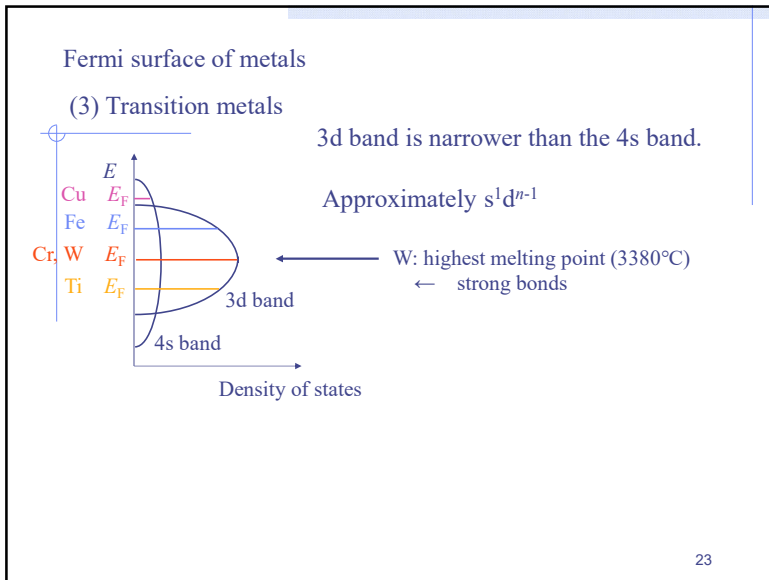
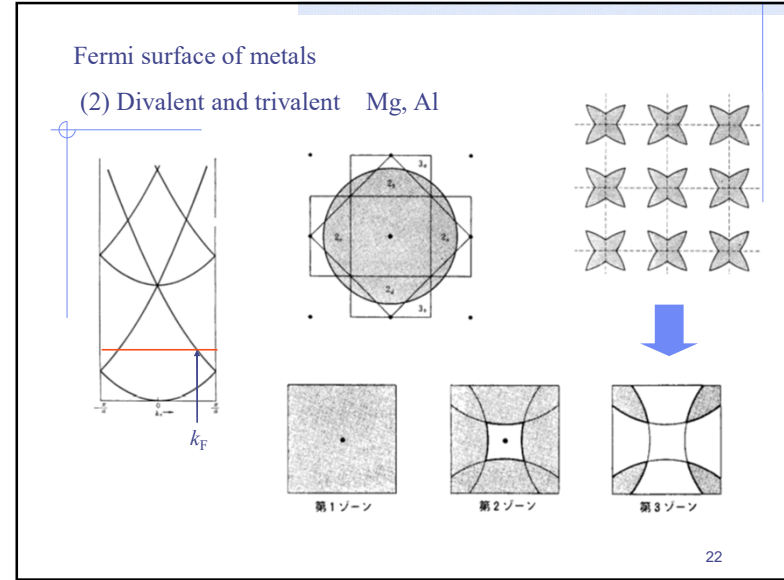
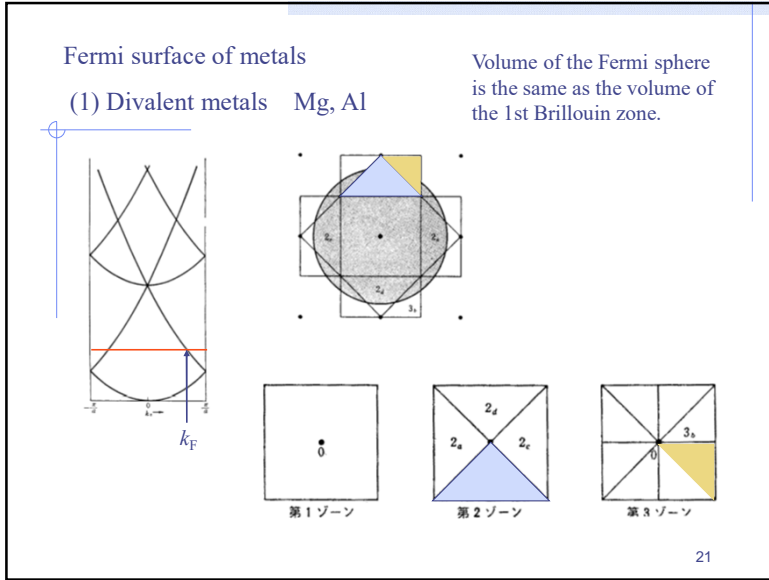
leads to a sphere in the  $k$ -space.

Energy interval in the  $k$ -space is  $\Delta k = \frac{2\pi}{Na}$

Volume of the Fermi sphere is half of the volume of the 1st Brillouin zone.

Fermi surface of alkali metals is not deviated from the perfect sphere by 1%.

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1D metal

$$E = \frac{\hbar^2 k_x^2}{2m} = \text{const.} \quad \text{leads to } k_x = k_F = \text{const.}$$

(No momentum for other  $k_y$  and  $k_z$  directions.  
= cannot move.)

The Fermi surface consists of a pair of planes.

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Examples of 1D metals

(1) 1D Platinum Complex KCP  
K2[Pt(CN)4]Br0.40xH2O

Pt surrounded by CN  
Metal 1D Chain

Metal at room temp.  
Insulator at low temp.

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Examples of 1D metals

(2) NbSe<sub>3</sub>

(3) Polyacetylene

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Examples of 1D metals

(4) Organic Charge-Transfer Complex (TTF)(TCNQ)

Current flow

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### Examples of 2D metals

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2) = \text{const.} \quad \text{leads to } k_x^2 + k_y^2 = k_F^2 = \text{const.} \rightarrow \text{circle}$$

占有

Cylindrical Fermi surface

Examples  
Graphite  
Organic superconductors

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### Organics : energy levels → energy bands

A single molecule of TMTSF

A crystal of (TMTSF)<sub>2</sub>PF<sub>6</sub>

Energy (eV)

Energy levels

Energy bands

伝導バンド  
↓  
LUMO バンド

HOMO バンド  
↓  
価電子バンド

Consider only HOMO (for donors) or LUMO (for acceptors)

Energy band of organic conductors consists of only HOMOs.

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### Fermi surface of the first organic superconductor

(TMTSF)<sub>2</sub>PF<sub>6</sub>

Direction	Interaction
1→1	± b
2→2	± b
1→2	a/2
	- a/2
	a/2 - b
	- a/2 + b

$$\beta_{11} = \beta_{22} = \beta_b e^{ikb} + \beta_b e^{-ikb} = 2\beta_b \cos(kb)$$

$$\beta_{12} = \beta_{21}^* = \beta_{a1} e^{ika/2} + \beta_{a2} e^{-ika/2} + \beta_{p1} e^{ika/2 - kb} + \beta_{p2} e^{-ika/2 + kb}$$

Put these in  $\begin{vmatrix} \beta_{11} - E & \beta_{12} \\ \beta_{21} & \beta_{22} - E \end{vmatrix} = 0$  and solve to give:

β (meV)	HOMO
a1	200
a2	230
b	35
p1	20
p2	7

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### (TMTSF)<sub>2</sub>PF<sub>6</sub>

$$E(k) = 2\beta_b \cos(kb) \pm \sqrt{\Delta}$$

$$\Delta = [(\beta_{a1} + \beta_{a2}) \cos(\frac{ka}{2}) + (\beta_{p1} + \beta_{p2}) \cos(\frac{ka}{2} - kb)]^2 + [(\beta_{a1} - \beta_{a2}) \sin(\frac{ka}{2}) + (\beta_{p1} - \beta_{p2}) \sin(\frac{ka}{2} - kb)]^2$$

方向	β (meV)
a1	200
a2	230
b	35
p1	20
p2	7

Calculated from MO

Energy/eV

EF

0.5

-0.5

Direction: a1, a2, b, p1, p2

Quasi-1D conductor

Considerable waving reflects the 2D character.

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### Fermi surface of organic superconductor

$\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>

方向	相互作用	$\beta$ (meV)
1→1	$\pm c$	c
2→2	$\pm c$	c
1→2	$b+c$	p1
	$c$	p2
	$b$	c
		q1
		q2
		q1
		q2

Transfer integrals  
 $\beta$  (meV)  
 方向 HOMO  
 p1 245  
 p2 84  
 c 50  
 q1 127  
 q2 68  
 From MO calc.

$$\beta_{11} = \beta_{22} = \beta_c e^{ikc} + \beta_c e^{-ikc} = 2\beta_c \cos(kc)$$

$$\beta_{12} = \beta_{21} = \beta_{p1} + \beta_{p2} e^{i(kb+kc)} + \beta_{q2} e^{ikc} + \beta_{q1} e^{ikb}$$

Cylindrical Fermi surface indicated 2D.

Program available from <http://www.op.titech.ac.jp/lab/mori/lib/program.html>

### Different $\beta$ for single and double bonds

$\beta_1 = \beta_2$

$\beta_1 \neq \beta_2$

Reduced zone

Extended zone

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### Peierls Insulator: Long periodicity generates a new energy gap and makes the system insulating.

$\beta_1 = \beta_2$

Metal

$\beta_1 \neq \beta_2$

Insulator

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