## Energy Band (Tight-Binding Approximation)

LCAO-MO of a one-dimensional polymer

$$
\begin{array}{lllll}
\chi_{1} & \chi_{2} & \chi_{3} & \chi_{4} & \chi_{5}
\end{array}
$$

$$
\varphi=\sum_{n} c_{n} \chi_{n}
$$

The secular equation is

$$
\underbrace{\left\lvert\, \begin{array}{ccc}
\alpha-E & \beta & 0 \\
\beta & \alpha-E & \beta \\
0 & \beta & \alpha-E
\end{array}\right.}_{N \times N \text { 次 }} \quad \cdots . . . \mid
$$

We can directly solve this, but we use another way:

$$
\phi=\sum_{n} c_{n} \chi_{n}
$$

translation by one unit cell, $\boldsymbol{r} \rightarrow \boldsymbol{r}+\boldsymbol{a}$
should not change the physics, because it only changes the atom number.
So the electron density $\rho=\phi^{*} \phi$ does

not change. Accordingly, $c_{n+1}{ }^{*} c_{n+1}=c_{n}{ }^{*} c_{n}$
or only the phase of $c_{n}$ may change. Thus, we can put
$c_{n+1}=c_{n} e^{i \theta}=c_{n} e^{i k a}$, Consequently $\phi$ is:

$$
\begin{aligned}
\phi & =c_{0}\left[\chi_{0}+e^{i k a} \chi_{1}+e^{i 2 k a} \chi_{2}+e^{i 3 k a} \chi_{3}+e^{i 4 k a} \chi_{4}+\ldots .\right] \\
& =c_{0} \sum_{n} e^{i n k a} \chi_{n}
\end{aligned}
$$

(Bloch function)
$c_{0}$ is mere a normalization constant.

$$
\begin{aligned}
& \text { Energy of } \phi=\sum e^{i n k a} \chi_{n} \quad \text { is } \\
& E=\frac{\int \phi^{*} H \phi d \tau}{\int \phi^{*} \phi d \tau}=\frac{\int\left(\sum_{m} e^{-i m k a} \chi_{m}^{*}\right) H\left(\sum_{n} e^{i n k a} \chi_{n}\right) d \tau}{\int\left(\sum_{m} e^{-i m k a} \chi_{m}^{*}\right)\left(\sum_{n} e^{i n k a} \chi_{n}\right) d \tau} \\
& =\frac{\sum_{n} \sum_{m} e^{i(n-m) k a} \int \chi_{m}^{*} H \chi_{n} d \tau}{\sum_{n}^{m} \sum_{m} e^{i(n-m) k a} \int \chi_{m}^{*} \chi_{n} d \tau} \\
& n \\
& =\frac{N\left(e^{i k a} \beta+\alpha+e^{-i k a} \beta\right)}{N} \\
& E=\alpha+2 \beta \cos k a
\end{aligned}
$$

## $E=\alpha+2 \beta \cos k a$

Owing to the periodicity, we only consider
( $\quad \begin{aligned}-\pi<k a<\pi \\ \text { or } \\ \text { or }\end{aligned}$ )

(2) Owing to $\beta<0$,
$\begin{array}{ll}\text { Maximum of } E \text { is (at } k=\pi / a) & E=(\quad) \\ \text { Minimum of } E \text { is (at } k=0) & E=(\quad)\end{array}$
(3) As a whole, the energy band has the bandwidth,

## $E=\alpha+2 \beta \cos k a$

$$
\phi=\sum_{n} e^{i n k a} \chi_{n}
$$


(4) Make a ring.
(Otherwise, "edge state"

## appears.)

When the total atoms are $N, N$-the atom $=0$-th atom, so
$e^{i N k a}=1 \rightarrow N k a=2 \pi n \quad(n$ : integer $) k=(\quad) \begin{aligned} & \text { Periodical } \\ & \text { boundary }\end{aligned}$
boundary condition


Very fine for large $N$.
$\rightarrow$ Nearly continuous (Energy band)

## $E=\alpha+2 \beta \cos k a$

(5) $\phi=\sum e^{\text {inka }} \chi_{n}$
$k=0$ leads to $\quad \phi=\chi_{0}+\chi_{1}+\chi_{2}+\chi_{3}+\ldots$.
$k=\pi / a$ leads to

$$
\begin{aligned}
& \phi=\chi_{0}+\chi_{1}+\chi_{2}+\chi_{3}+\ldots . \\
& \phi=[
\end{aligned}
$$



## All intervals have nodes.

$\rightarrow$ Completely antibonding


Completely bonding
The state next to $k=0$ has extra $e^{i \frac{2 \pi}{N}} \quad$ phase. When rotated around the solid, the phase shifts by $2 \pi$. So the whole solid has only one node.
(8) For $2 N$ electrons

$$
2 \frac{2 k_{\mathrm{F}}}{\frac{2 \pi}{N a}}=2 N \rightarrow k_{\mathrm{F}}=()
$$

All states are occupied I


Two electrons, $\uparrow$ and $\downarrow$, enter in one atomic orbital $\chi$.
(9) For $N=6$


$\pi$ orbitals (Hückel method) for benzene
Similarly, we can calculate Hückel molecular orbitals for $N$-carbon rings.

Cyclopentadienyl anion (right) is pentagon
and has delocalized negative charge.
Calculate the energy levels from the
equation of the tight-binding band, $E=\alpha+2 \beta \cos k a$.
( 1 ) When $N=5, k$ takes the values of $0, ~ \pm \mathrm{A}, ~ \pm \mathrm{B}$. Show A and B .
( 2 ) Obtain the energy levels.
Use $\cos (2 \pi / 5)=\cos 72^{\circ}=0.309, ~ \cos (4 \pi / 5)=\cos 144^{\circ}=-0.809$
( 3 ) Calculate energies of the anion, the radical and the cation.

## Free electron approximation

(1) Simple free electron approximation derived from the first principle of quantum mechanics.
(2) Electrons in metals, particularly the energy and momentum distribution, are investigated starting from a large number of free electrons.
(3) Distribution of electrons at finite temperatures are discussed in view of the Fermi statistics:
statistical mechanics.


Wave number $k=2 \pi / \lambda$ is inverse of the wavelength.
The number of waves in unit $\times 2 \pi$ length.
$E=\frac{p_{x}^{2}+p_{y}^{2}+p_{z}^{2}}{2 m}+V$ in three dimension.
Schrödinger equation is,
$\left[-\frac{\hbar^{2}}{2 m}\left(\frac{\partial^{2}}{\partial x^{2}}+\frac{\partial^{2}}{\partial y^{2}}+\frac{\partial^{2}}{\partial z^{2}}\right)+V\right] \phi=E \phi$
Eigenfunction (solution) for $V=0$ is $\phi(x, y, z)=e^{i\left(k_{x} x+k_{y} y+k_{z} z\right)}$
Eignevalue (energy) is $E=($


We cannot depict $k_{z}$ at the same time.

Instead of an infinite space, consider a box with a finite length $L$, and the $x=L$ edge is connected to $x=0$.
$\bigcirc$ (Otherwise, the edge generates a
"surface" state.)
$\phi(x+L, y, z)=\phi(x, y, z)$

$$
e^{i k_{x} L}=1 \rightarrow k_{x} L=2 \pi n \rightarrow k_{x}=(\quad)
$$

( $n$ : integer)
Similarly for $y, z$,
$k_{x}=\frac{2 \pi}{L} n_{x} \quad k_{y}=\frac{2 \pi}{L} n_{y} \quad k_{z}=\frac{2 \pi}{L} n_{z}$
(Consider a cube with $L$ edges.)



Interval of energy levels
$\rightarrow$ continuous for large $L$.
$\rightarrow$ Energy band

Fill $N$ electrons according to the Pauli's exclusion principle.
Starting from the origin with the minimum energy, to the inside of a sphere with radius $k=\sqrt{ } k_{x}{ }^{2}+k_{y}^{2}+k_{y}^{2}$

Volume of a sphere with radius $k$ is


One energy level has two electrons with $\uparrow$ and $\downarrow$ spins


Electron with the highest energy
(Fermi energy) is
$k_{\mathrm{F}}{ }^{2}=k_{x}^{2}+k_{y}^{2}+k_{y}^{2}$ $E_{\mathrm{F}}=\frac{\hbar^{2}}{2 m} k_{\mathrm{F}}^{2}=\frac{\hbar^{2}}{2 m} \times(\square)$
is solved as for $N$ to give,

$$
N=\frac{V}{3 \pi^{2}} \times(
$$

Differentiate as for $E$, and the number of energy levels per unit energy (density of states or states density) is


Another derivation of states density
Surface of the sphere
$2 \frac{4 \pi k^{2} d k}{\left(\frac{2 \pi}{L}\right)^{3}}=d N$

$$
E=\frac{\hbar^{2} k^{2}}{2 m} \text { より } d E=\square
$$

$$
\begin{array}{r}
D(E)=\frac{d N}{d E}=2 \frac{4 \pi k^{2}}{\left(\frac{2 \pi}{L}\right)^{3}} \frac{1}{\frac{\hbar^{2} k}{m} d k}=\frac{V}{2 \pi^{2}} \frac{2 m}{\hbar^{2}} k=\frac{V}{2 \pi^{2}}\left(\frac{2 m}{\hbar}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \\
k=\left(\frac{2 m E}{\hbar^{2}}\right)^{\frac{1}{2}} \quad \text { The same } \\
\text { conclusion }
\end{array}
$$

