

Lecture 6

①

Solid-state physics

* Unit cell & reciprocal space

* Bloch's theorem

* MO picture of solids - band theory

So far, we have focused on molecular systems.

Nevertheless, the quantum mechanical methods used to

study the electronic structures of molecules can be

generalized to study electronic structures of solids.

QM is actually very successful in solid-state

physics. Note that the success of DFT

theory is first recognized in solid-state physics

in the 80s. Here we will introduce key
notations in solid-state physics; for chemical
properties of "Bulk" system often depends on solid-state
physics, timeless

③

Even now, chemistry is more & more depending on devices that require considering a extensive structures. ~~esp~~ examples of solid state stuff in chemistry:

⇒ organic materials → DMO, CNT, Graphene.

⇒ surface chemistry.

⇒ molecular assemblies, periodic solution as a zeroth order approximation.

⇒ Inorganic chemistry, nanostructures (QD, QW)...

The objective is to give a general introduction on terms & notations that are not familiar to ~~the~~ common chemistry students.

So we can later read ~~the~~ literature ~.

3

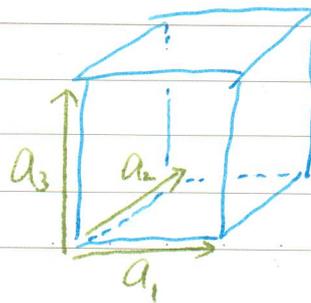
Note that we will mainly focus on crystals.

What is special about a crystal?

translational symmetry, ^{a crystal} is an extensive structure with a well-defined "unit cell" meaning all atoms in the crystal can

be identified by the following relationship:
a set of basis vectors that defines the unit cell — $\vec{r} = \vec{r}_0 + (n_1 \cdot \vec{a}_1 + n_2 \cdot \vec{a}_2 + n_3 \cdot \vec{a}_3)$,
where $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ denote the unit cell vectors, and when a unit cell and atoms in it are

specified, the structure & all atomic positions are specified.



④

In real space, there are 14 possible unit cells \Rightarrow 14 Bravais lattices.

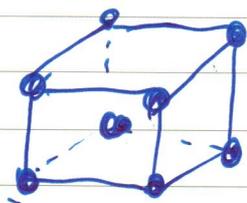
If including atom filling pattern, there can be 230 different space groups. i.e. 230 types of real space structures. These real space unit cells are common and have been introduced in general chemistry or high-school chemistry.

examples are :

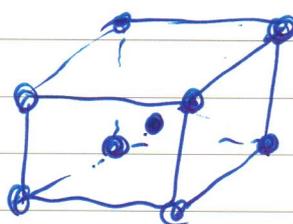
* $a=b=c, \alpha=\beta=\gamma=90^\circ$ (cubic)

Cubic
class

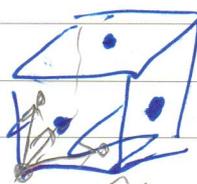
simple cubic



body centered cubic (BCC)



face-centered cubic (FCC)



determine $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$?

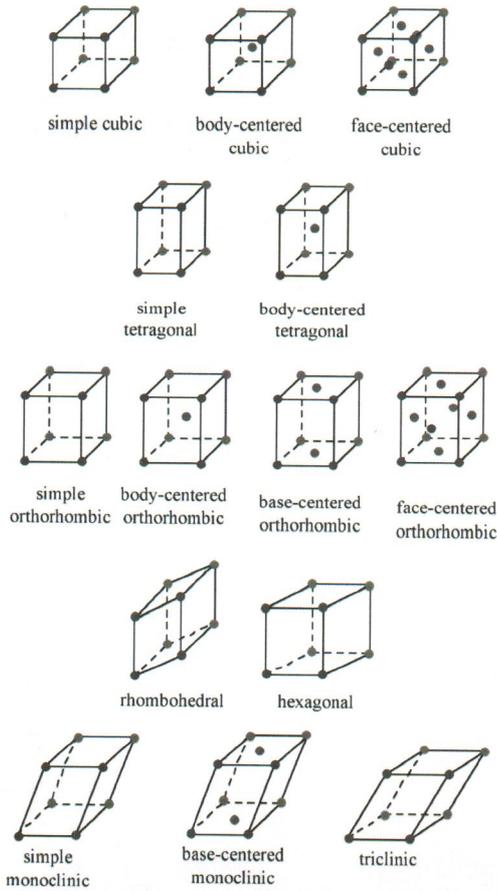
$$\begin{aligned} a_1 &= \frac{a}{2}(\hat{y} + \hat{z}) \\ a_2 &= \frac{a}{2}(\hat{x} + \hat{z}) \\ a_3 &= \frac{a}{2}(\hat{x} + \hat{y}) \end{aligned}$$

timeless

* $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$. (orthorhombic).



graphics8.png (PNG Image, 750x1363 pixels) - Scaled (86%)



<http://cnx.org/content/m16927/latest/graphics8.png>

referred to as primitive vectors. timeless

⇒ mathematically, these cells are defined by "primitive vectors". timeless

What are plane waves??

In general, we describe crystals in the reciprocal space.

plane waves are natural basis for solving

Because a plane wave with appropriate wave-vector ~~will~~ ~~in the~~ will have the periodicity of the Bravais lattice, it is natural to represent the solution to the Schrodinger equation using plane wave solutions.

problems in crystals

Considering $\vec{R} = (a_1, b, c)$ representing a Bravais lattice, the plane wave solution $e^{i\vec{k} \cdot \vec{r}}$ will satisfy the symmetry of the lattice if

$$e^{i\vec{k} \cdot (\vec{r} + \vec{R})} = e^{i\vec{k} \cdot \vec{r}}$$

$$\Rightarrow e^{i\vec{k} \cdot \vec{R}} = 1$$

direct lattice

shows \vec{k} 's form a reciprocal lattice

$$\begin{aligned} (a^*, b^*, c^*) &\rightarrow (b_1, b_2, b_3) \\ (a, b, c) &\rightarrow (a_1, a_2, a_3) \end{aligned}$$

(6)

such $\{\vec{k}\}$ form reciprocal lattice. There is

a standard way to construct them given

$$\vec{R} = (a_1, a_2, a_3) \leftarrow \text{primitive cell vectors.}$$

$$b_1^* = \frac{b \times c}{a \cdot b \times c} \times 2\pi, \quad b_2^* = \frac{a \times c}{b \cdot a \times c} \times 2\pi, \quad b_3^* = \frac{a \times b}{c \cdot a \times b} \times 2\pi$$

It is easy to verify that cross terms vanish (i.e., $\vec{a}_i \cdot \vec{b}_j = \delta_{ij} \cdot 2\pi$)
 so that $\vec{k} \cdot \vec{R} = e = 1$.

now any vector in the reciprocal space can

be written as

$$\vec{k} = k_1 \cdot b_1^* + k_2 \cdot b_2^* + k_3 \cdot b_3^*$$

any ~~point~~ ^{atomic position} in the real space can be written as

$$\vec{r} = n_1 \cdot a_1 + n_2 \cdot a_2 + n_3 \cdot a_3$$

when n_1, n_2, n_3 are integers. It follows

that

$$\vec{k} \cdot \vec{r} = 2\pi (h_1 n_1 + h_2 n_2 + h_3 n_3) \quad \text{--- (1)}$$

we choose h_1, h_2, h_3 to be integers so that the reciprocal lattice is sampled.

note that $\vec{a}^*, \vec{b}^*, \vec{c}^*$ form a "primitive cell"

called the Wigner-Seitz cell, which is

often called the first Brillouin zone,

example 1,

cubic

$$\vec{a}_1 = a \hat{x}, \vec{a}_2 = b \hat{y}, \vec{a}_3 = c \hat{z}$$

$$\text{then } \vec{a}_1^* = \frac{2\pi}{a} \hat{x}, \vec{a}_2^* = \frac{2\pi}{b} \hat{y}, \vec{a}_3^* = \frac{2\pi}{c} \hat{z}$$

← what is the unit cell of FCC??

FCC lattice

$$\vec{a}_1 = \frac{a}{2} (\hat{y} + \hat{z}), \vec{a}_2 = \frac{a}{2} (\hat{x} + \hat{z}), \vec{a}_3 = \frac{a}{2} (\hat{x} + \hat{y})$$

then

$$\vec{b}_1 = \frac{4\pi}{a} \times \frac{1}{2} (\hat{y} + \hat{z} - \hat{x}), \vec{b}_2 = \frac{4\pi}{a} \times \frac{1}{2} (\hat{z} + \hat{x} - \hat{y}), \vec{b}_3 = \frac{4\pi}{a} \times \frac{1}{2} (\hat{x} + \hat{y} - \hat{z})$$

⇒ reciprocal lattice of a FCC lattice is a BCC lattice with cell size $\frac{4\pi}{a}$ ✓

Bloch's theorem

In summary, periodic, crystal structures are described by primitive vectors in a Bravais lattice:

$$\vec{R} = \{\vec{a}_1, \vec{a}_2, \vec{a}_3\} \quad (\text{real space})$$

and in the reciprocal space

$$\vec{K} = \{\vec{b}_1, \vec{b}_2, \vec{b}_3\}$$

defines all the "possible" \vec{K} points.

single-electron
states,

ie,

lattice
orbitals

first

Now we can turn to consider physics.

For the electronic structure problem, consider a one-electron lattice Hamiltonian:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}).$$

this is a "one-electron" Hamiltonian that

naturally occurs, for example, if one considers

the Hartree-Fock solution to a crystal system.

In which $U(r)$ has the periodicity of
the underlying Bravais lattice:

any primitive vector

$$U(\vec{r} + \vec{a}_i \cdot n) = U(\vec{r})$$

↑ integers

A example is:



The eigenstate of this one electron Hamiltonian

must have the translational symmetry represented

by the potential. Mathematically, this

~~is presented~~ leads to the

Bloch's theorem.

Bloch's Theorem

The eigenstates of \hat{H} can be chosen so that associated with each ψ is a wavevector k such that

$$\psi_{\frac{k}{h}}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}} \psi_{\frac{k}{h}}(\vec{r})$$

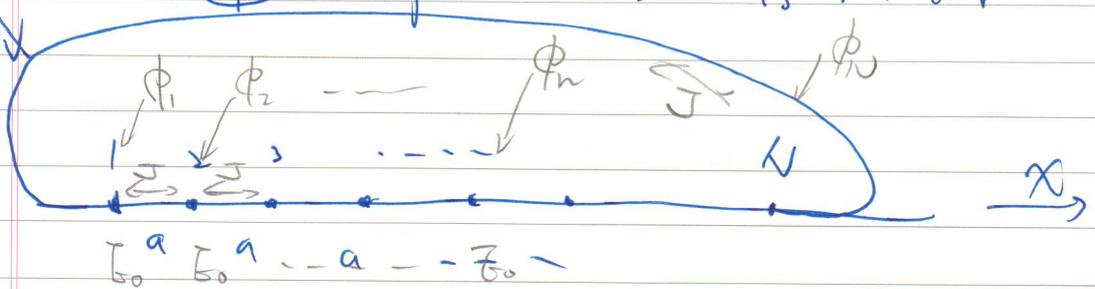
\vec{k} labels eigenstates
 \vec{R} any Bravais lattice vector in the lattice

For simplicity, hereafter we consider a 1-D lattice with lattice constant a .

The simple example is enough to demonstrate the basic ideas & the generalization to

~~more complex~~ higher dimensions is not complicated.

periodical boundary condition



Assume N sites $\Rightarrow N$ very large so

\Rightarrow it is the same as infinite \Rightarrow we can actually adopt a periodic boundary condition **timeless**

periodic wave function

$$\psi_k(x) = \sum_n C_n \phi(x - n \cdot a) \quad \leftarrow \text{--- ①}$$

shift $x \rightarrow x+a$

$$\psi_k(x+a) = \sum_n C_n \phi(x - (n-1) \cdot a)$$

$$= \sum_{m=0}^{N-1} C_{m+1} \cdot \phi(x - ma)$$

PBC, $C_N = C_0$

$$= \sum_{n=1}^N C_{n+1} \cdot \phi(x - na) \quad \leftarrow \text{--- ②}$$

Compare ① & ②

$$C_{n+1} = C_n \cdot e^{i k a}$$

note that the total phase does not

matter, $\rightarrow C_1 = C_0 \cdot e^{i k a}$

$$\therefore C_n \propto e^{i k n a}$$

M.O. picture of solids (also called the tight-binding limit). (4)

Wave function
 \hbar spin
 \rightarrow discrete
 $E-T$
of the bands
site
dynamics

If we further associate a ^{localized} one-electron wave function $\phi(x)$ to each ~~site~~ site, i.e. atomic orbitals, then the Bloch theorem

~~requires~~ yields directly the equations:

$$\psi_e(x) = \sum_n c_n \cdot \phi(x-na)$$

$$\psi_e(x) = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ikna} \cdot \phi(x-na)$$

$$\Rightarrow \psi_e = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ikna} \cdot \phi_n$$

It is easy to verify that ~~with the~~ ~~periodic boundary~~ ~~condition~~

The eigenfunctions satisfy the Bloch's theorem

Also, given the periodic boundary conditions, the values of k are limited to specific values!

the coefficient of the $n=N+1$ must equal to $n=1$
i.e. $C_1 = C_{N+1}$

$$\text{So } e^{i k a} = e^{i k (N+1) a} \Rightarrow e^{i k N a} = 1 \quad (\oplus)$$

due to PBC $\rightarrow k \cdot N \cdot a = 2\pi$, $k = \frac{m}{N} \times \frac{2\pi}{a}$, $m = 1, 2, \dots, N$

Note that:

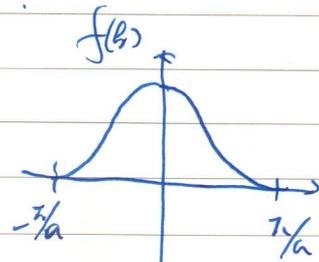
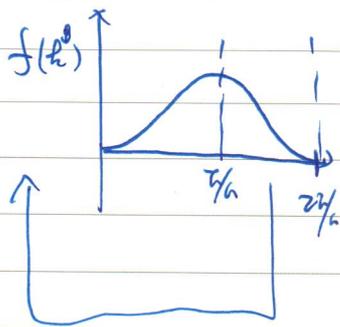
① totally N k states from N basis site functions.

② range of k is from $0 \dots \frac{2\pi}{a}$, however,

since $e^{i\pi - k'} = e^{-k'}$, any function in the k'

space can be folded from $(\pi \dots 2\pi)$ to

$(-\pi \dots 0)$ and we symmetrized $k' = -\pi \dots \pi$ apply to the waveform too.



← this range is the first Brillouin zone.

band structure

Now we can calculate energy of the k -states.

~~$\hat{H}_k = \hat{H}_k$~~

Here, we assume that

$$\langle \phi_n | \phi_n \rangle = \delta_{nm}$$

$$\langle \phi_n | \hat{H} | \phi_n \rangle = E_0 \leftarrow \text{site energy, equalize sites.}$$

$$\langle \phi_n | \hat{H} | \phi_m \rangle = \pm \delta_{n, m \pm 1} \leftarrow \text{nearest-neighbor coupling, PBC.}$$

Transfer Integral.

$$\therefore E_k = \langle \psi_k | \hat{H} | \psi_k \rangle$$

N diagonal terms
 \leftarrow $\pm N$ off-diagonal terms

$$= \sum_{n,m} \frac{1}{N} \cdot e^{-ikna} \cdot e^{ikna} \cdot \langle \phi_m | \hat{H} | \phi_n \rangle$$

$$= \frac{1}{N} E_0 \oplus E_0 \quad \pm (\delta_{n, m=n+1} + \delta_{n, m=n-1})$$

$$+ \frac{1}{N} \sum_{n \neq m} e^{i k(n-m)a} \cdot \langle \phi_m | \hat{H} | \phi_n \rangle$$

$$= E_0 + \left(\frac{1}{N} \right) \times \text{circled terms} \cdot \sum_n \sum_{m \neq n} \pm \left\{ e^{i k(n-m)a} \cdot \delta_{m=n+1} + e^{i k(n-m)a} \cdot \delta_{m=n-1} \right\}$$

goes away

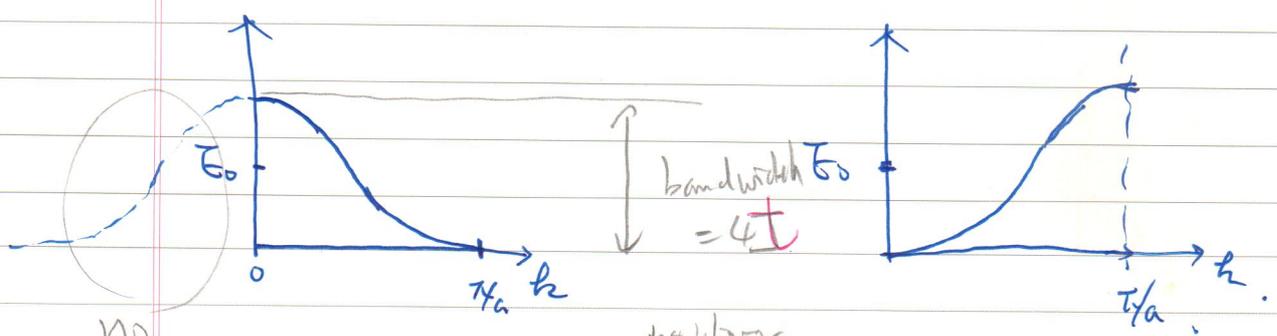
$$= E_0 + \pm (e^{-ika} + e^{ika})$$

$$= E_0 + 2J \cdot \cos(ka)$$

now depending on the sign of J
 the energy became:

$J > 0$

$J < 0$

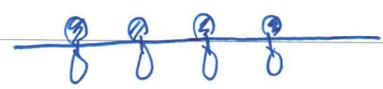
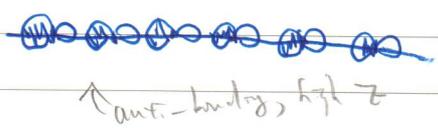


no need to eq.

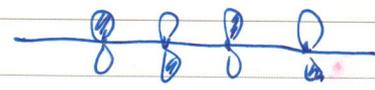
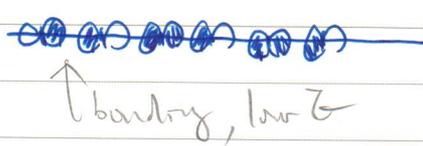
p_x bands:

eg. s band or p_z bands.

plot this E_0 because of



even $z = \pi/a$ lower

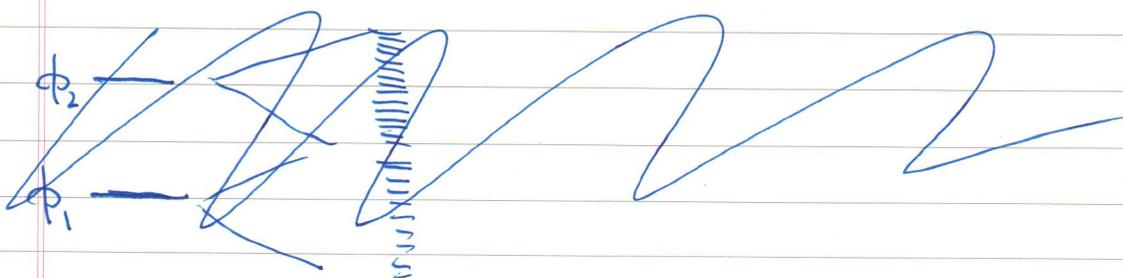


energy band !!

when $N \rightarrow \infty$.

~~this is the~~

Note that the idea can be easily generalized
 to multiple ~~AOs~~ AOs, per unit cell. ~~if you~~
~~at the one then consider HOMO & LUMO.~~



In these case, ~~one~~ multiple bands could be generated,
 minimal p-orbital model for
 for example, consider polyacetylene.

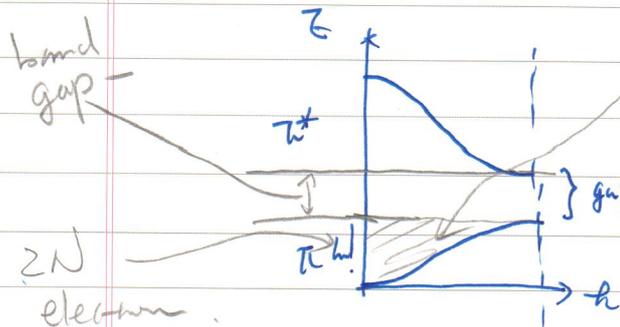


\therefore basis orbital: $\pi \Rightarrow$ $\leftarrow E_{\pi}$

$\pi^* \Rightarrow$ $\leftarrow E_{\pi^*}$

$E_{\pi^*} \gg E_{\pi}$

the band structure:



one electron thus,
 & there are N
 h states here!
 \Rightarrow and $2N$ electrons
 \uparrow just make!!

gap because $E_{\pi^*} - 2J_{\pi^*} > E_{\pi} + 2J_{\pi}$

the electronic structure \rightarrow fill n e^-

In this case, the π -band is filled \Rightarrow valance band.

π^* -band is empty \Rightarrow conducting band.

Note that polycarbonate is a semiconductor as predicted

by this theory. It can be turn into conductor by

"doping".

The band structure idea can be easily generalize to multiple dimensions, with now difference \vec{k} along reciprocal lattice vectors.

However, since multidimensional PESs are difficult to picture, in literatures one often see ~~the~~

~~multiple dimensional~~ energy bands display as Cuts through reciprocal space, ^{provides}

example:

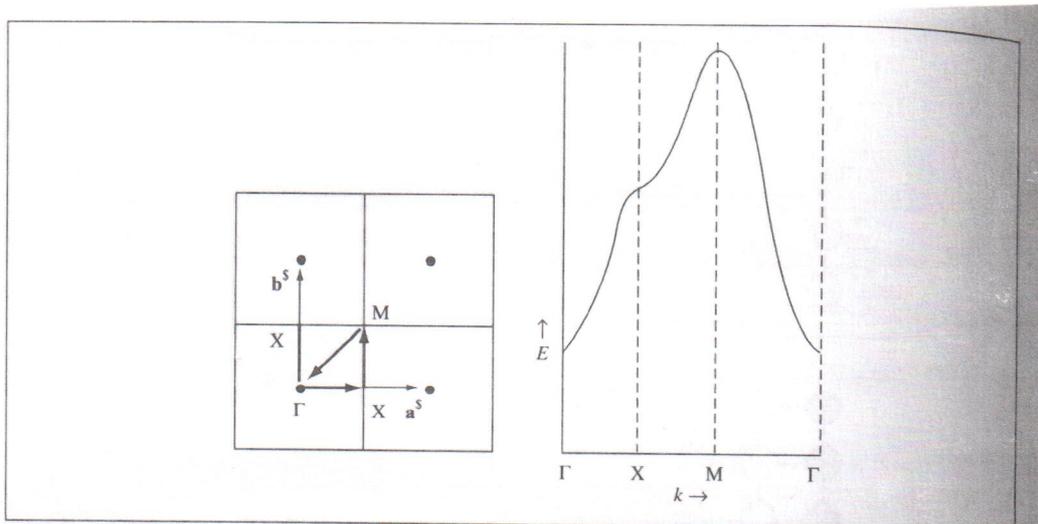


Fig. 3.14: Variation in energy for a 'tour' (Γ -X-M- Γ) of the reciprocal lattice for a 2D square lattice of hydrogen atoms. (Figure adapted in part from Hoffmann R 1988. Solids and Surfaces: A Chemist's View on Bonding in Extended Structures. New York, VCH Publishers.)

~~properties of Solids~~

(2)

The energy band of a solid provides much:

- ① group velocity of a Bloch state with wave vector k is the derivative in band energy:

$$v(k) = \frac{1}{\hbar} \nabla_k \cdot E(k)$$

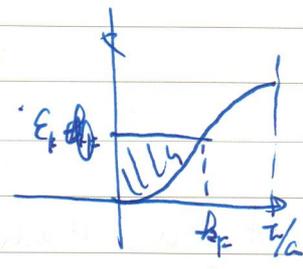
this is the "mean ~~vel~~ velocity" of a traveling wave \Rightarrow often called band-like motion of electrons.

- ②, very often a free-electron approximation can be used at the bottom of the band.

$$\text{i.e. } E(k) = \frac{\hbar^2}{2m^*} k^2$$

$$\text{where } m^* = \frac{\hbar^2}{\left(\frac{\partial^2 E(k)}{\partial k^2} \right) \Big|_{k=0}}$$

③ When a band is partially filled, then we define Fermi surface & Fermi energy



↑ defines Fermi surface in the reciprocal space.

④ Density of States

⇒ See Ashcroft, 10143 - 145

⇒ ~~the~~ example combined band structure + DOS explains many solid state properties.

↑ 这是通常看到的计算结果