IX. Electron States in Solids

A. The Problem

- Free electron model : ignored periodic potential
  ignored el-el interactions
- What is the influence of the periodic potential on electronic states?

Approximate the many-electron problem ($\sim 10^{23}/\text{cm}^3$) as a single electron problem, but account for the discrete translational symmetry

$\psi(\vec{r})$ = single-electron wavefunction

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

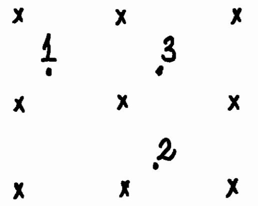
where $V(\vec{r})$ is a periodic potential energy function with the periodicity of the lattice

$$V(\vec{r}) = V(\vec{r}+\vec{R}) \quad , \quad \vec{R} = \text{lattice vectors}$$

How to solve this problem?
Properties of $\mathcal{E}$ and $\psi(\vec{r})$?

Underlying physics in $V(\vec{r})$?

- Due to regular array of nuclei or ions
  How about lattice vibrations?
- How about the effects of other electrons?
  These electrons, on the average, also contribute to $V(\vec{r})$.



$V(1) = V(2) = V(3)$
same environment

QM: $|\psi(\vec{r})|^2 \propto$ probability of finding particle at $\vec{r}$ (Born

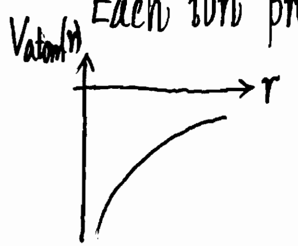
- By discrete translational symmetry, we expect
  $|\psi(1)|^2 = |\psi(2)|^2 = |\psi(3)|^2$
- $|\psi(\vec{r})|^2$ is the same at equivalent positions

$$\boxed{|\psi(\vec{r})|^2 = |\psi(\vec{r}+\vec{R})|^2}$$

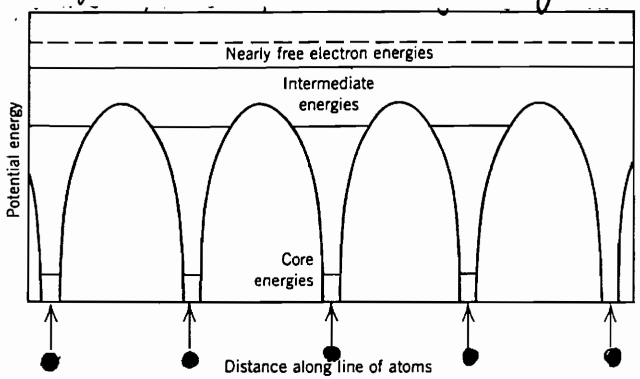
But this does NOT imply $\psi(\vec{r}) = \psi(\vec{r}+\vec{R})$
In fact $\psi(\vec{r}) \neq \psi(\vec{r}+\vec{R})$,
they are related by a phase factor (Bloch's theorem)

B. What do we expect qualitatively?

Each ion provides a potential of the form



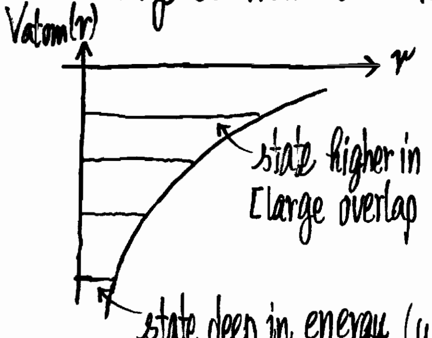
Putting ions together to form a regular array,



Give periodic $V(\vec{r})$

Electron potential energy along a line of atoms in a crystal. The dotted line indicates the energy for an electron outside the solid. Positions of nuclei are marked by arrows and representative allowed energy levels are shown as solid horizontal lines. Core states have energies deep in the potential wells near each nucleus. Nearly free electrons have energies well above the potential energy maxima.

Solving electron states for each ion:

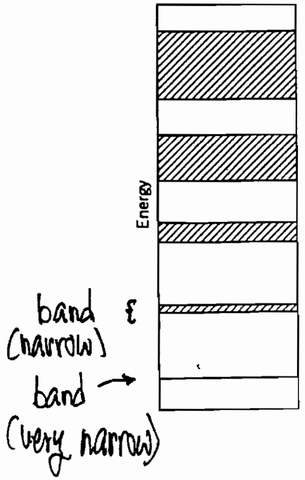


state higher in energy (wavefn more extended)
[large overlap with wavefns of neighboring atoms]

state deep in energy (wavefn closer to ion)
[small overlap with wavefns of neighboring atoms]

- Putting atoms together (~3 Å apart) ⇒ wavefunctions overlap
  smaller overlap ⇒ smaller spread in energies of eigenstates
  larger overlap ⇒ larger spread in energies of eigenstates

∴ Bands of eigenstates separated by band gaps



} band (wide)

} band gap (no allowed states for electrons in this range of energies)

Energy levels for an electron bound in a crystalline solid. Shaded regions indicate groups of allowed energy values. Each group actually consists of a large number of discrete levels, too close together to distinguish on the diagram. The groups are narrow for low energy and wide for high energy. No electron may have energy in a gap.

C. The Bloch's theorem

Aim: How is $\psi(\vec{r}+\vec{R})$ related to $\psi(\vec{r})$?
[in electron problem]

How is $u_{\vec{R}}$ related to $u_{\vec{R}=0}$?
[in normal mode problem of lattice vibrations]

Similarity between the electron and lattice vibration problems

Electron: $\hat{H}\,\psi(\vec{r}) = \mathcal{E}\,\psi(\vec{r})$

shows discrete translational symmetry

[QM: $\hat{H}$ commutes with all translational operators that translate the coordinates by $\vec{R}$]

An eigenvalue problem

Lattice vibrations

$$\underbrace{\frac{K}{M}\begin{pmatrix} -1 & +2 & -1 & & & & \\ & -1 & +2 & -1 & & & \\ & & -1 & +2 & -1 & & \\ & & & -1 & +2 & -1 & \\ & & & & -1 & +2 & -1 \end{pmatrix}\begin{pmatrix}\vdots \\ \bar{u}_2 \\ \bar{u}_1 \\ \bar{u}_0 \\ \bar{u}_{-1} \\ \bar{u}_{-2} \\ \vdots\end{pmatrix}}_{\overleftrightarrow{M}\,\vec{u} \,=\, \omega^2\vec{u}} = \omega^2\begin{pmatrix}\vdots \\ \bar{u}_2 \\ \bar{u}_1 \\ \bar{u}_0 \\ \bar{u}_{-1} \\ \bar{u}_{-2} \\ \vdots\end{pmatrix}$$

(see p. VI-⑯)

$$\overleftrightarrow{M}\,\vec{u} = \omega^2\vec{u}$$

↳ shows discrete translational symmetry

[$\overleftrightarrow{M}$ commutes with all translational operators]

An eigenvalue problem

∴ The electron problem and the normal mode problem are the same type of problems mathematically!

Recall: $u_{\vec{R}} = u_{\vec{R}=0}\,e^{i\vec{q}\cdot\vec{R}}$

Bloch's theorem

$$\psi(\vec{r}) \neq \psi(\vec{r}+\vec{R})$$

But $\psi(\vec{r})$ and $\psi(\vec{r}+\vec{R})$ can differ by a phase factor

Write: $$\psi(\vec{r}+\vec{R}) = e^{i\theta(\vec{R})}\,\psi(\vec{r})$$

where $\theta(\vec{R})$ is real and depends on $\vec{R}$

This form satisfies

$$|\psi(\vec{r}+\vec{R})|^2 = |\psi(\vec{r})|^2$$ as required.

- By considering the property of discrete translational symmetry, we get the form of $\theta(\vec{R})$.
- Consider two lattice translations: $\vec{R}_1$ and $\vec{R}_2$

$\psi(\vec{r}+\vec{R}_1+\vec{R}_2)$ can be evaluated in 2 ways[+]

$$\text{(i)}\quad \psi(\vec{r}+(\vec{R}_1+\vec{R}_2)) = e^{i\theta(\vec{R}_1+\vec{R}_2)}\psi(\vec{r})$$

$$\text{(ii)}\quad \psi(\vec{r}+\underset{\uparrow}{\vec{R}_1}+\underset{\nearrow}{\vec{R}_2}) = e^{i\theta(\vec{R}_2)}\psi(\vec{r}+\vec{R}_1)$$

$$\text{one by one} \quad = e^{i\theta(\vec{R}_2)}e^{i\theta(\vec{R}_1)}\psi(\vec{r})$$

$$\text{(i)}=\text{(ii)} \Rightarrow \theta(\vec{R}_1+\vec{R}_2) = \theta(\vec{R}_1)+\theta(\vec{R}_2)$$

This can be the case, if <u>$\theta(\vec{R})$ is linear in $\vec{R}$</u>

By linear, we mean θ is of the form:

$$\theta(\vec{R}) = A R_x + B R_y + C R_z,$$ where A, B, C are independent of $\vec{R}$

⌜Check: $\theta(\vec{R}_1)+\theta(\vec{R}_2)$

$$= AR_{1x}+BR_{1y}+CR_{1z}+AR_{2x}+BR_{2y}+CR_{2z}$$

$$= A(R_{1x}+R_{2x})+B(R_{1y}+R_{2y})+C(R_{1z}+R_{2z}) = \theta(\vec{R}_1+\vec{R}_2) ⌟$$

$$\therefore \boxed{\begin{array}{c}\psi(\vec{r}+\vec{R}) = e^{i\theta(\vec{R})}\psi(\vec{r}) \\ \text{with } \theta(\vec{R}) \text{ being linear in } \vec{R}\end{array}}$$

[+] The discussion also gives the mathematical form of the eigenvalues of the translational operator. The eigenvalues must be exponential in form.

Since $\theta(\vec{R})$ is linear in $\vec{R}$, we can write

$$\theta(\vec{R}) = \vec{k}\cdot\vec{R}$$

where $\vec{k}$ is a real constant vector

$$\boxed{\begin{array}{l}\underline{\text{Bloch's theorem}}: \\ \quad \psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) \\ \text{for any lattice vector } \vec{R}\end{array}}$$

The most important theorem in solid state physics.

c.f.: In treating lattice vibrations, we used

$$\vec{u}_{\vec{R}} = e^{i\vec{q}\cdot\vec{R}}\vec{u}_{\vec{R}=0}$$

this is a consequence of the Bloch's theorem.

∴ Many results in lattice vibrations can directly be used here.

D. <u>Comparing the normal mode and electron states problems</u>

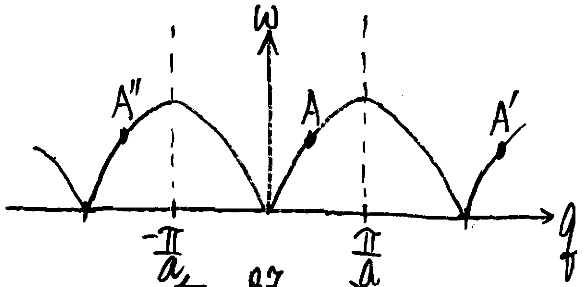
Lattice Vibrations (Normal Modes)

$$\vec{u}_{\vec{R}} = e^{i\vec{q}\cdot\vec{R}}\,\vec{u}_{\vec{R}=0}$$

$\vec{q}$ serves as a label for a normal mode

$\vec{q}$ lives in the reciprocal space

As a label, some $\vec{q}$'s are redundant! $\vec{q}$ and $\vec{q}+\vec{G}$ are redundent, since $e^{i\vec{G}\cdot\vec{R}}=1$



modes A, A', A'' are redundent

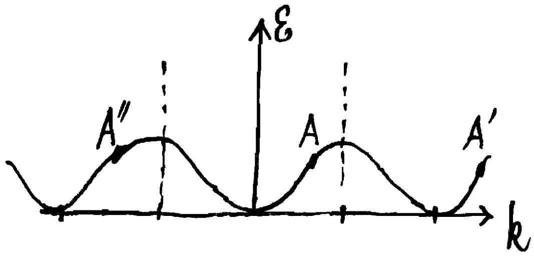
Electron States

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

$\vec{k}$ serves as a label for an electron state

$\vec{k}$ lives in the reciprocal space

As a label, some $\vec{k}$'s are redundent! $\vec{k}$ and $\vec{k}+\vec{G}$ are redundent, since $e^{i\vec{G}\cdot\vec{R}}=1$



states A, A', A'' are redundent

Lattice vibrations (normal modes)

sufficient to include $\vec{q} \in$ 1st B.Z.

$\omega_s(\vec{q})$

↖ branch index

$$\omega_s(\vec{q}) = \omega_s(\vec{q}+\vec{G})$$

$$\omega_s(\vec{q}) = \omega_s(-\vec{q})$$

Finite sample ⇒ Periodic boundary condition

⇒ discrete $\vec{q}$'s in 1st B.Z.

allowed $\vec{q}$'s per unit "volume" of reciprocal space $= \frac{V}{(2\pi)^3}$

N = # allowed $\vec{q}$'s in 1st B.Z.
= # primitive cells in sample

Electron States

sufficient to include $\vec{k} \in$ 1st B.Z.

$\mathcal{E}_n(\vec{k})$

↑ band index

$$\mathcal{E}_n(\vec{k}) = \mathcal{E}_n(\vec{k}+\vec{G})$$

$$\mathcal{E}_n(\vec{k}) = \mathcal{E}_n(-\vec{k})$$

Finite sample ⇒ Periodic boundary condition

⇒ discrete $\vec{k}$'s in 1st B.Z.

allowed $\vec{k}$'s per unit "volume" of reciprocal space $= \frac{V}{(2\pi)^3}$

N = # allowed $\vec{k}$'s in 1st B.Z.
= # primitive cells in sample

Lattice Vibrations (Normal Modes)

N modes per branch

$D(\omega)d\omega$ = # normal modes in the interval ω to $\omega + d\omega$

Electron States

N electron states labelled by different $\vec{k}$'s per band

$\Rightarrow$ 2N electron states per band ("2" comes from spin)

$g(\varepsilon)d\varepsilon$ = # electron states in the interval ε to $\varepsilon + d\varepsilon$

same method of calculation

BUT THERE IS ONE KEY DIFFERENCE

$\omega_s(\vec{q})$

finite number of branches

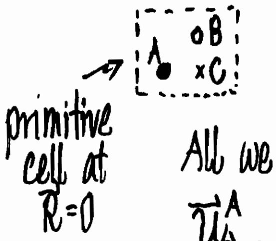
Why? finite number of degrees of freedom

$\varepsilon_n(\vec{k})$

infinite number of bands

Why? Infinite number of degrees of freedom

Lattice vibrations (Normal modes)



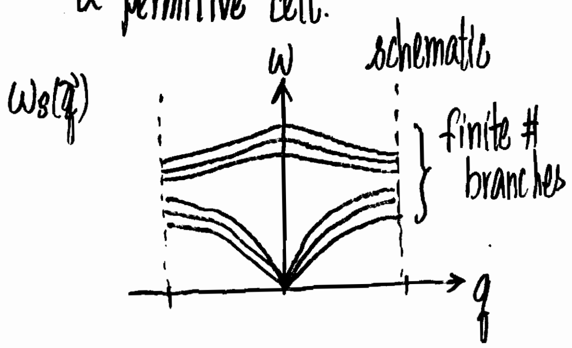
All we need to find is

$\vec{u}^{A}_{\vec{R}=0}$, $\vec{u}^{B}_{\vec{R}=0}$, $\vec{u}^{C}_{\vec{R}=0}$

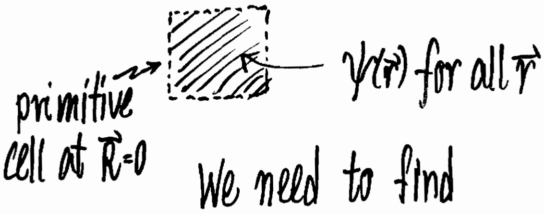
9 branches (3 atoms in basis)

3s branches (s atoms in basis)

$\therefore$ Only need to find the displacement of a finite number of atoms in a permitive cell.

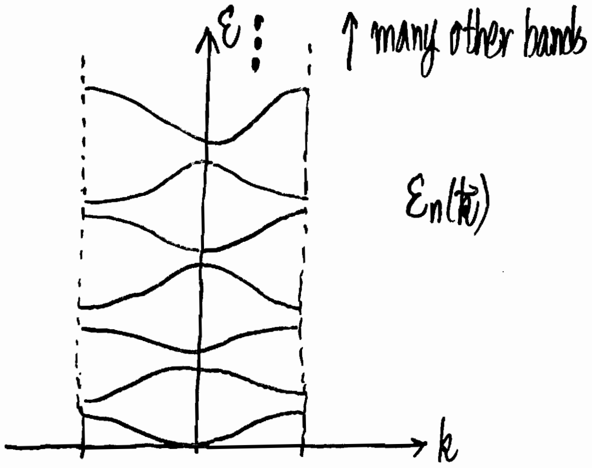


Electron States



We need to find $\psi(\vec{r})$ for all $\vec{r}$ (infinitely many)

$\therefore$ Infinite number of bands (c.f. atomic states)



E. An equivalent form of Bloch's Theorem

Bloch's theorem: $\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r})$

Recall: Free electrons (ignore $V(\vec{r})$) have $\psi(\vec{r}) \sim e^{i\vec{k}\cdot\vec{r}}$

Q: With periodic $V(\vec{r})$, how does $\psi(\vec{r})$ differ from $e^{i\vec{k}\cdot\vec{r}}$?

Writing: $\boxed{\psi(\vec{r}) = \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{\text{plane wave}} \cdot u_{\vec{k}}(\vec{r})}$ "Bloch form"

Bloch's theorem requires:

$$\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{R}} \cdot u_{\vec{k}}(\vec{r}+\vec{R}) \overset{\text{Bloch's theorem}}{=} e^{i\vec{k}\cdot\vec{R}} e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

$\Rightarrow u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$

$\Rightarrow$ $\boxed{u_{\vec{k}}(\vec{r}) \text{ is a periodic function with the periodicity of the lattice}}$

We call the form:

$$\boxed{\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \underbrace{u_{\vec{k}}(\vec{r})}_{\text{periodic}} \quad \text{a "Bloch function"}}$$

Thus, the Bloch's theorem says that the solutions (energy eigenstates) to the problem:

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

with $V(\vec{r}) = V(\vec{r}+\vec{R})$ are of the form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{where } u_{\vec{k}}(\vec{r}) \text{ is periodic}$$

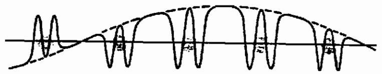
$\vec{k} \in 1^{st}$ B.Z. N allowed $\vec{k}$'s in 1^{st} B.Z.

Each crystal ⇒ its own $V(\vec{r})$

Solving this QM energy eigen-value problem is referred to as solving the electronic band structure for the material concerned.

Remarks on the form $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$

(a) a traveling plane wave ($\sim e^{i\vec{k}\cdot\vec{r}}$ as for free particle) modulated by a periodic function $u_{\vec{k}}(\vec{r})$ (due to $V(\vec{r})$) that oscillates periodically from one cell to the next cell.



(b) Just as $\hbar\vec{q}$ is the phonon crystal momentum, $\hbar\vec{k}$ is called the <u>electron crystal momentum</u> or the crystal momentum of the electron in the state $\psi_{\vec{k}}$ (or $\psi_{n\vec{k}}$).

(c) <u>Very important point</u>

$\psi_{\vec{k}}(\vec{r})$ is <u>delocalized throughout the solid</u>

[<u>not</u> localized around any particular atom]

i.e. Bloch functions are extended states

(<u>NOT</u> localized states)

(d) <u>Normalization</u>

$$\int_V |\psi_{\vec{k}}(\vec{r})|^2 \, d^3r = 1$$

In many books, the normalization is carried out by the trick of "box normalization", with "box" = volume of sample. In this case,

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

F. <u>What is the equation that $u_{\vec{k}}(\vec{r})$ satisfies?</u>

Consider
$$\nabla^2\psi_{\vec{k}}(\vec{r}) = \nabla^2\left(e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})\right)$$
$$= \vec{\nabla}\cdot\left[\vec{\nabla}\left(e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})\right)\right]$$
$$= \vec{\nabla}\cdot\left[i\vec{k}\, e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\vec{\nabla}u_{\vec{k}}(\vec{r})\right]$$
$$= -k^2 e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\, i\vec{k}\cdot\vec{\nabla}u_{\vec{k}}(\vec{r})$$
$$+ e^{i\vec{k}\cdot\vec{r}}\, i\vec{k}\cdot\vec{\nabla}u_{\vec{k}}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\nabla^2 u_{\vec{k}}(\vec{r})$$
$$= e^{i\vec{k}\cdot\vec{r}}\left(\nabla^2 + 2i\vec{k}\cdot\vec{\nabla} - k^2\right)u_{\vec{k}}(\vec{r})$$
$$= e^{i\vec{k}\cdot\vec{r}}\left(\vec{\nabla} + i\vec{k}\right)^2 u_{\vec{k}}(\vec{r})$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) + V(\vec{r})\psi_{\vec{k}}(\vec{r}) = \mathcal{E}(\vec{k})\psi_{\vec{k}}(\vec{r})}$$

$$\boxed{\left[-\frac{\hbar^2}{2m}\left(\vec{\nabla} + i\vec{k}\right)^2 + V(\vec{r})\right]u_{\vec{k}}(\vec{r}) = \mathcal{E}(\vec{k})\,u_{\vec{k}}(\vec{r})} \quad (*)$$

In Q.M., $\vec{p} \to \frac{\hbar}{i}\vec{\nabla}$,

$$\boxed{\left[\frac{1}{2m}\left(\vec{p} + \hbar\vec{k}\right)^2 + V(\vec{r})\right]u_{\vec{k}}(\vec{r}) = \mathcal{E}(\vec{k})\,u_{\vec{k}}(\vec{r})} \quad (*)$$

(*) is the equation that $u_{\vec{k}}(\vec{r})$ satisfies.

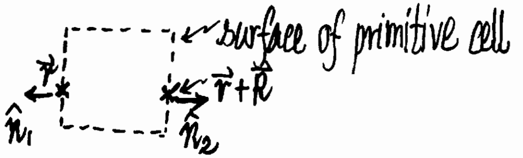
Solving (*) is equivalent to solving the Schrödinger Equation.

Since $\underline{u(\vec{r})}$ is periodic

$\Rightarrow$ need to solve $u(\vec{r})$ only in one primitive cell,

Like any QM problem, (✱) is solved with appropriate boundary conditions

⌜



continuity conditions

$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R})$ for $\vec{r}$ and $\vec{r}+\vec{R}$ on surface of primitive cell

$$\underset{\substack{\uparrow\\ \text{outward normal}\\ \text{at } \vec{r}}}{\hat{n}_1} \cdot \vec{\nabla} u_{\vec{k}}(\vec{r}) = -\underset{\substack{\uparrow\\ \text{outward normal at } \vec{r}+\vec{R}}}{\hat{n}_2} \cdot \vec{\nabla} u_{\vec{k}}(\vec{r})$$

[these are analogous to ψ and $\frac{d\psi}{dx}$ being continuous in 1D problems] ⌟

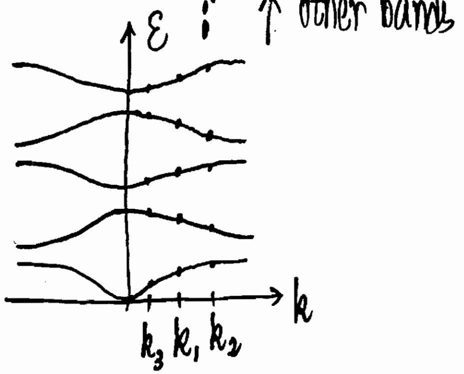
- (✱) is one equation for each $\vec{k}$
- For each $\vec{k}$, (✱) gives infinitely many eigenvalues

$$\begin{array}{cccccccc} \varepsilon_1(\vec{k}) & \varepsilon_2(\vec{k}) & \varepsilon_3(\vec{k}) & \cdots & \varepsilon_n(\vec{k}) & \cdots & \text{eigenvalues} \\ \downarrow & \downarrow & \downarrow & & \downarrow & & \\ u_{1\vec{k}}(\vec{r}) & u_{2\vec{k}}(\vec{r}) & u_{3\vec{k}}(\vec{r}) & \cdots & u_{n\vec{k}}(\vec{r}) & \cdots & \text{eigenstates} \end{array}$$

- Lining up the eigenvalues as

$$\varepsilon_1(\vec{k}) < \varepsilon_2(\vec{k}) < \varepsilon_3(\vec{k}) < \cdots$$

for each $\vec{k}$



- One QM calculation for each $\vec{k}$
- Plot $\varepsilon(\vec{k})$ for all allowed $\vec{k}$'s

$\Rightarrow$ infinitely many bands

$\therefore$ $\varepsilon_n(\vec{k})$ "band structure" of a material

$\quad\uparrow$ band index

- An electronic state is thus labelled by $(n, \vec{k})$

$$\begin{cases} \text{the eigenvalue is } \varepsilon_n(\vec{k}) \\ \text{the eigenstate is } \psi_{n\vec{k}}(\vec{r}) \end{cases}$$

- The Bloch functions can be made orthogonal to each other

$$\int_V \psi^*_{n'\vec{k}'}(\vec{r})\, \psi_{n\vec{k}}(\vec{r})\, d^3r \sim \delta_{nn'} \delta_{\vec{k}\vec{k}'}$$

- The set of all Bloch functions forms a complete set

$$\{\psi_{n\vec{k}}(\vec{r})\} \quad \text{for all } n \text{ and all } \vec{k}$$

$E_n(\vec{k})$ infinitely many bands!

- <u>Do we need to worry about infinitely many bands?</u>

<u>Fill Electrons</u> into the bands

↑ Fermi-Dirac distribution

⇒ Only several bands of lowest energies will contain electrons

↙ the very low energy filled bands

↓ will <u>not</u> affect the physics

(∵ "blocked" by Pauli Exclusion Principle)

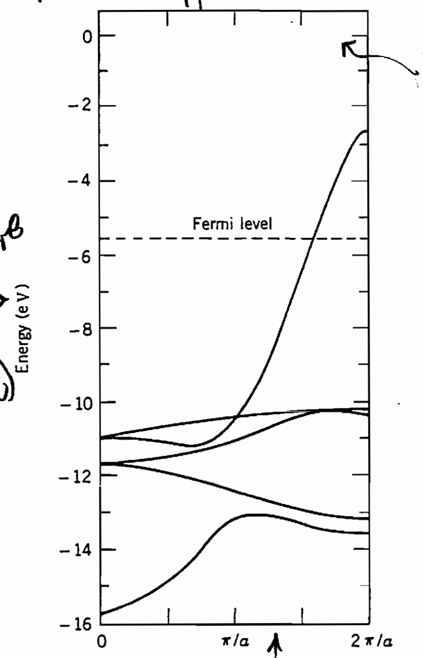
↘ the very high energy empty bands

↓ will <u>not</u> affect the physics

(∵ remain empty practically) due to Fermi-Dirac distribution

∴ The physics of a material is mostly determined by the <u>bands near E_F</u>, i.e. the highest band with electrons and the empty band just above it!

<u>Example:</u> <u>Copper</u>



Note: typical scale is eV (electronvolt)

there are higher bands (not shown)

In 3D, we need a 4-Dim plot for the energy bands.

Usually, band structures are shown along highly symmetrical directions in the reciprocal space (1st B.Z.)

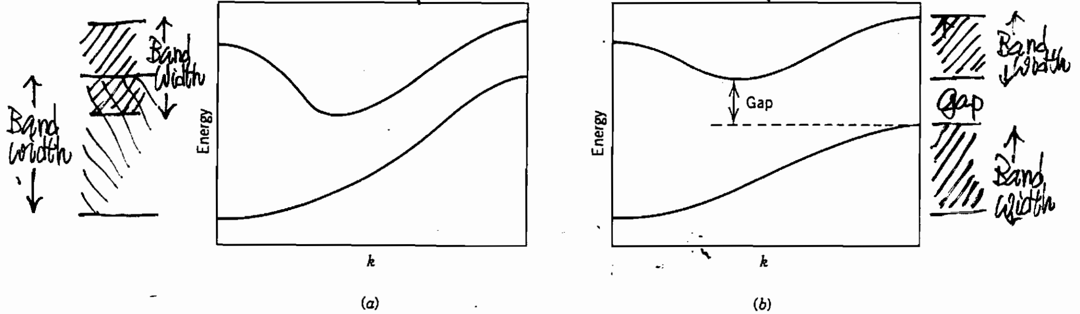
Electron energy bands for crystalline copper. The propagation vector is in the [100] direction. Bands associated with core states are not shown. The potential energy is zero at points outside the crystal.

k each k ⇓ many $E(\vec{k})$

Electrons are filled in according to the Pauli Exclusion Principle.

<u>Energy Gap</u>

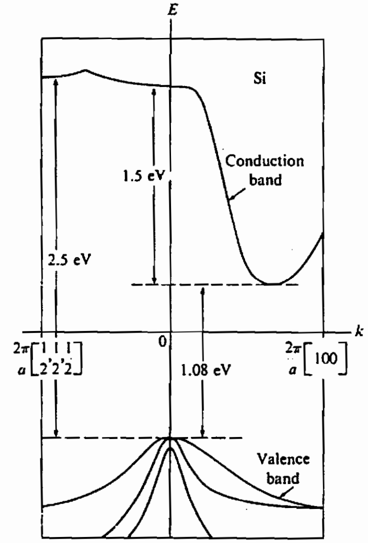
<u>No Gap</u> <u>Gap</u>



(a) The minimum of the second band is below the maximum of the first. For each propagation vector the second band energy is above the first band energy, but the energy spectrum has no gap. Compare with the situation shown in (b), for which the two bands are separated by a gap.

Example:

Silicon



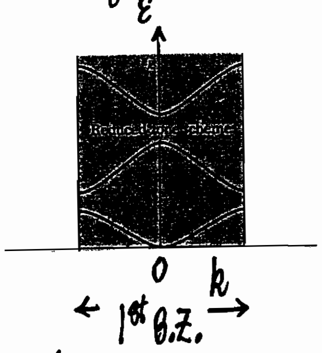
↑ all bands (many not shown) are empty at T=0

↑ "Band Gap" of silicon ↓

↓ all bands are filled completely (many not shown) up to here at T=0

↑ The physics of silicon is determined by these few highest filled bands and lowest empty band(s).

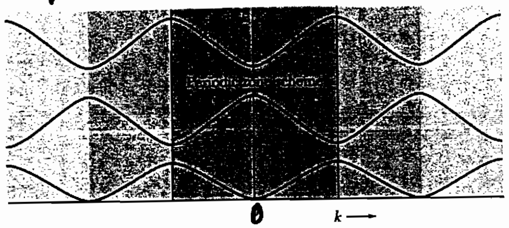
G. Ways of showing $\mathcal{E}_n(\vec{k})$



- Reduced zone scheme
- show $\mathcal{E}_n(\vec{k})$ with $\vec{k}$ in 1st B.Z.

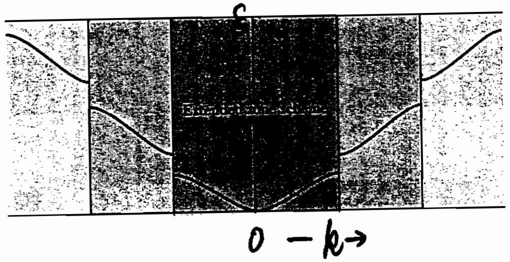
"standard scheme"

displace by $\vec{G}$'s and using $\mathcal{E}_n(\vec{k}+\vec{G}) = \mathcal{E}_n(\vec{k})$



- Periodic zone scheme or repeated zone scheme
- emphasize $\mathcal{E}_n(\vec{k}+\vec{G}) = \mathcal{E}_n(\vec{k})$

Start with reduced zone scheme, re-plot it as
1st band in 1st B.Z.
2nd band in 2nd B.Z.
3rd band in 3rd B.Z., and so on



- extended zone scheme

All schemes contain same information.

H. A proof of $\mathcal{E}_n(\vec{k}) = \mathcal{E}_n(-\vec{k})$ in a band

$u_{\vec{k}}(\vec{r})$ satisfies:

$$\left[\frac{1}{2m}(\vec{p}+\hbar\vec{k})^2 + V(\vec{r})\right] u_{n\vec{k}}(\vec{r}) = \mathcal{E}_n(\vec{k})\, u_{n\vec{k}}(\vec{r}) \qquad (*)$$

- Changing $\vec{k}$ to $-\vec{k}$, equation $(*)$ becomes

$$\left[\frac{1}{2m}(\vec{p}-\hbar\vec{k})^2 + V(\vec{r})\right] u_{n-\vec{k}}(\vec{r}) = \mathcal{E}_n(-\vec{k})\, u_{n-\vec{k}}(\vec{r}) \qquad (A)$$

- $V(\vec{r})$ is real, $\mathcal{E}_n(\vec{k})$ is real [$\hat{H}$ is hermitian]

$$\psi^*_{n\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\, u^*_{n\vec{k}}(\vec{r})$$

Take complex conjugate of Schrödinger Equation:

$$\left[\frac{p^2}{2m} + V(\vec{r})\right]\left(e^{-i\vec{k}\cdot\vec{r}}\, u^*_{n\vec{k}}(\vec{r})\right) = \mathcal{E}_n(\vec{k})\left(e^{-i\vec{k}\cdot\vec{r}}\, u^*_{n\vec{k}}(\vec{r})\right)$$

$$\Rightarrow \left[\frac{1}{2m}(\vec{p}-\hbar\vec{k})^2 + V(\vec{r})\right] u^*_{n\vec{k}}(\vec{r}) = \mathcal{E}_n(\vec{k})\, u^*_{n\vec{k}}(\vec{r}) \qquad (B)$$

But $\psi^*_{n\vec{k}}(\vec{r}) = e^{+i(-\vec{k})\cdot\vec{r}}\, u^*_{n\vec{k}}(\vec{r})$ should be a Bloch function of wavevector $-\vec{k}$, i.e. $u_{n-\vec{k}}(\vec{r}) = u^*_{n\vec{k}}(\vec{r})$

Comparing (A) and (B), they are the same eigenvalue eqn.

$$\therefore\ \mathcal{E}_n(\vec{k}) = \mathcal{E}_n(-\vec{k})$$

Summary

- Reduce to one-electron problem: $\left[\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi = \mathcal{E}\psi$
  with periodic $V(\vec{r})$, i.e. $V(\vec{r}+\vec{R}) = V(\vec{r})$
- Bloch's theorem $\Rightarrow$ $\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\psi_{\vec{k}}(\vec{r})$
  $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_n(\vec{k},\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{n\vec{k}}(\vec{r})$
  with n = band index
- Each allowed $\vec{k}$ $\Rightarrow$ $\mathcal{E}_n(\vec{k})$ (infinitely many)
- $\mathcal{E}_n(\vec{k}) = \mathcal{E}_n(-\vec{k})$; $\mathcal{E}_n(\vec{k}+\vec{G}) = \mathcal{E}_n(\vec{k})$
- $\psi_{n\vec{k}+\vec{G}}(\vec{r}) = \psi_{n\vec{k}}(\vec{r})$ [for given n, sufficient to include one of them
- Periodic B.C. $\Rightarrow$ $\vec{k} = \frac{h}{N_1}\vec{b}_1 + \frac{k}{N_2}\vec{b}_2 + \frac{l}{N_3}\vec{b}_3$
  (densely populated discrete $\vec{k}$'s in reciprocal space)
- To avoid over-counting, $\vec{k}$ can be chosen to be in the 1st B.Z.
  (reduced zone scheme)
- There are $N = N_1 \cdot N_2 \cdot N_3$ allowed $\vec{k}$'s in 1st B.Z.
  ↳ number of unit cells in the sample
- To fill the electrons into these bands, we use the Fermi-Dirac distribution.
- With $\mathcal{E}_n(\vec{k})$, one can calculate $g(\mathcal{E})$ [the electronic DOS]

Refs: Kittel: Ch.7 ; Christman: Secs. 7.1-7.2
Ch.9 (early pages) Omar: Ch.5