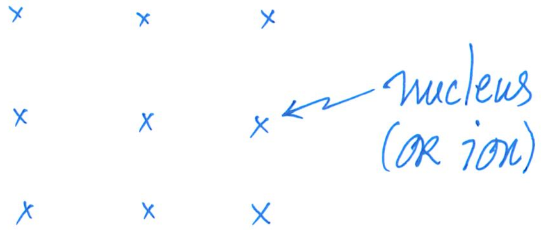
D. Tight-Binding Model : LCAO extended to solids

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + \underbrace{V(\vec{r})}_{\text{periodic } V(\vec{r}) = V(\vec{r}+\vec{R})} \qquad (25)$$



$$= \frac{-\hbar^2}{2m}\nabla^2 + \underbrace{\sum_{\vec{R}} U_{atom}(\vec{r}-\vec{R})}_{\substack{\text{array of nuclei}\\ \text{each contributing}\\ U_{atom}(\vec{r}-\vec{R})}} \qquad (25)$$

(special case (simpler) of $\underbrace{\text{one atom}}$ per primitive unit cell)

(semiconductor Si : 2 atoms per primitive cell
OR 8 atoms per conventional cell)

$$\boxed{\begin{array}{l} \hat{H}\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\,\psi_{\vec{k}}(\vec{r}) \\[2ex] \psi_{\vec{k}}(\vec{r}) \text{ satisfies the Bloch's theorem} \end{array}} \qquad (26)$$

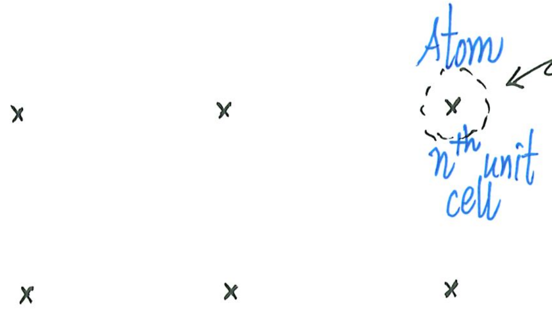
This is the Band problem

$\{\vec{R}\}$ periadicity in real space

$\Rightarrow \{\vec{G}_i\}$ reciprocal lattice

$\underbrace{1^{st}\text{ B.Z.}}_{\text{N allowed } \vec{k}\text{-values}}$

N = # unit cells in crystal



Consider how many atomic orbitals are to be used as basis functions in LCAO

e.g. $\phi_{1s}(\vec{r}-\vec{R}_n)$, $\phi_{2s}(\vec{r}-\vec{R}_n)$, $\cdots$

[or ϕ_1, ϕ_2, $\cdots$]

The atomic orbitals satisfy the atom's TISE, i.e.

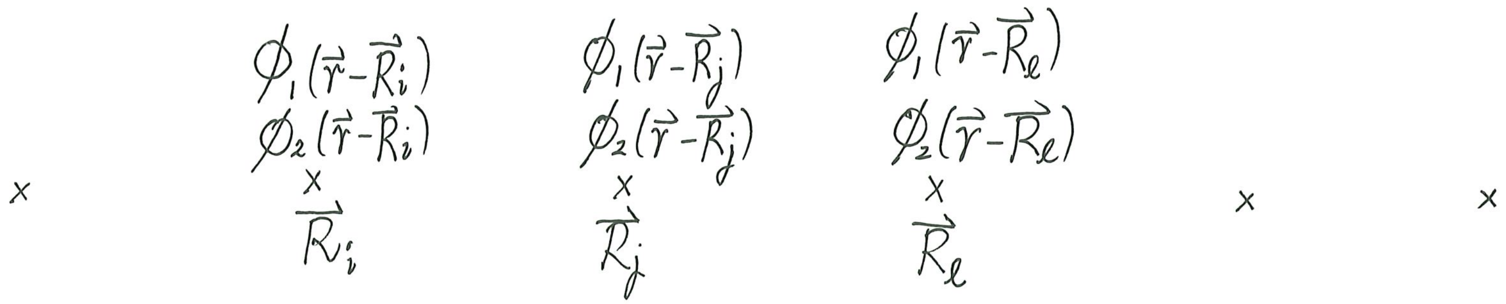
$$\left[\frac{-\hbar^2}{2m}\nabla^2 + \underbrace{U_{atom}(\vec{r})}_{\text{nucleus at } \vec{0}}\right]\phi_i(\vec{r}) = \mathcal{E}_i\,\phi_i(\vec{r}) \quad (27a)$$

e.g. $\mathcal{E}_i = \mathcal{E}_{2s}$, $\phi_i = \phi_{2s}(\vec{r})$

$\mathcal{E}_i = \mathcal{E}_{2p}$, $\phi_i = \phi_{2p}(\vec{r})$

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + \underbrace{U_{atom}(\vec{r}-\vec{R})}_{\text{nucleus at } \vec{R}}\right]\phi_i(\vec{r}-\vec{R}) = \mathcal{E}_i\,\phi_i(\vec{r}-\vec{R}) \quad (27b)$$

Idea: Linear Combination of $\phi_i(\vec{r}-\vec{R}_n)$ from different sites $\vec{R}_n$ to form $\psi_{\vec{k}}$, but $\psi_{\vec{k}}$ must obey Bloch's theorem



- Linearly Combine $\underbrace{\phi_1(\vec r-\vec R_n)}_{\text{N of them (1 from each atom)}}$ [e.g. linearly combine $\phi_{2s}(\vec r-\vec R_n)$]

$$\psi_{\vec k,1}(\vec r) = \cdots + e^{i\vec k\cdot\vec R_i}\phi_1(\vec r-\vec R_i) + \underbrace{e^{i\vec k\cdot\vec R_j}}_{\substack{\uparrow \\ \text{attach} \\ \text{prefactor}}}\underbrace{\phi_1(\vec r-\vec R_j)}_{\substack{\text{take AO} \\ \text{at } \vec R_j}} + e^{i\vec k\cdot\vec R_\ell}\phi_1(\vec r-\vec R_\ell) + \cdots \quad (28a)$$

- Linearly combine $\phi_2(\vec r-\vec R_n)$

$$\psi_{\vec k,2}(\vec r) = \cdots + e^{i\vec k\cdot\vec R_i}\phi_2(\vec r-\vec R_i) + e^{i\vec k\cdot\vec R_j}\phi_2(\vec r-\vec R_j) + e^{i\vec k\cdot\vec R_\ell}\phi_2(\vec r-\vec R_\ell) + \cdots \quad (28b)$$

The particular way makes $\psi_{\vec k,1}(\vec r)$ [$\psi_{\vec k,2}(\vec r)$] satisfy the Bloch's theorem

Bloch Sums

normalize the Bloch Sum

from atom at $\vec{R}_n$ (primitive cell)

$$\text{Form}\quad \psi_{\vec{k},i}(\vec{r}) = (\text{Normalization}) \sum_{\vec{R}_n} \underbrace{e^{i\vec{k}\cdot\vec{R}_n}} \phi_i(\vec{r}-\vec{R}_n) \qquad (29)$$

a $\vec{k}$-value in 1st B.Z.

sum over all atoms (labelled by locations)

factor depends on $\vec{R}_n$ (where atom is)

a particular AO

(thus can form one such $\psi_{\vec{k},i}$ for each of N allowed-$\vec{k}$ values)

Key Concept

normalization

$$\text{Check:}\quad \psi_{\vec{k},i}(\vec{r}+\vec{R}) = \mathcal{A}\sum_{\vec{R}_n} e^{i\vec{k}\cdot\vec{R}_n}\phi_i(\vec{r}-(\overbrace{\vec{R}_n-\vec{R}}^{\vec{R}'})) = \mathcal{A}\sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}} e^{i\vec{k}\cdot\vec{R}'}\phi_i(\vec{r}-\vec{R}')$$

some lattice vector

sum over all atoms

also sum over all atoms

$$= e^{i\vec{k}\cdot\vec{R}}\left(\mathcal{A}\sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'}\phi_i(\vec{r}-\vec{R}')\right) = e^{i\vec{k}\cdot\vec{R}}\,\psi_{\vec{k},i}(\vec{r}) \qquad (30)$$

∴ Eq. (29) satisfies the Bloch's theorem

- Formally, the normalization constant should be worked out carefully because $\int \phi_i^*(\vec{r}-\vec{R}_n)\,\phi_i(\vec{r}-\vec{R}_m)\,d^3r = S_{i,nm} \neq 0$ $\underbrace{\text{in general}}_{\text{especially, } \vec{R}_n \text{ and } \vec{R}_m \text{ are neighbors}}$

centered at different sites

If we regard $|S_{i,nm}| \ll 1$ so that $|S_{i,nm}| \approx 0$, then

$$\boxed{\psi_{\vec{k},i}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_n} e^{i\vec{k}\cdot\vec{R}_n}\,\phi_i(\vec{r}-\vec{R}_n)} \qquad (31)$$

sum over ϕ_i centered at all N lattice sites

<u>Recall</u>: if each atom contributes $i=1,2$ $(\phi_1(\vec{r}-\vec{R}_n), \phi_2(\vec{r}-\vec{R}_n))$ AO's, then Eq.(31) contributes $\psi_{\vec{k},1}(\vec{r})$ and $\psi_{\vec{k},2}(\vec{r})$ for a given $\vec{k} \in$ 1st B.Z.

For Band problem, each $\vec{k}$ is a separate TISE problem

$$\hat{H}\,\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\,\psi_{\vec{k}}(\vec{r}) \qquad (26)$$

- For a $\vec{k}$-value, form

$$\boxed{\psi_{\vec{k}}(\vec{r}) = C_1\,\overset{\text{Bloch sum}}{\psi_{\vec{k},1}(\vec{r})} + C_2\,\overset{\text{Bloch sum}}{\psi_{\vec{k},2}(\vec{r})}} \qquad (32)^{+}$$

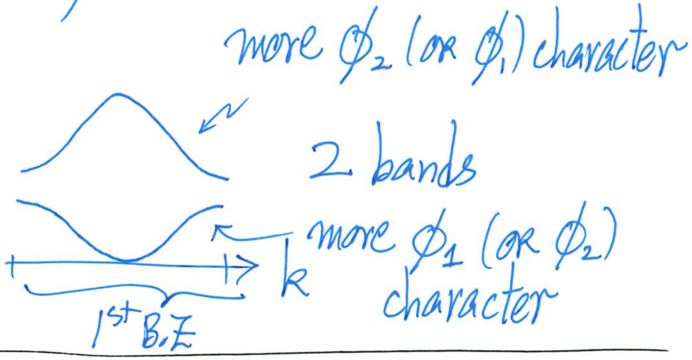
a trial wavefunction (linear combination of Bloch sums)

Using Eq. (32) in Eq. (26), TISE becomes[+] formally

$$\begin{pmatrix} H_{11}(\vec{k}) - ES_{11}(\vec{k}) & H_{12}(\vec{k}) - ES_{12}(\vec{k}) \\ H_{21}(\vec{k}) - ES_{21}(\vec{k}) & H_{22}(\vec{k}) - ES_{22}(\vec{k}) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad (33)$$

Basically Done!

Each $\vec{k} \in 1^{st}$ B.Z. $\Rightarrow$ two values of E

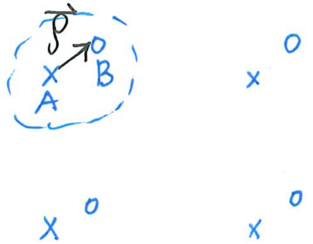


[+] Readily generalize to cases in which each atom contributing more AO's

- Start with $\underbrace{\phi_1,\ \phi_2,\ \phi_3}_{3N\ \text{AO's}}$ per atom? Then $\underbrace{3\ \text{bands}}_{3N\ \text{electronic states}}$

- Crystal with a $\underbrace{\text{basis of atoms}}$?

e.g.



→

$$\overbrace{\underbrace{\phi_A(\vec r-\vec R_n)}_{\substack{\text{one AO from}\\ \text{atom A}\\ \text{[can be more]}}} \ \text{and}\ \underbrace{\phi_B(\vec r-(\vec R_n+\vec\rho))}_{\substack{\text{one AO from atom B}\\ \text{[can be more]}}}}^{\text{two AO's per unit cell}}$$

Form Bloch Sum　　Form Bloch Sum

$$\psi_{\vec k}(\vec r) = C_A\,\psi_{\vec k,A}(\vec r) + C_B\,\psi_{\vec k,B}(\vec r)$$

2×2 problem for each $\vec k$ (N unit cells ⇒ N $\vec k$-values)

⇒ 2 bands

(a) 1D chain of identical atoms

Simplest case : 1 AO from every atom $\Rightarrow$ Only 1 Block sum

$\Rightarrow$ "1×1" problem

$$H_{11}(\vec k) - E\,S_{11}(\vec k) = 0 \;\Rightarrow\; E = \frac{H_{11}(\vec k)}{S_{11}(\vec k)} \quad \text{formally}$$

$$\therefore\; E \approx H_{11}(\vec k)$$

Let's look at $H_{11}(\vec k)$ formally (1D, 2D, 3D)

$$H_{11}(\vec k) = \frac{1}{N}\sum_{\vec R}\sum_{\vec R'} e^{i\vec k\cdot(\vec R-\vec R')}\int \phi^*(\vec r-\vec R')\,\hat H\,\phi(\vec r-\vec R)\,d^3r \qquad \text{(definition)}$$

$$= \frac{1}{N}\sum_{\vec R}\sum_{\vec R'} e^{i\vec k\cdot(\vec R-\vec R')}\int \phi^*(\vec r-\vec R')\Big[\underbrace{-\frac{\hbar^2}{2m}\nabla^2+\mathrlap{\overbrace{\phantom{U_{atom}(\vec r-\vec R)+\sum_{\vec R''\neq\vec R}U_{atom}(\vec r-\vec R'')}}^{V(\vec r)}}U_{atom}(\vec r-\vec R)}_{}+\sum_{\vec R''\neq\vec R}U_{atom}(\vec r-\vec R'')\Big]\underbrace{\phi(\vec r-\vec R)}_{\text{AO}}\,d^3r$$

$$H_{11}(\vec{k}) = \frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\int \phi^*(\vec{r}-\vec{R}')\,\varepsilon_{atom}\,\phi(\vec{r}-\vec{R})\,d^3r$$

$$+\frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\sum_{\vec{R}''\neq\vec{R}}\int \phi^*(\vec{r}-\vec{R}')\,U_{atom}(\vec{r}-\vec{R}'')\,\phi(\vec{r}-\vec{R})\,d^3r$$

$$= \underset{\substack{\uparrow \\ \text{"on-site" energy}}}{\varepsilon_{atom}} + \frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\sum_{\vec{R}''\neq\vec{R}}\underbrace{\int \phi^*(\vec{r}-\vec{R}')\,U_{atom}(\vec{r}-\vec{R}'')\,\phi(\vec{r}-\vec{R})\,d^3r}_{\text{in general, 3-center integrals}^{+}}$$

- Hard NOT to be zero if 3 centers are different
- Keep those 2-center terms only and ignore others

[+] When each atom contributes ϕ_1, ϕ_2 AO's, H_{12} will have this 3-center integral with ϕ_1^*, ϕ_2 on LHS and RHS.

- One type of 2-center terms has NO $\vec{k}$-dependence $\Rrightarrow$ just a shift

These will be the $\vec{R}=\vec{R}'$ cases. These terms are

$$\frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}''\neq\vec{R}}\underbrace{\int \phi^*(\vec{r}-\vec{R})\,U_{atom}(\vec{r}-\vec{R}'')\,\phi(\vec{r}-\vec{R})\,d^3r}_{\text{function of }(\vec{R}-\vec{R}'')}$$

Diagonal elements
[For LHS ϕ = RHS ϕ, this has classical interpretation]

N of them (cancels 1/N)

$$=\frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}''\neq\vec{R}} f(\vec{R}-\vec{R}'') = \frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}'\neq 0} f(\vec{R}') = \sum_{\vec{R}'\neq 0} f(\vec{R}')$$

$$=\underbrace{\sum_{\vec{R}\neq 0}\int \phi^*(\vec{r})\,U_{atom}(\vec{r}-\vec{R})\,\phi(\vec{r})\,d^3r}$$

- gives no dispersion (no $\vec{k}$-dependence) [but we want $E(\vec{k})$, band structure]
- just an unimportant shift [no information on $E(\vec{k})$]

- Another (crucial) type of 2-center terms HAS $\vec{k}$-dependence ⇒ band structure

These will be the cases with $\vec{R}' = \vec{R}''$

$$\frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\sum_{\vec{R}''\neq\vec{R}}\int \phi^*(\vec{r}-\vec{R})\, U_{atom}(\vec{r}-\vec{R}'')\,\phi(\vec{r}-\vec{R})\,d^3r \qquad \text{[3-center]}$$

$$\approx \frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}''\neq\vec{R}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}'')}\underbrace{\int \phi^*(\vec{r}-\vec{R}'')\, U_{atom}(\vec{r}-\vec{R}'')\,\phi(\vec{r}-\vec{R})\,d^3r}_{\text{some function } \mathcal{J}(\vec{R}-\vec{R}'')} \qquad \text{[2-center]}$$

$$= \frac{1}{N}\sum_{\vec{R}}\sum_{\vec{R}''\neq\vec{R}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}'')}\,\mathcal{J}(\vec{R}-\vec{R}'') = \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}}\,\mathcal{J}(\vec{R})$$

$$= \underset{\substack{\Uparrow \\ \text{gives } \vec{k}\text{-dependence}}}{\sum_{\vec{R}\neq 0}} e^{i\vec{k}\cdot\vec{R}}\underbrace{\int \phi^*(\vec{r}-\vec{R})\, U_{atom}(\vec{r}-\vec{R})\,\phi(\vec{r})\,d^3r}_{\substack{\text{determines band width (pushing)} \\ \text{"hopping integrals"}}} \qquad (34) \leftarrow \text{this is a function of } \vec{k} \text{ after doing the sum}$$

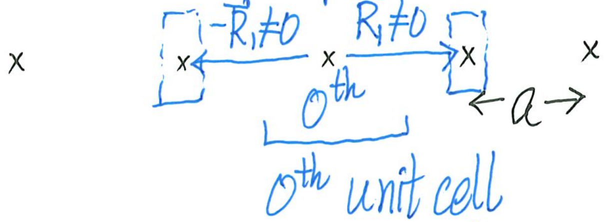
Summary

- close analogy (LCAO and TBM) [same types of integrals]
- Readily generalized to H_{ij} $(i \neq j)$ [(i) No ε_{atom} term; (ii) a shift, (iii) a k-dependent term]
- General for 1D, 2D, 3D; several AO's per atom for 1 atom per unit cell, several AO's per atom for several atoms for unit cell (more symbols)

e.g. see $$\int \underset{\substack{\uparrow \\ \text{A-atom}}}{\phi}{}^{*}_{A,\underset{\substack{\uparrow \\ \text{s-orbital}}}{s}}(\vec{r}-\vec{R})\, U_{atom}(\vec{r}-\vec{R})\, \phi_{\underset{\substack{\uparrow \\ \text{B atom}}}{B},\underset{\substack{\uparrow \\ \text{p-orbital}}}{p}}(\vec{r}-\underset{\substack{\uparrow \\ \text{in } 0^{th} \text{ unit cell}}}{\vec{\rho}_B})\, d^3r$$ etc. in H_{ij}

Go Back to 1D simplest case

$$E(\vec{k}) = H_{11}(\vec{k}) = \varepsilon_{atom} + (a\ shift) + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}}\, \underbrace{J(\vec{R})}_{\underbrace{\int \phi^*(\vec{r}-\vec{R})\, U_{atom}(\vec{r}-\vec{R})\, \phi(\vec{r})\, d^3r}_{\text{most important terms are the shortest } \vec{R}\text{'s}}}$$



$(\vec{R}_1 = a\hat{x})$

nearest-neighbor hopping (most important!)

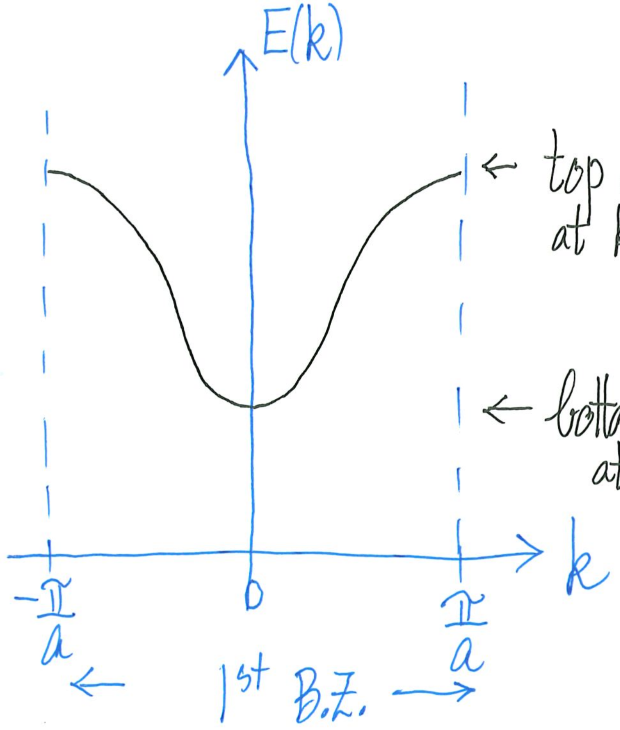
- Taking the nearest-neighboring (n.n.) hopping terms only:

$$E(\vec{k}) = \varepsilon_{atom} + (shift) + e^{ika}\underbrace{J(a)} + e^{-ika}\underbrace{J(-a)}$$

inspecting integrals' meaning (they are the same) [call it "$-t$"]

$$= \varepsilon_{atom} - \alpha - t\,(e^{ika} + e^{-ika}) = \underbrace{\boxed{\varepsilon_{atom} - \alpha - 2t\cos ka = E(k)}}_{\text{1D TB Band}\quad (k\in 1^{st}\ B.Z.)} \quad (35)$$

1D



← top of band $\mathcal{E}_{atom}-\alpha+2t$ at $k=\pm\frac{\pi}{a}$

← bottom of band $\mathcal{E}_{atom}-\alpha-2t$ at $k=0$

$$\uparrow\ \boxed{\text{Band Width} = 4t}\ \downarrow \qquad (36)$$

Near bottom of band $E(k) = \text{constant} - 2t\left(1-\frac{k^2a^2}{2}\right)$

$$= \underbrace{(\mathcal{E}_{atom}-\alpha-2t)}_{\text{bottom of band}} + ta^2\cdot \underbrace{k^2}_{\text{quadratic in } k}$$

like free electron

c.f. $\frac{\hbar^2k^2}{2m^*} \Rightarrow \boxed{m^* = \frac{\hbar^2}{2a^2t}}$ (37)

$$\boxed{\begin{array}{l}|t| = \left|\overbrace{\int \phi^*(\vec{r}-\vec{R}_{shortest})\, U_{atom}(\vec{r}-\vec{R}_{shortest})\, \phi(\vec{r})\, d^3r}^{\text{"local" (bonding)}}\right| \\ \text{determines band width} \\ \text{and effective mass!}\end{array}}$$

Ex: Include next nearest neighbors and Obtain E(k)

(b) 3D Cubic Lattice

- 1 atom, 1 AO, at lattice points

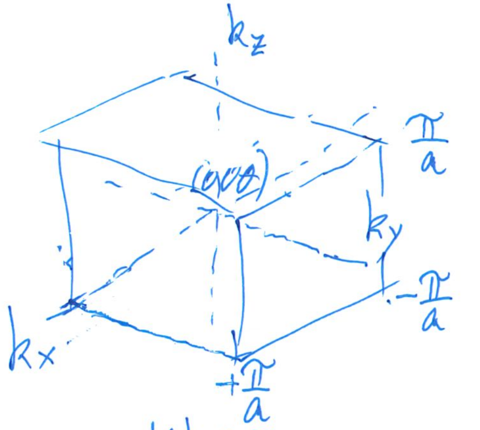
$$E(\vec{k}) = \varepsilon_{atom} - \alpha - t \sum_{\substack{\text{6 shortest } \vec{R}\text{'s to n.n.}}} e^{i\vec{k}\cdot\vec{R}}$$

(n.n. terms Only)

(at $\pm a\hat{x}, \pm a\hat{y}, \pm a\hat{z}$)

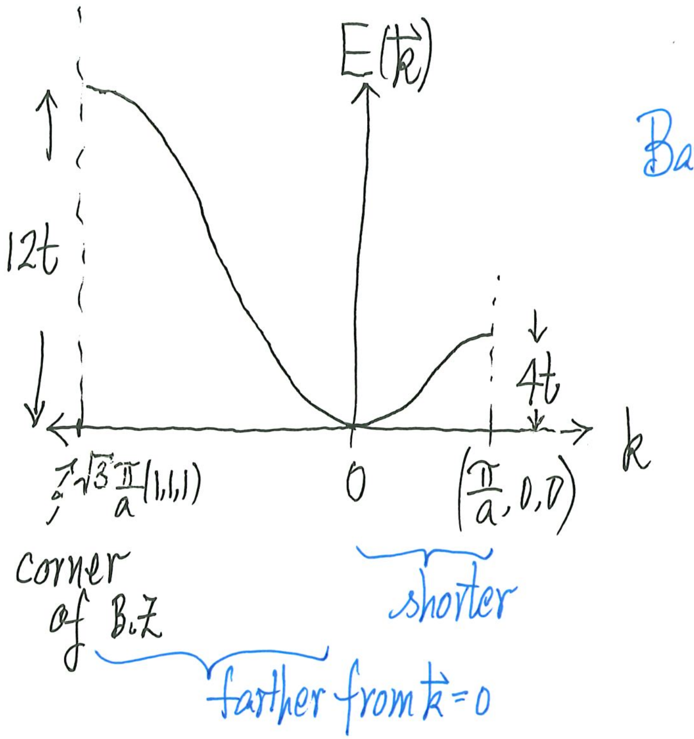
$$= \varepsilon_{atom} - \alpha - t\left(e^{ik_xa} + e^{-ik_xa} + e^{ik_ya} + e^{-ik_ya} + e^{ik_za} + e^{-ik_za}\right)$$

$$= \varepsilon_{atom} - \alpha - 2t\left[\cos k_xa + \cos k_ya + \cos k_za\right] \quad (38)$$

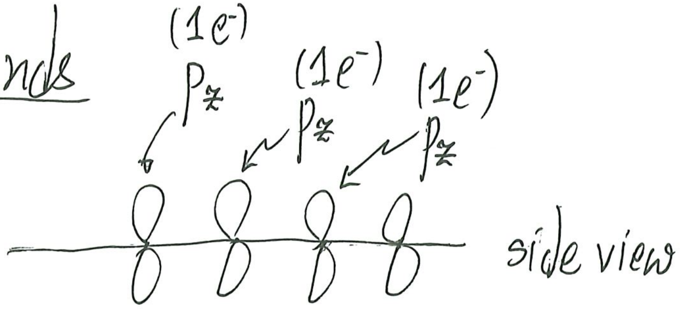


1st B.Z.
(Cube of edges $\frac{2\pi}{a}$)

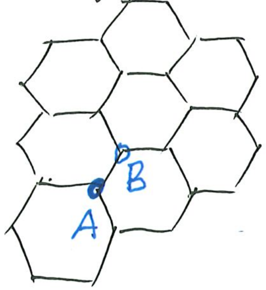
Band Width = 12t



(c) Graphene p_z bands : The most famous 2D bands



- sp^2 form the framework →



2 carbon atoms docurating each lattice point ("A" carbon, "B" carbon)

p_z atomic orbitals

$$\underbrace{\phi_A(\vec{r}),\ \phi_B(\vec{r}-\vec{\rho})}_{\text{two AO's per unit cell}}$$

$$\psi_{\vec{k}}(\vec{r}) = C_1 \underbrace{\psi_{\vec{k},A}(\vec{r})}_{\substack{\text{Bloch sum A} \\ \frac{1}{\sqrt{N}}\sum_{R} e^{i\vec{k}\cdot\vec{R}}\phi_A(\vec{r}-\vec{R})}} + C_2 \underbrace{\psi_{\vec{k},B}(\vec{r})}_{\substack{\text{Bloch sum B} \\ \frac{1}{\sqrt{N}}\sum_{R} e^{i\vec{k}\cdot\vec{R}}\phi_B(\vec{r}-(\vec{R}+\vec{\rho}))}}$$

(2×2) problem for each $\vec{k}$ ⇒ 2 bands from p_z carbon AO's

Note!

P. R. Wallace, Phys. Rev. 71, 622 (1947)

$$E(\vec{k}) = E(k_x, k_y) = (\text{constant}) \pm t\sqrt{1+\cos\left(\frac{\sqrt{3}\,k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+4\cos^2\left(\frac{k_y a}{2}\right)} \qquad (39)$$

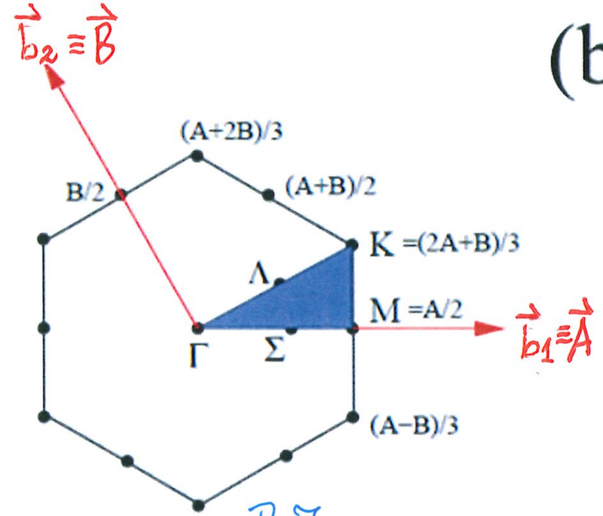
This was re-discovered many times after the experimental works on obtaining graphene.

$t =$

2-center integral (single parameter of the bands)

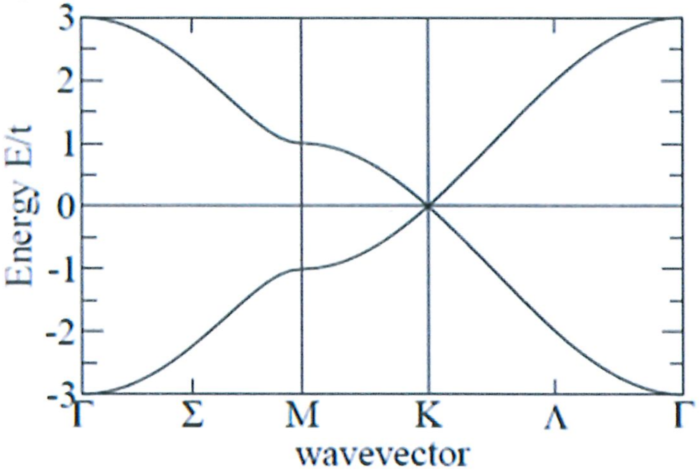
$\sim V_{pp\pi}$ in ETBM

(a)



B.Z.

(b)



Two bands by tight-binding $2p_z$ AO's of carbon atoms

2N states in each band

[2N electrons, each from every atom]

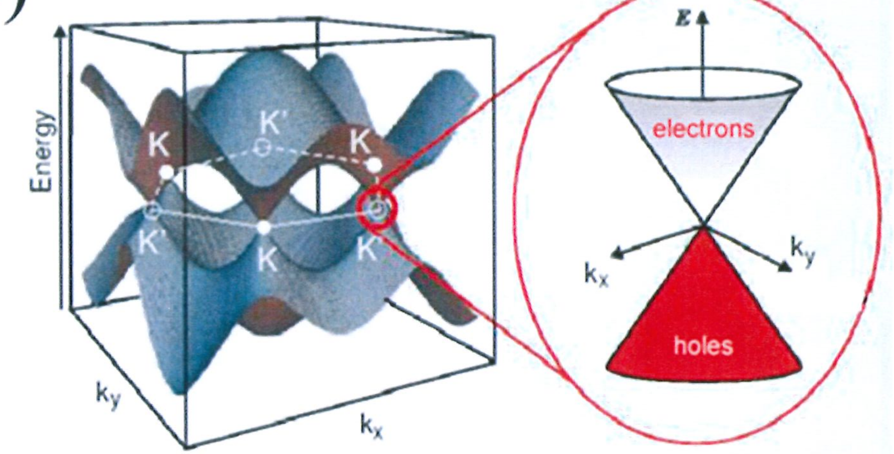
⇓

Just touch at K-point { lower band is full / upper band is empty

"gapless" semiconductor

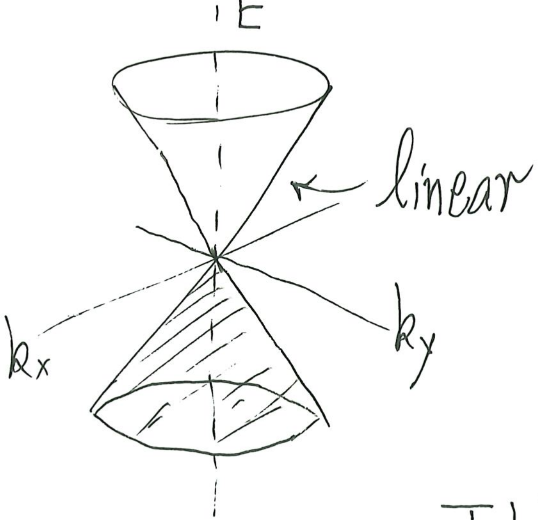
(c)

$E(k_x, k_y)$



↑

around K-point in B.Z.



$$E = \underbrace{v\hbar k}_{\text{like massless fermions!}} \text{ near K-point}$$

Table-Top Dirac electrons physics!

- The hottest topics in condensed matter physics:
  - twisted graphene bilayer (two layer, one is slightly twisted (rotated) by 1.1° relative to the other)

    → superconductor vs insulator in ~0.1°!

Nature 556, 43 (2018) [MIT experiment seeing superconductivity]

[See review by Andrei and MacDonald, Nature Materials 19, 1265 (2020)]

Latest (Feb. 2021): Superconductivity in twisted trilayer graphene (MIT group) Nature (2021)

(d) Silicon, Germanium, GaAs, ...

- Diamond or zincblende structure ⇒ Two atoms decorating every lattice point

"A", "B" atoms or "cation/anion"

zincblende (different atoms)

Si : [Ne] $3s^2 2p^2$

$$\boxed{\begin{array}{l} \text{"A" atom : } 3s,\ 3p_x,\ 3p_y,\ 3p_z \ \text{(at lattice point)} \\ \text{"B" atom : } 3s,\ 3p_x,\ 3p_y,\ 3p_z \ \text{(at } \vec{g} \text{ from a lattice point)} \end{array}} \quad (39)$$

→ 8 AO's per unit cell ⇒ form 8 Bloch Sums

TISE ⇒ 8×8 matrix eigenvalue problem for every $\vec{k}$ in 1st B.Z.

⇒ 8 bands

Including spins ⇒ 2N states per band

4 electrons from "A" atom + 4 electrons from "B" atoms ⇒ 8N electrons into states

Schematically, the 8×8 matrix for each $\vec{k}$ looks like (TB Hamiltonian)

	s^c	s^a	p_x^c	p_y^c	p_z^c	p_x^a	p_y^a	p_z^a
s^c	ε_s^c	$E_{ss}g_0$	0	0	0	$E_{sp}g_1$	$E_{sp}g_2$	$E_{sp}g_3$
s^a	$E_{ss}g_0^*$	ε_s^a	$-E_{sp}g_1^*$	$-E_{sp}g_2^*$	$-E_{sp}g_3^*$	0	0	0
p_x^c	0	$-E_{sp}g_1$	ε_p^c	0	0	$E_{xx}g_0$	$E_{xy}g_3$	$E_{xy}g_2$
p_y^c	0	$-E_{sp}g_2$	0	ε_p^c	0	$E_{xy}g_3$	$E_{xx}g_0$	$E_{xy}g_1$
p_z^c	0	$-E_{sp}g_3$	0	0	ε_p^c	$E_{xy}g_2$	$E_{xy}g_1$	$E_{xx}g_0$
p_x^a	$E_{sp}g_1^*$	0	$E_{xx}g_0^*$	$E_{xy}g_3^*$	$E_{xy}g_2^*$	ε_p^a	0	0
p_y^a	$E_{sp}g_2^*$	0	$E_{xy}g_3^*$	$E_{xx}g_0^*$	$E_{xy}g_1^*$	0	ε_p^a	0
p_z^a	$E_{sp}g_3^*$	0	$E_{xy}g_2^*$	$E_{xy}g_1^*$	$E_{xx}g_0^*$	0	0	ε_p^a

Obtained from form given by Chadi and Cohen (1975).

s^c : s-orbital of cation (Atom A)
p_z^a : p_z-orbital of anion (Atom B)

$$g_0 = g_0(\vec{k}) = e^{i\vec{k}\cdot\vec{d}_1} + e^{i\vec{k}\cdot d_2} + e^{i\vec{k}\cdot\vec{d}_3} + e^{i\vec{k}\cdot d_4}$$

$\vec{d}_1, \vec{d}_2, \vec{d}_3, \vec{d}_4$ point to n.n. atom

$\vec{d}_1 = \frac{a}{4}[111]$, $\vec{d}_2 = \frac{a}{4}[1\bar{1}\bar{1}]$, $\vec{d}_3 = \frac{a}{4}[\bar{1},1,\bar{1}]$, $\vec{d}_4 = \frac{a}{4}[\bar{1}\bar{1}1]$

$g_1(\vec{k})$, $g_2(\vec{k})$, $g_3(\vec{k})$ have signs in $g_0(\vec{k})$ changed to $(+,+,-,-)$, $(+,-,+,-)$ $(+,-,-,+)$.

E_{sp}, E_{xy} ($E_{p_xp_y}$, etc) have empirical values

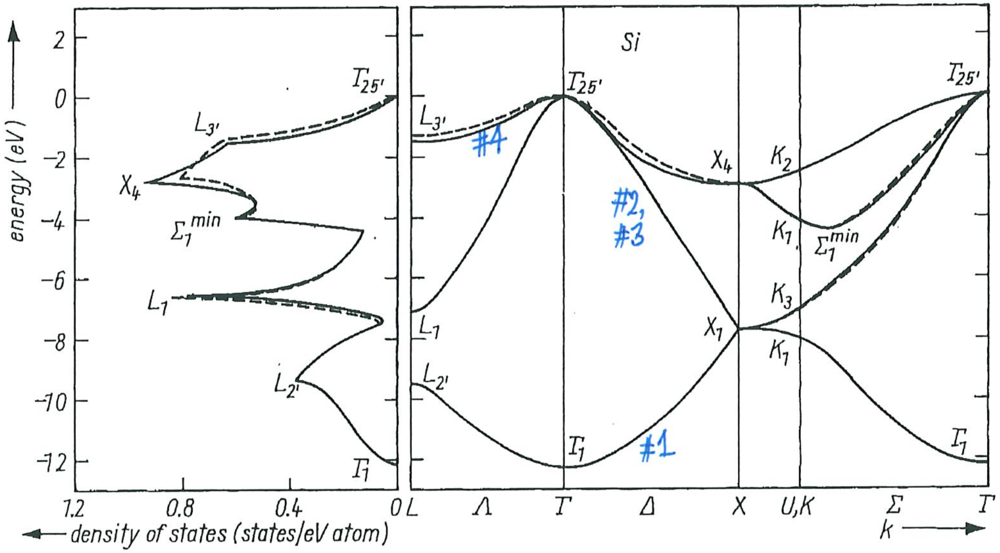
Classic TBM paper: Chadi and Cohen, "Tight-binding calculations of the valence bands of diamond and zincblende crystals", Physica Status Solidi 86, 405 (1975)

(hybridization will emerge if we want to interpret the results that way!)

Chadi and Cohen (1975)

Tight-Binding Calculations of the Valence Bands of Crystals

Valence Bands (Silicon)



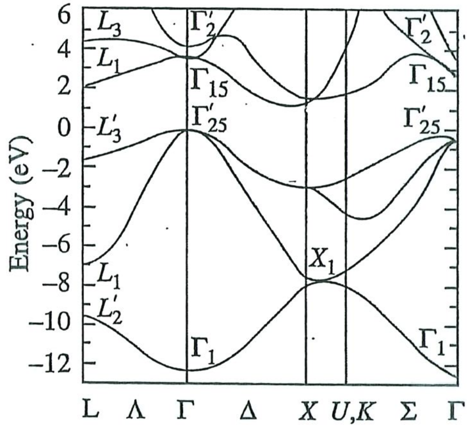
Tight-binding band structure and density of states of Si as compared to the results obtained from empirical pseudopotential calculations , ——— Tight binding, – – – EPM

↑ 4 other (conduction) bands are not shown (8N states)

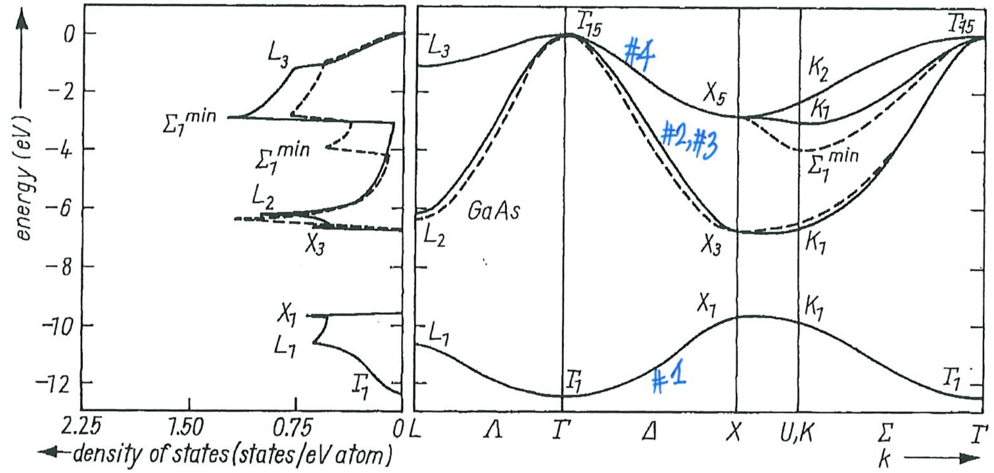
8N electrons filled the lower $\underbrace{\text{4 bands}}_{\text{8N states}}$ shown here

Silicon

conduction bands ↑

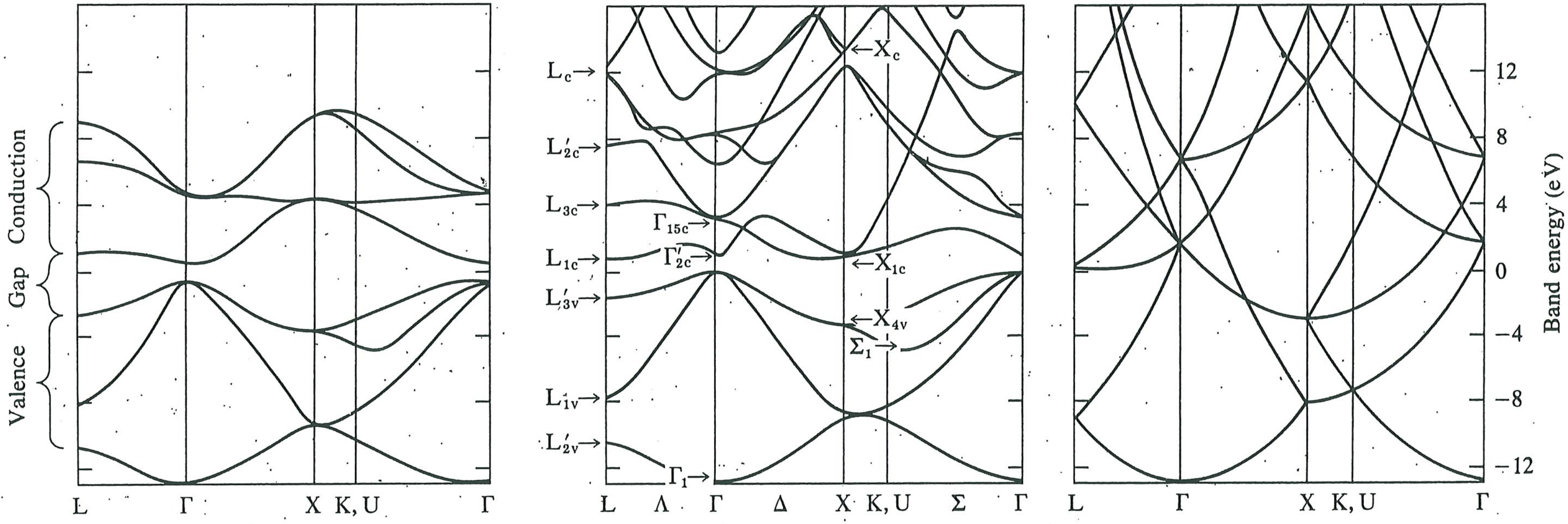


Valence Bands (Germanium)



Tight-binding band structure and density of states of Ge as compared to the results obtained from empirical pseudopotential calulations. ——— Tight binding, – – – EPM

Germanium



(8×8) Tight-Binding Bands (a)

True bands (b)

Free-electron bands (c)

[From Harrison, "Electronic Structure"]

The energy bands of germanium. Part (a) gives the bands based upon s and p valence states and matrix elements taken from the Solid State Table. Second-neighbor interatomic matrix elements are neglected but otherwise the calculation is exact. Part (b) gives the bands obtained by Grobman, Eastman, and Freeouf by combining pseudopotential calculations with experimental optical studies; the points indicated with arrows were associated with experimental determinations. Part (c) gives the free-electron bands, $\hbar^2k^2/(2m)$ with each state shifted into the Brillouin Zone by addition of the appropriate lattice wave number.

(3-fold degenerate) (anti-bonding p)

(non-degenerate) (anti-bonding s)

(3-fold degenerate) (bonding p)

(non-degenerate) (bonding s)

valence bands (full)

$\vec{k}=0$

$\vec{k}=0$ (see matrix)

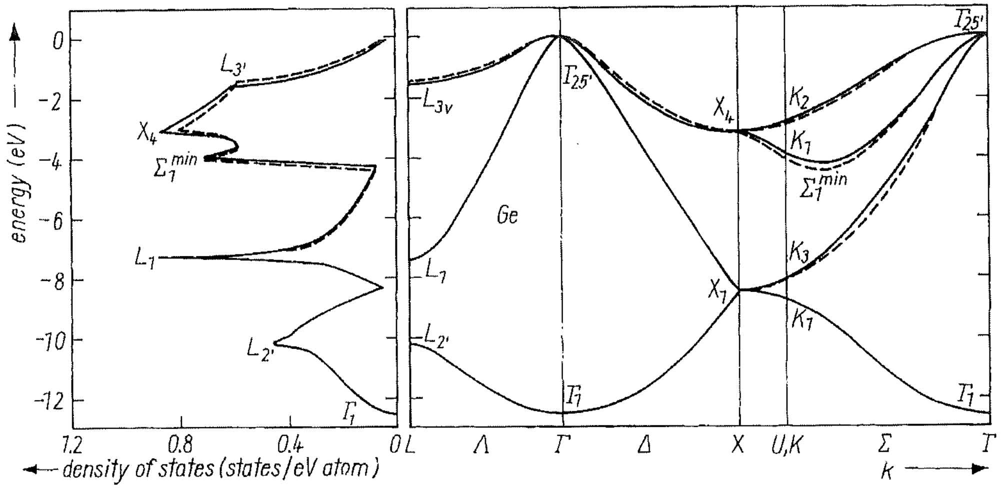
$s^c \leftrightarrow s^a$ coupled

$p_x^c \leftrightarrow p_x^a$ coupled ($p_y^c \leftrightarrow p_y^a$, $p_z^c \leftrightarrow p_z^a$)

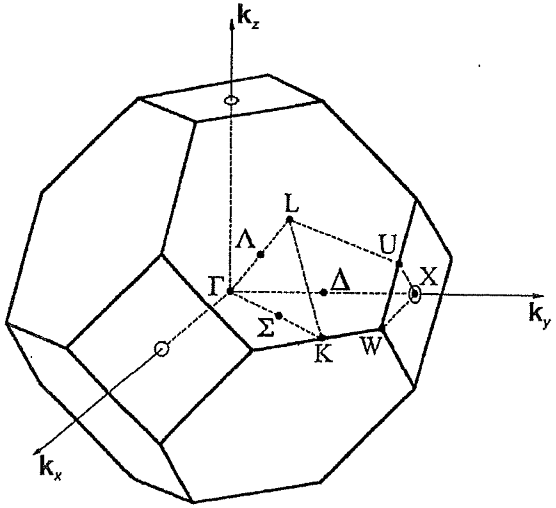
↓

4 "2×2" blocks

Valence Bands
of GaAs
(Chadi and Cohen 1975)

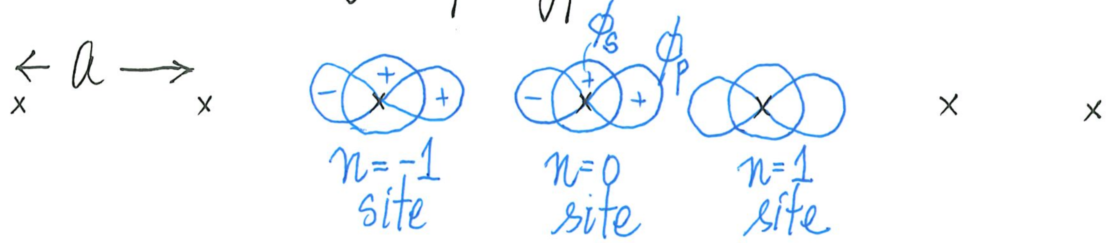


Tight-binding band structure and density of states of GaAs compared to the results of EPM calculations ——— Tight binding, – – – EPM.



1st B.Z.

(e) A 1D Model of sp-type semiconductor



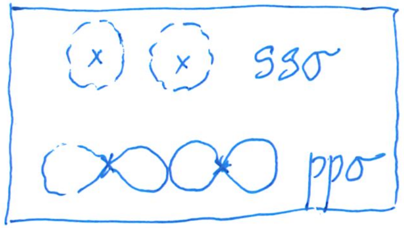
Bloch Sums

$$\boxed{\begin{aligned}\psi_{k,s} &= \frac{1}{\sqrt{N}}\sum_n e^{ikna}\phi_s(x-na)\\ \psi_{k,p} &= \frac{1}{\sqrt{N}}\sum_n e^{ikna}\phi_p(x-na)\end{aligned}} \qquad (40)$$

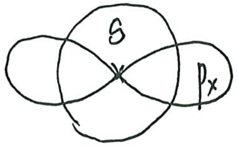
Set up 2x2 matrix problem $[H_{ij}]$ (retain n.n. hopping)

$$\begin{pmatrix} \varepsilon_{atom\,s} + 2V_{ss\sigma}\cos ka - E & i\,2V_{sp\sigma}\sin ka \\ -2i\,V_{sp\sigma}\sin ka & \varepsilon_{atom\,p} + 2V_{pp\sigma}\cos ka - E \end{pmatrix}\begin{pmatrix} C_s \\ C_p \end{pmatrix} = 0 \qquad (41)$$

$$\boxed{\begin{aligned}E_\pm(k) = {} & \frac{\varepsilon_{atom\,s}+\varepsilon_{atom\,p}}{2} + (V_{pp\sigma}+V_{ss\sigma})\cos ka \\ & \pm\sqrt{\left[\left(\frac{\varepsilon_{atom\,p}-\varepsilon_{atom\,s}}{2}\right) + (V_{pp\sigma}-V_{ss\sigma})\cos ka\right]^2 + 4V_{sp\sigma}^2\sin^2 ka}\end{aligned}} \qquad (42)$$



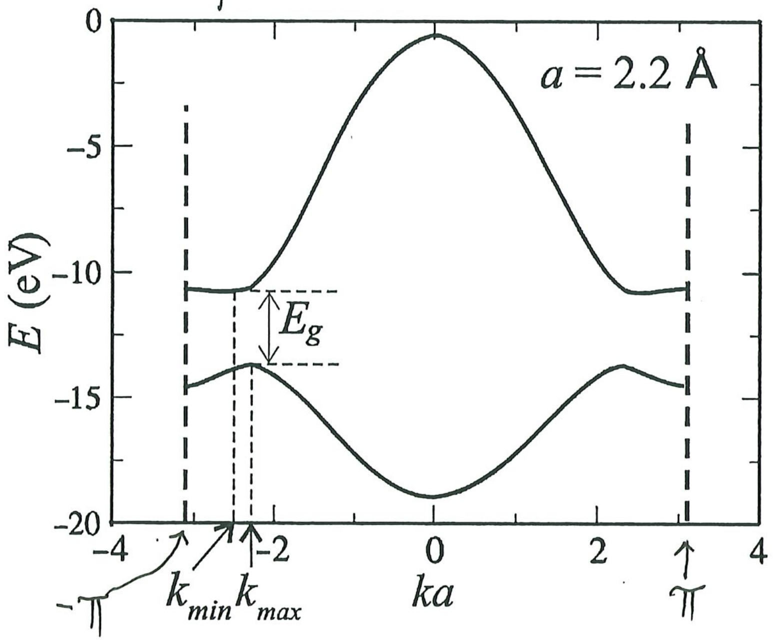
(Recall: 2x2 matrix problem can be solved exactly)



is to mimic Si (sp^3)

So, interesting to take ETBM (just like Empirical LCAO) parameters for Si (and $a = 2.2$ Å (about distance between neighboring atoms in Si))

A "sp" Semiconductor

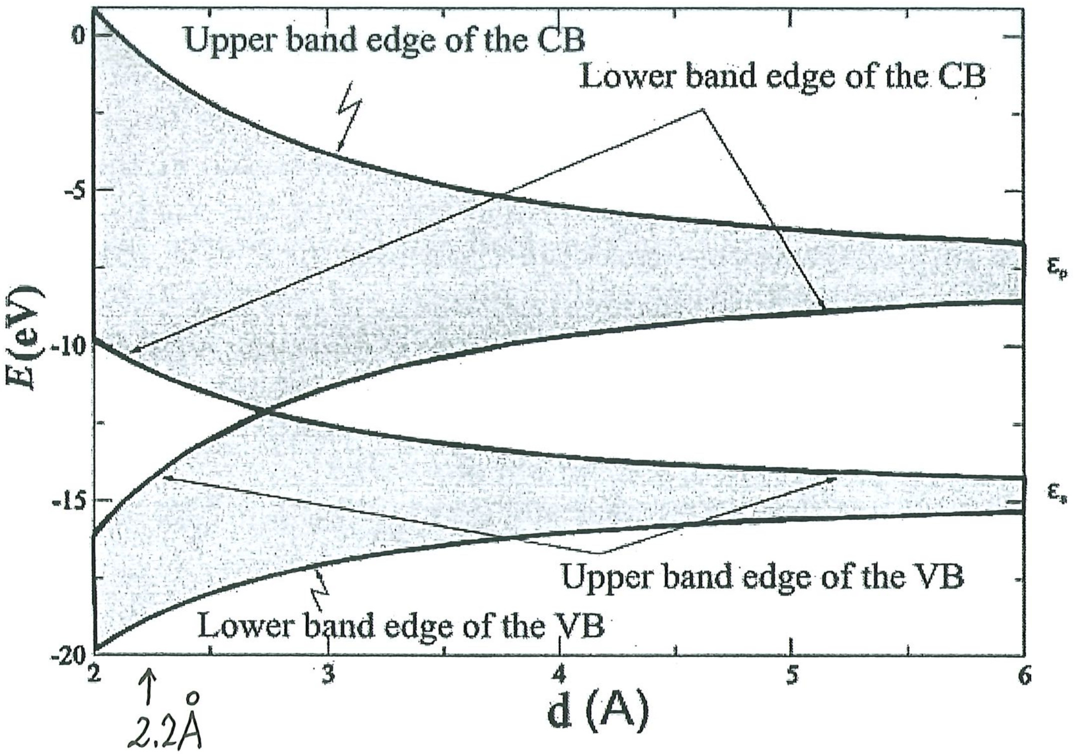


The band structure $E_\pm(k)$ according to ETBM describing qualitatively the behavior of an elemental semiconductor. Notice that the maximum of the VB occurs at $k_{\max}$ and the minimum of the CB at $k_{\min}$ with $k_{\max} \neq k_{\min} \neq \pm\pi/d$. Semiconductors for which $k_{\max} \neq k_{\min}$ are called *indirect gap* semiconductors, while *direct gap* are the semiconductors for which $k_{\max} = k_{\min}$

- Indirect gap → bottom of CB, → top of VB } different $\vec{k}$'s
- For even smaller a, E_g increases
- From eigenvectors [($C_s(k)$, $C_p(k)$) for a $\vec{k}$]:
  Top of VB: largely p-character
  Bottom of CB: largely s-character

Si has n.n. separation of 0.235 nm (2.35 Å)

Educational to see how Band Structure/Band Gap varies with separation a



Evolution of conduction and valence bands and the gap as the equilibrium lattice constant $a = d$ varies in a one-dimensional model of elemental semiconductor with two orbitals and two electrons per atom and one atom per primitive cell. Only at a single value of the lattice constant $a = a_1$ the gap closes. With the present choices of $\varepsilon_p, \varepsilon_s, V_{pp\sigma}, V_{ss\sigma}$, and $V_{sp\sigma}$, $a_1 = 2.734$ A. The nearest neighbor separation for Si is $d = 2.35$ A

one regime

another regime

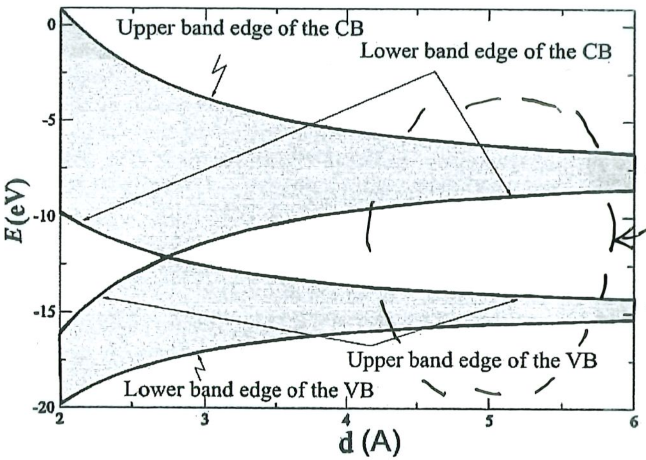
Two regimes both with a gap

But the physics is quite different! Real Semiconductors correspond to the small a (or d) regime

From Economou, "The Physics of Solids" Ch.6

Large a ($a > 2.7$ Å) regime

- s orbital closer to nucleus ⇒ small (tiny) overlap (hopping) between s-orbitals and small (tiny) spσ integral
  ⇒ s orbitals form a narrow (flat) band ($-2t_s \cos ka$ with small t_s)
- s and p don't affect each other
- p orbitals affect each other ⇒ p band ($-2t_p \cos ka$, with $t_p > t_s$)



Large a regime

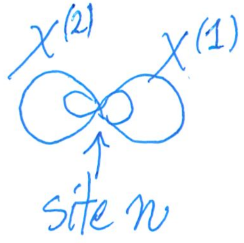
▨ p-band (2N states) [empty]

s-band ▨ ↓↑ 2N states (full)

(no sign of "sp hybridization")

Small a (a< 2.7 Å) regime

- note that the top of VB carries p-character
- Interpretation (of 2x2 matrix math)
  - Every site: form $\underbrace{sp}_{\text{s and p (in)}}$ hybridized orbitals $\underbrace{\chi^{(1)}, \chi^{(2)}}_{\text{(out)}}$



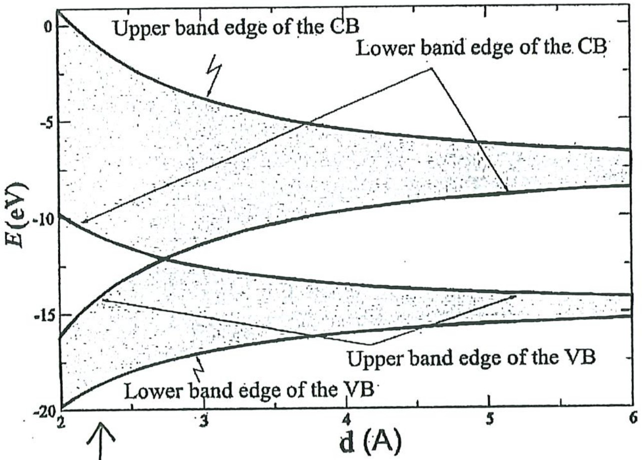
Can form Bloch sums for $\underbrace{\chi^{(1)}(x-na)}_{\text{centered at different sites}}, \chi^{(2)}(x-na)$

then encounter $\underbrace{\int \chi^{*(1)}(x-a)\, u_{atom}(x-a)\, \chi^{(2)}(x)\, dx}_{\text{this is the term that gives bonding and antibonding MO's for atoms at "0" and at "a"}}$ type of integrals

then system becomes

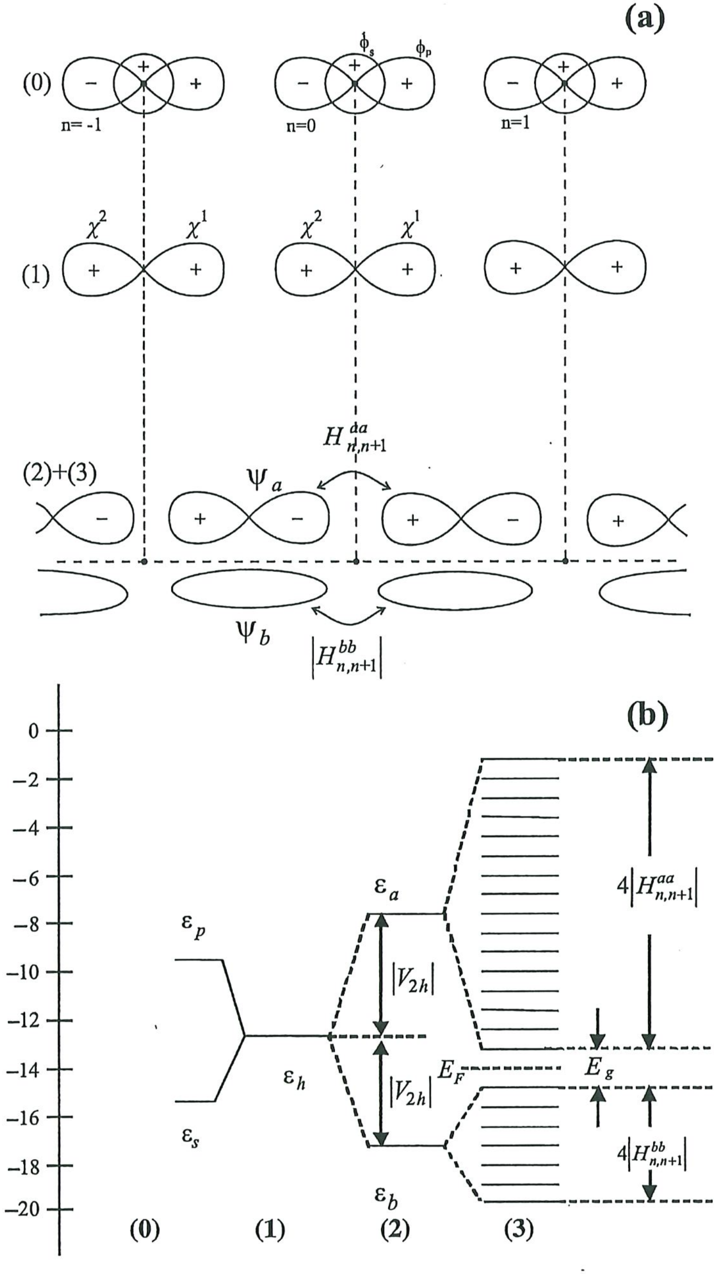
anti-bonding (Tight-Binding them to form a band)

bonding (Tight-Binding them to form a band)



"What is the physics here?"

This is the physical picture relevant to Semiconductors



Successive changes of the basis orbitals produced by step 1 [from ϕ_s, ϕ_p to χ^1, χ^2] and step 2 [from χ^1, χ^2 to ψ_b, ψ_a] (panel **a**) and the corresponding energy levels accompanying these changes (panel **b**) for the 1-D model shown in the top of the figure. The VB and the CB are formed around the bonding ε_b and the antibonding ε_a molecular levels respectively. Recall that the top of both bands is of pure p-character, while the bottom of both bands is of pure s-character.

s and p AO's

sp hybrids $\chi^{(1)}, \chi^{(2)}$

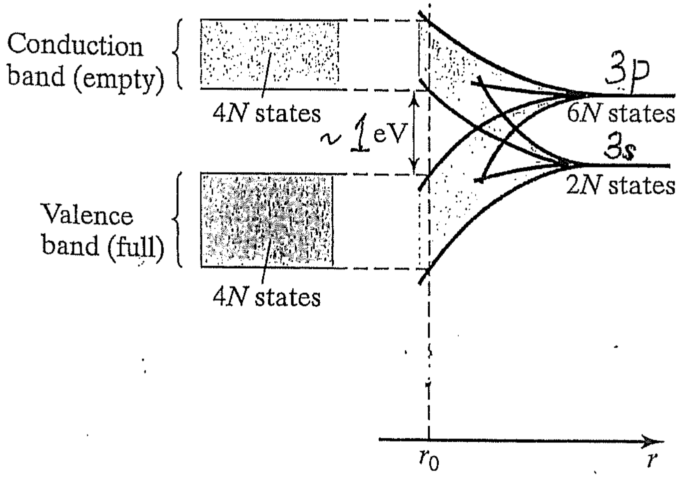
Tight-bind to form CB

Antibonding MO's (node at midpoint between atoms)

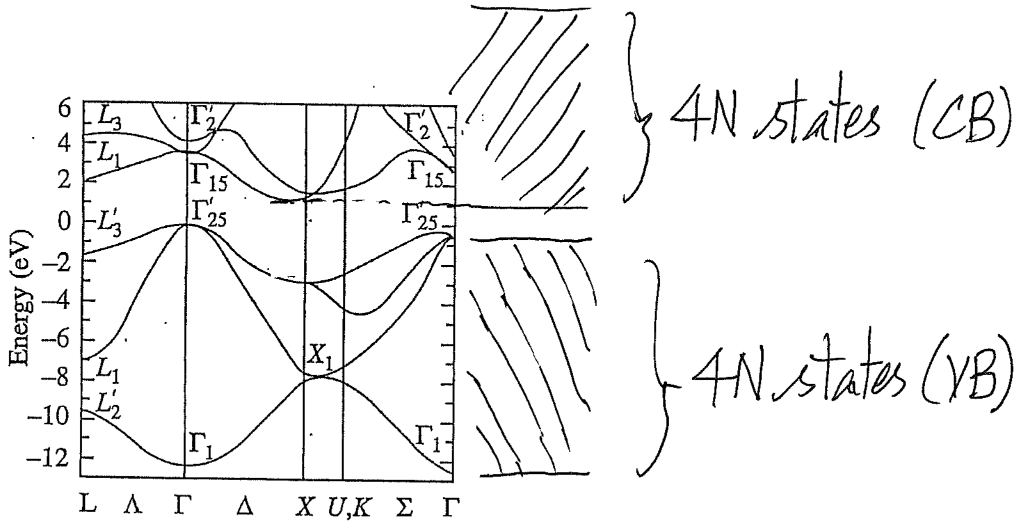
Bonding MO's, tight-bind to form VB

Extending this physical picture to Silicon (Germanium)

Silicon (semiconductor)



TBM provides the physical understanding of the band structure and the nature of the band-edge states



E. The Wannier Functions

Motivation: Used $\underbrace{\text{atomic orbitals}}$ in TBM to form bands

Physically Transparent, but AO's from different atoms are in general NOT orthogonal!

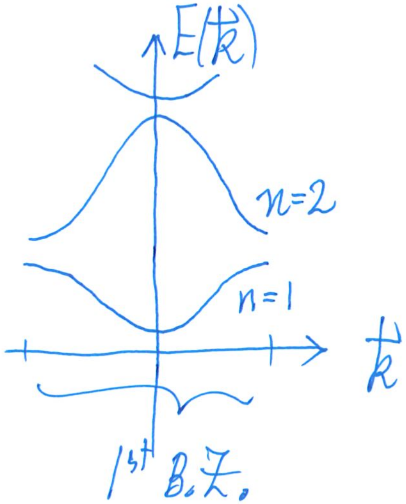
$$\left.\begin{aligned} &\int \phi_{3s}^{*}(\vec{r}-\vec{R})\ \phi_{3s}(\vec{r})\, d^3r \neq 0 \\ &\int \phi_{3p}^{*}(\vec{r}-\vec{R})\ \phi_{3s}(\vec{r})\, d^3r \neq 0 \end{aligned}\right\} \text{ in general}$$

although we usually approximate them as $S_{ij} = \delta_{ij}$

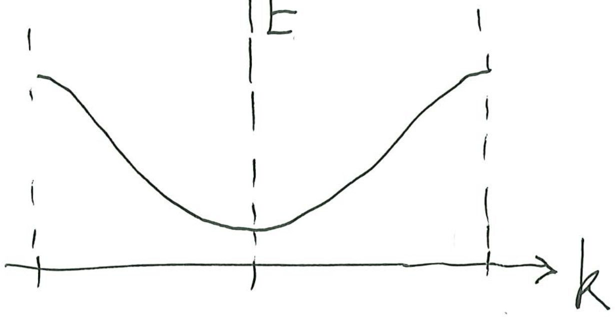
Question: Bloch States $\psi_{n\vec{k}}(\vec{r})$ are orthonormal. They are extended states. Can there be a set of states that are localized at the unit cells and are also orthonormal?

Wannier Functions

- Defined for each band
- Take a band (band index n)



There are N Bloch states in each band, because there are N allowed $\vec k$-values in 1^{st} B.Z.



extended ($e^{i\vec k\cdot\vec r}\cdot u_{n\vec k}(\vec r)$)

Each $\vec k$: Bloch state $\psi_{n\vec k}(\vec r)$

Form linear combination(s) of Bloch states within a band:

$$w_n(\vec r-\vec R) = \frac{1}{\sqrt N}\sum_{\vec k\in 1^{st} B.Z.} e^{-i\vec k\cdot\vec R}\,\psi_{n\vec k}(\vec r) \qquad (42)$$

one lattice vector (meaning: specifying a location in direct lattice)

- Can define N such functions for a band, one for each $\underbrace{\vec{R}}_{}$

N unit cells ⇒ N different $\vec{R}$'s

- $w_n(\vec{r}-\vec{R})$ is a localized function about lattice site $\vec{R}$

[one such localized function for every lattice site, for every band]

- They are orthonormal $\displaystyle\int_{\text{whole crystal}} w_n^*(\vec{r}-\vec{R})\, w_{n'}(\vec{r}-\vec{R}')\, d^3r = \delta_{\vec{R}\vec{R}'}\,\delta_{nn'}$

They work like atomic orbitals at $\vec{R}$ but with nice orthonormal property

Refs: Wannier, "Dynamics of Band Electronics in Electric and Magnetic Fields", Rev. Mod. Phys. 34, 645 (1962) (a classic in Electron Dynamics)

Kohn, "Analytic Properties of Bloch Waves and Wannier Functions", Phys. Rev. 115, 809 (1959).

From the definition, the Bloch states can be "constructed" by LC"WF":

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r}-\vec{R}) \qquad (43)$$

[c.f.: Bloch Sum in TBM, with $w_n(\vec{r}-\vec{R})$ work as atomic orbitals]

What for?

$\{w_n(\vec{r}-\vec{R})\}$ for all $\vec{R}$ and all n can be used to expand any functions in solid state physics problems

"Crystal coordinate representation" (CCR)

Useful in problems where alternations to periodicity are local, e.g. impurities.

Summary

- Tight-Binding Model is a handy way of obtaining band structures for semiconductors
- Nature of the states near band edges (top of valence bands) and $\vec{k}=0$ of conduction band is useful in understanding optical properties
- Empirical TBM gives a quick way for getting approximate band structures
- TBM applied to graphene is starting point of some fancy physics

References

- Economou, "The Physics of Solids"
- Harrison, "Solid State Theory"
- Harrison, "Electronic Structure"
- BW: Ch.3