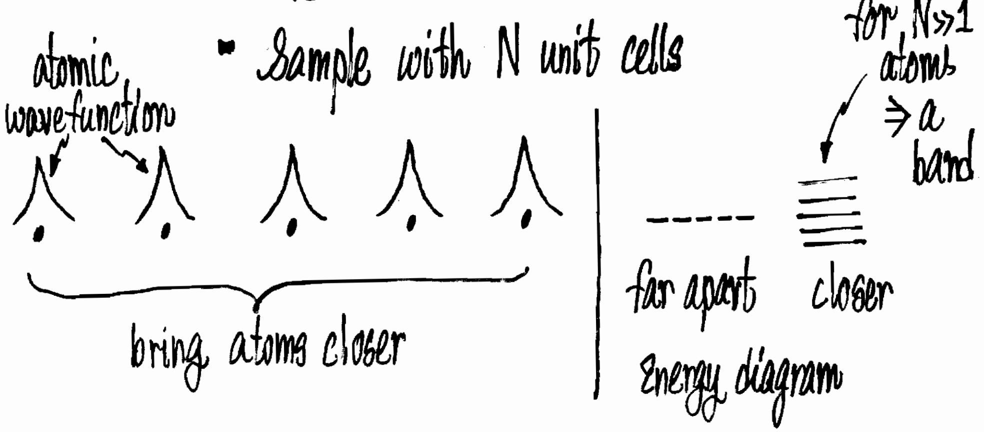
D. Tight-Binding Model (TBM)

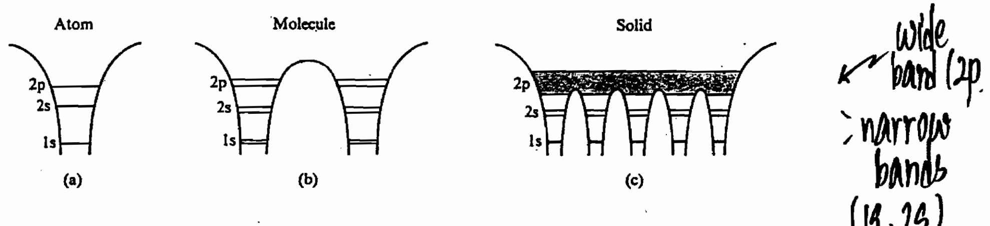
- Starting point: Electronic states associated with each atom (e.g., 1s, 2s, 2p, 3s, 3p, 3d, ...)

- We illustrate the idea by considering the simplest case:
  - each atom is contributing one particular atomic wavefunction to the formation of a band
    [Note: We may repeat the argument for each atomic wavefunction.]
  - One atom in a unit cell
  - Sample with N unit cells



- Formation of bands can be thought of as the "mixing" or "combinations" of atomic orbitals as atoms come closer to each other.

2 atoms forming molecular orbitals



The evolution of the energy spectrum of Li from an atom (a), to a molecule (b), to a solid (c).

Wide bands: situation closer to that considered of nearly free electron model

Narrow bands:
- those come from core electrons
- those come from atomic orbitals closer to nucleus (e.g. f-orbitals, d-orbitals)

better to start with the picture of electronic states belonging to each atom (i.e. atomic orbitals)

- One atomic wavefunction from each atom

$\chi(\vec{r}-\vec{R})$ = atomic wavefunction for the atom with nucleus at $\vec{R}$

E_{atom} = energy of the atomic state

⌜ <u>Example:</u>

Hydrogen 1s state

<u>Nucleus at (0,0,0)</u>	<u>Nucleus at $\vec{R}$</u>
$\chi_{1s}(\vec{r}) \sim e^{-r/a_0}$	$\chi_{1s}(\vec{r}-\vec{R}) \sim e^{-\lvert\vec{r}-\vec{R}\rvert/a_0}$
$E_{atom} = -13.6\,eV$	$E_{atom} = -13.6\,eV$

But usually TBM is good for d-orbitals in transition metals, or f-orbitals. ⌟

$U_{atom}(\vec{r}-\vec{R})$ = potential energy function for an electron in an <u>isolated atom</u> sitting at $\vec{R}$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\chi(\vec{r}-\vec{R}) + U_{atom}(\vec{r}-\vec{R})\,\chi(\vec{r}-\vec{R}) = E_{atom}\,\chi(\vec{r}-\vec{R})}$$

↑ Schrödinger Equation for an isolated atom

- Atomic $\chi(\vec{r}-\vec{R}) \neq 0$ only for $\vec{r}$ very close to $\vec{R}$ ($\chi(\vec{r}-\vec{R}) \to 0$ exponentially as $\vec{r}$ goes away from $\vec{R}$)

- In crystalline <u>solids</u>, we want to solve:

$$\boxed{\begin{array}{c} -\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) + V(\vec{r})\,\psi_{\vec{k}}(\vec{r}) = \mathcal{E}(\vec{k})\,\psi_{\vec{k}}(\vec{r}) \\ \text{where } V(\vec{r}) \text{ is periodic}^{\dagger} \end{array}}$$

We know that $\psi_{\vec{k}}(\vec{r})$ should satisfy the Bloch's theorem.

<u>Key step</u>: <u>LCAO</u>, <u>forming a Bloch Sum</u>

<u>Recall</u>: Molecular orbitals are formed by linearly combining atomic orbitals of different atoms

We expect:

$$\underset{\text{Bloch function}}{\psi_{\vec{k}}(\vec{r})} = \sum_{\vec{R}} \overbrace{C(\vec{R})}^{\text{some coefficient}}\ \overbrace{\chi(\vec{r}-\vec{R})}^{\text{atomic orbitals}}$$

<u>L</u>inear <u>C</u>ombination of <u>A</u>tomic <u>O</u>rbitals (LCAO

[†] One may regard $V(\vec{r}) = \sum_{\vec{R}} U_{atom}(\vec{r}-\vec{R})$, i.e. $V(\vec{r})$ is the sum of the influence at $\vec{r}$ due to all the atoms.

- <u>Bloch's theorem</u> requires $\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{\vec{k}}(\vec{r})$

$\therefore$ $C(\vec{R})$ should be chosen to satisfy the Bloch's theorem.

<u>Bloch Sum</u>

- LCAO that satisfies the Bloch's theorem

$$\psi_{\vec{k}}(\vec{r}) = \underset{\uparrow}{\Gamma} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \chi(\vec{r}-\vec{R})$$

normalization constant

Let's check:

$$\psi_{\vec{k}}(\vec{r}+\vec{R}') = \Gamma \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \chi(\vec{r}+\vec{R}'-\vec{R})$$

$$= \Gamma \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \chi(\vec{r}-(\vec{R}-\vec{R}'))$$

$$\underset{\uparrow}{\vec{R}-\vec{R}' \equiv \vec{R}''}$$

also a lattice vector

$$= \Gamma \sum_{\vec{R}''} e^{i\vec{k}\cdot(\vec{R}''+\vec{R}')} \chi(\vec{r}-\vec{R}'')$$

$$= e^{i\vec{k}\cdot\vec{R}'} \cdot \underbrace{\Gamma \sum_{\vec{R}''} e^{i\vec{k}\cdot\vec{R}''}\chi(\vec{r}-\vec{R}'')}_{\psi_{\vec{k}}(\vec{r})}$$

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

which is the Bloch's theorem.

<u>The normalization constant Γ</u>

Γ follows from the normalization of $\psi_{\vec{k}}(\vec{r})$

$$\int_V \psi^*_{\vec{k}}(\vec{r})\,\psi_{\vec{k}}(\vec{r})\,d^3r = 1$$

(integrate over the whole sample of vol. V)

$$\Rightarrow |\Gamma|^2 \sum_{\vec{R}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \underbrace{\int_V \chi^*(\vec{r}-\vec{R}')\,\chi(\vec{r}-\vec{R})\,d^3r}_{\text{this integral depends on } \vec{R}-\vec{R}'} = 1$$

$$\Rightarrow |\Gamma|^2 \sum_{\vec{R}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \underbrace{\int \chi^*(\vec{r}')\,\chi(\vec{r}'-(\vec{R}-\vec{R}'))\,d^3r'}_{B(\vec{R}-\vec{R}')} = 1$$

$$\Rightarrow |\Gamma|^2 \sum_{\vec{R}}\sum_{\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} B(\vec{R}-\vec{R}') = 1$$

$$\Rightarrow |\Gamma|^2 \sum_{\vec{R}'}\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} B(\vec{R}) = 1$$

$$\Rightarrow N|\Gamma|^2 \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} B(\vec{R}) = 1 \qquad \sum_{\vec{R}'} 1 = \overset{\#\text{unit cells}}{\underset{\downarrow}{N}}$$

$$\Rightarrow \boxed{|\Gamma|^2 = \frac{1}{N\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}B(\vec{R})} \quad \text{where } B(\vec{R}) = \int_V \chi^*(\vec{r})\,\chi(\vec{r}-\vec{R})\,d^3r}$$

formally

Expected Behavior of $B(\vec{R})$

$$B(\vec{R}) = \int_V \underset{\substack{\text{centered at}\\ \vec{R}=0}}{\chi^*(\vec{r})}\, \underset{\text{centered at } \vec{R}}{\chi(\vec{r}-\vec{R})}\, d^3r$$

~ Overlap of atomic wavefunctions centered at nuclei separated by $\vec{R}$

- For large $\vec{R}$,
  $B(\vec{R})$ is very small ≈ 0
  (when $\chi^*(\vec{r})$ is not small, $\chi(\vec{r}-\vec{R})$ is small; and vice versa)

∴ The most important $B(\vec{R})$ is $B(\vec{0})$.

For $\vec{R}=0$, $B(\vec{0}) = \int_V \chi^*(\vec{r})\,\chi(\vec{r})\,d^3r$ (centered at the same nucleus)

$= 1$ (normalization of atomic orbitals)

Any $\vec{R} \neq 0$, even the shortest $\vec{R}$,

$B(\vec{R}) \ll 1$

∴ $\boxed{\begin{array}{l} B(\vec{R}=0) \text{ is appreciable } (=1) \\ B(\vec{R}\neq 0) \text{ is tiny.} \end{array}}$ $\Rightarrow |\Gamma|^2 \approx \frac{1}{N}$

or $\boxed{\Gamma = \frac{1}{\sqrt{N}}}$

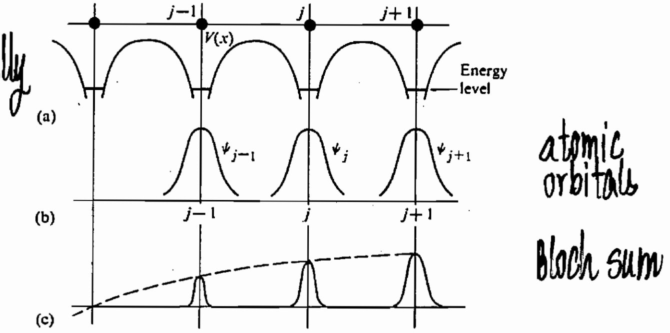
∴

Bloch sum

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\, \chi(\vec{r}-\vec{R})$$

- satisfies Bloch's theorem
- linearly combine N atomic orbitals centered at different $\vec{R}$'s
- one such combination for each $\vec{k}$

Schematically



The tight-binding model. (a) The crystal potential. (b) The atomic wave functions. (c) The corresponding Bloch function.

Next, we substitute $\psi_{\vec{k}}(\vec{r})$ into the Schrödinger Equation to find $\mathcal{E}(\vec{k})$.

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}) + V(\vec{r})\psi_{\vec{k}}(\vec{r}) = \underbrace{\mathcal{E}(\vec{k})}_{\uparrow \text{find } \mathcal{E}(\vec{k})}\psi_{\vec{k}}(\vec{r})$$

Substituting:

$$\psi_{\vec{k}}(\vec{r}) = \Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\chi(\vec{r}-\vec{R}) \text{ into Schrödinger Eq.}$$

$$\text{LHS} = -\frac{\hbar^2}{2m}\Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\nabla^2\chi(\vec{r}-\vec{R}) + V(\vec{r})\Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\chi(\vec{r}-\vec{R})$$

$$= \Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + U_{atom}(\vec{r}-\vec{R})\right)\chi(\vec{r}-\vec{R})}_{E_{atom}\,\chi(\vec{r}-\vec{R})} + \Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\left(V(\vec{r}) - U_{atom}(\vec{r}-\vec{R})\right)\chi(\vec{r}-\vec{R})$$

$$= E_{atom}\,\psi_{\vec{k}}(\vec{r}) + \Gamma\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\left(V(\vec{r}) - U_{atom}(\vec{r}-\vec{R})\right)\chi(\vec{r}-\vec{R})$$

$$= \text{RHS} = \mathcal{E}(\vec{k})\,\psi_{\vec{k}}(\vec{r})$$

Multiply both sides by $\psi^*_{\vec{k}}(\vec{r})$ and $\int_V d^3r$:

$$\mathcal{E}(\vec{k}) = E_{atom} - |\Gamma|^2\sum_{\vec{R}'}\sum_{\vec{R}} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\underbrace{\int_V \chi^*(\vec{r}-\vec{R}')\left(U_{atom}(\vec{r}-\vec{R}) - V(\vec{r})\right)\chi(\vec{r}-\vec{R})\,d^3r}_{\text{depends on } \vec{R}-\vec{R}'}$$

$$\Rightarrow \mathcal{E}(\vec{k}) = E_{atom} - N|\Gamma|^2\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}A(\vec{R}) \qquad (N|\Gamma|^2 = 1)$$

where $A(\vec{R}) \equiv \int_V \chi^*(\vec{r})\left(U_{atom}(\vec{r}-\vec{R}) - V(\vec{r})\right)\chi(\vec{r}-\vec{R})\,d^3r$

Thus, through LCAO, the atomic orbitals from different atoms linearly combine to form <u>a band</u> with

$$\boxed{\mathcal{E}(\vec{k}) = E_{atom} - \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}A(\vec{R})}$$

↖ Key result for a <u>tight-binding band</u>

<u>Behaviour of $A(\vec{R})$</u>

$$A(\vec{R}) \equiv \int_V \chi^*(\vec{r})\left(U_{atom}(\vec{r}-\vec{R}) - V(\vec{r})\right)\chi(\vec{r}-\vec{R})\,d^3r$$

- $A(\vec{R})$ is negligible unless $|\vec{R}|$ is small
- $A(\vec{R})$ is important only for
  - (i) $\vec{R} = 0$
  - (ii) shortest $\vec{R}$'s (nearest neighbors)
  - (iii) next shortest $\vec{R}$'s (next nearest neighbors)
  - ⋮

(usually take (i) and (ii))

$A(\vec{R})$ is called the <u>hopping integral</u>

Look at $A(\vec{R}=0) \equiv A(\vec{0})$:

$$A(\vec{0}) = \int \chi^*(\vec{r})\left(U_{atom}(\vec{r}) - V(\vec{r})\right)\chi(\vec{r})\,d^3r$$

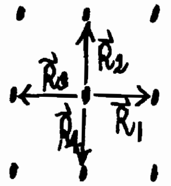
$$\equiv \alpha = \text{a number} \quad (\text{no dependence on } \vec{k})$$

$$\therefore \boxed{\mathcal{E}(\vec{k}) = E_{atom} - \alpha - \sum_{\vec{R}(\vec{R}\neq 0)} e^{i\vec{k}\cdot\vec{R}} A(\vec{R})}$$

Key result in TBM

take $\vec{R}=0$ term only does not give any dispersion (no $\vec{k}$-dependence)

i.e. to get a dispersive $\mathcal{E}(\vec{k})$, we need to consider $A(\vec{R})$ for the shortest $\vec{R}'s$ (at least)



2D square lattice

$\vec{R}_1, \vec{R}_2, \vec{R}_3, \vec{R}_4$ are the shortest $\vec{R}'s$ in a 2D square lattice.

Including them is to include <u>nearest-neighbor hopping</u>

Example: Simple Cubic lattice

- Include nearest-neighbor interactions only,

  $\Rightarrow$ include the 6 shortest $\vec{R}'s$

  $$\vec{R} = \pm a\hat{x} \;;\; \pm a\hat{y} \;;\; \pm a\hat{z}$$

For $\vec{k}$ in the B.Z., $\vec{k} = (k_x, k_y, k_z)$

Let $A(\vec{R}) \equiv t$ for these 6 shortest $\vec{R}'s$

$$\mathcal{E}(\vec{k}) = E_{atom} - \alpha - t\left(e^{ik_xa} + e^{-ik_xa} + e^{ik_ya} + e^{-ik_ya} + e^{ik_za} + e^{-ik_za}\right)$$

$$\Rightarrow \boxed{\mathcal{E}(\vec{k}) = E_{atom} - \alpha - 2t(\cos k_xa + \cos k_ya + \cos k_za)}$$

- <u>3D SC nearest neighbors TBM</u>
- standard n.n. TB form
- For $\vec{k} \in 1^{st}$ B.Z., (2N electronic states)

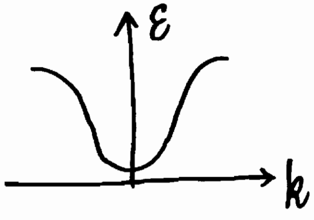
$\left\{ \begin{array}{l} \text{lowest energy: } \mathcal{E}(\vec{k}=0) = E_{atom} - \alpha - 6t \quad \text{at } \vec{k}=0 \\ \text{highest energy: } \mathcal{E}(\vec{k}) = E_{atom} - \alpha + 6t \quad \text{at } \vec{k} = \left(\pm\frac{\pi}{a}, \pm\frac{\pi}{a}, \pm\frac{\pi}{a}\right) \end{array} \right.$

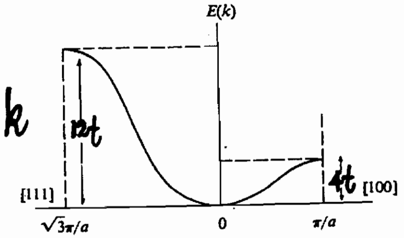
zone center

zone corners

Band Width $= 12t \propto t$

For a cut





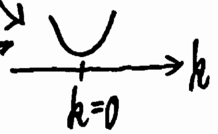
Behavior near bottom of band

- bottom of band is at $\vec{k}=0$
- near $\vec{k}=0$, $\cos k_x a \sim 1 - \frac{(k_x a)^2}{2}$, etc.

$$\mathcal{E}(\vec{k}) = \underbrace{E_{atom} - \alpha - 6t}_{} + (k_x^2 + k_y^2 + k_z^2)a^2 t$$

$$= \text{constant} + k^2 a^2 t$$

$\sim k^2 \Rightarrow$ parabolic near bottom of band



similar to free electron

But $V(\vec{r})$ effect is included!

The $V(\vec{r})$ effect is represented by the curvature (near $\vec{k}=0$)

Write: $\frac{\hbar^2 k^2}{2m^*} = k^2 a^2 t \Rightarrow \frac{\hbar^2}{2a^2 t} = m^*$ ← effective mass (the lazy way to include effect of $V(\vec{r})$)

Remarks

- How about 2D TBM? 1D TBM? other 3D Bravais lattices?
- How about basis with 2 atoms? How to formulate TBM?
- How about several atomic orbitals/atom?
- Empirical TBM (ETBM)
  - In recent years, many physicists applied TBM empirically to all materials (metals with rather free electrons as well as transition metals with tightly-binding electrons) by treating α and t as simply parameters. Values of α and t are found by fitting TB bands to results of other computationally intensive and accurate band structure calculations.
    [See W. Harrison, "Electronic Structure"]

Refs. Kittel Ch.7 and Ch.9
Christman Sec.7.1-7.5
Omar Ch.5