Band Theory: Nearly free energy model

- The problem: $-\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi = \varepsilon\psi$

  where $V(\vec{r}) = V(\vec{r}+\vec{R})$

  Bloch's theorem: $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r})$

  $\vec{k} \in 1^{st}$ B.Z.

- Problem becomes:

$$\left[\sum_{\vec{G}} \frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2 \delta_{\vec{G},\vec{G}'} + \sum_{\vec{G}} V(\vec{G}'-\vec{G})\right] u_{\vec{k}}(\vec{G}) = \varepsilon(\vec{k})\, u_{\vec{k}}(\vec{G})$$

OR

$$\left[\sum_{\vec{G}} \left[\frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2 + \bar{V}\right] \delta_{\vec{G},\vec{G}'} + \sum_{\vec{G}\neq\vec{G}'} V(\vec{G}'-\vec{G})\right] u_{\vec{k}}(\vec{G}) = \varepsilon(\vec{k})\, u_{\vec{k}}(\vec{G})$$

- Idea: $\{e^{i\vec{G}\cdot\vec{r}}\}$ basis set

$$V(\vec{G}) = \frac{1}{\Omega_c}\int_{\Omega_c} V(\vec{r})\, e^{-i\vec{G}\cdot\vec{r}}\, d^3r$$

$$
\begin{array}{c|ccccc}
 & 1 & e^{i\vec{G}_1\cdot\vec{r}} & e^{i\vec{G}_2\cdot\vec{r}} & e^{i\vec{G}_3\cdot\vec{r}} & \cdots \\
\hline
1 & \varepsilon^0(\vec{k})+\overline{V} & V(-\vec{G}_1) & V(-\vec{G}_2) & V(-\vec{G}_3) & \cdots \\
e^{i\vec{G}_1\cdot\vec{r}} & V(\vec{G}_1) & \varepsilon^0(\vec{k}+\vec{G}_1)+\overline{V} & V(\vec{G}_1-\vec{G}_2) & V(\vec{G}_1-\vec{G}_3) & \cdots \\
e^{i\vec{G}_2\cdot\vec{r}} & V(\vec{G}_2) & V(\vec{G}_2-\vec{G}_1) & \varepsilon^0(\vec{k}+\vec{G}_2)+\overline{V} & V(\vec{G}_2-\vec{G}_3) & \\
e^{i\vec{G}_3\cdot\vec{r}} & V(\vec{G}_3) & V(\vec{G}_3-\vec{G}_1) & V(\vec{G}_3-\vec{G}_2) & \varepsilon^0(\vec{k}+\vec{G}_3)+\overline{V} & \\
\vdots & \vdots & & & & \ddots
\end{array}
\begin{pmatrix} u_{\vec{k}}(\vec{0}) \\ u_{\vec{k}}(\vec{G}_1) \\ u_{\vec{k}}(\vec{G}_2) \\ u_{\vec{k}}(\vec{G}_3) \\ \vdots \end{pmatrix}
= \varepsilon(\vec{k})
\begin{pmatrix} u_{\vec{k}}(\vec{0}) \\ u_{\vec{k}}(\vec{G}_1) \\ u_{\vec{k}}(\vec{G}_2) \\ u_{\vec{k}}(\vec{G}_3) \\ \vdots \end{pmatrix}
$$

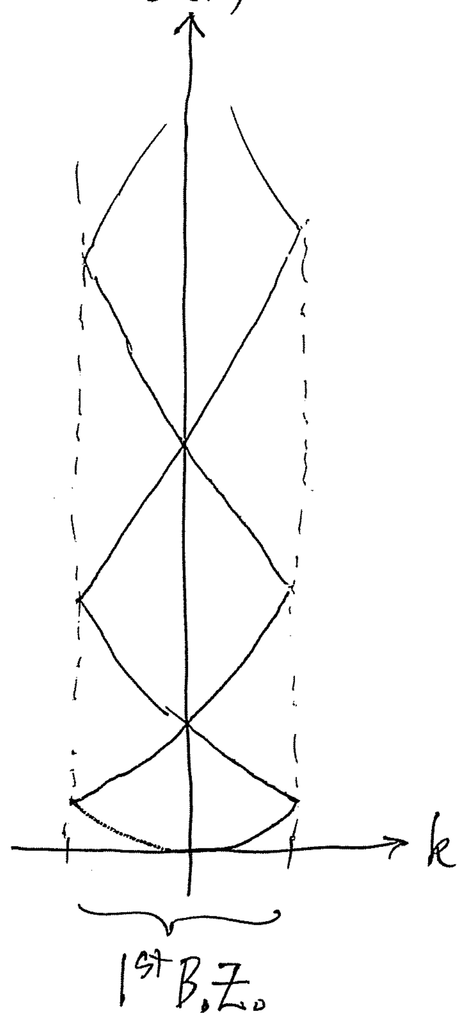
- Exact
- Each $\vec{k}$: a problem
- $\varepsilon^0(\vec{k}) = \frac{\hbar^2}{2m}k^2$
- $V(-\vec{G}) = \frac{1}{\Omega_c}\int_{\Omega_c} V(\vec{r})e^{i\vec{G}\cdot\vec{r}}d^3r = V(\vec{G})^*$

Turn off $V(\vec{r})$

	1	$e^{i\vec{G}_1\cdot\vec{r}}$	$e^{i\vec{G}_2\cdot\vec{r}}$	$e^{i\vec{G}_3\cdot\vec{r}}$	$\cdots$
1	$\varepsilon^0(\vec{k})$	0	0	0	$\cdots$
$e^{i\vec{G}_1\cdot\vec{r}}$	0	$\varepsilon^0(\vec{k}+\vec{G}_1)$	0	0	$\cdots$
$e^{i\vec{G}_2\cdot\vec{r}}$	0	0	$\varepsilon^0(\vec{k}+\vec{G}_2)$	0	$\cdots$
$e^{i\vec{G}_3\cdot\vec{r}}$	0	0	0	$\varepsilon^0(\vec{k}+\vec{G}_3)$	
					$\ddots$

- Give energies of folded bands at a particular $\vec{k}$
- These states are related through some $\vec{G}$

Band Folding



Empty Lattice Approximation

2 x 2 Matrices cover much physics

(a) Find the eigenvalues of

$$\begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ab} & \varepsilon_b \end{pmatrix}, \quad \text{i.e. } (\varepsilon_a - \varepsilon)(\varepsilon_b - \varepsilon) - V_{ab}^2 = 0$$

solve for ε

$$\varepsilon = \frac{\varepsilon_a + \varepsilon_b}{2} \pm \frac{1}{2}\sqrt{(\varepsilon_a + \varepsilon_b)^2 - 4(\varepsilon_a \varepsilon_b - V_{ab}^2)} \quad (*)$$

$$= \frac{\varepsilon_a + \varepsilon_b}{2} \pm \frac{\varepsilon_a - \varepsilon_b}{2} \cdot \sqrt{1 + \frac{4V_{ab}^2}{(\varepsilon_a - \varepsilon_b)^2}}$$

exact so far.

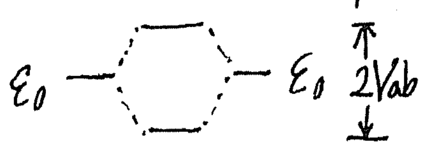
Two special cases

(b) $\varepsilon_a = \varepsilon_b = \varepsilon_0$

Start from (*), we have

$$\varepsilon = \begin{cases} \varepsilon_0 + V_{ab} \\ \varepsilon_0 - V_{ab} \end{cases}$$

i.e., Two degenerate states push each other apart

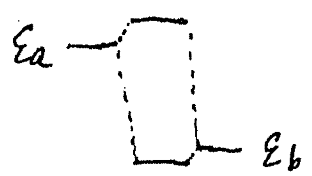


e.g. H_2

(c) $|\varepsilon_a - \varepsilon_b| \gg V_{ab}$

$$\varepsilon \approx \frac{\varepsilon_a + \varepsilon_b}{2} \pm \frac{\varepsilon_a - \varepsilon_b}{2}\left(1 + \frac{2V_{ab}^2}{(\varepsilon_a - \varepsilon_b)^2}\right)$$

$$\approx \begin{cases} \varepsilon_a + \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \\ \varepsilon_b - \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \end{cases}$$



e.g. HF

$$\varepsilon \approx \begin{cases} \varepsilon_a + \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \\ \varepsilon_b - \dfrac{V_{ab}^2}{\varepsilon_a - \varepsilon_b} \end{cases}$$

"A Pictorial Image in mind"...

- States repel each other in energy

  i.e., state of high energy (e.g. ε_a) is pushed up in energy by the state(s) of lower energy (energies)

  <u>AND</u>

  state of lower energy (e.g. ε_b) is pushed down in energy by the state(s) of high energy (energies)

- Case (c) is essentially the 2nd order non-degenerate ($\varepsilon_a \neq \varepsilon_b$) perturbation theory in QM
- Case (b) is essentially the degenerate ($\because \varepsilon_a = \varepsilon_b$) perturbation theory in QM

Applications

- Two atoms far apart $\Rightarrow$ one is not affecting the other

energy of atomic orbital of relevance in atom A (e.g. 1s orbital in H)

$$\begin{pmatrix} \varepsilon_a & 0 \\ 0 & \varepsilon_b \end{pmatrix}$$

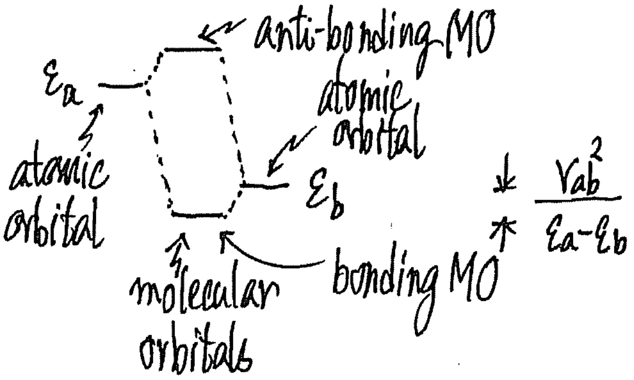
Far apart, atoms A & B are not influcencing each other

energy of atomic orbital of relevance in atom B

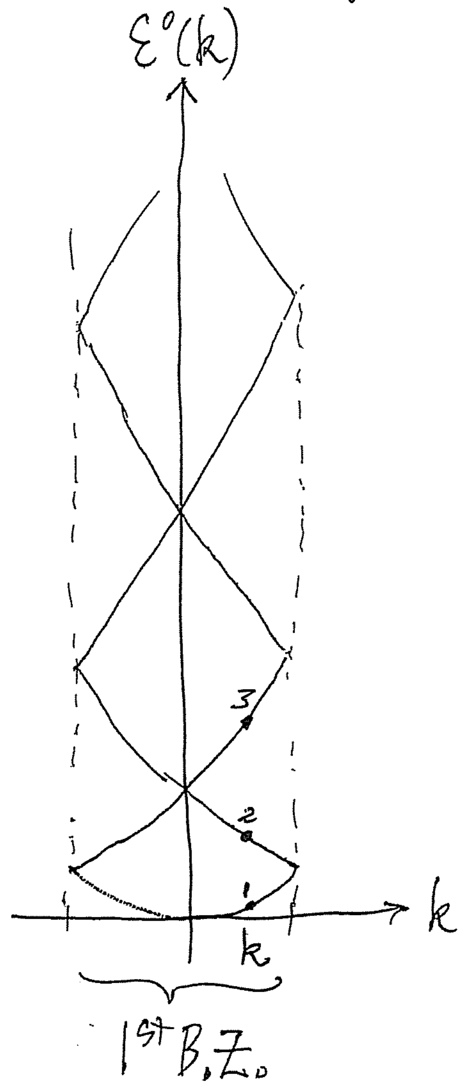
- Two atoms get closer $\Rightarrow$ $\begin{cases} \text{one is affecting the other} \\ \text{formation of molecule} \end{cases}$

$$\begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ab} & \varepsilon_b \end{pmatrix}$$

describes how atoms A & B influence each other : "interaction energy"



Band Folding



- Question:
  - What does a finite $V(\vec{r})$ do to state 1?
- "Neighboring" (above/below) not too close
- Can use 2x2 matrix and consider effects of other states one by one
- Largest effect comes from state closest in energy ("2")

Pick the 2x2 out:

$$\begin{pmatrix} \varepsilon^0(\vec{k}) + \overline{V} & V(\vec{G})^* \\ V(\vec{G}) & \varepsilon^0(\vec{k}+\vec{G}) + \overline{V} \end{pmatrix}$$

some $\vec{G}$ relating 1 & 2

Eigenvalues:
Change $\varepsilon^0(\vec{k})$ of "1" to:

$$\varepsilon(\vec{k}) = \varepsilon^0(\vec{k}) + \overline{V} - \frac{|V(\vec{G})|^2}{\varepsilon^0(\vec{k}+\vec{G}) - \varepsilon^0(\vec{k})}$$

Empty Lattice Approximation
(2^{nd} order perturbation)

Including effects of other states one by one:

$$\varepsilon(\vec{k}) = \varepsilon^0(\vec{k}) + \bar{V} + \underbrace{\sum_{\vec{G}\neq 0} \frac{|V(\vec{G})|^2}{\varepsilon^0(\vec{k}) - \varepsilon^0(\vec{k}+\vec{G})}}_{\text{this is 2nd perturbation result in QM}}$$

1^{st} order perturbation

- no effect
- no gap opening

Band Folding

- When there are states <u>close</u> or <u>equal</u> in $\mathcal{E}^0$, <u>Be Careful!</u>
- Don't worry, do the same thing and pick the 2x2 (or n×4) out

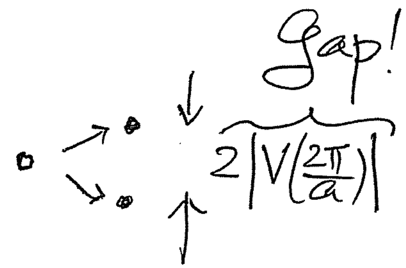
<u>E.g.</u>
$$\begin{pmatrix} \mathcal{E}^0\left(\frac{\pi}{a}\right)+\overline{V} & V\left(\frac{2\pi}{a}\right)^* \\ V\left(\frac{2\pi}{a}\right) & \mathcal{E}^0\left(\frac{\pi}{a}\right)+\overline{V} \end{pmatrix}$$

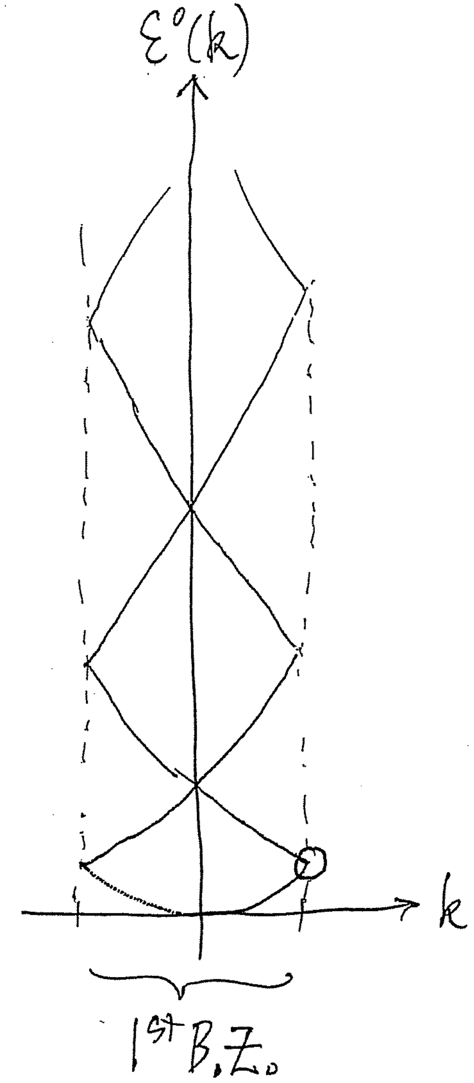
Exact eigenvalues:

$$\mathcal{E}^0\left(\frac{\pi}{a}\right)+\overline{V}+\left|V\left(\frac{2\pi}{a}\right)\right|$$

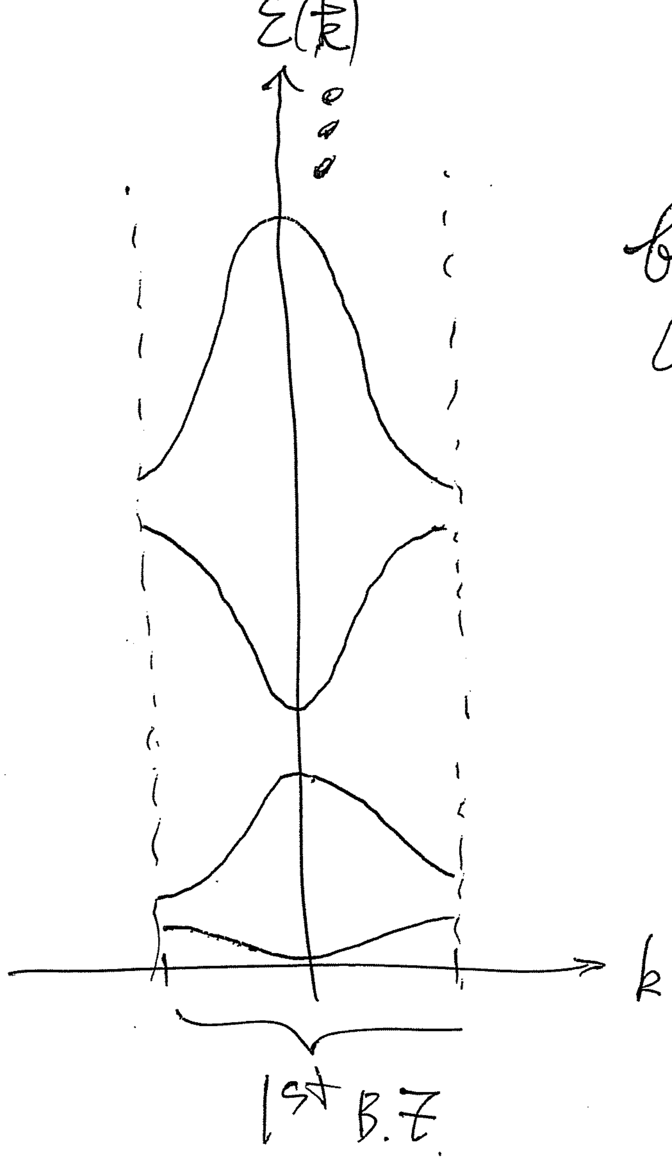
and

$$\mathcal{E}^0\left(\frac{\pi}{a}\right)+\overline{V}-\left|V\left(\frac{2\pi}{a}\right)\right|$$





Empty Lattice Approximation



band structure
with bands & band gaps!

This is the essence of the
nearly free electron model!