Nearly Free electrons <u>NFE</u>

Notation: $\vec{G} = RLV$

$\vec{G} = \sum_i l_i \vec{b}_i$ with $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$

$$\psi_k = \sum_G C_{k-G}\, e^{i(k-G)r} \longleftarrow \text{A Bloch WF}$$

Prove: $\psi_k(r+\vec{R}) = \sum_G C_{k-G}\, e^{\overbrace{i(k-G)(r+R)}^{ikr - iGr + ikR - \cancel{iGR}}} = e^{ikR}\,\psi_k(r)$ QED

These states satisfy the equation of e^- in a periodic potential

$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$; $H\psi_k = \varepsilon_k \psi_k$

$$\left[\frac{\hbar^2}{2m}(k-G)^2 - \varepsilon_k\right] C_{k-G} + \sum_{G'} V_{G'-G}\, C_{k-G'} = 0 \quad (1)$$

This is the eq. That we solve To compute The eigenvalues for each k point.

→ For Fixed k There are G equations like (1)

n = # of eigenstates = # G's or plane waves in the expansion.

. Free e^- : $U(r) = \sum_G U_G e^{iGr} \Rightarrow U_0 = U(r) = 0$

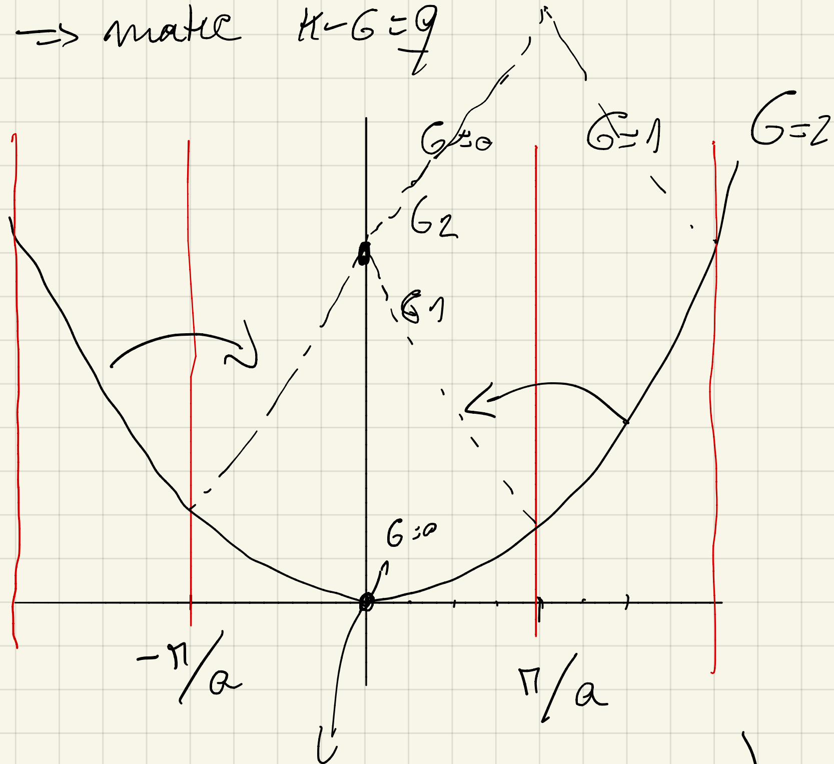
Then (1) $\Rightarrow \left(\frac{\hbar^2}{2m}(k-G)^2 - \varepsilon\right) C_{k-G} = 0$

$$\left[\frac{\hbar^2}{2m}\sum_{G}(k-G)^2 C_{k-G} + \sum_{GG'} V_{G'} C_{k-G}\right] e^{i(k-G)r} = \varepsilon_k \sum_{G} C_{k-G}\, e^{i(k-G)r}$$

$$= \sum_{G} C_{k-G}\, e^{i(k-G)r} \left[\frac{\hbar^2}{2m}(k-G)^2 - \varepsilon_k\right] + \sum_{G'} V_{G'}$$

$$\mathcal{E}(k-G) = \frac{\hbar^2}{2m}(k-G)^2 \Rightarrow \text{make } k-G=q$$

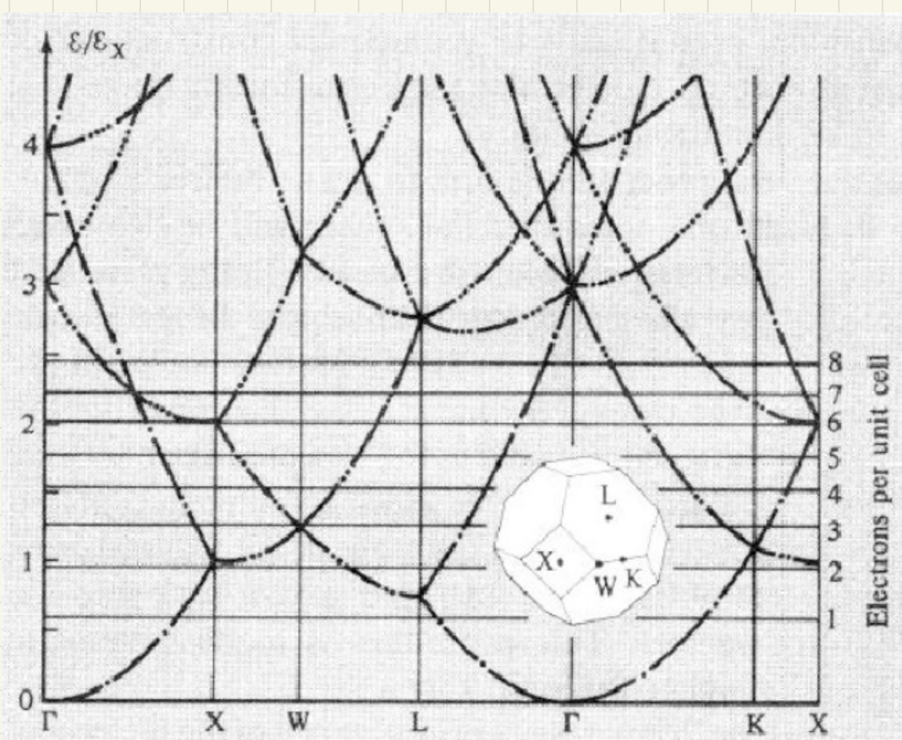
$$\mathcal{E}(q) = \frac{\hbar^2}{2m}q^2$$



$$G=0 \quad \frac{\hbar^2 k^2}{2m} \quad k \in (0, \pi/a)$$

$$G=1\ (\pi/a) \rightarrow \mathcal{E} = \frac{\hbar^2 (k-\pi/a)^2}{2m} \quad k \in (0, \pi/a)$$

→ This is the free electron solution



What happens if we have more than one C_{k-G} for which $\epsilon^{0}_{k-G} = \epsilon^{0}_{k-G'}$

Note $\epsilon^{0}(k-G) = \dfrac{\hbar^2 (k-G)^2}{2m}$

Free electron solution.

Nearly Free electrons

. What happens when the external potential is periodic, but very week. We can solve our problem by applying perturbation th. to the free e^- approximation.

. We still have:

$$\psi_k(r) = \sum_G C_{k-G}\, e^{i(k-G)r}$$

$$\left[\frac{\hbar^2}{2m}(k-G)^2 - \mathcal{E}\right] C_{k-G} + \sum_{G'} V_{G-G'}\, C_{k-G'} = 0$$

. We solved this for the energy, obtaining

$$\mathcal{E}_{\underline{q}} = \mathcal{E}^\circ_{\underline{q}} = \frac{\hbar^2}{2m}\underline{q}^2 \quad \text{with } \underline{q} = k - G$$

The wave functions for each energy, when there is no degeneracy ($\mathcal{E}^\circ_{k-G} \neq \mathcal{E}^\circ_{k-G'}$ for <u>all</u> G')

Then $\psi_k = \frac{1}{\sqrt{V}} e^{i(k-G)r}$

→ If there are degeneracies, then ψ_k will be a linear combination of all G's that have the same eigenvalue

→ That is, the $\{C_{k-G}\}$ will be a set of size m, m being the degeneracy.

. Let's do this, will use perturbation th, and the notation as in Ziman (chapter 3).

- $V(r) \to$ Periodic potential $\to V(r) = \sum_G V_G e^{iGr}$
- $|k\rangle \to \psi_k(r) = \frac{1}{\sqrt{V}} e^{ikr}$
- $\mathcal{E}^\circ(k) \to$ Free e^- energies $= \frac{\hbar^2 k^2}{2m}$

1st order perturbation th.

$$\mathcal{E}(k) = \mathcal{E}^\circ_k + \langle k|V|k\rangle + \sum_{k'} \frac{|\langle k|V|k'\rangle|^2}{\mathcal{E}^\circ(k) - \mathcal{E}^\circ(k')} + \mathcal{O}(V^3)$$

$$\langle k|V|k'\rangle = \frac{1}{V}\int_V e^{-ikr}\left(\sum_G V_G e^{iGr}\right) e^{ik'r} d^3r$$

$$= \sum_G V_G \frac{1}{V}\int_V e^{i(G+k'-k)r} dr = \sum_G V_G \delta_{k',k-G}$$

$$\langle k|V|k\rangle = \sum_G V_G \delta_{k,0} = V_0 = 0 \text{ (by definition)}$$

This gives us:

$$\mathcal{E}(k) = \mathcal{E}^0(k) + \sum_{G\neq 0} \frac{|V_G|^2}{\mathcal{E}^0(k) - \mathcal{E}^0(k-G)}$$

This expansion is valid if $|\mathcal{E}^0(k) - \mathcal{E}^0(k-G)| \gg |V_G| \ \forall k$

i.e is valid not near a degeneracy

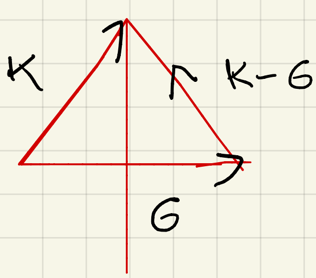
also $V_G \longrightarrow \emptyset$ for large G (The actual potential seen by e^- is smooth!)

$$\mathcal{E}(k) = \mathcal{E}^0(k) + \mathcal{O}(V^2)$$

- Degeneracy condition

$\Longrightarrow |K| = |K-G|$ $\rightarrow$ This is The Laue Condition!

$\rightarrow$ Bragg difraction $k = k - G$



$\Rightarrow k$ lies on The perpendicular bisector of a reciprocal lattice vector G.

This perpendicular bisector defines The zone boundaries

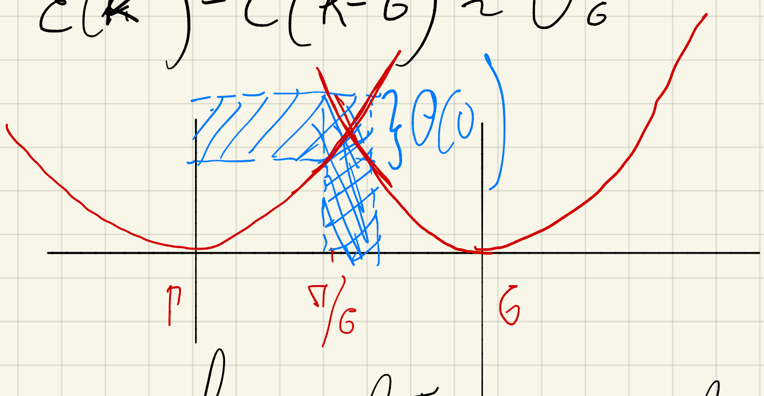
→ Perturbative expansion fails near the zone boundaries

k and k-G are strongly coupled → we need to find a linear combination of these two states that are decoupled at low order.

Note: Valence e^- in crystals are diffracted by the crystal exactly the same as if they would be diffracted if they were incident with wave vector k from outside

. Simplest degeneracy $(m=2)$ $|k\rangle, |k-G\rangle$

$$\mathcal{E}(k) - \mathcal{E}(k-G) \sim U_G$$



$U \to 0$

$\mathcal{E}_k - \mathcal{E}_{k-G} \to 0$

→ Find a solution near the zone Boundary

$$\left(\frac{\hbar^2}{2m}(k-G)^2 - \mathcal{E}(k)\right) C_{k-G} + \sum_{G' \neq G} V_{G'-G}\, C_{k-G'} = 0$$

→ Potential only mixes states that differ by a RLV

· Now we consider in our solution only the 2D space spanned by $|k\rangle$ and $|k-G\rangle$, we ignore the coupling to all other states

(solution is a linear combination of incident & difracted (Bragg) states)

$$\begin{cases} \left(\dfrac{\hbar^2}{2m}(k-G)^2 - \mathcal{E}(k)\right) C_{k-G} + V_{-G}\, C_k = 0 & G=G \quad G'=0 \\ \left(\dfrac{\hbar^2}{2m}k^2 - \mathcal{E}(k)\right) C_k + V_G\, C_{k-G} = 0 & G=0 \quad G'=G \end{cases}$$

$$V_{-G} = V_G^* \Rightarrow V \text{ is real}$$

$$\begin{cases} \left(\mathcal{E}^0_{k-G} - \mathcal{E}_k\right) C_{k-G} + V_G^* C_k = 0 \\ \left(\mathcal{E}^0_k - \mathcal{E}_k\right) C_k + V_G C_{k-G} = 0 \end{cases}$$

$$\begin{vmatrix} \mathcal{E}_k - \mathcal{E}^0_k & -V_G \\ -V_G^* & \mathcal{E}_k - \mathcal{E}^0_{k-G} \end{vmatrix} = 0$$

$$\mathcal{E}_k^{\pm} = \frac{1}{2}\left(\left(\mathcal{E}^0_k + \mathcal{E}^0_{k-G}\right) \pm \sqrt{\left(\mathcal{E}^0_k - \mathcal{E}^0_{k-G}\right) + 4|V_G|^2}\right.$$

$$\psi^{\pm} = C_k^{\pm} e^{ikr} + C_{k-G}^{\pm} e^{i(k-G)r}$$

$\Rightarrow$ The two states e^{ikr} and $e^{i(k-G)r}$ are combined into two other states ψ^+ and ψ^-

This is the dominant effect of a weak periodic potential for nearly degenerated levels when they are close to a Bragg plane (only there degeneracies happen)

- Exact degeneracy $|k| = |\cancel{k} - G|$ $\varepsilon^0_k = \varepsilon^0_{k-G}$

$$\varepsilon^{\pm}_k = \varepsilon^0_k \pm |V_G|$$

- At all points on the Bragg plane we open a gap
$E_g = 2|V_G| \propto |V_g|$ (1st order effect)

- Wave function coefficient?

$$\left(\varepsilon - \varepsilon^0_k\right) C_k = V_G C_{k-G} \xrightarrow{\varepsilon^+} |V_G| C_k = V_G C_{k-G} \; ; \; \varepsilon^-$$

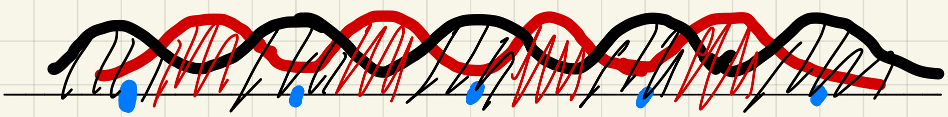
$$\left(\varepsilon - \varepsilon^0_{k-G}\right) C_{k-G} = V^*_G C_k \qquad C_k = \pm \operatorname{sing} V_G \, C_{k-G}$$

$$V_G < 0 \implies \psi^+ = C_k \left(e^{ikr} - e^{i(k-G)r}\right) \overset{k=1/2\,G}{=} \frac{1}{\sqrt{2}} \left(e^{i\frac{G}{2}r} - e^{-i\frac{G}{2}r}\right.$$

$$\psi^+ = \sqrt{2} \sin \tfrac{1}{2} G r \; ; \; \psi^- = \sqrt{2} \cos \tfrac{1}{2} G r$$

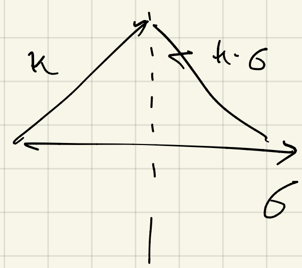
$\psi^- \to e^-$ around atoms $\Rightarrow$ s-like states $(\varepsilon^- < \varepsilon^0)$

$\psi^+ \to e^-$ in between atoms $\to$ p-like states $(\varepsilon^+ > \varepsilon^0)$



$\to$ charge densities

- All this can be easily generated for $n > 2$ degenerated states.
- Gaps are formed if tip of $\vec{k}$ lies on a Bragg plane (perpendicular bisector of G)



- The faces of the 1st BZ are Bragg planes, This is where gaps open!

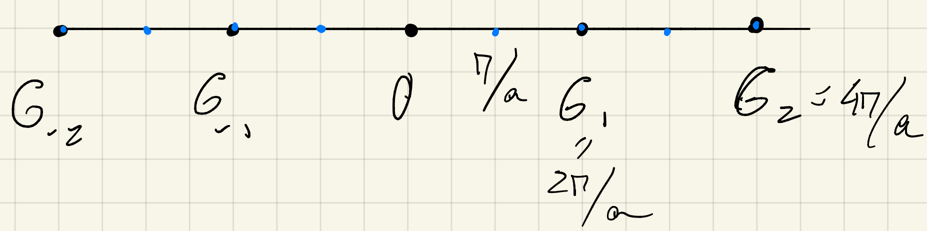
. Summary: (let's review the NFE model in 1D)

① K away from BZ boundaries (Bragg planes)

$$\mathcal{E}(K) = \mathcal{E}^0(k) + O(U^2)$$

② K on Bragg planes $\left(1D \to k = \frac{G_n}{2} = \frac{n\,2\pi}{2\,a} = n\frac{\pi}{a}\right.$

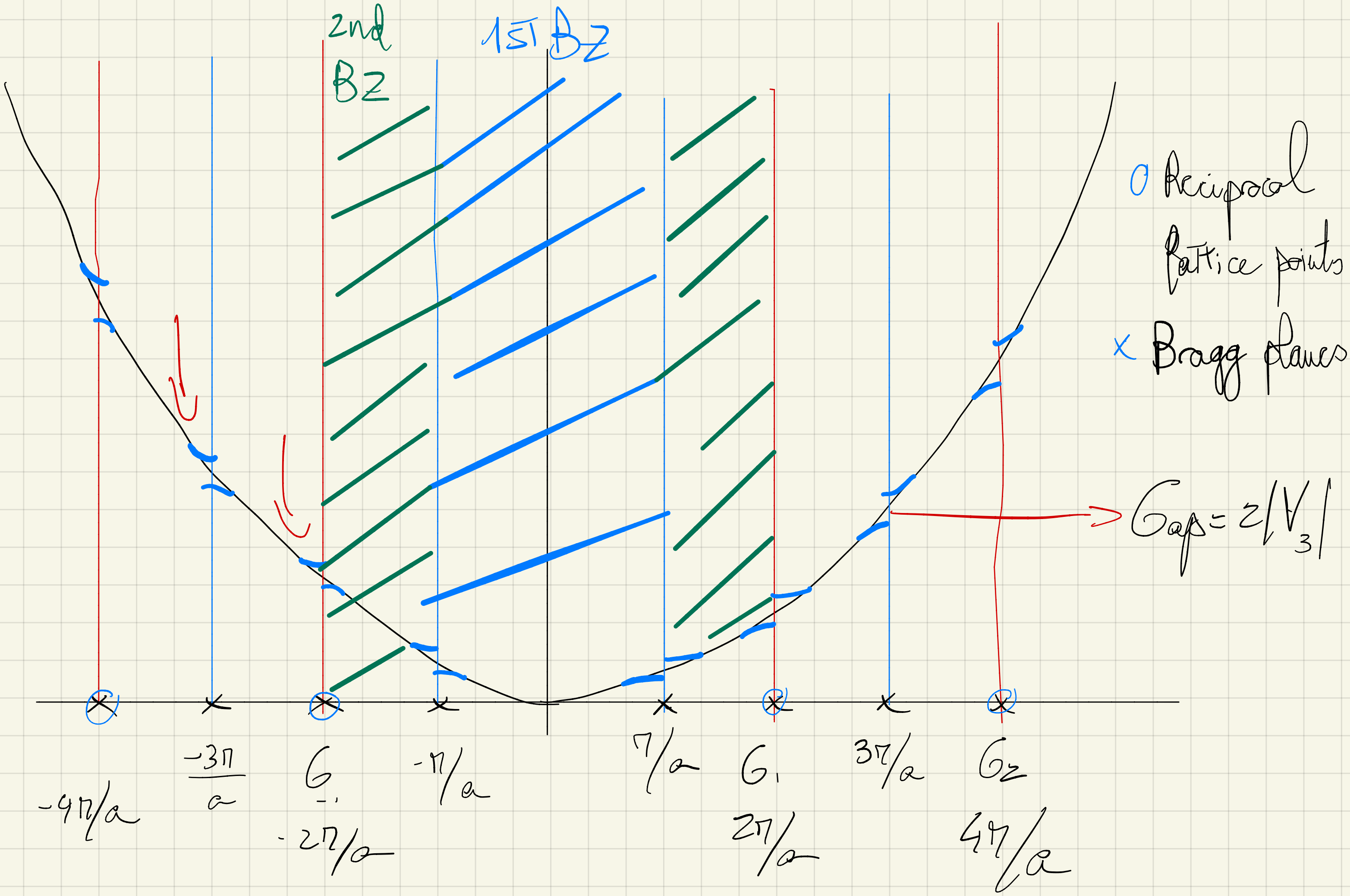
$|K| = |K - G|$, Two and only 2 degenerate states$\left.\right)$

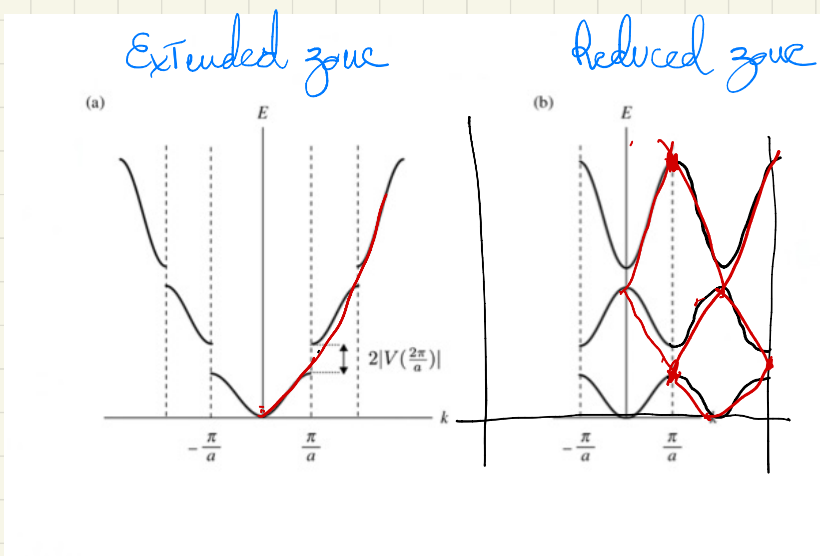


$$\mathcal{E}\left(K = \frac{G_n}{2}\right) = \mathcal{E}^0\left(K = \frac{G_n}{2}\right) \pm |V_n| \quad ; \quad V_n = \frac{1}{V}\int_{V_p} V(r)\, e^{-iG_n r}$$

③ K very close To G_n.

$$\mathcal{E}_K^{\pm} = \frac{1}{2}\left[\mathcal{E}^0_K + \mathcal{E}^0_{K-G_n} \pm \sqrt{\left(\mathcal{E}^0_K - \mathcal{E}^0_{K-G_n}\right)^2 + 4|V_n|^2}\right.$$


2nd BZ
1st BZ
o Reciprocal lattice points
x Bragg planes
Gap = 2|V_3|
-4π/a
-3π/a
G_{-1}
-2π/a
-π/a
π/a
G_1
2π/a
3π/a
G_2
4π/a


Extended zone
Reduced zone
(a)
(b)
E
k
2|V(2π/a)|
-π/a
π/a

$\mathcal{E}(k)$ is a smooth function

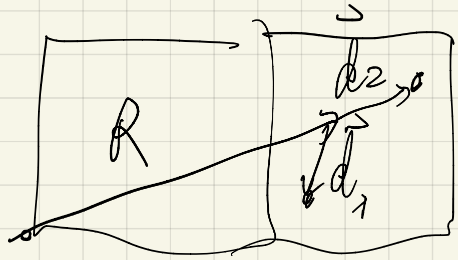
1st BZ bands: Pieces of $\mathcal{E}(k)$ in n-th BZ. Using the extended zone scheme, reduce (unfold) them to 1st Brillouin zone and join smoothly, represents the n'th band in the reduced zone scheme.

- Reduced zone: each level is indexed with a $\vec{k}$ within the 1st BZ
- Extended zone: emphasizes the continuity of $\mathcal{E}(k)$. It is extremely redundant.
- 3D: $\mathcal{E}$ Vs k is plotted for free e^- along high symmetry directions in k space. There are highly degenerated bands. Not all degeneracies are broken by the free e^- model, some remain.

- Geometrical structure factor in monoatomic lattices with basis

$U(r) \Rightarrow$ atomic potentials at the atomic positions repeated periodically

Basis of identical atoms at $\vec{d}_j$



$$U(r) = \sum_R \sum_j \phi(r-R-d_j)$$

$$U_G = \frac{1}{V}\int_{V_p} dr\, e^{-iGr} \sum_{R,j} \phi(r-R-d_j)$$

$$\int_{V_p}\sum_R F(R,r) = \int_{-\infty}^{\infty} d^3r\, F(r)$$

$$= \frac{1}{V}\int_{\text{all space (supercell Volume)}} dr\, e^{-iGr} \sum_j \phi(r-d_j)$$

$r' = r - d_j$; $e^{-iG(r'+d_j)} = e^{-iGr'} \cdot e^{iGd_j}$

$$U_G = \frac{1}{V}\phi(\vec{G})\, S^*_G$$

$$\phi_G = \int_{-\infty}^{\infty} d^3r\, e^{-iGr}\phi(r)$$

$\downarrow$ Fourier Transform of the atomic potential

$$S_G = \sum_j e^{iGd_j}$$

$\downarrow$ Geometrical structure factor

So if the basis leads to a $S(G)=0$ for some Bragg planes then the Fourier component of the periodic potential associated with those planes is $=0$ $\Longrightarrow$ the lowest order splitting disappears

Symmetry operations and $\mathcal{E}(k)$

- if a crystal is invariant under rotation

$$O_R \equiv \text{Rotation operator} \quad O_R \psi(r) = \psi(R^{-1} r)$$

R = Rot. matrix

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$O_R H O_{R^{-1}} = H \qquad H O_R = O_R H$$

$$O_R H \psi_k(r) = O_R \mathcal{E}_k \psi_k(r)$$

$$H[O_R \psi_k(r)] = \mathcal{E}_k [O_R \psi_k(r)]$$

$\Rightarrow O_R \psi_k$ is also an eigenfunction, with the same eigenvalue

$$O_R \psi_k(R) = O_R\left[e^{ikr} u_k(r)\right] = e^{ikR^{-1}r} \underbrace{u_k(R^{-1}r)}_{\text{still periodic}}$$

$$\vec{k}(R^{-1}r) = (R\vec{k}) \cdot (RR^{-1}r) = R\vec{k}\vec{r}$$

$$O_R \psi_k(r) = e^{i(R\vec{k})\cdot\vec{r}} u_k(R^{-1}r) \Rightarrow O_R \psi_k(\vec{r})$$ is a Bloch state with $\vec{k}' = Rk$

$\Rightarrow \mathcal{E}(R\vec{k}) = \mathcal{E}(\vec{k})$; $\mathcal{E}_n(R\vec{k}) = \mathcal{E}_m(\vec{k})$ with n properly chosen

Theorem : $\mathcal{E}_n(R\vec{k}) = \mathcal{E}_n(\vec{k})$ if The crystal is invariant under O_R

O_R = rotation, reflection, inversion, any point operation

$$\mathcal{E}_n(R\vec{k}) = O_R^{-1}\,\mathcal{E}_n(k) = \mathcal{E}_n(k)$$

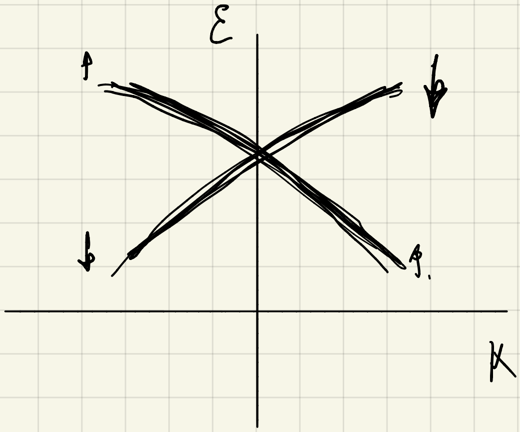
Theorem : $\mathcal{E}_n(k)$ surfaces in $\vec{k}$ space have The point symmetries of The crystal in real space.

Examples

- inversion symmetry $\mathcal{E}_n(k) = \mathcal{E}_n(-k)$
- reflection about $y-z$: $\mathcal{E}_n(k_x, k_y, k_z) = \mathcal{E}_n(-k_x, k_y, k_z)$
- Time Reversal symmetry :

1. ignore spin $\Rightarrow \psi_k$ and ψ_{-k} are degenerate $\mathcal{E}(k) = \mathcal{E}(-k)$
2. if spin orbit interaction is included $\Rightarrow \psi_{k\uparrow} \neq \psi_{k\downarrow}$

Time reversal $\Rightarrow \mathcal{E}_{k\uparrow} = \mathcal{E}_{-k\downarrow}$



· Translational symmetry :

$\psi_{\vec{k}}$ can be written as $\psi_{k+\vec{G}}$, $\vec{G}$ a RL vector.

$\mathcal{E}_n(k) = \mathcal{E}_n(k+\vec{G}) \Longrightarrow \psi_{nk} = \psi_{n(k+G)}$

$\Longrightarrow \mathcal{E}_n(\vec{k})$ is periodic in reciprocal space.

Summary : $\mathcal{E}_n(k)$ has Translational Sym. $\mathcal{E}_n(k) = \mathcal{E}_n(k+G)$

$\mathcal{E}_n(\vec{k})$ has the point symmetry of the crystal