Estructura de la Materia 2

Clase 9 - Teoría

Docentes

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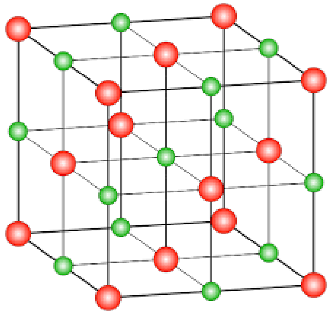
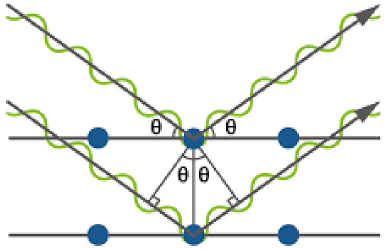
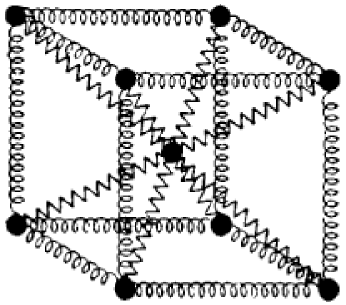
Web: http://materias.df.uba.ar/edlm2a2020c1

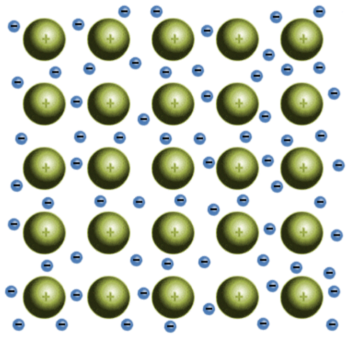
Programa de la materia

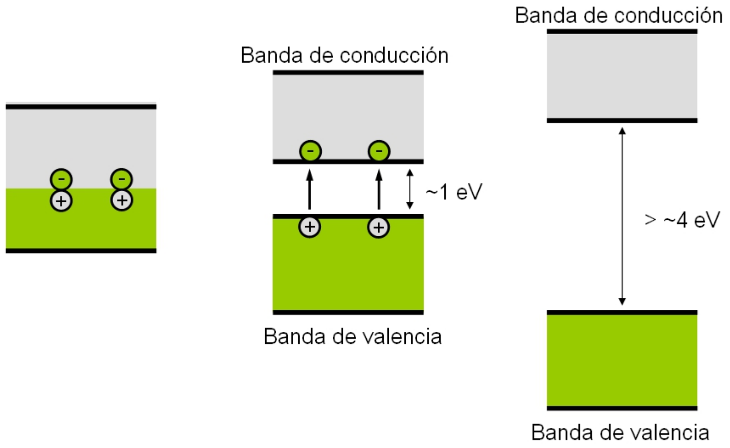
- Red cristalina y red recíproca ✔
- Difracción de rayos X ✔
- Cohesión en sólidos ✔
- Vibraciones, fonones y propiedades térmicas ✔
- Electrones en sólidos
  - Electrones libres ✔
  - Electrones en un potencial periódico
    - Potencial débil
    - Enlaces fuertes
- Semiconductores







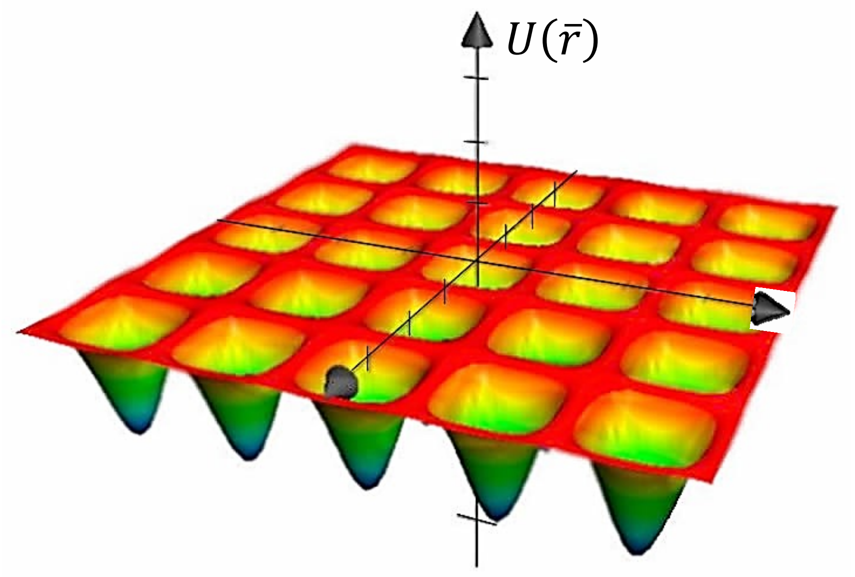




Electrones en un potencial periódico

Potencial periódico

Los iones de la red generan un potencial periódico, en el cual se encuentran inmersos los e⁻ más externos.



$$U(\bar{r}+\bar{R}) = U(\bar{r}), \qquad \forall \bar{R} \in RB$$

Trabajamos en un modelo de e⁻ independientes, donde $U(\bar{r})$ es un potencial efectivo que también incluye las interacciones e⁻-e⁻.

$$\underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\bar{r})\right)}_{\mathcal{H}}\psi(\bar{r}) = \varepsilon\psi(\bar{r}) \quad \text{(Ec. de Shcrödinger de 1 e}^-\text{)}$$

Teorema de Bloch

Los autoestados de $\mathcal{H}$ pueden elegirse como: $\psi_{n\bar{k}}(\bar{r}) = e^{i\bar{k}\cdot\bar{r}}u_{n\bar{k}}(\bar{r})$ con $u_{n\bar{k}}(\bar{r}+\bar{R}) = u_{n\bar{k}}(\bar{r})$

Índice de banda

$$\rightarrow \psi_{n\bar{k}}(\bar{r}+\bar{R}) = e^{i\bar{k}\cdot(\bar{r}+\bar{R})}u_{n\bar{k}}(\bar{r}+\bar{R}) = e^{i\bar{k}\cdot\bar{R}}e^{i\bar{k}\cdot\bar{r}}u_{n\bar{k}}(\bar{r}) = e^{i\bar{k}\cdot\bar{R}}\psi_{n\bar{k}}(\bar{r})$$

Teorema de Bloch

Condiciones de contorno periódicas (Born-von Karman)

$\psi(\bar{r}+N_i\bar{a}_i)=\psi(\bar{r});\ i=1,2,3$ $\quad \bar{a}_i$:VP de la RD; $\quad N_1N_2N_3=N$ (N° total de CP en el cristal)

$$\psi(\bar{r}+\bar{R})=e^{i\bar{k}\cdot\bar{R}}\psi(\bar{r}) \longrightarrow \psi(\bar{r}+N_i\bar{a}_i)=e^{i\bar{k}\cdot N_i\bar{a}_i}\psi(\bar{r}) \longrightarrow e^{i\bar{k}N_i\bar{a}_i}=1$$

$\bar{k}=x_1\bar{b}_1+x_2\bar{b}_2+x_3\bar{b}_3,\ \bar{b}_i$: VP de la RR, $x_i \in \mathbb{R} \longrightarrow 2\pi x_i N_i=2\pi m_i, m_i \in \mathbb{Z} \longrightarrow x_i=\dfrac{m_i}{N_i}$

$\bar{k}=\dfrac{m_1}{N_1}\bar{b}_1+\dfrac{m_2}{N_2}\bar{b}_2+\dfrac{m_3}{N_3}\bar{b}_3 \longrightarrow$ Volumen por $\bar{k}$ permitido: $\Delta\bar{k}=\dfrac{\bar{b}_1}{N_1}\left(\dfrac{\bar{b}_2}{N_2}\times\dfrac{\bar{b}_3}{N_3}\right)=\dfrac{1}{N}\dfrac{(2\pi)^3}{v}=\dfrac{(2\pi)^3}{V}$

Demostración del Teorema de Bloch

$\psi(\bar{r})=\sum_{\bar{q}} c_{\bar{q}}\, e^{i\bar{q}\cdot\bar{r}};\quad U(\bar{r})=\sum_{\bar{K}} U_{\bar{K}}\, e^{i\bar{K}\cdot\bar{r}} \longrightarrow$ Coeficiente de Fourier $U_{\bar{K}}=\frac{1}{v}\int_{CP} e^{-i\bar{K}\cdot\bar{r}}U(\bar{r})d\bar{r}$

$\bar{K}$ $\in RR\ (U(\bar{r}+\bar{R})=U(\bar{r}))$

$\bar{q}$ Satisface condiciones de contorno

Simetría de inversión

Elegimos $U_0=\frac{1}{v}\int_{CP}U(\bar{r})d\bar{r}=0;\ U(\bar{r})$ real $\longrightarrow U_{-\bar{K}}={U_{\bar{K}}}^*;\ \ U(\bar{r})=U(-\bar{r}) \longrightarrow U_{-\bar{K}}=U_{\bar{K}}={U_{\bar{K}}}^*$

Teorema de Bloch

Demostración del Teorema de Bloch

Energía cinética: $$-\frac{\hbar^2}{2m}\nabla^2\left(\sum_{\bar q} c_{\bar q}\, e^{i\bar q\cdot\bar r}\right) = \sum_{\bar q}\frac{\hbar^2}{2m} q^2 c_{\bar q}\, e^{i\bar q\cdot\bar r}$$

Energía potencial: $$\sum_{\bar K} U_{\bar K}\, e^{i\bar K\cdot\bar r}\left(\sum_{\bar q} c_{\bar q}\, e^{i\bar q\cdot\bar r}\right) = \sum_{\bar K\bar q} U_{\bar K} c_{\bar q}\, e^{i(\bar K+\bar q)\cdot\bar r} \overset{\bar q' = \bar K + \bar q}{=} \sum_{\bar K\bar q'} U_{\bar K} c_{\bar q'-\bar K}\, e^{i\bar q'\cdot\bar r}$$

$$\xrightarrow{\bar q' \to \bar q,\ \bar K \to \bar K'} \sum_{\bar q} e^{i\bar q\cdot\bar r}\overbrace{\left\{\left(\frac{\hbar^2}{2m}q^2 - \varepsilon\right)c_{\bar q} + \sum_{\bar K'} U_{\bar K'} c_{\bar q-\bar K'}\right\}}^{=0} = 0 \xrightarrow{\bar q = \bar k - \bar K,\, \bar k \in 1ZB,\, \bar K \in RR} \left(\frac{\hbar^2}{2m}(\bar k-\bar K)^2 - \varepsilon\right)c_{\bar k-\bar K} + \sum_{\bar K'} U_{\bar K'} c_{\bar k-\bar K-\bar K'} = 0$$

$$\xrightarrow{\bar K' \to \bar K' - \bar K} \left(\underbrace{\frac{\hbar^2}{2m}(\bar k-\bar K)^2}_{\varepsilon^0_{\bar k-\bar K}} - \varepsilon\right)c_{\bar k-\bar K} + \sum_{\bar K'} U_{\bar K'-\bar K} c_{\bar k-\bar K'} \overset{\forall \bar K \in RR}{=} 0 \longrightarrow$$

Tenemos *N* problemas independientes, uno para cada $\bar k$ permitido en la 1ZB. Cada problema tiene como soluciones superposiciones de ondas planas con vectores de onda que solo pueden diferir de $\bar k$ en un vector de la RR.

$$\longrightarrow \psi_{n\bar k}(\bar r) = \sum_{\bar K} c_{\bar k-\bar K}\, e^{i(\bar k-\bar K)\cdot\bar r} = e^{i\bar k\cdot\bar r}\underbrace{\sum_{\bar K} c_{\bar k-\bar K}\, e^{-i\bar K\cdot\bar r}}_{u_{n\bar k}(\bar r)}$$

Potencial periódico débil

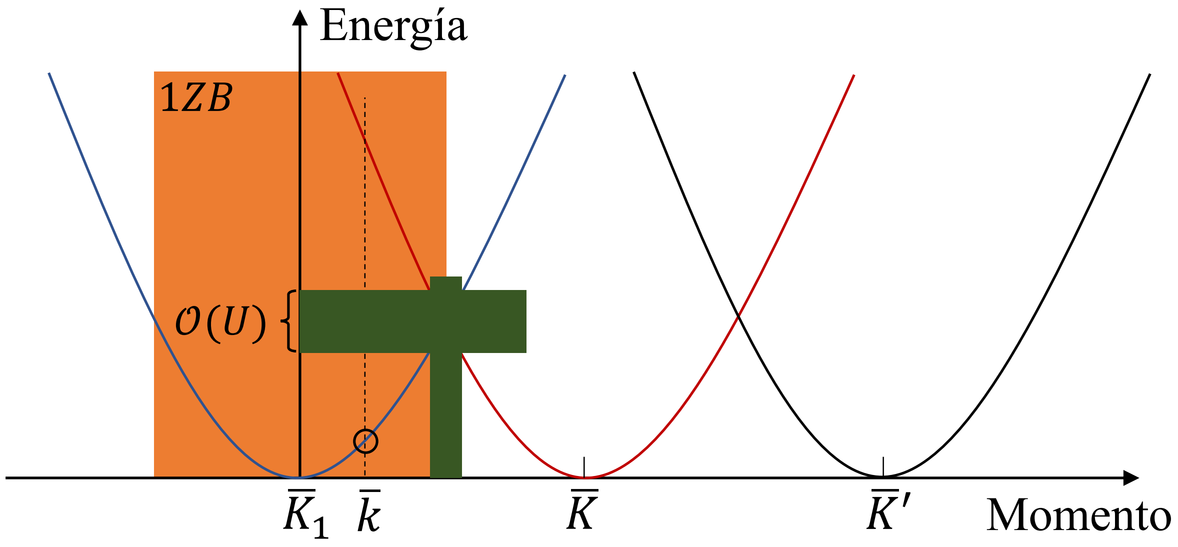
Potencial débil

$$\begin{cases} \psi_{n\bar{k}}(\bar{r}) = \sum_{\bar{K}} c_{\bar{k}-\bar{K}}\, e^{i(\bar{k}-\bar{K})\cdot\bar{r}} \\ \left(\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}\right) c_{\bar{k}-\bar{K}} = \sum_{\bar{K}'} U_{\bar{K}'-\bar{K}}\, c_{\bar{k}-\bar{K}'} \end{cases}$$

Tomamos $\bar{k}$ y $\bar{K}_1$ tal que:

$$\left|\varepsilon^0_{\bar{k}-\bar{K}_1} - \varepsilon^0_{\bar{k}-\bar{K}}\right| \gg U, \forall \bar{K} \neq \bar{K}_1$$

Valor típico de $U_{\bar{K}}$



Queremos ver cómo afecta el potencial al estado de e$^-$ libre dado por: $\varepsilon = \varepsilon^0_{\bar{k}-\bar{K}_1}, c_{\bar{k}-\bar{K}} = 0, \forall \bar{K} \neq \bar{K}_1$

$\underline{\bar{K} = \bar{K}_1}$: $$\left(\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}_1}\right) c_{\bar{k}-\bar{K}_1} = \sum_{\bar{K}} U_{\bar{K}-\bar{K}_1} c_{\bar{k}-\bar{K}} \approx \sum_{\bar{K}} \frac{U_{\bar{K}-\bar{K}_1} U_{\bar{K}_1-\bar{K}}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}} c_{\bar{k}-\bar{K}_1} \rightarrow \boxed{\varepsilon = \varepsilon^0_{\bar{k}-\bar{K}_1} + \sum_{\bar{K}} \frac{\left|U_{\bar{K}-\bar{K}_1}\right|^2}{\varepsilon^0_{\bar{k}-\bar{K}_1} - \varepsilon^0_{\bar{k}-\bar{K}}}}$$

$U_{-\bar{K}} = U_{\bar{K}} = U_{\bar{K}}^*$

$\underline{\bar{K} \neq \bar{K}_1}$: $$c_{\bar{k}-\bar{K}} = \frac{U_{\bar{K}_1-\bar{K}} c_{\bar{k}-\bar{K}_1}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}} + \sum_{\bar{K}' \neq \bar{K}_1} \frac{U_{\bar{K}'-\bar{K}} c_{\bar{k}-\bar{K}'}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}} \approx \frac{U_{\bar{K}_1-\bar{K}} c_{\bar{k}-\bar{K}_1}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}}$$

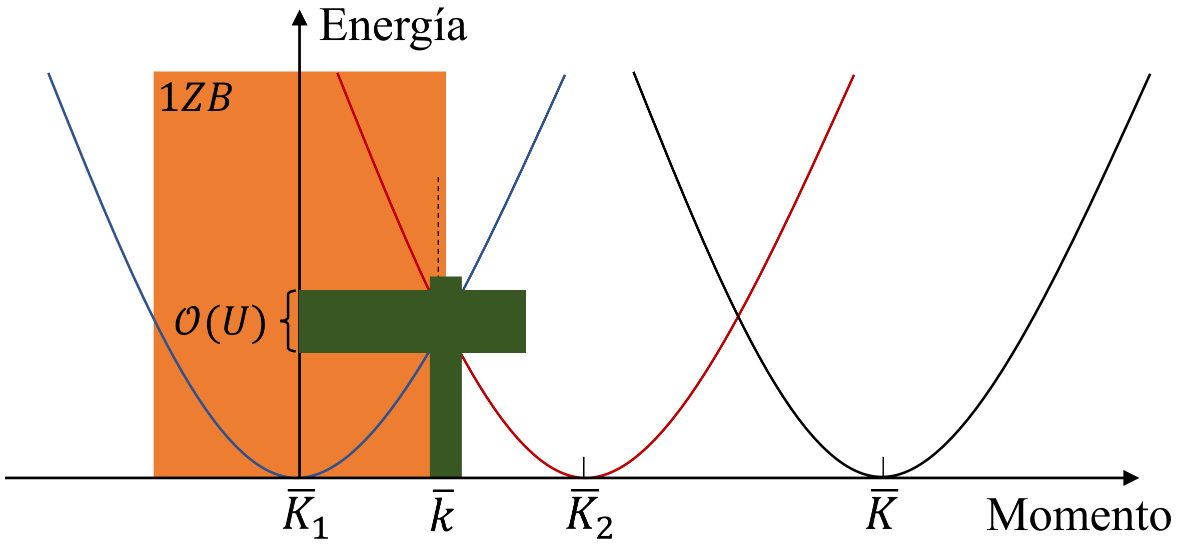
$= 0$ cuando $U = 0$

→ Las bandas se repelen entre sí

Potencial periódico débil

Potencial débil

$$
\begin{cases}
\psi_{n\bar{k}}(\bar{r}) = \displaystyle\sum_{\bar{K}} c_{\bar{k}-\bar{K}}\, e^{i(\bar{k}-\bar{K})\cdot\bar{r}} \\
\left(\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}\right) c_{\bar{k}-\bar{K}} = \displaystyle\sum_{\bar{K}'} U_{\bar{K}'-\bar{K}}\, c_{\bar{k}-\bar{K}'}
\end{cases}
$$



Tomamos $\bar{k}$ y $\bar{K}_1, \dots, \bar{K}_m$ tal que:

$\varepsilon^0_{\bar{k}-\bar{K}_1}, \dots, \varepsilon^0_{\bar{k}-\bar{K}_m}$ se encuentran en $\mathcal{O}(U)$ entre sí

$$\left|\varepsilon^0_{\bar{k}-\bar{K}} - \varepsilon^0_{\bar{k}-\bar{K}_i}\right| \gg U, \;\; i = 1, \dots, m, \;\; \forall \bar{K} \neq \bar{K}_1, \dots, \bar{K}_m$$

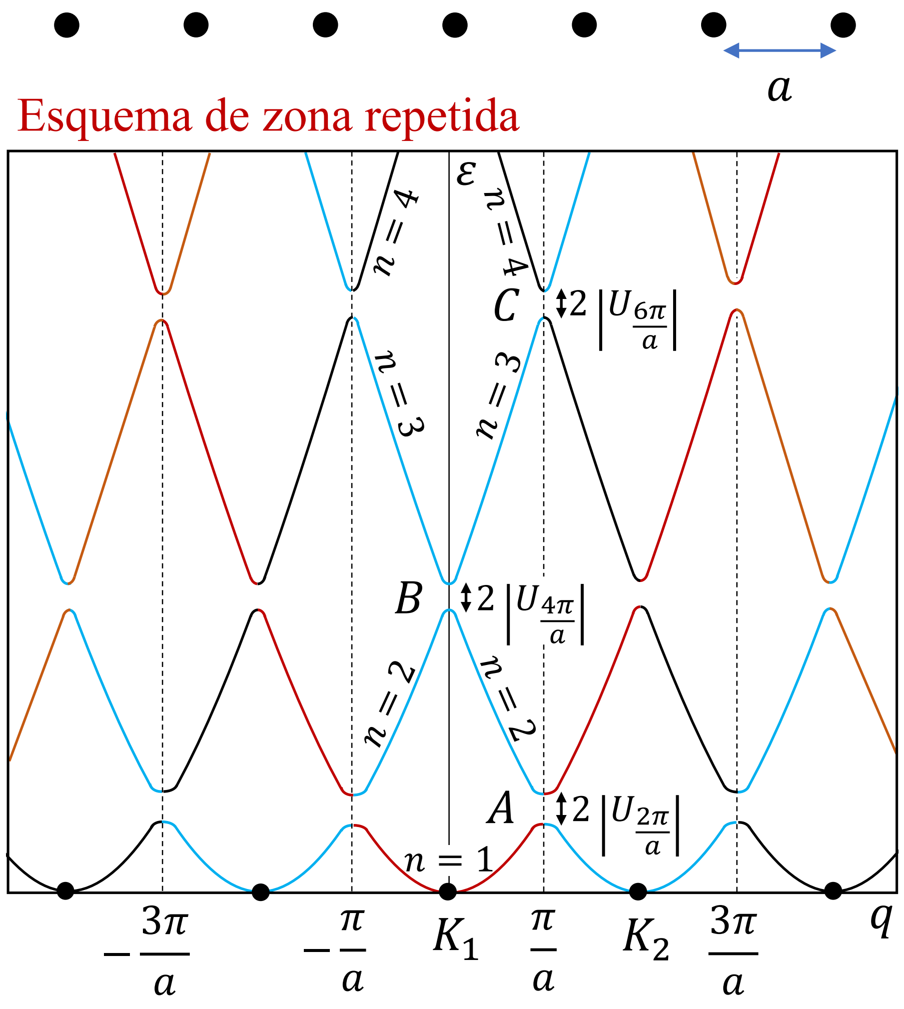
$\underline{\bar{K} = \bar{K}_i}$: $$\left(\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}_i}\right) c_{\bar{k}-\bar{K}_i} = \sum_{j=1}^{m} U_{\bar{K}_j-\bar{K}_i} c_{\bar{k}-\bar{K}_j} + \sum_{\bar{K}\neq\bar{K}_1,\dots,\bar{K}_m} U_{\bar{K}-\bar{K}_i} c_{\bar{k}-\bar{K}} \approx \boxed{\sum_{j=1}^{m} U_{\bar{K}_j-\bar{K}_i} c_{\bar{k}-\bar{K}_j} + \mathcal{O}(\cancel{U}^2)}$$

$\underline{\bar{K} \neq \bar{K}_i}$: $$c_{\bar{k}-\bar{K}} = \sum_{j=1}^{m} \frac{U_{\bar{K}_j-\bar{K}} c_{\bar{k}-\bar{K}_j}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}} + \sum_{\bar{K}'\neq\bar{K}_1,\dots,\bar{K}_m} \frac{U_{\bar{K}'-\bar{K}} \overset{\mathcal{O}(U)}{c_{\bar{k}-\bar{K}'}}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}} \approx \sum_{j=1}^{m} \frac{U_{\bar{K}_j-\bar{K}} c_{\bar{k}-\bar{K}_j}}{\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}}}$$

Para niveles cuasi-degenerados tenemos correcciones de $\mathcal{O}(U)$

Potencial periódico débil

Potencial débil: RB 1D



$$\left(\varepsilon - \varepsilon^0_{\bar{k}-\bar{K}_i}\right) c_{\bar{k}-\bar{K}_i} = \sum_{j=1}^{m} U_{\bar{K}_j-\bar{K}_i} c_{\bar{k}-\bar{K}_j} \quad (m = 2)$$

$$\begin{cases} \left(\varepsilon - \varepsilon^0_{k-K_1}\right) c_{k-K_1} = U_{K_2-K_1} c_{k-K_2} \\ \left(\varepsilon - \varepsilon^0_{k-K_2}\right) c_{k-K_2} = U_{K_1-K_2} c_{k-K_1} \end{cases} \quad \left(K_1 = 0; K_2 = \frac{2\pi}{a}\right)$$

$$\rightarrow \begin{vmatrix} \varepsilon - \varepsilon^0_{k-K_1} & -U_{K_2-K_1} \\ -U_{K_2-K_1} & \varepsilon - \varepsilon^0_{k-K_2} \end{vmatrix} = 0$$

$$\rightarrow \varepsilon^2 - \varepsilon\left(\varepsilon^0_{k-K_1} + \varepsilon^0_{k-K_2}\right) + \varepsilon^0_{k-K_1}\varepsilon^0_{k-K_2} - \left|U_{K_2-K_1}\right|^2 = 0$$

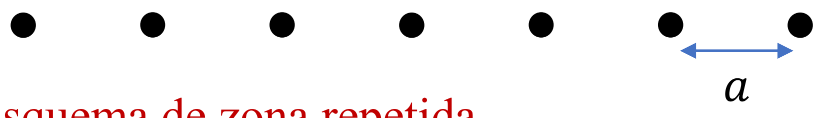
$$\rightarrow \varepsilon = \frac{\varepsilon^0_{k-K_1} + \varepsilon^0_{k-K_2}}{2} \pm \sqrt{\left(\frac{\varepsilon^0_{k-K_1} - \varepsilon^0_{k-K_2}}{2}\right)^2 + \left|U_{K_2-K_1}\right|^2}$$

$$\varepsilon^0_{k-K_1} \overset{k = \pi/a}{=} \varepsilon^0_{k-K_2} \rightarrow \varepsilon = \varepsilon^0_{k-K_1} \pm \left|U_{K_2-K_1}\right|$$

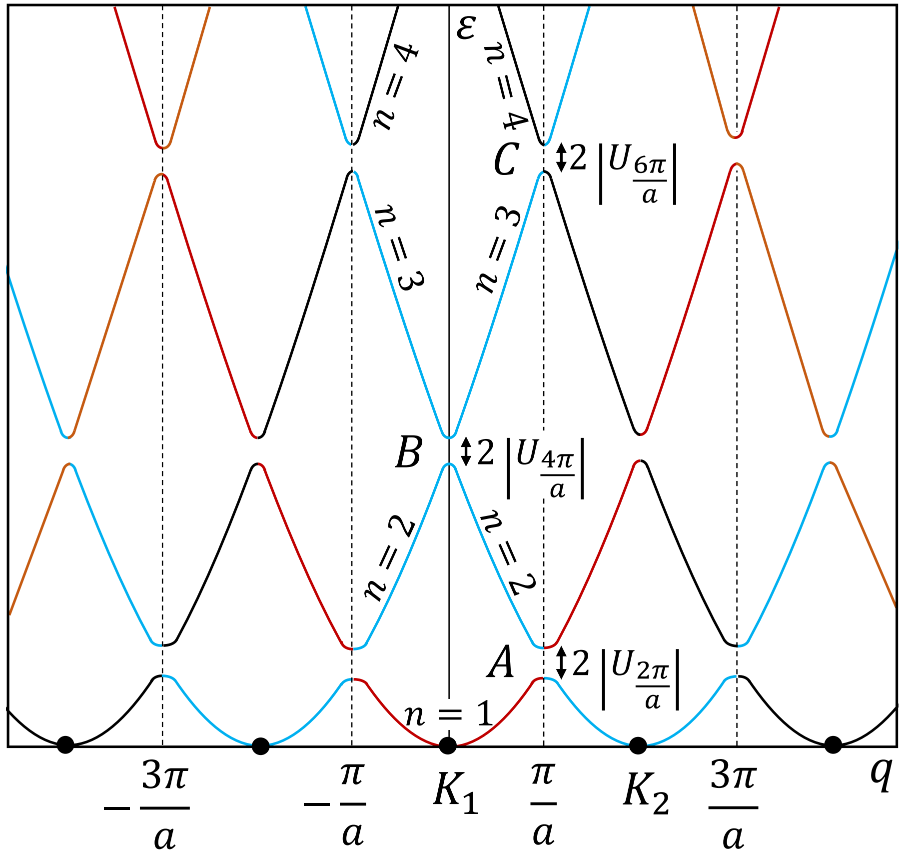
$\boxed{\text{¡Se abre un } \textit{gap}!}$

Potencial periódico débil

<u>Potencial débil</u>: RB 1D



Esquema de zona repetida



$$\left(\varepsilon-\varepsilon^0_{\bar{k}-\bar{K}_i}\right)c_{\bar{k}-\bar{K}_i}=\sum_{j=1}^{m}U_{\bar{K}_j-\bar{K}_i}c_{\bar{k}-\bar{K}_j}\quad (m=2)$$

$$\begin{cases}\left(\varepsilon-\varepsilon^0_{k-K_i}\right)c_{k-K_i}=U_{K_j-K_i}c_{k-K_j}\\ \left(\varepsilon-\varepsilon^0_{k-K_j}\right)c_{k-K_j}=U_{K_i-K_j}c_{k-K_i}\end{cases}$$

$\forall\, i,j$ tal que $\varepsilon^0_{k-K_i}$ y $\varepsilon^0_{k-K_j}$ difieren entre sí en $\mathcal{O}(U)$

$$\varepsilon^0_{k-K_i}=\varepsilon^0_{k-K_j}\rightarrow\varepsilon=\varepsilon^0_{k-K_i}\pm\left|U_{K_j-K_i}\right|$$

<u>Ejemplo</u>

$$U=-2V_0\cos\left(\frac{2\pi x}{a}\right)$$

$$U(\bar{r})=\sum_{\bar{K}}U_{\bar{K}}\,e^{i\bar{K}\cdot\bar{r}}\rightarrow U_{\frac{2\pi}{a}}=U_{-\frac{2\pi}{a}}=-V_0$$

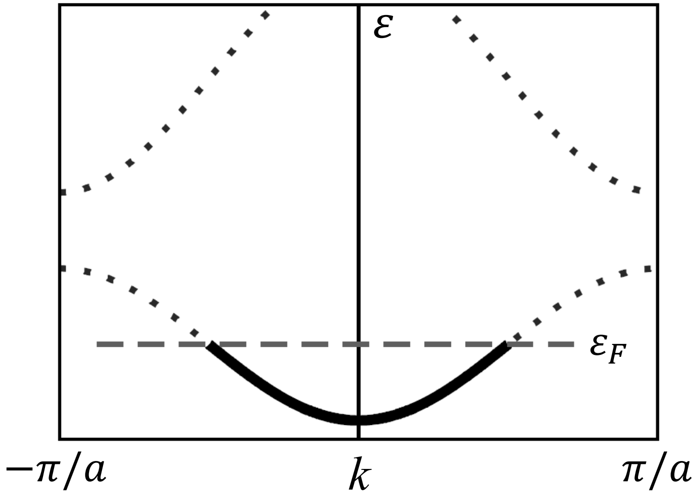
¿Se abren *gaps* en *A*,*B*,*C*? $\rightarrow$ ¡Sí, pero solo en *A*!

Comportamiento eléctrico

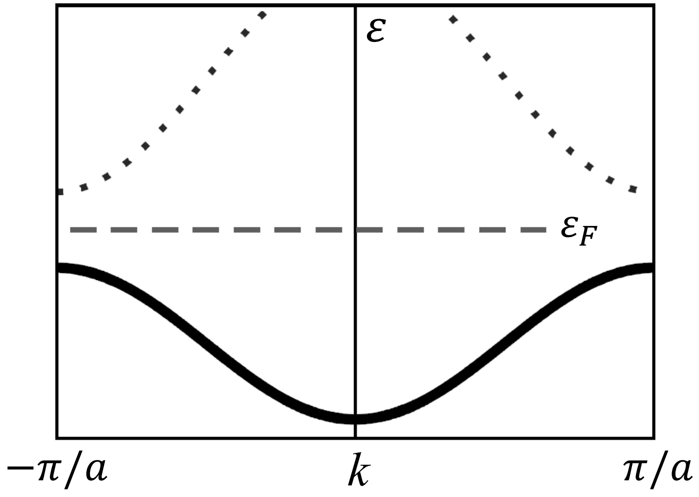
<u>¿Metal o aislante?</u>

En cada banda podemos acomodar $2N$ e^- (N: N° de CP en el cristal).

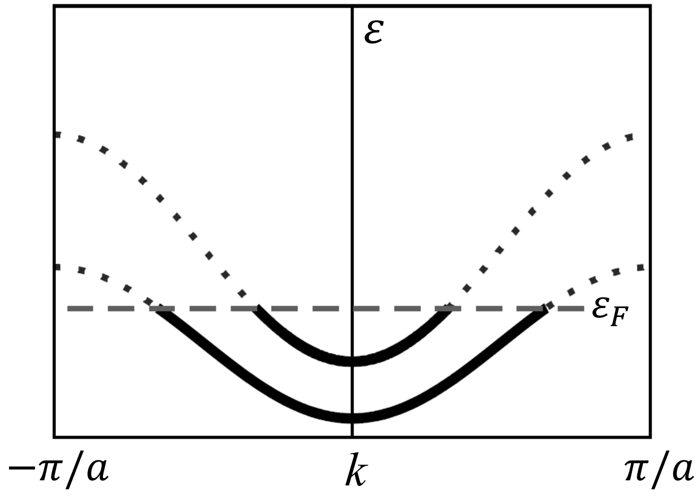
Cada CP aporta 1e^-: N e^-
Banda semi-llena → Metal



Cada CP aporta 2e^-: Banda llena
¿Hay *gap*? → Sí → Aislante



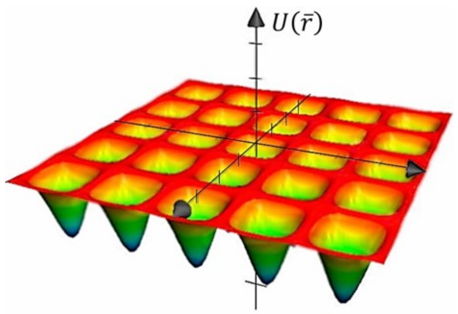
Cada CP aporta 2e^-, pero las bandas se solapan → Metal



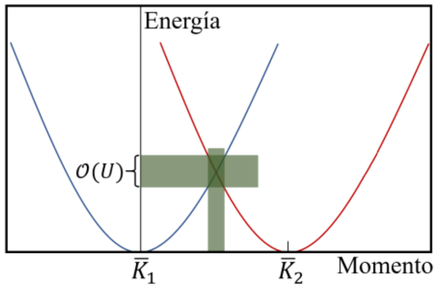
Si cada CP aporta un N° impar de e^- → Metal
Si cada CP aporta un N° par de e^- → Metal o aislante
Si el material es aislante → Cada CP aporta un N° par de e^-

Resumen

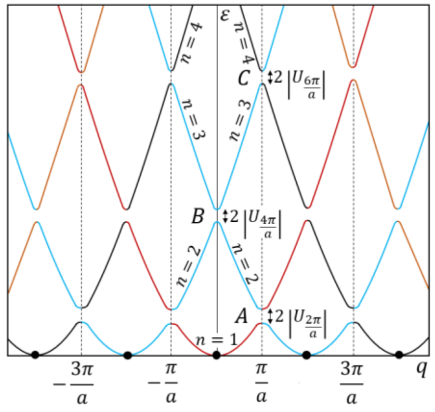
- Potencial periódico y teorema de Bloch



- Potencial periódico débil



- Estructura de bandas de RB 1D



- Comportamiento eléctrico