GUÍA 4: Métodos de cálculo de estructura electrónica (Enlaces Fuertes)

HOJA

FECHA

1.

$\psi_{nk}(\vec{r})$: Función de Block (son ortonormales)

Función de Wannier $\rightarrow$ $\phi_n(\vec{r}-\vec{R}) = \frac{1}{\sqrt{N}} \sum_k \psi_{nk}(\vec{r}) \cdot e^{-i\vec{k}\cdot\vec{R}}$

$$\phi_n^*(\vec{r}-\vec{R}) \cdot \phi_m(\vec{r}-\vec{R}) = \frac{1}{\sqrt{N}} \frac{1}{\sqrt{N}} \sum_k \psi_{nk}^*(\vec{r}) e^{+i\vec{k}\cdot\vec{R}} \sum_l \psi_{ml}(\vec{r}) e^{-i\vec{l}\cdot\vec{R}}$$

$$= \frac{1}{N} \sum_k \sum_l \psi_{nk}^*(\vec{r}) \psi_{ml}(\vec{r}) e^{-i(\vec{l}-\vec{k})\cdot\vec{R}}$$

$$= \frac{1}{N} \sum_k \sum_l \delta_{nm} \delta_{kl} e^{-i(\vec{l}-\vec{k})\cdot\vec{R}}$$

$$= 0 \quad \text{si } k \neq l$$

$$= \frac{1}{N} \sum_k^N \delta_{nm} = 1 \quad \text{si } \begin{matrix} m=n \\ k=l \end{matrix}$$

NOTA

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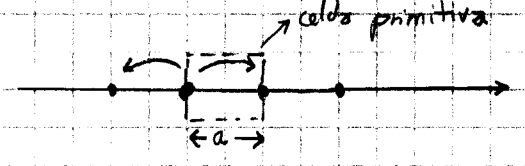
2.



1 tipo átomo A en 1 estado determinado

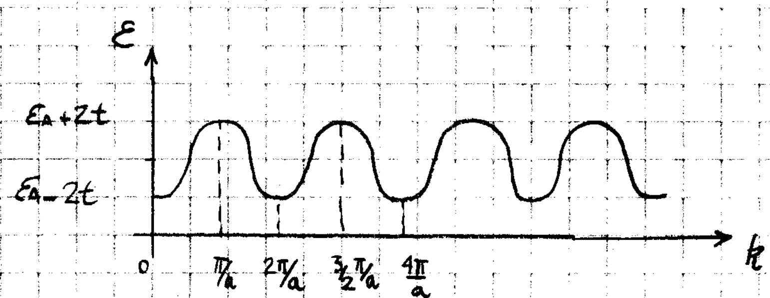
$$(\varepsilon_A - \varepsilon)\, b_A - \beta_{AA}\, b_A - \left(\gamma_{AA}\, e^{ika} + \gamma_{AA}\, e^{-ika}\right) b_A = 0$$

$$\varepsilon_A - \varepsilon - 2t\cos(ka) = 0$$

$$\boxed{\varepsilon = \varepsilon_A - 2\cos(ka)\, t}$$

Relación de dispersión

1)



ii)

$$\frac{d\varepsilon}{dk} = 2t\,\mathrm{sen}(ka)\, a \quad\rightarrow\quad g(k) = \frac{\cancel{2}/\pi}{\cancel{2}ta\,\mathrm{sen}(ka)}$$

$$\left(\frac{\varepsilon - \varepsilon_A}{2t}\right)^2 = \cos^2(ka) \Rightarrow$$

$n = \frac{2k}{\pi}$ densidad de electrones (1D)

$N_q = \frac{2ka}{\pi}$ electrones por sitio

$$\mathrm{sen} = \sqrt{1 - \cos^2}$$

$$1 = \frac{2ka}{\pi} \rightarrow k = \frac{\pi}{2a}$$

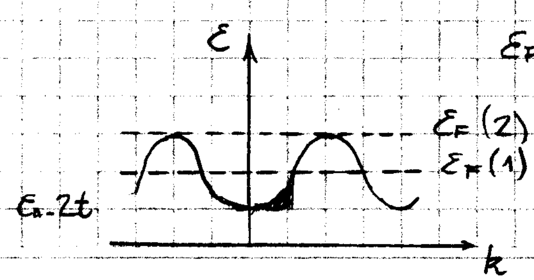
$$\boxed{g(\varepsilon) = \frac{1}{\pi t a \sqrt{1 - \frac{(\varepsilon - \varepsilon_A)^2}{4t^2}}}}$$

iii)

$$n = \frac{2k}{\pi} \rightarrow \frac{N_q}{a} = \frac{2k}{\pi} \rightarrow k = \frac{\pi N_q}{2a} \rightarrow$$

$$N_q = 2 \rightarrow k = \frac{\pi}{a}$$

$$\varepsilon_F = \varepsilon_A - 2\cos(\pi)\, t = \boxed{\varepsilon_A + 2t = \varepsilon_F\,(N_q = 2)}$$

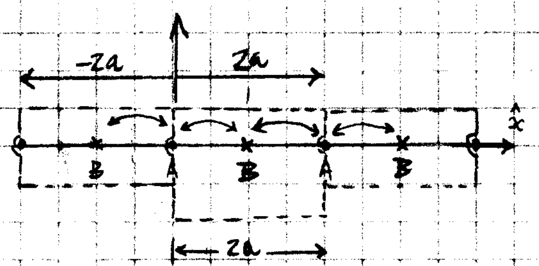


con $N_q = 1 \rightarrow$

$$\varepsilon_F(1) = \varepsilon_A - 2\cos\left(\frac{\pi}{2}\right) t$$

NOTA

3.



términos diagonales ε
términos no diagonales entre 1eros vecinos t

Átomo A

donde está la celda primitiva → esto lo ~~determina el~~ vector $\vec{R}$ de la celda cuyo átomo B estoy teniendo en cuenta para la interacción

$$(\varepsilon_A^0-\varepsilon)b_A - \overset{=0}{\beta_{AA}}.b_A - \beta_{AB}.b_B - \left[\gamma_{AB}(-2a)e^{-ik(-2a)}\right]b_B = 0$$

$$(\varepsilon_A^0-\varepsilon)b_A - \beta_{AB}.b_B - \gamma_{AB}(-2a)e^{ik2a}.b_B = 0$$

Átomo B

$$(\varepsilon_B^0-\varepsilon)b_B - \overset{=0}{\beta_{BB}}.b_B - \beta_{BA}.b_A - \gamma_{BA}(2a)e^{-ik(2a)}b_A = 0$$

$$(\varepsilon_B^0-\varepsilon)b_B - \beta_{BA}.b_A - \gamma_{BA}^{(a)}e^{-ika}b_A = 0$$

$$(\varepsilon_A^0-\varepsilon)b_A - t\,b_B - t.e^{ik2a}b_B = 0$$

$$(\varepsilon_B^0-\varepsilon)b_B - t.b_A - t.e^{-ik2a}b_A = 0$$

$$\begin{bmatrix} (\varepsilon_A^0-\varepsilon) & -t(1+e^{ika2}) \\ -t(1+e^{-ika2}) & (\varepsilon_B^0-\varepsilon) \end{bmatrix}\begin{pmatrix} b_A \\ b_B \end{pmatrix} = \vec{0}$$

Pidiendo determinante nulo →

$$(\varepsilon_A^0-\varepsilon)(\varepsilon_B^0-\varepsilon) - t^2(1+e^{ika2})(1+e^{-ika2}) = 0$$

$$\varepsilon_A^0\varepsilon_B^0 - \varepsilon\varepsilon_B^0 + \varepsilon^2 - \varepsilon_A^0\varepsilon - t^2\left[1+e^{ika2}+e^{-ika2}+1\right] = 0$$

$c^2+s^2=1$

$\cos(2ka) = \cos^2(ka) - \operatorname{sen}^2(ka)$

$\cos(2ka) = 2\cos^2(ka) - 1$

$$\varepsilon^2 - \varepsilon(\varepsilon_B^0+\varepsilon_A^0) + \varepsilon_A^0\varepsilon_B^0 - t^2 2(1+\cos(2ka)) = 0$$

$$\varepsilon = \frac{(\varepsilon_B^0+\varepsilon_A^0) \pm \sqrt{(\varepsilon_B^0+\varepsilon_A^0)^2 - 4(\varepsilon_A^0\varepsilon_B^0 - 2t^2(2\cos^2 ka))}}{2}$$

$$\varepsilon = \frac{\sqrt{\varepsilon_B^{0\,2}+\varepsilon_A^{0\,2} - 2\varepsilon_A^0\varepsilon_B^0 + 16t^2[\cos^2 ka]}}{2}$$

$$\boxed{\varepsilon = \frac{(\varepsilon_B^0+\varepsilon_A^0) \pm (\varepsilon_B^0-\varepsilon_A^0)\sqrt{1+\frac{[4t\cos(ka)]^2}{(\varepsilon_B^0-\varepsilon_A^0)^2}}}{2}}$$

i) Tenemos $\varepsilon = \varepsilon(k)$ ⇒ hay que dibujar esto con soft

$$2\varepsilon - (\varepsilon_B+\varepsilon_A) = \left([\varepsilon_B-\varepsilon_A]^2 + 16t^2\cos^2 ka\right)^{1/2}$$

$$\frac{[2\varepsilon-(\varepsilon_B+\varepsilon_A)]^2 - [\varepsilon_B-\varepsilon_A]^2}{16t^2} = \cos^2(ka)$$

ii) $$g(\varepsilon) = \frac{dn}{d\varepsilon} = \frac{dn}{dk}\cdot\frac{dk}{d\varepsilon} = \frac{dn}{dk}\cdot\frac{1}{\left(\frac{d\varepsilon}{dk}\right)}$$

$$\frac{d\varepsilon}{dk} = \frac{1}{\cancel{4}}\,\frac{1}{\left(1+\frac{16t^2\cos^2 ka}{(\varepsilon_B-\varepsilon_A)^2}\right)^{1/2}}\cdot\frac{\cancel{16}^{4}t^2\,2\cos(ka)\,\mathrm{sen}(ka)\,a}{(\varepsilon_B-\varepsilon_A)^2}$$

En electrón libre (1D) es:

$$n = \sqrt{2m\varepsilon}\,\frac{2}{\hbar\pi} \rightarrow n = \frac{\cancel{\hbar}k\,2}{\cancel{\hbar}\pi} \rightarrow \frac{dn}{dk} = \frac{2}{\pi}$$

$$\frac{d\varepsilon}{dk} = \frac{8a\,t^2\cos(ka)\,\mathrm{sen}(ka)}{\sqrt{(\varepsilon_B-\varepsilon_A)^2+(16t^2\cos^2 ka)}\,(\varepsilon_B-\varepsilon_A)}$$

$$2\varepsilon - (\varepsilon_B+\varepsilon_A) = \left[(\varepsilon_B-\varepsilon_A)^2 + 16t^2\cos^2 ka\right]^{1/2}$$

$$\cos\alpha\cdot\mathrm{sen}\,\alpha = \frac{1}{2}\mathrm{sen}(2\alpha)$$

$$\frac{[2\varepsilon-(\varepsilon_B+\varepsilon_A)]^2-(\varepsilon_B-\varepsilon_A)^2}{16t^2} = \cos^2(ka) = 1-\mathrm{sen}^2(ka)$$

$$\cos^2\alpha\,\mathrm{sen}^2\alpha = \frac{1}{4}\left(1-\cos^2(2\alpha)\right)$$

$$\cos\alpha\cdot\mathrm{sen}\,\alpha = \frac{\sqrt{1-\cos^2(2\alpha)}}{2}$$

$$\frac{4\varepsilon^2 - 4\varepsilon(\varepsilon_B+\varepsilon_A) + \overbrace{(\varepsilon_B+\varepsilon_A)^2-(\varepsilon_B-\varepsilon_A)^2}^{4\varepsilon_A\varepsilon_B}}{16t^2} = \cos^2(ka)$$

$$\frac{d\varepsilon}{dk} = \frac{\cancel{8}^{2}\cancel{a}\cancel{t^2}\sqrt{[2\varepsilon-(\varepsilon_B+\varepsilon_A)]^2-(\varepsilon_B-\varepsilon_A)^2}\cdot\sqrt{16t^2-[2\varepsilon-(\varepsilon_B+\varepsilon_A)]^2+(\varepsilon_B-\varepsilon_A)^2}}{[2\varepsilon-(\varepsilon_B+\varepsilon_A)](\varepsilon_B-\varepsilon_A)\,\cancel{4t}_{2}\,\cancel{4t}_{1}}$$

$$\sqrt{\mathbb{C}_1-\mathbb{C}_2}\cdot\sqrt{16t^2-\mathbb{C}_1+\mathbb{C}_2} = 16t^2(\mathbb{C}_1-\mathbb{C}_2)-\mathbb{C}_1^2+\mathbb{C}_1\mathbb{C}_2+\mathbb{C}_2\mathbb{C}_1-\mathbb{C}_2^2$$
$$= \left[16t^2(\mathbb{C}_1-\mathbb{C}_2)-(\mathbb{C}_1-\mathbb{C}_2)^2\right]^{1/2}$$

$$\frac{d\varepsilon}{dk} = \frac{a\left[16t^2(\mathbb{C}_1-\mathbb{C}_2)-(\mathbb{C}_1-\mathbb{C}_2)^2\right]^{1/2}}{2\sqrt{\mathbb{C}_1}\sqrt{\mathbb{C}_2}}$$

$$\mathbb{C}_1 \equiv [2\varepsilon-(\varepsilon_B+\varepsilon_A)]^2$$

$$\boxed{g(\varepsilon) = \frac{a}{\pi}\sqrt{\frac{[16t^2(\mathbb{C}_1-\mathbb{C}_2)-(\mathbb{C}_1-\mathbb{C}_2)^2]}{(\mathbb{C}_1\cdot\mathbb{C}_2)}}}$$

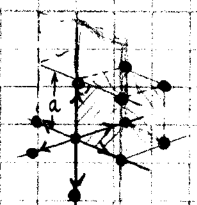
$$\mathbb{C}_2 \equiv [\varepsilon_B-\varepsilon_A]^2$$

iii) $$k_F = \frac{\pi}{2}\frac{N_q}{a} \rightarrow k_F(1) = \frac{\pi}{2a} \rightarrow \cos\left(\frac{\pi a}{2a}\right) = 0 \rightarrow \varepsilon_F = \frac{(\varepsilon_B+\varepsilon_A)\pm(\varepsilon_B-\varepsilon_A)}{2}$$

$$\boxed{\varepsilon_F = \begin{cases}\varepsilon_B\\ \varepsilon_A\end{cases}}$$

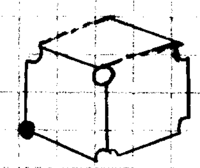
4. Sc parámetro a

1 sitio ≡ 1 orbital tipo s con ε



t ≡ interacción a 1eros vecinos

No tiene 1eros vecinos en la celda primitiva



$(\varepsilon - \varepsilon_n)$

$R_1 = (a,0,0)$
$R_2 = (-a,0,0)$
$R_3 = (0,a,0)$
$R_4 = (0,-a,0)$
$R_5 = (0,0,a)$
$R_6 = (0,0,-a)$

Átomo A en todas las celdas prim.

$$(\varepsilon_A^0 - \varepsilon) b_A - \left(\gamma_{A1} e^{ik_x a} + \gamma_{A2} e^{-ik_x a} + \gamma_{A3} e^{ik_y a} + \gamma_{A4} e^{-ik_y a} + \gamma_{A5} e^{ik_z a} + \gamma_{A6} e^{-ik_z a}\right) b_A$$

$$(\varepsilon_A^0 - \varepsilon) b_A - t2\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right] b_A = 0$$

$$\boxed{\varepsilon = \varepsilon_A^0 - 2t\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right]}$$

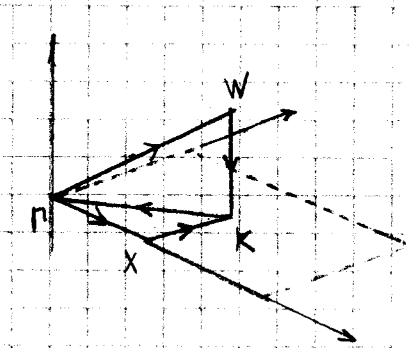
Esto serán las bandas de energía en 3D

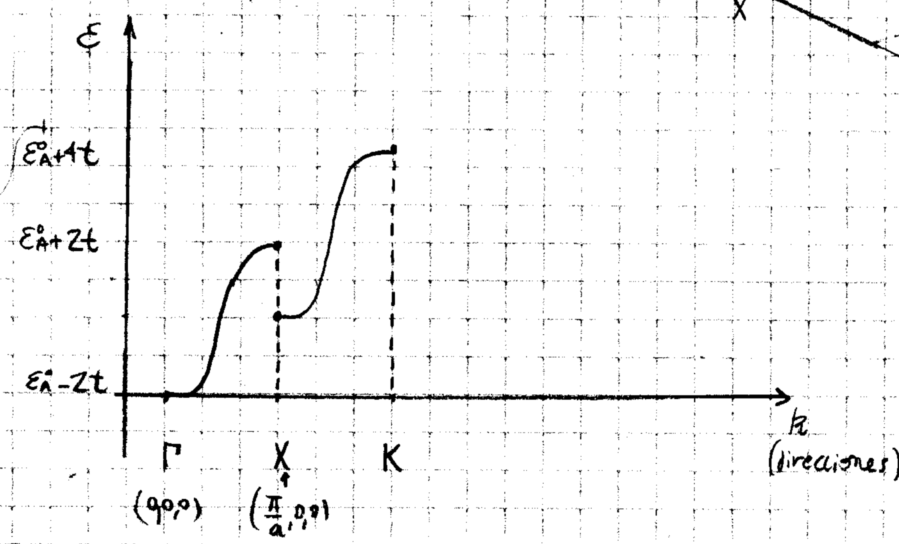
$\Gamma = (0,0,0)$

$k = \pi/a$

$\Gamma \to X \quad \varepsilon = \varepsilon_A^0 - 2t \cos(k_x a)$

$X \to K \quad \varepsilon = \varepsilon_A^0 - 2t \cos(k_y a) + 2t.$





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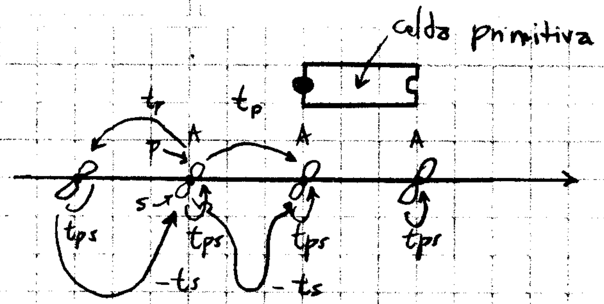

2 orbitales $\begin{cases} s \to \varepsilon_s \\ p \to \varepsilon_p \end{cases}$

t_{ps} mismo sitio
$-t_s$ (s de 1eros vecinos)
t_p (p de 1eros vecinos)

1 tipo de átomo

As

$$(\varepsilon_s^\circ - \varepsilon) b_s - \beta_{sp} \cdot b_p - \left(\gamma_{ss}(a)\, e^{ika} + \gamma_{ss}(-a) \cdot e^{-ika}\right) b_s = 0$$

$$(\varepsilon_p^\circ - \varepsilon) b_p - \beta_{ps} \cdot b_s - \left(\gamma_{pp}(a)\, e^{ika} + \gamma_{pp}(-a)\, e^{-ika}\right) b_p = 0$$

$$(\varepsilon_s^\circ - \varepsilon) b_s - t_{ps} \cdot b_p + \left(t_s \cdot e^{ika} + t_s\, e^{-ika}\right) b_s = 0$$

$$(\varepsilon_p^\circ - \varepsilon) b_p - t_{ps} \cdot b_s - \left(t_p \cdot e^{ika} + t_p\, e^{-ika}\right) b_p = 0$$

$$(\varepsilon_s^\circ - \varepsilon) b_s - t_{ps} \cdot b_p + 2 t_s \cdot \cos(ka) \cdot b_s = 0$$

$$(\varepsilon_p^\circ - \varepsilon) b_p - t_{ps} \cdot b_s - 2 t_p \cdot \cos(ka) \cdot b_p = 0$$

$$\begin{vmatrix} (\varepsilon_s^\circ - \varepsilon) + 2 t_s \cos(ka) & -t_{ps} \\ -t_{ps} & (\varepsilon_p^\circ - \varepsilon) - 2 t_p \cos(ka) \end{vmatrix} = 0$$

ii) Si $t_s = t_p = 0 \rightarrow \quad (\varepsilon_s^\circ - \varepsilon)(\varepsilon_p^\circ - \varepsilon) - t_{ps}^2 = 0$

$$\varepsilon^2 - \varepsilon(\varepsilon_p^\circ + \varepsilon_s^\circ) + \varepsilon_s^\circ \varepsilon_p^\circ - t_{ps}^2 = 0$$

$$\varepsilon = \frac{\varepsilon_p^\circ + \varepsilon_s^\circ \pm \sqrt{(\varepsilon_p^\circ + \varepsilon_s^\circ)^2 - 4 \cdot (\varepsilon_s^\circ \varepsilon_p^\circ - t_{ps}^2)}}{2}$$

$\boxed{\text{La relación de dispersión es independiente de } k}$

¿La densidad de estados es 0?

NOTA