

Física de Semiconductores

Lección 6

On site integrals I

- Supondremos que

$$\langle a', \mathbf{0} | H | a, \mathbf{0} \rangle = \int d\mathbf{r} \phi_{a', \mathbf{0}}^*(\mathbf{r}) H \phi_{a, \mathbf{0}}(\mathbf{r}) = \varepsilon_a \delta_{aa'}$$

- Esto no es necesariamente cierto, porque H no es el hamiltoniano atómico.
- Esto lo absorberemos parcialmente en la definición de ε_a , pero no podemos garantizar la ortogonalidad, ni que se mantengan las degeneraciones atómicas. (Relevante para los niveles p)
- Podemos suponer que el hamiltoniano real es la suma de el hamiltoniano atómico (para el cual la expresión es correcta) más una corrección de primeros vecinos, más una corrección más pequeña de segundos vecinos, etc.
- A cada nivel, la teoría de grupos nos permitirá encontrar el número de integrales distintas de cero que podemos esperar.

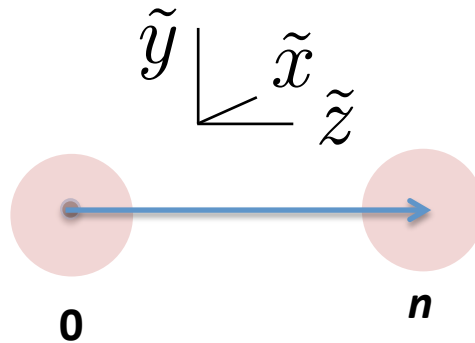
Matrix elements in bond coordinates

- El paso siguiente es calcular elementos de matriz de la forma

$$\langle a', \mathbf{0} | H | a, \mathbf{n} \rangle = \int d\mathbf{r} \phi_{a',0}^*(\mathbf{r}) H \phi_{aj,\mathbf{n}}(\mathbf{r})$$

- entre un átomo ubicado en el origen y otro ubicado en la punta del vector \mathbf{n} . Para ello utilizamos un systemas de coordenadas cartesianos elegido de modo que el eje positivo \tilde{z} coincide con el vector \mathbf{n} .

Elemento de matriz s-s


$$\langle s, 0 | H | s, \mathbf{n} \rangle = V_{ss\sigma}$$

Esperamos que este elemento de matriz sea negativo, porque el hamiltoniano aplicado al estado s, n dará aproximadamente la energía ϵ_s (negativa) multiplicada por el mismo estado, y la integral de solapamiento entre dos estados s es positiva.

Elemento de matriz s-p matrix

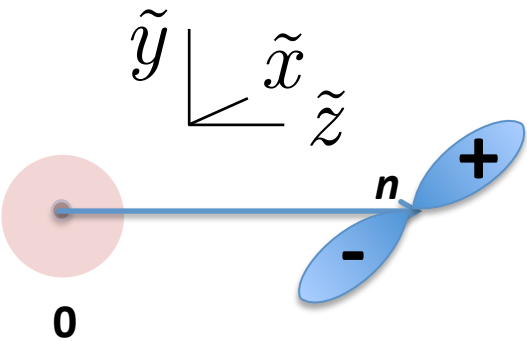


Diagram showing the overlap of an s orbital (red sphere, labeled 0) and a p _{\tilde{x}} orbital (blue dumbbell, labeled n). The coordinate system has axes \tilde{y} , \tilde{x} , and \tilde{z} . The p orbital is oriented along the \tilde{x} axis. The s orbital is centered at the origin, and the p orbital is centered at a distance n along the \tilde{x} axis. The p orbital has a positive lobe on the right and a negative lobe on the left.

$$\langle s, 0 | H | p_{\tilde{x}}, n \rangle = 0$$

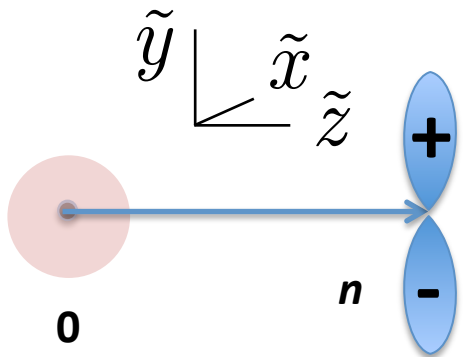


Diagram showing the overlap of an s orbital (red sphere, labeled 0) and a p _{\tilde{y}} orbital (blue dumbbell, labeled n). The coordinate system has axes \tilde{y} , \tilde{x} , and \tilde{z} . The p orbital is oriented along the \tilde{y} axis. The s orbital is centered at the origin, and the p orbital is centered at a distance n along the \tilde{y} axis. The p orbital has a positive lobe on top and a negative lobe on the bottom.

$$\langle s, 0 | H | p_{\tilde{y}}, n \rangle = 0$$

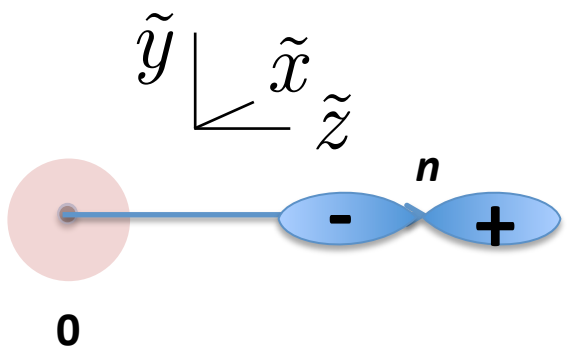
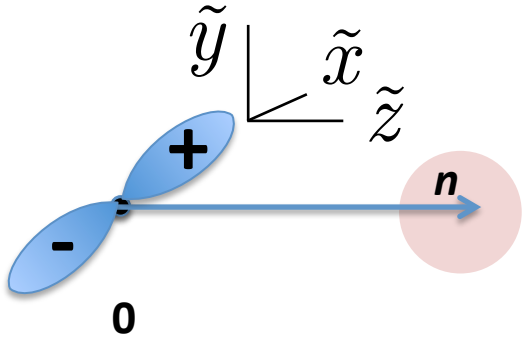


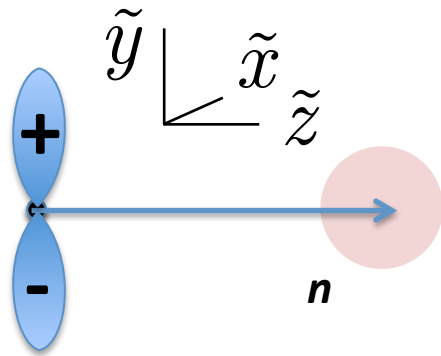
Diagram showing the overlap of an s orbital (red sphere, labeled 0) and a p _{\tilde{z}} orbital (blue dumbbell, labeled n). The coordinate system has axes \tilde{y} , \tilde{x} , and \tilde{z} . The p orbital is oriented along the \tilde{z} axis. The s orbital is centered at the origin, and the p orbital is centered at a distance n along the \tilde{z} axis. The p orbital has a positive lobe on the right and a negative lobe on the left.

$$\langle s, 0 | H | p_{\tilde{z}}, n \rangle = V_{sp\sigma}$$

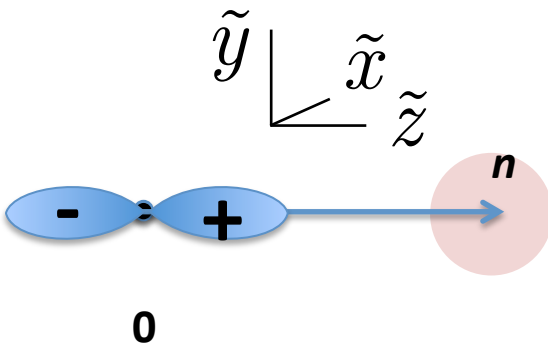
Elemento de matriz p-s



$$\langle p_{\tilde{x}}, 0 | H | s, \mathbf{n} \rangle = 0$$

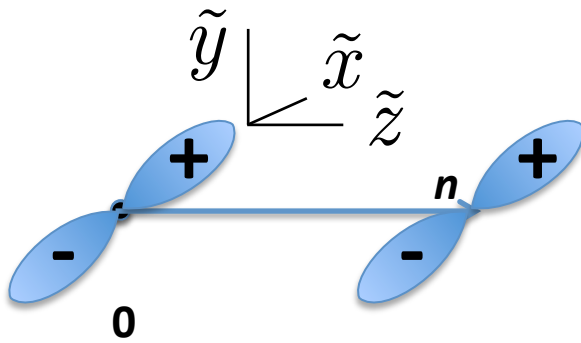


$$\langle p_{\tilde{y}}, 0 | H | s, \mathbf{n} \rangle = 0$$

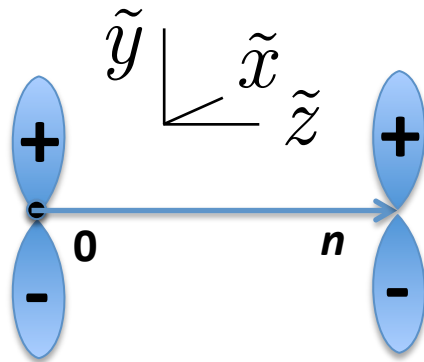


$$\langle s, 0 | H | p_{\tilde{z}}, \mathbf{n} \rangle = -V_{sp\sigma}$$

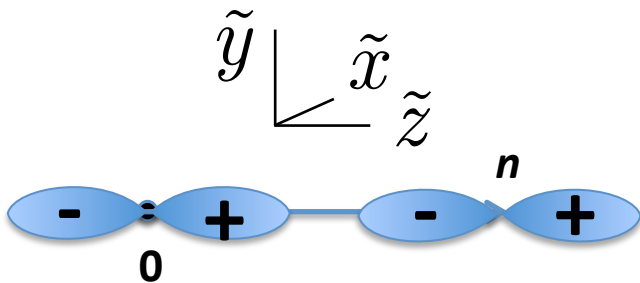
Elementos de matriz p-p distintos de zero



$$\langle p_{\tilde{x}}, 0 | H | p_{\tilde{x}}, n \rangle = V_{pp\pi}$$



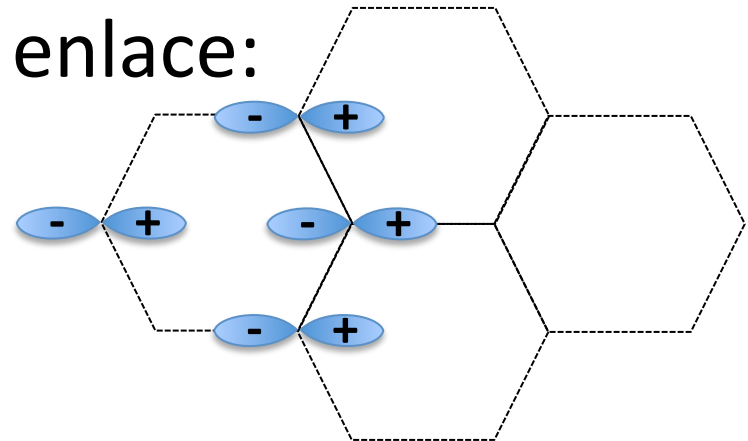
$$\langle p_{\tilde{y}}, 0 | H | p_{\tilde{y}}, n \rangle = V_{pp\pi}$$



$$\langle p_{\tilde{z}}, 0 | H | p_{\tilde{z}}, n \rangle = V_{pp\sigma}$$

Problema con estados p

- Las funciones p que seleccionamos para formar sumas de Bloch deben ser idénticas en cada punto de la red, por lo que deberán estar orientadas en la misma dirección, por ejemplo en la dirección de los ejes cristalinos. De modo que necesitaremos elementos de matriz entre estados de la siguiente forma, no ortogonales al sistema cartesiano del enlace:



Orbitales rotados

- Necesitamos entonces funciones p (p_x, p_y, p_z) orientadas a lo largo de los ejes cristalinos. Podemos entonces escribir

$$p_x = \hat{l}_x p_{\tilde{x}} + \hat{m}_x p_{\tilde{y}} + \hat{n}_x p_{\tilde{z}}$$

$$p_y = \hat{l}_y p_{\tilde{x}} + \hat{m}_y p_{\tilde{y}} + \hat{n}_y p_{\tilde{z}}$$

$$p_z = \hat{l}_z p_{\tilde{x}} + \hat{m}_z p_{\tilde{y}} + \hat{n}_z p_{\tilde{z}}$$

- Donde $\hat{n} = \mathbf{n}/|\mathbf{n}|$ un vector unidad en la dirección \tilde{z} , \hat{l} un vector unidad en la dirección \tilde{x} y \hat{m} es otro vector unidad a lo largo de eje \tilde{y} .

Elementos de matriz s-p en coordenadas del cristal.

- Expandiendo los orbitales como indicamos en la expresión anterior,

$$\begin{aligned}\langle s, 0 | H | p_x, \mathbf{n} \rangle &= \langle s, 0 | H | p_{\tilde{x}}, \mathbf{n} \rangle \hat{l}_x \\ &\quad + \langle s, 0 | H | p_{\tilde{y}}, \mathbf{n} \rangle \hat{m}_x + \langle s, 0 | H | p_{\tilde{z}}, \mathbf{n} \rangle \hat{n}_x \\ &= V_{sp\sigma} \hat{n}_x\end{aligned}$$

$$\langle s, 0 | H | p_y, \mathbf{n} \rangle = V_{sp\sigma} \hat{n}_y$$

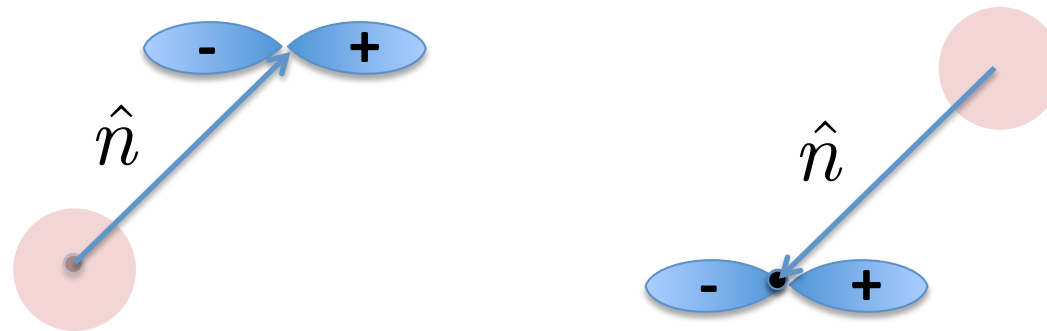
$$\langle s, 0 | H | p_z, \mathbf{n} \rangle = V_{sp\sigma} \hat{n}_z$$

Elementos de matriz p-p en coordenadas cristalinas

$$\begin{aligned}
 \langle p_x, 0 | H | p_x, \mathbf{n} \rangle &= (\hat{l}_x^2 + \hat{m}_x^2) V_{pp\pi} + \hat{n}_x^2 V_{pp\sigma} = (1 - \hat{n}_x^2) V_{pp\pi} + \hat{n}_x^2 V_{pp\sigma} \\
 \langle p_y, 0 | H | p_y, \mathbf{n} \rangle &= (\hat{l}_y^2 + \hat{m}_y^2) V_{pp\pi} + \hat{n}_y^2 V_{pp\sigma} = (1 - \hat{n}_y^2) V_{pp\pi} + \hat{n}_y^2 V_{pp\sigma} \\
 \langle p_z, 0 | H | p_z, \mathbf{n} \rangle &= (\hat{l}_z^2 + \hat{m}_z^2) V_{pp\pi} + \hat{n}_z^2 V_{pp\sigma} = (1 - \hat{n}_z^2) V_{pp\pi} + \hat{n}_z^2 V_{pp\sigma} \\
 \langle p_x, 0 | H | p_y, \mathbf{n} \rangle &= (\hat{l}_x \hat{l}_y + \hat{m}_x \hat{m}_y) V_{pp\pi} + \hat{n}_x \hat{n}_y V_{pp\sigma} = \hat{n}_x \hat{n}_y (V_{pp\sigma} - V_{pp\pi}) \\
 \langle p_x, 0 | H | p_z, \mathbf{n} \rangle &= (\hat{l}_x \hat{l}_z + \hat{m}_x \hat{m}_z) V_{pp\pi} + \hat{n}_x \hat{n}_z V_{pp\sigma} = \hat{n}_x \hat{n}_z (V_{pp\sigma} - V_{pp\pi}) \\
 \langle p_y, 0 | H | p_z, \mathbf{n} \rangle &= (\hat{l}_y \hat{l}_z + \hat{m}_y \hat{m}_z) V_{pp\pi} + \hat{n}_y \hat{n}_z V_{pp\sigma} = \hat{n}_y \hat{n}_z (V_{pp\sigma} - V_{pp\pi})
 \end{aligned}$$

Cambio de signo

- Las expresiones que derivamos indican que algunos de los elementos de matriz cambian de signo dependiendo de la orientación del vector que une los átomos. Esto tiene sentido:



Hamiltoniano de vecinos más cercanos

$$\begin{aligned}
 H_{a'j',aj}(\mathbf{k}) &= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{d}_j - \mathbf{d}_{j'})} \int d\mathbf{r} \phi_{a'j',0}^*(\mathbf{r}) H \phi_{aj,\mathbf{R}}(\mathbf{r}) \\
 &= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R} + \mathbf{d}_j - \mathbf{d}_{j'})} \int d\mathbf{r} \phi_{a'j',0}^*(\mathbf{r}) H \phi_{aj,\mathbf{R}}(\mathbf{r})
 \end{aligned}$$

Si nos limitamos a los N vecinos más cercanos:

$$H_{a'j',aj}(\mathbf{k}) = \langle a', 0 | H | a, 0 \rangle \delta_{jj'} + (1 - \delta_{jj'}) \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{j'j}^{(m)}} \langle a', 0 | H | a, \mathbf{n}_{j'j}^{(m)} \rangle$$

$$H_{a'j',aj}(\mathbf{k}) = \langle a', 0 | H | a', 0 \rangle \delta_{aa'} \delta_{jj'} + (1 - \delta_{jj'}) \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{j'j}^{(m)}} \langle a', 0 | H | a, \mathbf{n}_{j'j}^{(m)} \rangle$$

Donde $\mathbf{n}_{j'j}^{(m)} = \mathbf{R} + \mathbf{d}_j - \mathbf{d}_{j'}$ es uno de los N vectores que unen el átomo j' con el j .

Elementos de matriz $H(a_j, a_j)$

$$H_{aA, aA}(\mathbf{k}) = H_{aB, aB}(\mathbf{k}) = \varepsilon_a$$

Pero recordar que esto es solamente aproximado.

Elementos de matriz $H(sA,sB)$

$$H_{sA,sB}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | s, \mathbf{n}_{AB}^{(m)} \rangle = V_{ss\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}}$$

$$\begin{aligned} H_{sB,sA}(\mathbf{k}) &= \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | s, \mathbf{n}_{BA}^{(m)} \rangle = V_{ss\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{BA}^{(m)}} \\ &= H_{sB,sA}^*(\mathbf{k}) \end{aligned}$$

Elementos de matriz H(sA,pB)

$$H_{sA,p_xB}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | p_x, \mathbf{n}_{AB}^{(m)} \rangle = V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} n_{AB,x}^{(m)}$$

$$H_{sA,p_yB}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | p_y, \mathbf{n}_{AB}^{(m)} \rangle = V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} n_{AB,y}^{(m)}$$

$$H_{sA,p_zB}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | p_y, \mathbf{n}_{AB}^{(m)} \rangle = V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} n_{AB,z}^{(m)}$$

$$H_{sB,p_xA}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | p_x, \mathbf{n}_{BA}^{(m)} \rangle = V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{BA}^{(m)}} n_{BA,x}^{(m)}$$

$$H_{sB,p_yA}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | p_y, \mathbf{n}_{BA}^{(m)} \rangle = V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{BA}^{(m)}} n_{BA,y}^{(m)}$$

$$H_{sB,p_zA}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(m)}} \langle s, 0 | H | p_y, \mathbf{n}_{BA}^{(m)} \rangle = V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k}\cdot\mathbf{n}_{BA}^{(m)}} n_{BA,z}^{(m)}$$

Elementos de matriz $H(pA,sB)$

$$H_{p_x A, sB}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \langle p_x, 0 | H | s, \mathbf{n}_{AB}^{(m)} \rangle = -V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} n_{AB,x}^{(m)}$$

$$H_{p_y A, sB}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \langle p_y, 0 | H | s, \mathbf{n}_{AB}^{(m)} \rangle = -V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} n_{AB,y}^{(m)}$$

$$H_{p_z A, sB}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \langle p_z, 0 | H | s, \mathbf{n}_{AB}^{(m)} \rangle = -V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} n_{AB,z}^{(m)}$$

$$H_{p_x B, sA}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{BA}^{(m)}} \langle p_x, 0 | H | s, \mathbf{n}_{BA}^{(m)} \rangle = -V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{BA}^{(m)}} n_{BA,x}^{(m)}$$

$$H_{p_y B, sA}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{BA}^{(m)}} \langle p_y, 0 | H | s, \mathbf{n}_{BA}^{(m)} \rangle = -V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{BA}^{(m)}} n_{BA,y}^{(m)}$$

$$H_{p_z B, sA}(\mathbf{k}) = \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{BA}^{(m)}} \langle p_z, 0 | H | s, \mathbf{n}_{BA}^{(m)} \rangle = -V_{sp\sigma} \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{BA}^{(m)}} n_{BA,z}^{(m)}$$

Elementos de matriz $H(p_A, p_B)$

$$\begin{aligned}
 H_{p_x A, p_x B}(\mathbf{k}) &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left\langle p_x, 0 \left| H \right| p_x, \mathbf{n}_{AB}^{(m)} \right\rangle \\
 &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left[\left(1 - \left(\hat{n}_{AB,x}^{(m)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,x}^{(m)} \right)^2 V_{pp\sigma} \right]
 \end{aligned}$$

$$\begin{aligned}
 H_{p_y A, p_y B}(\mathbf{k}) &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left\langle p_y, 0 \left| H \right| p_y, \mathbf{n}_{AB}^{(m)} \right\rangle \\
 &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left[\left(1 - \left(\hat{n}_{AB,y}^{(m)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,y}^{(m)} \right)^2 V_{pp\sigma} \right]
 \end{aligned}$$

$$\begin{aligned}
 H_{p_z A, p_z B}(\mathbf{k}) &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left\langle p_z, 0 \left| H \right| p_z, \mathbf{n}_{AB}^{(m)} \right\rangle \\
 &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left[\left(1 - \left(\hat{n}_{AB,z}^{(m)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,z}^{(m)} \right)^2 V_{pp\sigma} \right]
 \end{aligned}$$

Elementos de matriz $H(pA, p'B)$

$$\begin{aligned}
 H_{p_x A, p_y B}(\mathbf{k}) &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left\langle p_x, 0 \left| H \right| p_y, \mathbf{n}_{AB}^{(m)} \right\rangle \\
 &= \left(V_{pp\sigma} - V_{pp\pi} \right) \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \hat{n}_{AB,x}^{(m)} \hat{n}_{AB,y}^{(m)}
 \end{aligned}$$

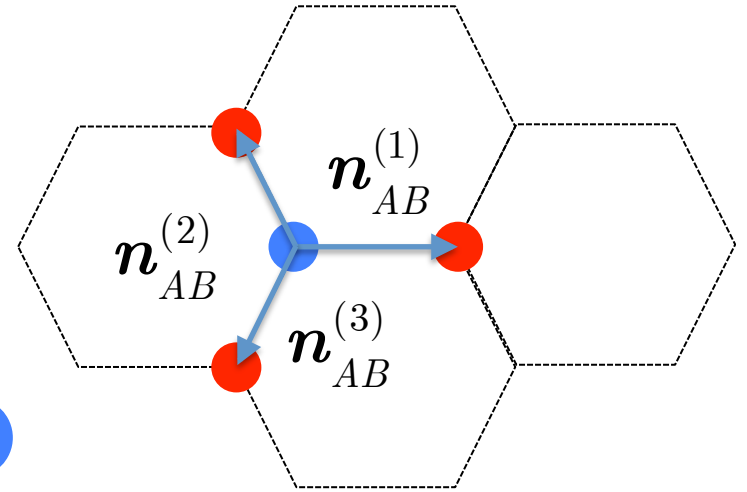
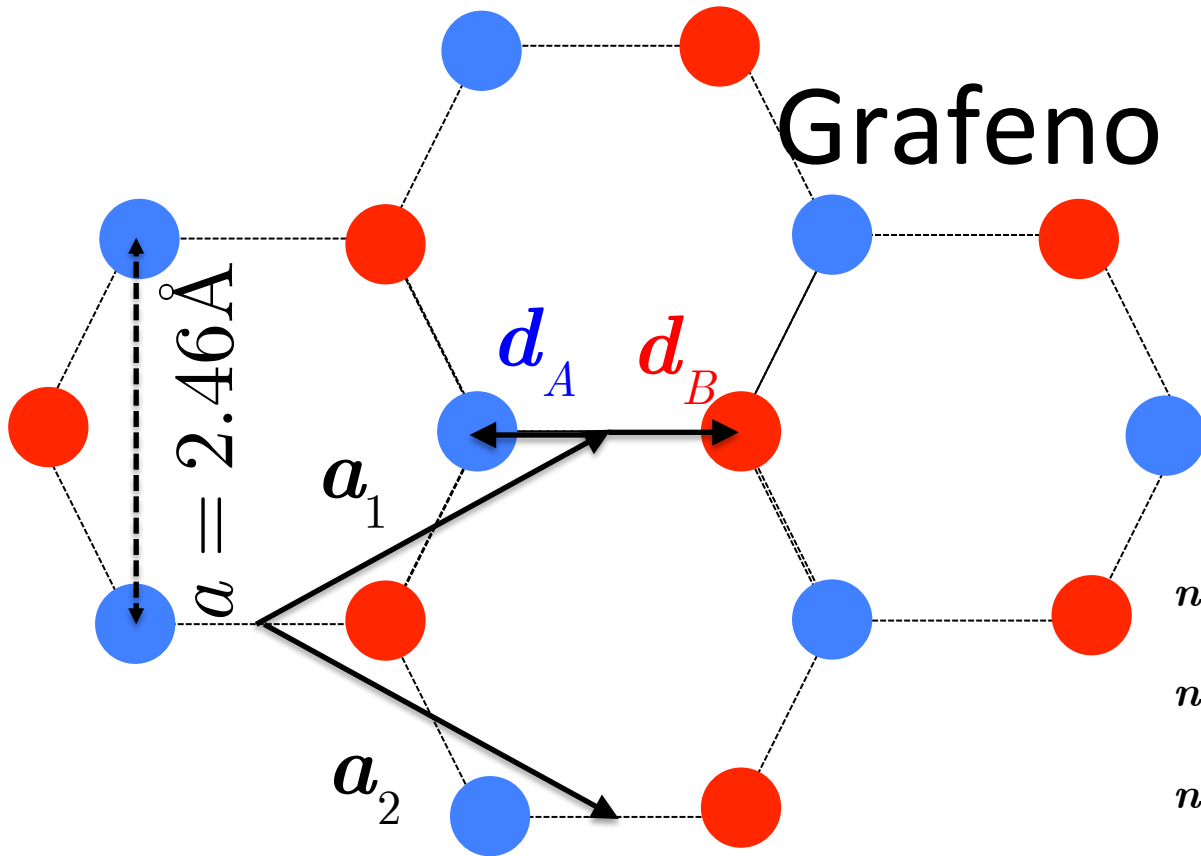
$$\begin{aligned}
 H_{p_x A, p_z B}(\mathbf{k}) &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left\langle p_x, 0 \left| H \right| p_z, \mathbf{n}_{AB}^{(m)} \right\rangle \\
 &= \left(V_{pp\sigma} - V_{pp\pi} \right) \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \hat{n}_{AB,x}^{(m)} \hat{n}_{AB,z}^{(m)}
 \end{aligned}$$

$$\begin{aligned}
 H_{p_y A, p_z B}(\mathbf{k}) &= \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \left\langle p_y, 0 \left| H \right| p_z, \mathbf{n}_{AB}^{(m)} \right\rangle \\
 &= \left(V_{pp\sigma} - V_{pp\pi} \right) \sum_{m=1}^N e^{i\mathbf{k} \cdot \mathbf{n}_{AB}^{(m)}} \hat{n}_{AB,y}^{(m)} \hat{n}_{AB,z}^{(m)}
 \end{aligned}$$

Casos de interés

- Los casos de interés que consideraremos en este curso contienen dos átomos por celda unidad, que denominaremos A y B.
- En el caso del grafeno, diamante, silicio, y germanio, los dos átomos son iguales (pero no equivalentes en la red).
- En el caso de materiales como el BN o el GaAs, los dos átomos son distintos.

Grafeno



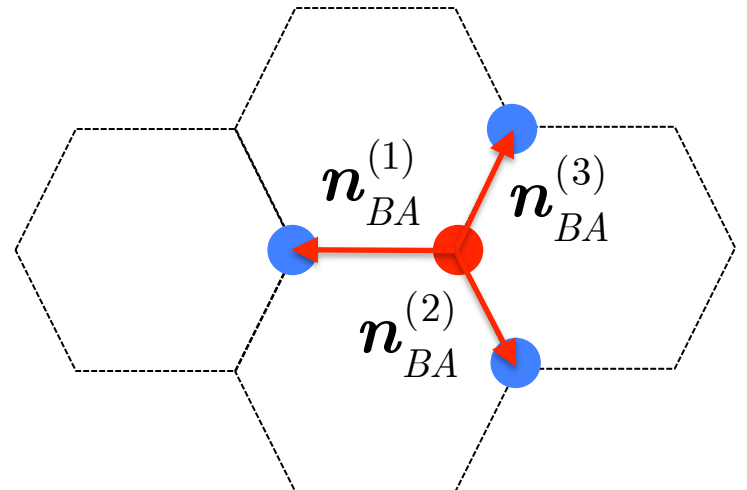
$$\mathbf{n}_{AB}^{(1)} = -\mathbf{n}_{BA}^{(1)} = \left(\frac{a}{\sqrt{3}}\right) \hat{\mathbf{i}}$$

$$\mathbf{n}_{AB}^{(2)} = -\mathbf{n}_{BA}^{(2)} = \left(\frac{a}{\sqrt{3}}\right) \left[-\left(\frac{1}{2}\right) \hat{\mathbf{i}} + \left(\frac{\sqrt{3}}{2}\right) \hat{\mathbf{j}} \right]$$

$$\mathbf{n}_{AB}^{(3)} = -\mathbf{n}_{BA}^{(3)} = \left(\frac{a}{\sqrt{3}}\right) \left[-\left(\frac{1}{2}\right) \hat{\mathbf{i}} - \left(\frac{\sqrt{3}}{2}\right) \hat{\mathbf{j}} \right]$$

$$\mathbf{a}_1 = \frac{a}{2} \left(\sqrt{3} \hat{\mathbf{i}} + \hat{\mathbf{j}} \right); \mathbf{a}_2 = \frac{a}{2} \left(\sqrt{3} \hat{\mathbf{i}} - \hat{\mathbf{j}} \right)$$

$$\mathbf{d}_A = -\frac{a}{2\sqrt{3}} \hat{\mathbf{i}}; \mathbf{d}_B = \frac{a}{2\sqrt{3}} \hat{\mathbf{i}}$$



Elementos de matriz $H(a_j, a_j)$

$$H_{sA, sA}(\mathbf{k}) = \langle s, 0 | H | s, 0 \rangle \delta_{ss} \delta_{AA} = \varepsilon_s = H_{sB, sB}(\mathbf{k})$$

$$H_{p_x A, p_x A}(\mathbf{k}) = \langle p_x, 0 | H | p_x, 0 \rangle \delta_{p_x p_x} \delta_{AA} = \varepsilon_{p\sigma} = H_{p_x B, p_x B}(\mathbf{k})$$

$$H_{p_y A, p_y A}(\mathbf{k}) = \langle p_y, 0 | H | p_y, 0 \rangle \delta_{p_y p_y} \delta_{AA} = \varepsilon_{p\sigma} = H_{p_y B, p_y B}(\mathbf{k})$$

$$H_{p_z A, p_z A}(\mathbf{k}) = \langle p_y, 0 | H | p_y, 0 \rangle \delta_{p_y p_y} \delta_{AA} = \varepsilon_{p\pi} = H_{p_z B, p_z B}(\mathbf{k})$$

Como la suma de los tres vectores que conectan con los vecinos es cero, podemos argumentar que la integral de p_x dará lo mismo que la integral de p_y , pero lo mismo no es cierto para la integral de p_z , de modo que en principio deberíamos permitir que los valores sean diferentes.

Elementos de matriz $H(sA,sB)$

Definimos, para simplificar la notación:

$$g_1 \equiv e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(1)}}$$

$$g_2 \equiv e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(2)}}$$

$$g_3 \equiv e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(3)}}$$

$$H_{sA,sB}(\mathbf{k}) = V_{ss\sigma} \left(e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(1)}} + e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(2)}} + e^{i\mathbf{k}\cdot\mathbf{n}_{AB}^{(3)}} \right) = V_{ss\sigma} (g_1 + g_2 + g_3)$$

$$H_{sB,sA}(\mathbf{k}) = H_{sB,sA}^*(\mathbf{k})$$

Elementos de matriz H(sA,pB)

$$H_{sA,p_x B}(\mathbf{k}) = V_{sp\sigma} \left(g_1 \hat{n}_{AB,x}^{(1)} + g_2 \hat{n}_{AB,x}^{(2)} + g_3 \hat{n}_{AB,x}^{(3)} \right)$$
$$= V_{sp\sigma} \left[g_1 (1) + g_2 \left(-\frac{1}{2} \right) + g_3 \left(-\frac{1}{2} \right) \right] = V_{sp\sigma} \left[g_1 - \frac{1}{2} (g_2 + g_3) \right]$$

$$H_{sA,p_y B}(\mathbf{k}) = V_{sp\sigma} \left(g_1 \hat{n}_{AB,y}^{(1)} + g_2 \hat{n}_{AB,y}^{(2)} + g_3 \hat{n}_{AB,y}^{(3)} \right)$$
$$= V_{sp\sigma} \left[g_1 (0) + g_2 \left(\frac{\sqrt{3}}{2} \right) + g_3 \left(-\frac{\sqrt{3}}{2} \right) \right] = \frac{\sqrt{3}V_{sp\sigma}}{2} (g_2 - g_3)$$

$$H_{sA,p_z B}(\mathbf{k}) = V_{sp\sigma} \left(g_1 \hat{n}_{AB,z}^{(1)} + g_2 \hat{n}_{AB,z}^{(2)} + g_3 \hat{n}_{AB,z}^{(3)} \right) = 0$$

Elementos de matriz H(pA,sB)

$$H_{p_x BA, sB}(\mathbf{k}) = -V_{sp\sigma} \left(g_1 \hat{n}_{AB,x}^{(1)} + g_2 \hat{n}_{AB,x}^{(2)} + g_3 \hat{n}_{AB,x}^{(3)} \right)$$
$$= -V_{sp\sigma} \left[g_1 (1) + g_2 \left(-\frac{1}{2} \right) + g_3 \left(-\frac{1}{2} \right) \right] = -V_{sp\sigma} \left[g_1 - \frac{1}{2} (g_2 + g_3) \right]$$

$$H_{p_y A, sB}(\mathbf{k}) = -V_{sp\sigma} \left(g_1 \hat{n}_{AB,y}^{(1)} + g_2 \hat{n}_{AB,y}^{(2)} + g_3 \hat{n}_{AB,y}^{(3)} \right)$$
$$= -V_{sp\sigma} \left[g_1 (0) + g_2 \left(\frac{\sqrt{3}}{2} \right) + g_3 \left(-\frac{\sqrt{3}}{2} \right) \right] = -\frac{\sqrt{3}V_{sp\sigma}}{2} (g_2 - g_3)$$

$$H_{p_z BA, sB}(\mathbf{k}) = V_{sp\sigma} \left(g_1 \hat{n}_{AB,z}^{(1)} + g_2 \hat{n}_{AB,z}^{(2)} + g_3 \hat{n}_{AB,z}^{(3)} \right) = 0$$

Elementos de matriz $H(pA, pB)$

$$\begin{aligned} H_{p_x A, p_x B}(\mathbf{k}) &= g_1 \left[\left(1 - \left(\hat{n}_{AB,x}^{(1)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,x}^{(1)} \right)^2 V_{pp\sigma} \right] \\ &+ g_2 \left[\left(1 - \left(\hat{n}_{AB,x}^{(2)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,x}^{(2)} \right)^2 V_{pp\sigma} \right] \\ &+ g_3 \left[\left(1 - \left(\hat{n}_{AB,x}^{(3)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,x}^{(3)} \right)^2 V_{pp\sigma} \right] \\ &= g_1 V_{pp\sigma} + (g_2 + g_3) \left[\frac{3}{4} V_{pp\pi} + \frac{1}{4} V_{pp\sigma} \right] \end{aligned}$$

Elementos de matriz $H(pA, pB)$

$$\begin{aligned}
 H_{p_y A, p_y B}(\mathbf{k}) &= g_1 \left[\left(1 - \left(\hat{n}_{AB,y}^{(1)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,y}^{(1)} \right)^2 V_{pp\sigma} \right] \\
 &+ g_2 \left[\left(1 - \left(\hat{n}_{AB,y}^{(2)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,y}^{(2)} \right)^2 V_{pp\sigma} \right] \\
 &+ g_3 \left[\left(1 - \left(\hat{n}_{AB,y}^{(3)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,y}^{(3)} \right)^2 V_{pp\sigma} \right] \\
 &= g_1 \left[V_{pp\pi} \right] + g_2 \left[\frac{1}{4} V_{pp\pi} + \frac{3}{4} V_{pp\sigma} \right] + g_3 \left[\frac{1}{4} V_{pp\pi} + \frac{3}{4} V_{pp\sigma} \right] \\
 &= g_1 V_{pp\pi} + (g_2 + g_3) \left[\frac{1}{4} V_{pp\pi} + \frac{3}{4} V_{pp\sigma} \right]
 \end{aligned}$$

Elementos de matriz $H(pA, pB)$

$$\begin{aligned} H_{p_z A, p_z B}(\mathbf{k}) &= g_1 \left[\left(1 - \left(\hat{n}_{AB,z}^{(1)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,z}^{(1)} \right)^2 V_{pp\sigma} \right] \\ &\quad + g_2 \left[\left(1 - \left(\hat{n}_{AB,z}^{(2)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,z}^{(2)} \right)^2 V_{pp\sigma} \right] \\ &\quad + g_3 \left[\left(1 - \left(\hat{n}_{AB,z}^{(3)} \right)^2 \right) V_{pp\pi} + \left(\hat{n}_{AB,z}^{(3)} \right)^2 V_{pp\sigma} \right] \\ &= \left(g_1 + g_2 + g_3 \right) V_{pp\pi} \end{aligned}$$

Elementos de matriz $H(pA, p'B)$

$$\begin{aligned} H_{p_x A, p_y B}(\mathbf{k}) &= \\ &= \left(V_{pp\sigma} - V_{pp\pi} \right) \left(g_1 \hat{n}_{AB,x}^{(1)} \hat{n}_{AB,y}^{(1)} + g_2 \hat{n}_{AB,x}^{(2)} \hat{n}_{AB,y}^{(2)} + g_3 \hat{n}_{AB,x}^{(3)} \hat{n}_{AB,y}^{(3)} \right) \\ &= \left(V_{pp\sigma} - V_{pp\pi} \right) \left[g_1 (1)(0) + g_2 \left(-\frac{1}{2} \right) \left(\frac{\sqrt{3}}{2} \right) + g_3 \left(-\frac{1}{2} \right) \left(-\frac{\sqrt{3}}{2} \right) \right] \\ &= \frac{\sqrt{3} \left(V_{pp\sigma} - V_{pp\pi} \right)}{4} \left(g_3 - g_2 \right) \end{aligned}$$

H(pA,p'B) matrix elements

$$\begin{aligned} H_{p_x A, p_z B}(\mathbf{k}) &= \\ &= \left(V_{pp\sigma} - V_{pp\pi} \right) \left(g_1 \hat{n}_{AB,x}^{(1)} \hat{n}_{AB,z}^{(1)} + g_2 \hat{n}_{AB,x}^{(2)} \hat{n}_{AB,z}^{(2)} + g_3 \hat{n}_{AB,x}^{(3)} \hat{n}_{AB,z}^{(3)} \right) \\ &= \left(V_{pp\sigma} - V_{pp\pi} \right) \left[g_1 (1)(0) + g_2 \left(-\frac{1}{2} \right) 0 + g_3 \left(-\frac{1}{2} \right) 0 \right] \\ &= 0 \end{aligned}$$

H(pA, p'B) matrix elements

$$\begin{aligned} H_{p_y A, p_z B}(\mathbf{k}) &= \\ &= \left(V_{pp\sigma} - V_{pp\pi} \right) \left(g_1 \hat{n}_{AB,y}^{(1)} \hat{n}_{AB,z}^{(1)} + g_2 \hat{n}_{AB,y}^{(2)} \hat{n}_{AB,z}^{(2)} + g_3 \hat{n}_{AB,y}^{(3)} \hat{n}_{AB,z}^{(3)} \right) \\ &= \left(V_{pp\sigma} - V_{pp\pi} \right) \left[g_1 (0)(0) + g_2 \left(\frac{\sqrt{3}}{2} \right) 0 + g_3 \left(-\frac{\sqrt{3}}{2} \right) 0 \right] \\ &= 0 \end{aligned}$$

Bloques del hamiltoniano

- Escribimos la matriz hamiltoniana en forma de bloque como

$$H = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

- donde cada bloque es una matriz de 4x4.
Entonces:

H_{AA}

$$H_{AA} = \begin{pmatrix} \varepsilon_s & 0 & 0 & 0 \\ 0 & \varepsilon_{p\sigma} & 0 & 0 \\ 0 & 0 & \varepsilon_{p\sigma} & 0 \\ 0 & 0 & 0 & \varepsilon_{p\pi} \end{pmatrix}$$

H_{BB}

$$H_{BB} = \begin{pmatrix} \varepsilon_s & 0 & 0 & 0 \\ 0 & \varepsilon_{p\sigma} & 0 & 0 \\ 0 & 0 & \varepsilon_{p\sigma} & 0 \\ 0 & 0 & 0 & \varepsilon_{p\pi} \end{pmatrix}$$

H_{AB}

$$\begin{aligned}
 H_{AB} = & \\
 & \begin{array}{cccc}
 V_{ss\sigma} (g_1 + g_2 + g_3) & V_{sp\sigma} \left[g_1 - \frac{1}{2}(g_2 + g_3) \right] & \frac{\sqrt{3}}{2} V_{sp\sigma} (g_2 - g_3) & 0 \\
 -V_{sp\sigma} \left[g_1 - \frac{1}{2}(g_2 + g_3) \right] & g_1 V_{pp\sigma} + (g_2 + g_3) \left[\frac{3}{4} V_{pp\pi} + \frac{1}{4} V_{pp\sigma} \right] & \frac{\sqrt{3}}{4} (V_{pp\sigma} - V_{pp\pi})(g_3 - g_2) & 0 \\
 -\frac{\sqrt{3}}{2} V_{sp\sigma} (g_2 - g_3) & \frac{\sqrt{3}}{4} (V_{pp\sigma} - V_{pp\pi})(g_3 - g_2) & g_1 V_{pp\pi} + (g_2 + g_3) \left[\frac{1}{4} V_{pp\pi} + \frac{3}{4} V_{pp\sigma} \right] & 0 \\
 0 & 0 & 0 & (g_1 + g_2 + g_3) V_{pp}.
 \end{array}
 \end{aligned}$$

H_{BA}

$$H_{BaAa'} = H_{Aa'Ba}^*$$

$$\begin{pmatrix} V_{ss\sigma} (g_1^* + g_2^* + g_3^*) & -V_{sp\sigma} \left[g_1^* - \frac{1}{2}(g_2^* + g_3^*) \right] & -\frac{\sqrt{3}}{2} V_{sp\sigma} (g_2^* - g_3^*) & 0 \\ V_{sp\sigma} \left[g_1^* - \frac{1}{2}(g_2^* + g_3^*) \right] & g_1^* V_{pp\sigma} + (g_2^* + g_3^*) \left[\frac{3}{4} V_{pp\pi} + \frac{1}{4} V_{pp\sigma} \right] & \frac{\sqrt{3}}{4} (V_{pp\sigma} - V_{pp\pi}) (g_3^* - g_2^*) & 0 \\ \frac{\sqrt{3}}{2} V_{sp\sigma} (g_2^* - g_3^*) & \frac{\sqrt{3}}{4} (V_{pp\sigma} - V_{pp\pi}) (g_3^* - g_2^*) & g_1^* V_{pp\pi} + (g_2^* + g_3^*) \left[\frac{1}{4} V_{pp\pi} + \frac{3}{4} V_{pp\sigma} \right] & 0 \\ 0 & 0 & 0 & (g_1^* + g_2^* + g_3^*) V_{pi} \end{pmatrix}$$

Caso $k=0$

En este caso el hamiltoniano se simplifica a

$$H_{AB} = \begin{pmatrix} 3V_{ss\sigma} & 0 & 0 & 0 \\ 0 & \frac{3}{2}(V_{pp\pi} + V_{pp\sigma}) & 0 & 0 \\ 0 & 0 & \frac{3}{2}(V_{pp\pi} + V_{pp\sigma}) & 0 \\ 0 & 0 & 0 & 3V_{pp\pi} \end{pmatrix}$$

Reordenamiento de estados

- Los resultados para $k=0$ sugieren un reordenamiento de la forma

$$|s_A\rangle, |s_B\rangle, |p_{Ax}\rangle, |p_{Bx}\rangle, |p_{Ay}\rangle, |p_{By}\rangle, |p_{Az}\rangle, |p_{Bz}\rangle$$

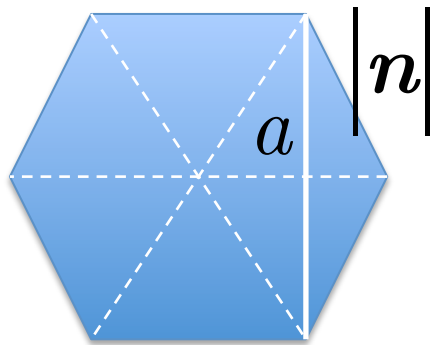
- Entonces el hamiltoniano correspondiente es

Bloques de 2x2

ε_s	$3V_{ss\sigma}$	0	0	0	0	0	0	0
$3V_{ss\sigma}$	ε_s	0	0	0	0	0	0	0
0	0	ε_p	$\frac{3}{2}(V_{pp\pi} + V_{pp\sigma})$	0	0	0	0	0
0	0	$\frac{3}{2}(V_{pp\pi} + V_{pp\sigma})$	ε_p	0	0	0	0	0
0	0	0	0	ε_p	$\frac{3}{2}(V_{pp\pi} + V_{pp\sigma})$	0	0	0
0	0	0	0	$\frac{3}{2}(V_{pp\pi} + V_{pp\sigma})$	ε_p	0	0	0
0	0	0	0	0	0	0	ε_p	$3V_{pp\pi}$
0	0	0	0	0	0	0	$V_{pp\pi}$	ε_p

Celda unidad del grafeno (geometría)

- Cada hexágono tiene 6 átomos. Cada átomo es compartido por tres hexágonos, de modo que hay 2 átomos por hexágono. Pero como la celda unidad tiene precisamente 2 átomos, el “volumen” de la celda unidad es el área A_H del hexágono:



$$|\mathbf{n}| \cos 30^\circ = |\mathbf{n}| \frac{\sqrt{3}}{2} = a$$

$$A_H = 6 \times \frac{1}{2} |\mathbf{n}| \frac{a}{2} = \frac{\sqrt{3}a^2}{2}$$

Unit cell volume

- Si queremos utilizar las fórmulas 3D para el volumen de la celda unidad, definimos un vector “fake” a_3 en la dirección z. Si definimos este vector como $a_3 = -\hat{\mathbf{k}}$, entonces

$$\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{a}{2} (\sqrt{3}\hat{\mathbf{i}} + \hat{\mathbf{j}}) \cdot \left[\frac{a}{2} (\sqrt{3}\hat{\mathbf{i}} - \hat{\mathbf{j}}) \times (-\hat{\mathbf{k}}) \right] =$$

$$\frac{a}{2} (\sqrt{3}\hat{\mathbf{i}} + \hat{\mathbf{j}}) \cdot \frac{a}{2} (\sqrt{3}\hat{\mathbf{j}} + \hat{\mathbf{i}}) = \left(\frac{a}{2} \right)^2 2\sqrt{3} = \frac{\sqrt{3}}{2} a^2$$

- El motivo por el cual tenemos que hacer la extraña selección de $-\mathbf{k}$ es la orientación de los otros dos vectores.

Graphene reciprocal lattice

- Using the same fake unit vector, the graphene reciprocal lattice vectors can be obtained as

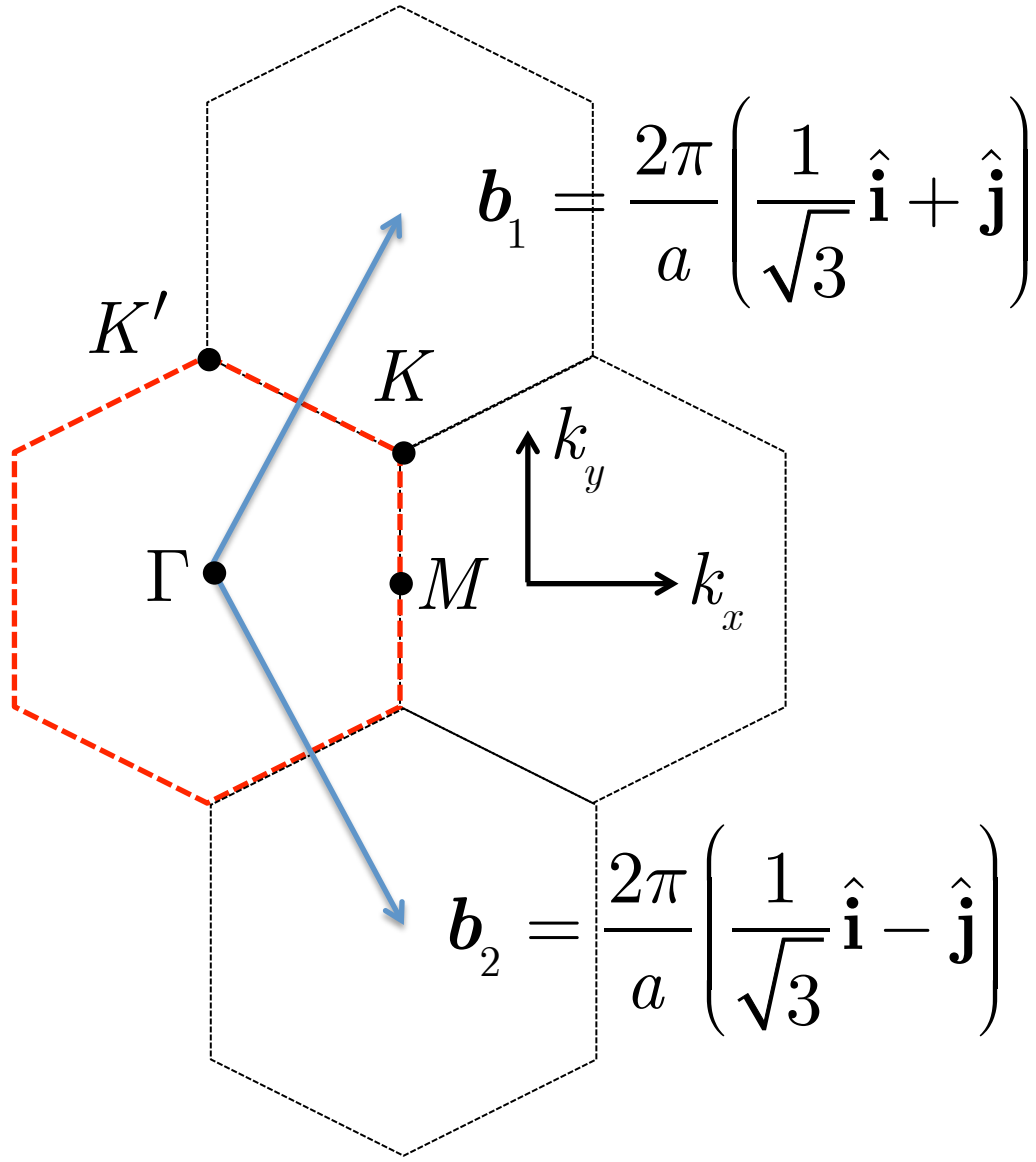
$$\mathbf{b}_1 = -\frac{2\pi}{A_H} (\mathbf{a}_2 \times \hat{\mathbf{k}}) = 2\pi \left(\frac{2}{\sqrt{3}a^2} \right) \frac{a}{2} (-\hat{\mathbf{i}} - \sqrt{3}\hat{\mathbf{j}}) = \frac{2\pi}{a} \left(\frac{1}{\sqrt{3}} \hat{\mathbf{i}} + \hat{\mathbf{j}} \right)$$

$$\mathbf{b}_2 = -\frac{2\pi}{A_H} (\hat{\mathbf{k}} \times \mathbf{a}_1) = 2\pi \left(\frac{2}{\sqrt{3}a^2} \right) \frac{a}{2} (-\hat{\mathbf{i}} + \sqrt{3}\hat{\mathbf{j}}) = \frac{2\pi}{a} \left(\frac{1}{\sqrt{3}} \hat{\mathbf{i}} - \hat{\mathbf{j}} \right)$$

- We verify that

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = \left[\frac{a}{2} (\sqrt{3}\hat{\mathbf{i}} + \hat{\mathbf{j}}) \right] \cdot \left[\frac{2\pi}{a} \left(\frac{1}{\sqrt{3}} \hat{\mathbf{i}} + \hat{\mathbf{j}} \right) \right] = 2\pi$$

Brillouin zone del grafeno



$$\Gamma = 0$$

$$M = \frac{2\pi}{a\sqrt{3}}$$

$$K = K' = \frac{2\pi}{a}$$