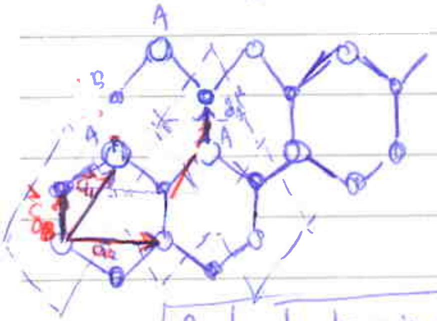
Out. 2017

Tight-binding para grafeno



Rede de bravais ≠ posição dos átomos!

$\ell = A, B$

orbitais π: $\phi_A(\vec{r})$, $\phi_B(\vec{r})$ $H_{at}\,\phi_\ell(\vec{r}) = \varepsilon\,\phi_\ell(\vec{r})$

base: com dois átomos na célula unitária!

função de Bloch
$$\begin{cases} \psi_{\vec{q}}^{(A)}(\vec{r}) = \sum_{\vec{R}'} e^{i\vec{q}\cdot\vec{R}}\,\phi_\ell(\vec{r}+\vec{\delta}_A-\vec{R}) \\ \psi_{\vec{q}}^{(B)}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}}\,\phi_\ell(\vec{r}+\vec{\delta}_B-\vec{R}) \end{cases}$$

onde $\vec{R}_\ell$ é o vetor de translação na sub rede ℓ. $(\ell = A, B)$

Sendo $\vec{a}_1$ e $\vec{a}_2$ os vetores de base (figura), temos $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2$ conecta apenas pontos na mesma sub-rede. $\vec{\delta}_A$ e $\vec{\delta}_B$ são os vetores que ligam os pontos da rede de Bravais aos átomos A e B.

Por conveniência, vamos escolher que os pontos da rede de bravais estão na sub rede $\underline{A}$ de modo que $\vec{\delta}_A = 0$ e $\vec{\delta}_B = a\hat{e}_y$

Temos então:
$$\begin{cases} \psi_{\vec{q}}^{(A)}(\vec{r}) = \sum_{\vec{R}'} e^{i\vec{q}\cdot\vec{R}'}\,\phi_A(\vec{r}-\vec{R}') \\ \psi_{\vec{q}}^{(B)}(\vec{r}) = \sum_{\vec{R}'} e^{i\vec{q}\cdot\vec{R}'}\,\phi_B(\vec{r}+\vec{\delta}_B-\vec{R}') \end{cases}$$

A função de onda será uma combinação linear destas duas funções de Bloch:
$$\boxed{\psi_{\vec{q}}(\vec{r}) = a_{\vec{q}}\,\psi_{\vec{q}}^{(A)}(\vec{r}) + b_{\vec{q}}\,\psi_{\vec{q}}^{(B)}(\vec{r})} \qquad H.$$

e queremos resolver $H\psi_{\vec{q}}(\vec{r}) = E(\vec{q})\,\psi_{\vec{q}}(\vec{r})$ $\quad (H = H_{at} + \Delta V).$

logo:
$$\begin{cases} \int \left(\psi_{\vec{q}}^{(A)}(\vec{r})\right)^* H\,\psi_{\vec{q}}(\vec{r})\,d^2\vec{r} = E(\vec{q}) \int \left(\psi_{\vec{q}}^{(A)}(\vec{r})\right)^* \psi_{\vec{q}}(\vec{r})\,d^2\vec{r} \\ \int \left(\psi_{\vec{q}}^{(B)}(\vec{r})\right)^* H\,\psi_{\vec{q}}(\vec{r})\,d^2\vec{r} = E(\vec{q}) \int \left(\psi_{\vec{q}}^{(B)}(\vec{r})\right)^* \psi_{\vec{q}}(\vec{r})\,d^2\vec{r} \end{cases}$$

Lembrando que $H_{at}\,\varphi_q(\vec r) = \varepsilon_0\,\varphi_q(\vec r)$ temos

$$\psi_q^*(\vec r)\,H\,\psi_q(\vec r) = a_q^*\left(\varphi_q^A(\vec r)\right)^* H\,\psi_q(\vec r) + b_q^*\left(\varphi_q^{(B)}(\vec r)\right)^* H\,\psi_q(\vec r)$$

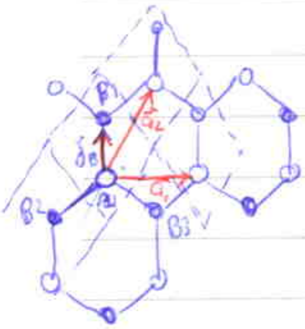
e onde

$$\boxed{H_q^{ij} = \int \psi_q^{(i)}(\vec r)^*\,H\,\psi_q^{(j)}(\vec r)\,d^2\vec r} = \sum_{\vec R'\vec R''} e^{i\vec q(\vec R'-\vec R'')}\Big(\varepsilon_0\int \phi_i^*(\vec r - \vec R'' + \vec\delta_i)\,\phi_j(\vec r+\vec\delta_j-\vec R')\,d^2\vec r$$

$$+ \int \phi_i^*(\vec r+\vec\delta_i-\vec R'')\,\Delta V\,\phi_j(\vec r+\vec\delta_j-\vec R')\,d^2\vec r$$

$$S_q^{ij} = \int\left(\psi_q^{(i)}(\vec r)\right)^*\psi_q^{(j)}(\vec r)\,d^2\vec r = \sum_{\vec R'\vec R''} e^{i\vec q(\vec R'-\vec R'')}\int \phi_i^*(\vec r+\vec\delta_i-\vec R'')\,\phi_j(\vec r+\vec\delta_j-\vec R')\,d^2\vec r$$

Vamos ver quais destes termos são zero / pequeno.



$$\begin{cases} \vec a_1 = \sqrt3\,a\,\hat e_x \\ \vec a_2 = \dfrac{\sqrt3}{2}\,a\,(\hat e_x + \sqrt3\,\hat e_y) \\ \vec R = n_1\vec a_1 + n_2\vec a_2. \end{cases} \qquad \delta_B = a\,\hat e_y$$

sítio A_1 em $\vec R = \vec R'$

1ºs vizinhos (B sites)	$\vec r_{B1} = \vec\delta_B$, $\vec r_{B2} = \vec R' - \vec a_2 + \vec\delta_B$, $\vec r_{B3} = \vec R' + \vec a_1 - \vec a_2 + \vec\delta_B$
2ºs vizinhos (A sites)	$r_A = \vec R' \pm \vec a_1 \pm \vec a_2$, $\vec R' \pm \vec a_1$, $\vec R' \pm \vec a_2$ (6)

Logo

$\boxed{S_q^{AA} = N}$

$$S_q^{BA} = \sum_{\vec R'\vec R''} e^{i\vec q\cdot(\vec R'-\vec R'')}\int \phi_B^*(\vec r+\vec\delta_B-\vec R'')\,\phi_A(\vec r-\vec R')\,)\,d^2\vec r$$

$$= \sum_{\vec R'} e^{i\vec q\cdot\vec R'}\Big(\int \phi_B^*(\vec r+\vec\delta_B-\vec R')\,\phi_A(\vec r-\vec R')\,d^2\vec r\;e^{-i\vec q\cdot\vec R'}$$

$$+ \int \phi_B^*(\vec r+\vec\delta_B-\vec a_2-\vec R)\,\phi_A(\vec r-\vec R)\;e^{-i\vec q\cdot(\vec R'+\vec a_2)}$$

$$+ \int \phi_B^*(\vec r+\vec\delta_B-\vec a_2+\vec a_1-\vec R)\,\phi_A(\vec r-\vec R)\;e^{-i\vec q(\vec R'+\vec a_2-\vec a_1)}\Big)$$

$$= \sum_{\vec R'}\underbrace{\left(\int \phi_B^*(\vec r-\vec R'+\vec\delta_B)\,\phi_A(\vec r-\vec R')\,d^2\vec r\right)}_{\equiv S_{AB}}\underbrace{\left(1 + e^{-i\vec q\cdot\vec a_2} + e^{-i\vec q\cdot(\vec a_2-\vec a_1)}\right)}_{\equiv \gamma_{\vec q}^*} = N\,S_{BA}\,\gamma_{\vec q}^*$$

nº sítios na rede.

E os hoppings? Mesma coisa; podemos ter 1^{os} e 2^{os} vizinhos

$$t_q^{ij} = \int (\Psi_q^{(i)}(\vec r)\,\Delta V (\Psi_q^{(j)}(\vec r)) = \sum_{\vec R' \vec R''} e^{i\vec q(\vec R' - \vec R'')} \int \phi_i^*(\vec r + \vec\delta_i - \vec R'')\,\Delta V\, \phi_j(\vec r + \vec \delta_j - \vec R')\, d^2 r$$

$$t_q^{BA} = \sum_{\vec R'} e^{i\vec q\cdot\vec R'} \Big(\int \phi_B^*(\vec r - \vec R' + \vec\delta_B)\,\Delta V\, \phi_A(\vec r - \vec R')\; e^{-i\vec q\cdot\vec R'}$$
$$+ \int \phi_B^*(\vec r - \vec R' + \vec\delta_B - \vec a_2)\,\Delta V\, \phi_A(\vec r - \vec R')\; e^{-i\vec q\cdot(\vec R' + \vec a_2)}$$
$$+ \int \phi_B^*(\vec r - \vec R' + \vec\delta_B - \vec a_2 + \vec a_1)\,\Delta V\, \phi_A(\vec r - \vec R')\; e^{-i\vec q\cdot(\vec R' + \vec a_2 - \vec a_1)} \Big) \quad 1^{os} \text{ vizinhos}$$

$$= \sum_{\vec R'} \underbrace{\Big(\int \phi_B^*(\vec r - \vec R' + \vec\delta_B)\,\Delta V\,\phi_A(\vec r - \vec R')\Big)}_{\equiv t_{BA}} \underbrace{\Big(1 + e^{-i\vec q\cdot\vec a_2} + e^{-i\vec q\cdot(\vec a_2 - \vec a_1)}\Big)}_{\equiv \gamma_{\vec q}^*} = N t_{BA}\, \gamma_{\vec q}^*$$

$$t_q^{AA} = \sum_{\vec R'} e^{i\vec q\cdot\vec R'} \Big(\overbrace{\int \phi_A^*(\vec r - \vec R')\,\Delta V\, \phi_A(\vec r - \vec R')\, d^2 r}^{\Delta\varepsilon}\; e^{-i\vec q\cdot\vec R'} \quad \text{(mesmo sítio)}$$
$$+ \int \phi_A^*(\vec r - \vec R' \pm \vec a_1)\,\phi_A(\vec r - \vec R')\, d^2 r\; e^{-i\vec q\cdot\vec R'}\big(e^{+i q a_1} + e^{-i q a_1}\big)$$
$$+ \int \phi_A^*(\vec r - \vec R' \pm \vec a_2)\,\phi_A(\vec r - \vec R')\, d^2 r\; e^{-i\vec q\cdot\vec R'}\big(e^{i q a_2} + e^{-i q a_2}\big) \quad 2^{os} \text{ vizinhos}$$
$$+ \int \phi_A^*(\vec r - \vec R' \pm (\vec a_2 - \vec a_1))\,\phi_A(\vec r - \vec R')\, d^2 r\; e^{-i\vec q\cdot\vec R'}\big(e^{i q (a_2 - a_1)} + e^{-i q (a_2 - a_1)}\big)\Big)$$

$$= N\Delta\varepsilon + 2N t_2^{AA}\big(\cos\vec q\cdot\vec a_1 + \cos\vec q\cdot\vec a_2 + \cos\vec q\cdot(\vec a_2 - \vec a_1)\big)$$

Now $\boxed{H_q^{ij} = \varepsilon_0 S_q^{ij} + t_q^{ij}}$; $\dfrac{H_q^{BA}}{N} = \left(\dfrac{H_q^{AB}}{N}\right)^* = (\varepsilon_0 S_{BA} + t_{BA})\,\gamma_q^*$ //

$$\frac{H_q^{AA}}{N} = (\varepsilon_0 + \Delta\varepsilon) + 2t_2\big(\cos\vec q\cdot\vec a_1 + \cos\vec q\cdot\vec a_2 + \cos\vec q\,(\vec a_2 - \vec a_1)\big) = \frac{H_q^{BB}}{N} \quad //$$

Voltemos à equação. Temos

$$\int \psi_q^*(\vec r)\,\frac{H}{N}\,\psi_q(\vec r)\,d^2\vec r = (a_q^*\ b_q^*)\begin{pmatrix} H_q^{AA} & H_q^{AB} \\ H_q^{BA} & H_q^{BB}\end{pmatrix}\begin{pmatrix} a_q \\ b_q\end{pmatrix} \qquad \vec a_3 \equiv \vec a_2 - \vec a_1$$

$$= (a_q^*\ b_q^*)\begin{pmatrix} \varepsilon_0 + \Delta\varepsilon + 2t_2\sum_{i=1}^{3}\cos\vec q\cdot\vec a_i & (\varepsilon_0 S + t_1)\gamma_q \\ (\varepsilon_0 S + t_1)\gamma_q^* & \varepsilon_0 + \Delta\varepsilon + 2t_2\sum_{i=1}^{3}\cos\vec q\cdot\vec a_i\end{pmatrix}\begin{pmatrix} a_q \\ b_q\end{pmatrix}$$

$$\boxed{\gamma_q = 1 + e^{-i\vec q\cdot\vec a_2} + e^{+i\vec q\cdot\vec a_3}}$$

$\boxed{\cdot\ \text{Caso } t_2 = 0 \quad (1^{os} \text{ vizinhos apenas})}$

Equação de auto-valores: $\quad \bar\varepsilon_0 \equiv \varepsilon_0 + \Delta\varepsilon$

$$\begin{vmatrix} \bar\varepsilon_0 - E & (\varepsilon_0 S + t_1)\gamma_q \\ (\varepsilon_0 S + t_1)\gamma_q^* & \bar\varepsilon_0 - E\end{vmatrix} = 0 \Rightarrow (\bar\varepsilon_0 - E)^2 - (\varepsilon_0 S + t_1)^2|\gamma_q|^2 = 0$$

$$\boxed{E(q) = \varepsilon_0 \pm (\varepsilon_0 S + t_1)|\gamma_q|}$$

Quem é $|\gamma_q|$?

$$|\gamma_q|^2 = \left(1 + e^{i\vec q\cdot\vec a_2} + e^{i\vec q\cdot\vec a_3}\right)\left(1 + e^{-i\vec q\cdot\vec a_2} + e^{-i\vec q\cdot\vec a_3}\right) = 3 + 2\cos(\vec q\cdot\vec a_2) + 2\cos(\vec q\cdot\vec a_3) + 2\cos(\vec q\cdot\vec a_1)$$

Lembrando que:
$$\begin{cases} \vec a_1 = \sqrt3\, a\, \hat e_x \\ \vec a_2 = \frac{\sqrt3}{2} a(\hat e_x + \sqrt3\,\hat e_y) \\ \vec a_3 = \vec a_2 - \vec a_1 = \frac{\sqrt3}{2} a(-\hat e_x + \sqrt3\,\hat e_y)\end{cases}$$

$$\vec q\cdot\vec a_2 = \frac{\sqrt3}{2}(q_x a + \sqrt3 q_y a)\ ;\quad \vec q\cdot\vec a_1 = \sqrt3 q_x a \quad \vec q\cdot\vec a_3 = \frac{\sqrt3}{2}(-q_x a + \sqrt3 q_y a)$$

$$|\gamma_q| = \sqrt{3 + \underbrace{2\cos\left(\frac{\sqrt3}{2}q_x a + \frac32 q_y a\right) + 2\cos\left(-\frac{\sqrt3}{2}q_x a + \frac32 q_y a\right)}_{4\cos\left(\frac{\sqrt3}{2}q_x a\right)\cos\left(\frac32 q_y a\right)} + 2\cos\sqrt3 q_x a}$$

Tarefa: encontrar os vetores $\vec A_1$ e $\vec A_2$ da rede recíproca, e os pontos (q_x, q_y) onde $|\gamma_q| = 0$