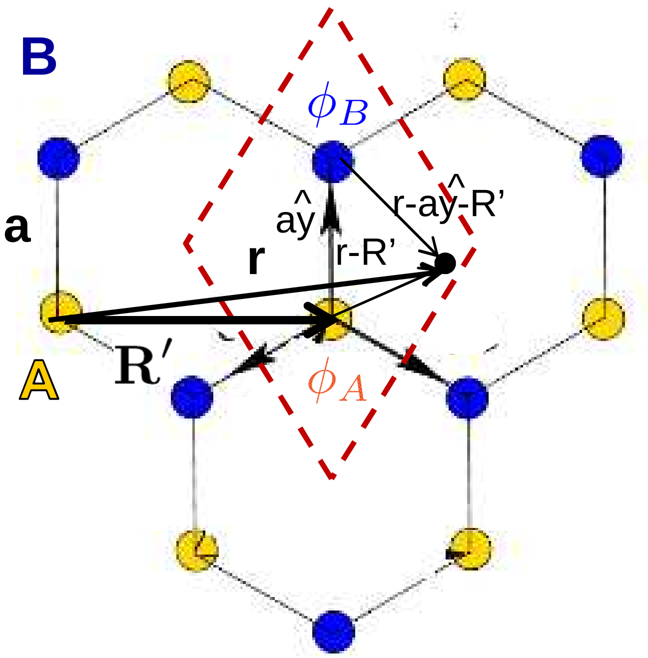
# Tight-binding para o grafeno: base de dois orbitais.




$$\mathbf{R}' = n_1'\mathbf{a}_1 + n_2'\mathbf{a}_2$$

$$\mathbf{a}_1 = \sqrt{3}a\hat{\mathbf{x}}$$

$$\mathbf{a}_2 = \frac{\sqrt{3}}{2}a\hat{\mathbf{x}} + \frac{3}{2}\hat{\mathbf{y}}$$

- Funções de Bloch para os orbitais A e B:

$$\Psi^{(A)}_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'}\phi_A(\mathbf{r}-\mathbf{R}')$$

$$\Psi^{(B)}_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'}\phi_B(\mathbf{r}-a\hat{\mathbf{y}}-\mathbf{R}')$$

- Combinação linear de orbitais atômicos (LCAO):

$$\Psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'}\left[a_{\mathbf{q}}\phi_A(\mathbf{r}-\mathbf{R}') + b_{\mathbf{q}}\phi_B(\mathbf{r}-a\hat{\mathbf{y}}-\mathbf{R}')\right]$$

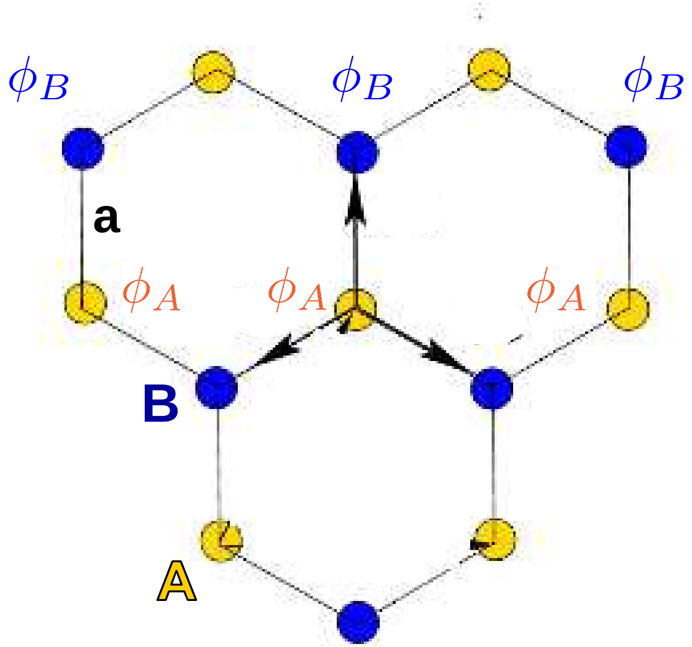
$$\boxed{\Psi_{\mathbf{q}}(\mathbf{r}) = a_{\mathbf{q}}\Psi^{(A)}_{\mathbf{q}}(\mathbf{r}) + b_{\mathbf{q}}\Psi^{(B)}_{\mathbf{q}}(\mathbf{r})}$$

- Base “ortonormal”:

$$\int \left(\Psi^A_{\mathbf{q}}(\mathbf{r})\right)^* \Psi^A_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} = \int \left(\Psi^B_{\mathbf{q}}(\mathbf{r})\right)^* \Psi^B_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} = 1$$

$$\int \left(\Psi^A_{\mathbf{q}}(\mathbf{r})\right)^* \Psi^B_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} = \int \left(\Psi^B_{\mathbf{q}}(\mathbf{r})\right)^* \Psi^A_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} = 0$$

# Tight-binding para o grafeno: Hamiltoniano.




- Eq. de Schrödinger: $H\Psi_{\mathbf{q}}(\mathbf{r}) = E(\mathbf{q})\Psi_{\mathbf{q}}(\mathbf{r})$

$$H = H_0 + \Delta V(r) \qquad H_0\phi_{A(B)} = \epsilon_0\phi_{A(B)}$$

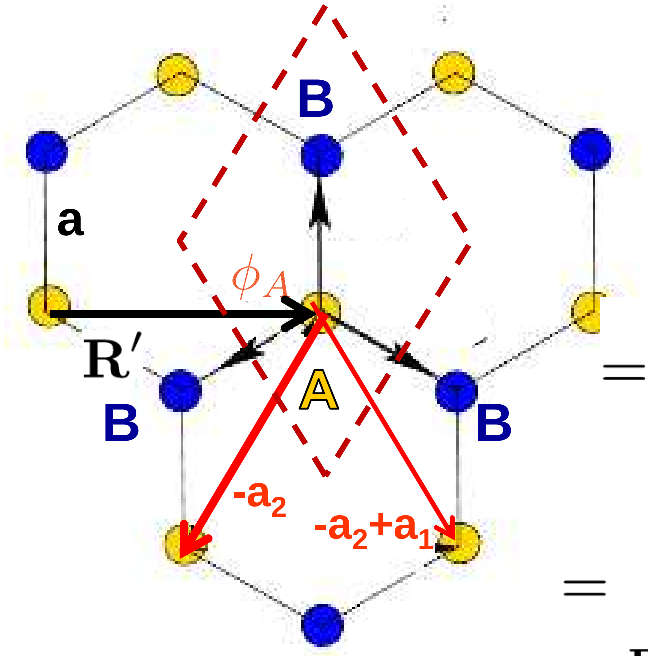
- Em forma "matricial": equação de auto-valores

$$\begin{pmatrix} H^{AA} & H^{AB} \\ H^{BA} & H^{BB} \end{pmatrix} \begin{pmatrix} a_{\mathbf{q}} \\ b_{\mathbf{q}} \end{pmatrix} = E(\mathbf{q}) \begin{pmatrix} a_{\mathbf{q}} \\ b_{\mathbf{q}} \end{pmatrix}$$

onde:

$$\begin{cases} H^{AA} = \int \left(\Psi^A_{\mathbf{q}}(\mathbf{r})\right)^* H\Psi^A_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} \\ H^{AB} = \int \left(\Psi^A_{\mathbf{q}}(\mathbf{r})\right)^* H\Psi^B_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} \\ H^{AB} = \int \left(\Psi^B_{\mathbf{q}}(\mathbf{r})\right)^* H\Psi^A_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} \\ H^{BB} = \int \left(\Psi^B_{\mathbf{q}}(\mathbf{r})\right)^* H\Psi^B_{\mathbf{q}}(\mathbf{r})d^2\mathbf{r} \end{cases}$$

# Calculando os elementos de matriz: $H^{BA}=H^{AB}$.




- Primeiramente, vamos calcular $H^{BA} = H^{AB}$ :

$$H^{BA} = \int \left(\Psi_{\mathbf{q}}^{B}(\mathbf{r})\right)^{*} H\Psi_{\mathbf{q}}^{A}(\mathbf{r})d^2\mathbf{r}$$

$$= \sum_{\mathbf{R}',\mathbf{R}''} e^{i\mathbf{q}\cdot(\mathbf{R}'-\mathbf{R}'')} \int \phi_B^*(\mathbf{r}-(\mathbf{R}''+a\hat{\mathbf{y}}))H\phi_A(\mathbf{r}-\mathbf{R}')d^2\mathbf{r}$$

$$= \sum_{\mathbf{R}',\mathbf{R}''} e^{i\mathbf{q}\cdot(\mathbf{R}'-\mathbf{R}'')} \left[\epsilon_0 \int \phi_B^*(\mathbf{r}-(\mathbf{R}''+a\hat{\mathbf{y}}))\phi_A(\mathbf{r}-\mathbf{R}')d^2\mathbf{r} + \int \phi_B^*(\mathbf{r}-(\mathbf{R}''+a\hat{\mathbf{y}}))\Delta V(r)\phi_A(\mathbf{r}-\mathbf{R}')d^2\mathbf{r}\right]$$

$$\mathbf{R}' = n_1'\mathbf{a}_1 + n_2'\mathbf{a}_2$$

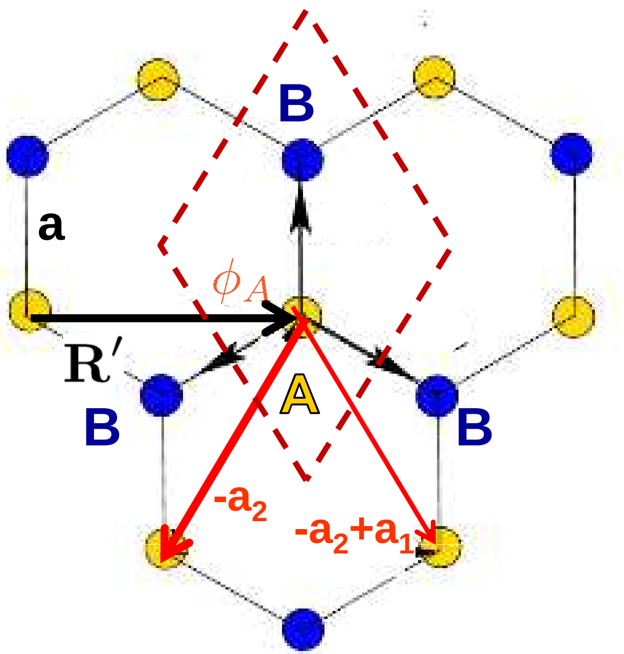
$$\mathbf{a}_1 = \sqrt{3}a\hat{\mathbf{x}}$$

$$\mathbf{a}_2 = \frac{\sqrt{3}}{2}a\hat{\mathbf{x}} + \frac{3}{2}\hat{\mathbf{y}}$$

- Dado um **R'**, vamos considerar apenas os **R''** tais que <u>os sítios B mais próximos do síto A em **R**' estejam em **R''+ay**</u>.
- São 3:

$$\mathbf{R}'' = \mathbf{R}'; \mathbf{R}'' = \mathbf{R}' - \mathbf{a}_2; \mathbf{R}'' = \mathbf{R}' - \mathbf{a}_2 + \mathbf{a}_1$$

# Calculando os elementos de matriz: $H^{BA}=H^{AB}$.




- Logo, teremos:

$$H^{BA} = \sum_{\mathbf{R}'} \left(1 + e^{i\mathbf{q}\cdot\mathbf{a}_2} + e^{i\mathbf{q}\cdot(\mathbf{a}_2-\mathbf{a}_1)}\right)[\epsilon_0 S_{BA} + t_{BA}]$$

onde, por simetria, $S_{BA}$ e $t_{BA}$ são independentes de **R'**:

$$S_{BA} = \int \phi_B^*(\mathbf{r} - a\hat{\mathbf{y}})\phi_A(\mathbf{r})d^2\mathbf{r}$$

$$t_{BA} = \int \phi_B^*(\mathbf{r} - a\hat{\mathbf{y}})\Delta V(r)\phi_A(\mathbf{r})d^2\mathbf{r}$$

$$\mathbf{R}' = n_1'\mathbf{a}_1 + n_2'\mathbf{a}_2$$

$$\mathbf{a}_1 = \sqrt{3}a\hat{\mathbf{x}}$$

$$\mathbf{a}_2 = \frac{\sqrt{3}}{2}a\hat{\mathbf{x}} + \frac{3}{2}\hat{\mathbf{y}}$$

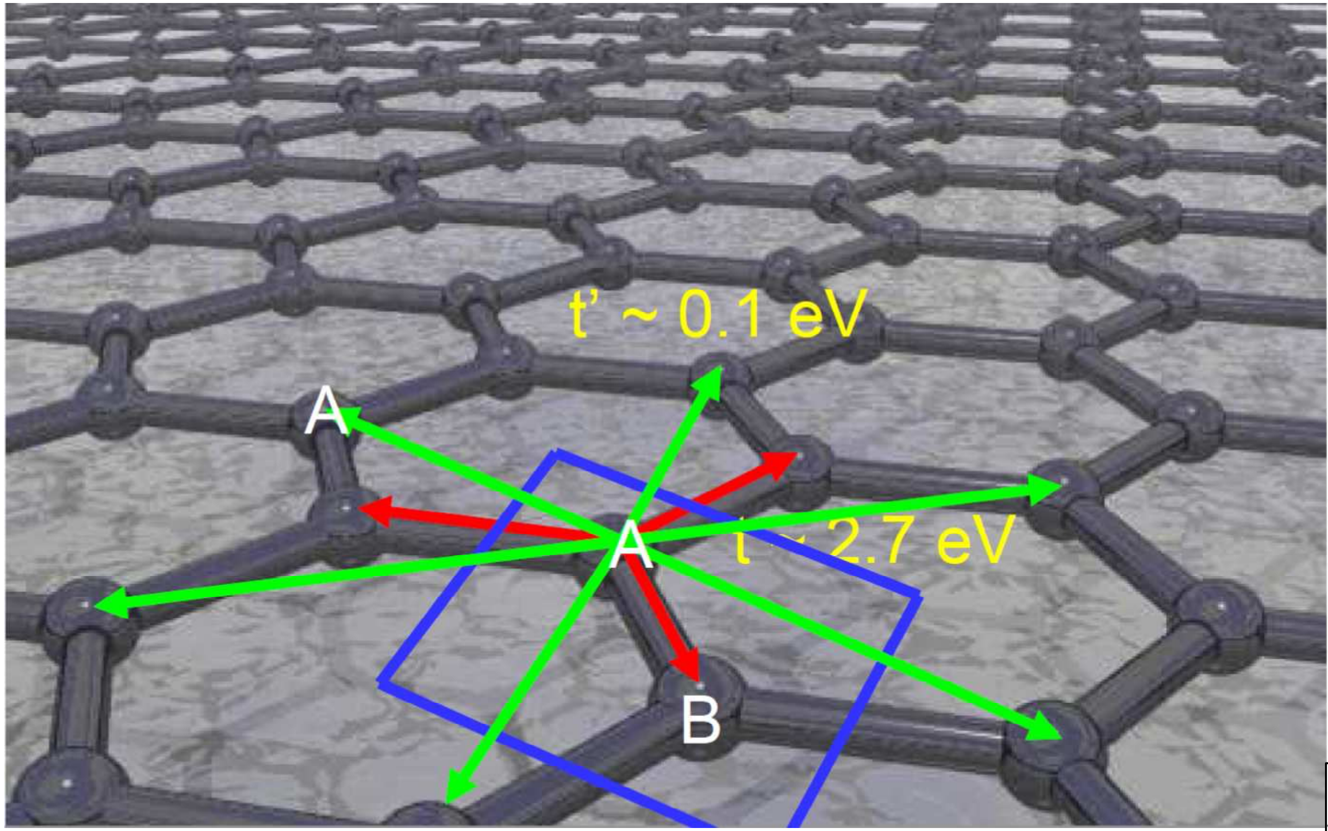
- Por fim, temos:

$$\boxed{\frac{H^{BA}}{N} = \gamma_{\mathbf{q}}[\epsilon_0 S_{BA} + t_{BA}]}$$

onde N é o número total de sítios e $\gamma_{\mathbf{q}}$ foi calculado na Tarefa 10:

$$\gamma_{\mathbf{q}} = \left(1 + e^{i\mathbf{q}\cdot\mathbf{a}_2} + e^{i\mathbf{q}\cdot(\mathbf{a}_2-\mathbf{a}_1)}\right)$$

# Tight-binding para o grafeno: duas bandas.




**Tight-binding de 1os…**

$$H = -t \sum_{\langle i,j \rangle, \sigma} \left( a^{\dagger}_{\sigma,i} b_{\sigma,j} + \text{H.c.} \right)$$

$$- t' \sum_{\langle\langle i,j \rangle\rangle, \sigma} \left( a^{\dagger}_{\sigma,i} a_{\sigma,j} + b^{\dagger}_{\sigma,i} b_{\sigma,j} + \text{H.c.} \right)$$

**…e 2os vizinhos**

$$0.02t \leq t' \leq 0.2t$$

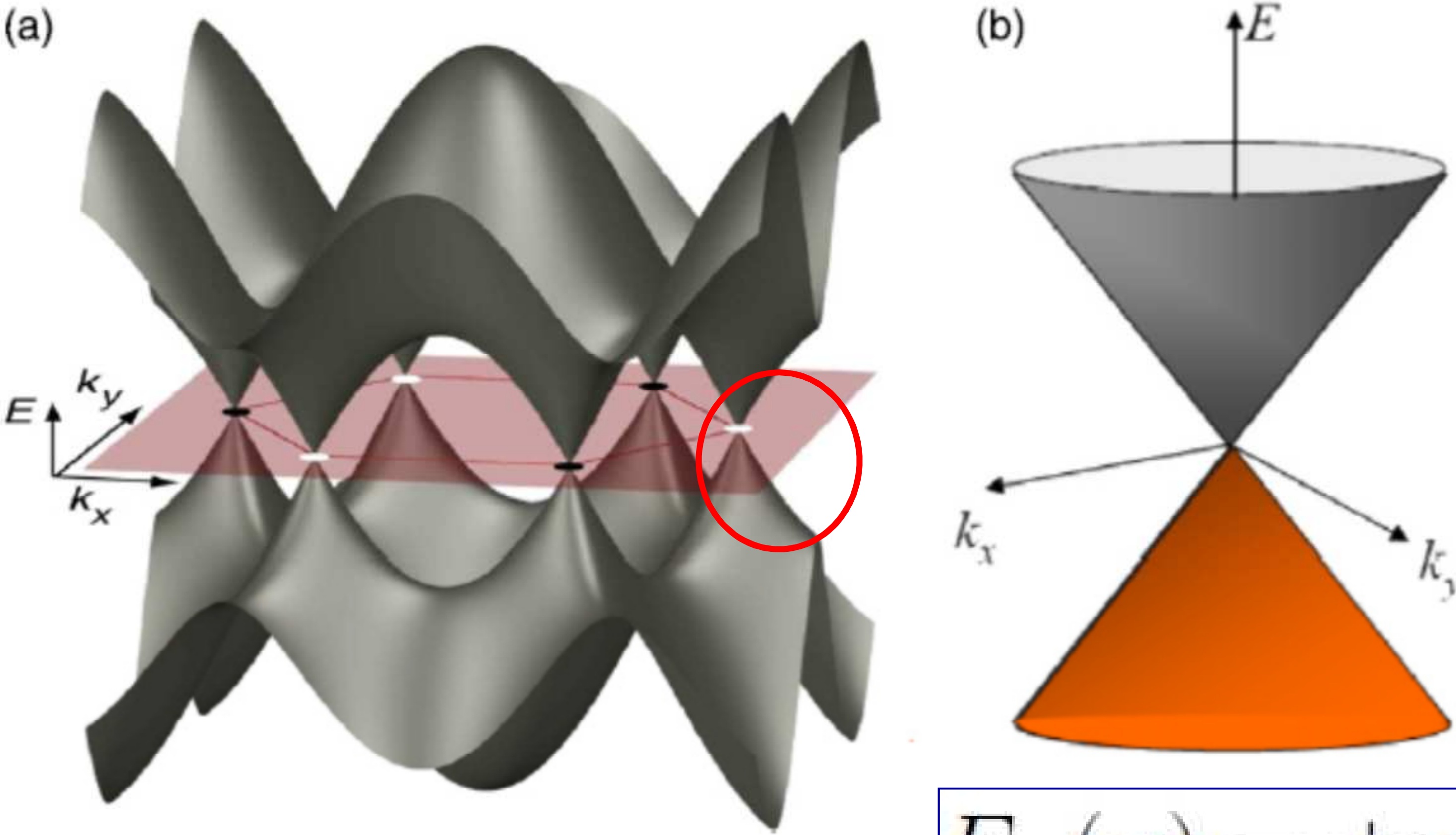
$$E_{\pm}(\mathbf{q}) = \pm t \sqrt{3 + f(\mathbf{q})} - t' f(\mathbf{q})$$

$$f(\mathbf{q}) = 2\cos\left(\sqrt{3} q_x a\right) + 4 \cos\left(\frac{\sqrt{3}}{2} q_x a\right) \cos\left(\frac{3}{2} q_y a\right)$$

**Resultado do final dos anos 40!**

Wallace, P.R., *Phys. Rev.* 71 622 (1947)

# Cones de Dirac.

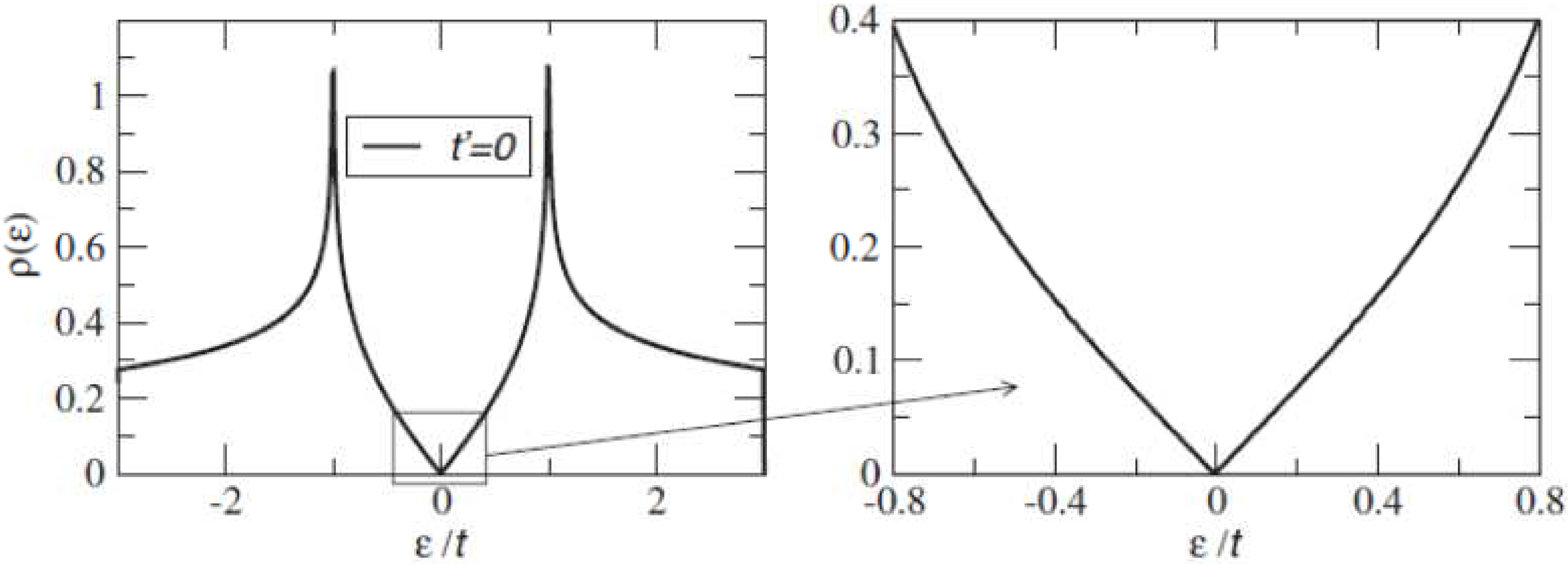



$$E_{\pm}(\mathbf{q}) = \pm v_F |\mathbf{q}|$$

$$E_{\pm}(\mathbf{q}) \approx \pm t\sqrt{3 + f(\mathbf{q})}$$

**Analogia: dispersão de férmions "relativísticos sem massa" ("E=pc")**

# Grafeno: densidade de estados




**ρ(E) ∝ |E| (*linear*)**
**próximo ao ponto**
**de neutralidade de carga.**

$$\rho(E) = \frac{2A_c}{\pi}\frac{|E|}{v_F^2}$$