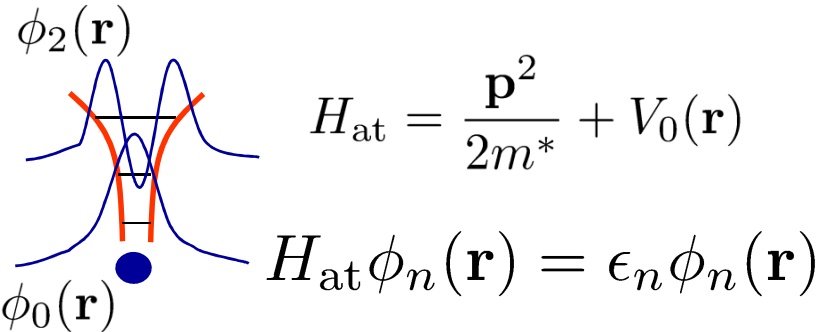


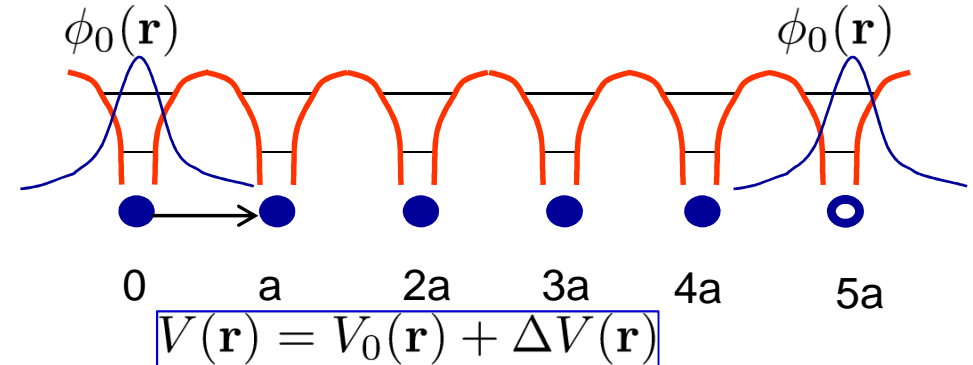
# O modelo de tight-binding.

Note que:  $\phi_n(\mathbf{r} + \mathbf{L}) = \phi_n(\mathbf{r})$   
 mas, em geral:  $\phi_n(\mathbf{r} \pm \mathbf{R}) \neq \phi_n(\mathbf{r})$

- Potenciais atômicos  $V_0(\mathbf{r})$ :



- Potencial cristalino  $V(\mathbf{r})$ :



$$\Delta V(\mathbf{r}) \approx V_0(\mathbf{r} - \mathbf{R}) \text{ para } \mathbf{r} = \mathbf{R}$$

$$\Delta V(\mathbf{r}) \approx 0 \text{ para } \mathbf{r} = 0$$

- Teorema de Bloch:  $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$

$$\Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}} u_{j,\mathbf{q}}(\mathbf{r}) \Rightarrow \Psi_{\mathbf{q}}^{(j)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}} \Psi_{\mathbf{q}}^{(j)}(\mathbf{r})$$

Procuramos uma expansão em termos dos orbitais  $\phi_n(\mathbf{r})$

Escolha da “base”:

$$\Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) = \sum_{\mathbf{R}', n} e^{i\mathbf{q}\cdot\mathbf{R}'} \mathcal{B}_{jn} \phi_n(\mathbf{r} - \mathbf{R}')$$

(Tarefa 8, agora!)

Mostre que esta escolha satisfaz:

$$\Psi_{\mathbf{q}}^{(j)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}} \Psi_{\mathbf{q}}^{(j)}(\mathbf{r})$$

Na verdade, *qualquer* função de Bloch pode ser escrita em uma expansão similar usando **funções de Wannier**.

Dica: lembre das condições periódicas de contorno na soma sobre  $\mathbf{R}'$

# Equação para os estados de Bloch.

- Hamiltoniano do cristal:  $H = \frac{\mathbf{p}^2}{2m^*} + V(\mathbf{r}) = H_{\text{at}} + \Delta V(\mathbf{r})$
- Orbitais atômicos:  $H_{\text{at}}\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r})$      $H_{\text{at}}\phi_n^*(\mathbf{r}) = \epsilon_n\phi_n^*(\mathbf{r})$
- Função de Bloch:  $\Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) = \sum_{\mathbf{R}',n} e^{i\mathbf{q}\cdot\mathbf{R}'} \mathcal{B}_{jn} \phi_n(\mathbf{r} - \mathbf{R}')$

Equação de auto-valores:  $H\Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) = E_j(\mathbf{q})\Psi_{\mathbf{q}}^{(j)}(\mathbf{r})$

Multiplica por  $\phi_m^*(\mathbf{r})$ , e integra:  $\int \phi_m^*(\mathbf{r}) H\Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) d^3\mathbf{r} = E_j(\mathbf{q}) \int \phi_m^*(\mathbf{r}) \Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) d^3\mathbf{r}$

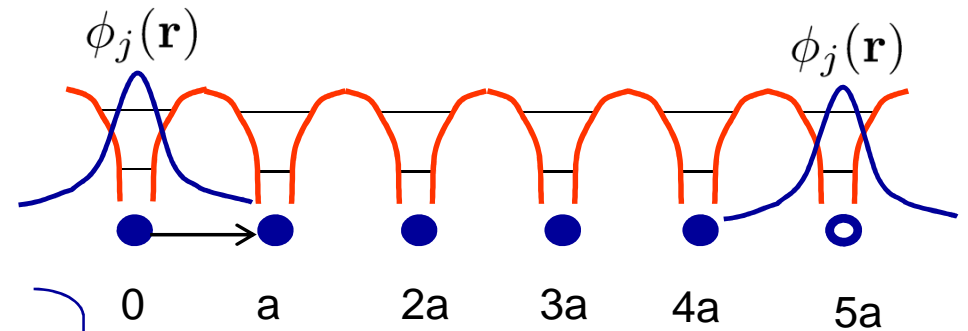
Temos então:

$$\sum_{\mathbf{R}',n} e^{i\mathbf{q}\cdot\mathbf{R}'} \mathcal{B}_{jn} \left[ \epsilon_n \int \phi_m^*(\mathbf{r}) \phi_n(\mathbf{r} - \mathbf{R}') d^3\mathbf{r} + \int \phi_m^*(\mathbf{r}) \Delta V(\mathbf{r}) \phi_n(\mathbf{r} - \mathbf{R}') d^3\mathbf{r} \right] = E_j(\mathbf{q}) \sum_{\mathbf{R}',n} e^{i\mathbf{q}\cdot\mathbf{R}'} \mathcal{B}_{jn} \int \phi_m^*(\mathbf{r}) \phi_n(\mathbf{r} - \mathbf{R}') d^3\mathbf{r}$$

# Integrais de transferência.

- Potencial cristalino  $V(\mathbf{r})$ :

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \Delta V(\mathbf{r}) \quad \Delta V(\mathbf{r}) \approx 0 \text{ para } \mathbf{r} = \mathbf{R}$$



Note que:  $\int \phi_m^*(\mathbf{r})\phi_n(\mathbf{r}) d^3\mathbf{r} = \delta_{mn}$

e  $\int \phi_m^*(\mathbf{r})\phi_n(\mathbf{r} - \mathbf{R}) d^3\mathbf{r} \approx 0$  se  $\mathbf{R} \neq \vec{0}$

$$\int \phi_m^*(\mathbf{r})\phi_n(\mathbf{r} - \mathbf{R}) d^3\mathbf{r} = \delta_{mn}\delta_{\mathbf{R},\vec{0}}$$

mas:

$$\int \phi_m^*(\mathbf{r})\Delta V(\mathbf{r})\phi_n(\mathbf{r} - \mathbf{R}) d^3\mathbf{r} \equiv -\gamma_{mn}(\mathbf{R}) \neq 0$$

Nos pontos em que  $\Delta V(\mathbf{r}) \approx 0$  o overlap dos orbitais é grande e vice-versa.

Logo, temos:

$$\sum_{\mathbf{R}',n} e^{i\mathbf{q}\cdot\mathbf{R}'} \mathcal{B}_{jm} [\epsilon_m \delta_{mn} \delta_{\mathbf{R}',\vec{0}} - \gamma_{mn}(\mathbf{R}')] = E_j(\mathbf{q}) \sum_{\mathbf{R}',n} e^{i\mathbf{q}\cdot\mathbf{R}'} \mathcal{B}_{jm} \delta_{mn} \delta_{\mathbf{R}',\vec{0}}$$

que leva a uma equação de auto-valores:

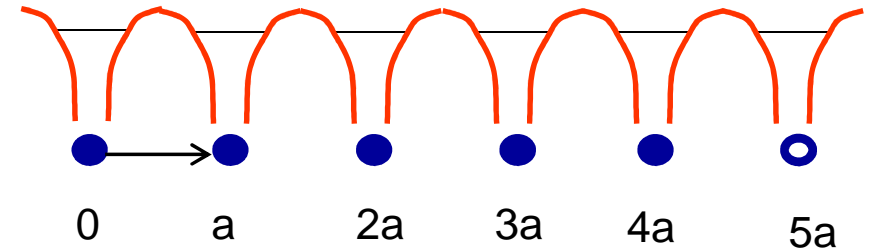
$$[E_j(\mathbf{q}) - \epsilon_m] \mathcal{B}_{jm} = - \sum_{\mathbf{R}',n} e^{i\mathbf{q}\cdot\mathbf{R}'} \mathcal{B}_{jn} \gamma_{mn}(\mathbf{R}')$$

# Modelo 1D com 1 orbital (1 banda).

- Caso 1D com 1 orbital por sítio:

$$\gamma(na) \equiv - \int \phi^*(x) \Delta V(x) \phi(x - na) dx$$

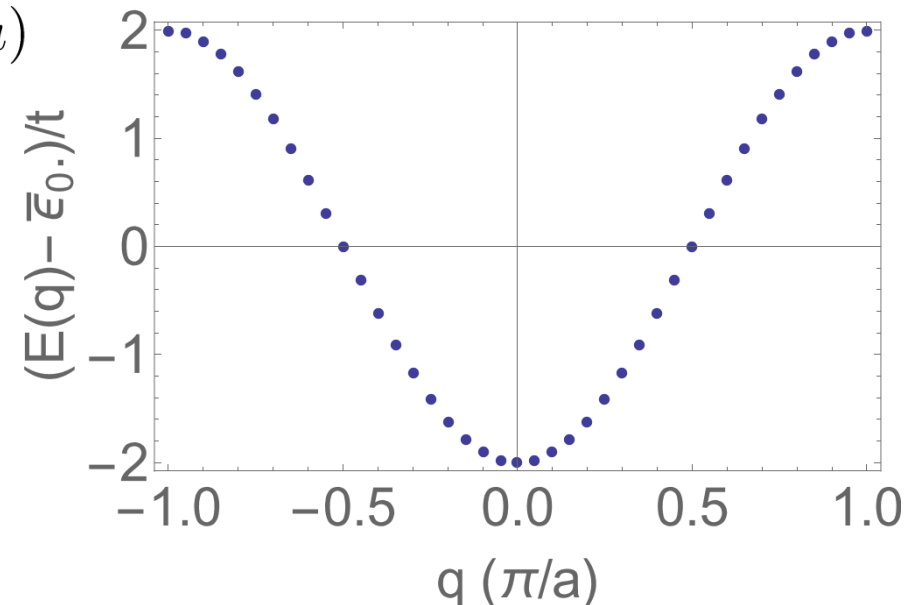
$$E(q) = \epsilon_0 - \sum_n e^{inqa} \gamma(na)$$



- Aproximação adicional: apenas  $n \pm 1$  contribuem para as integrais (“1os vizinhos”).
- Definimos:  $\bar{\epsilon}_0 \equiv \epsilon_0 - \gamma(0)$  e  $t \equiv \gamma(\pm a)$

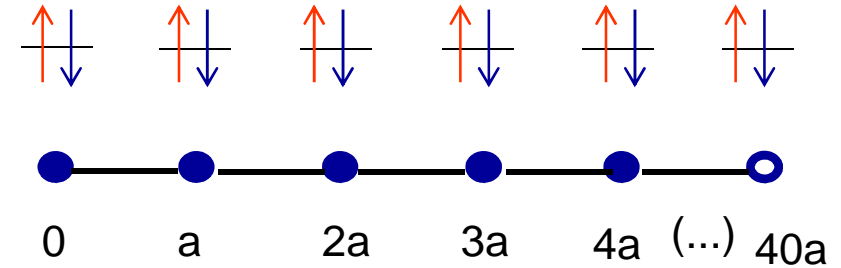
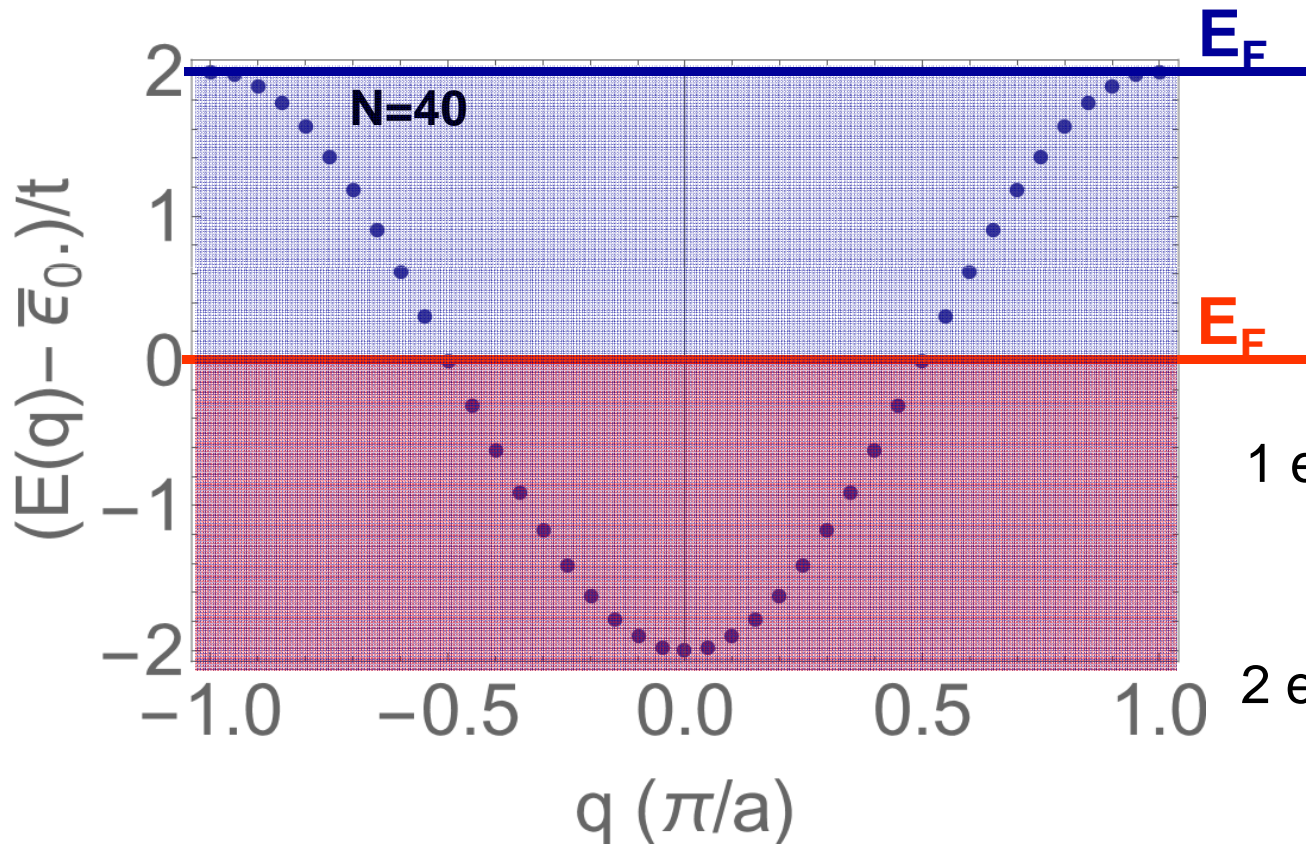
O resultado é a dispersão de tight-binding:

$$E(q) = \bar{\epsilon}_0 - 2t \cos(qa)$$



# Modelo 1D de 1 banda: discussão.

$$E(q_m) = \bar{\epsilon}_0 - 2t \cos(q_m a)$$



$$q_m = \frac{2m}{N} \left( \frac{\pi}{a} \right)$$

2t: largura da banda.

1 e- por sítio: banda semi-preenchida.

Comportamento metálico

2 e- por sítio: banda preenchida.

Comportamento isolante