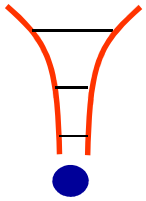
O modelo de tight-binding.

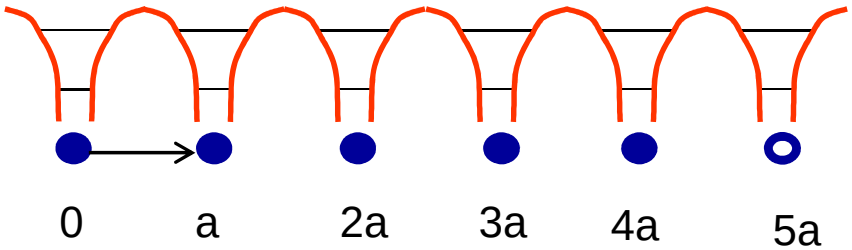
- Potenciais *atômicos* $V_0(r)$:



$$H_{\rm at} = \frac{\mathbf{p}^2}{2m^*} + V_0(\mathbf{r})$$

$$H_{\rm at}\phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r})$$

- Potencial cristalino V(r):



$$\boxed{V(\mathbf{r}) = V_0(\mathbf{r}) + \Delta V(\mathbf{r})}$$

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

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

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

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

Escolha:

$$\Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) = \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'} \phi_j(\mathbf{r}-\mathbf{R}')$$

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

(Tarefa de hoje)

Mostre que esta escolha satisfaz:

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

Dica: lembre das condições periódicas de contorno

Equação para os estados de Bloch.

- Hamiltoniano do cristal: $H = \frac{\mathbf{p}^2}{2m^*} + V(\mathbf{r}) = H_{\rm at} + \Delta V(\mathbf{r})$
- Orbitais atômicos: $H_{\rm at}\phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r})$
- Função de Bloch: $\Psi_{\mathbf{q}}^{(j)}(\mathbf{r}) = \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'} \phi_j(\mathbf{r}-\mathbf{R}')$

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

Multiplica por $\phi_i^*(\mathbf{r})$ e integra: :

$$\int \phi_i^*(\mathbf{r})\; H\Psi_{\mathbf{q}}^{(j)}(\mathbf{r})\; d^3\mathbf{r} = E_j(\mathbf{q}) \int \phi_i^*(\mathbf{r})\; \Psi_{\mathbf{q}}^{(j)}(\mathbf{r})\; d^3\mathbf{r}$$

Temos então:

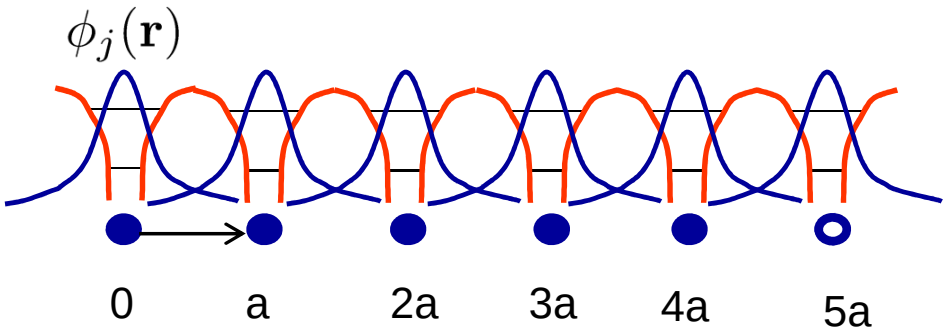
$$\epsilon_j \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'} \int \phi_i^*(\mathbf{r})\; \phi_j(\mathbf{r}-\mathbf{R}')\; d^3\mathbf{r} + \int \phi_i^*(\mathbf{r})\; \Delta V(\mathbf{r})\phi_j(\mathbf{r}-\mathbf{R}')\; d^3\mathbf{r} = E_j(\mathbf{q}) \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'} \int \phi_i^*(\mathbf{r})\; \phi_j(\mathbf{r}-\mathbf{R}')\; d^3\mathbf{r}$$

Integrais de transferência.

- Potencial cristalino V(r):

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \Delta V(\mathbf{r})$$

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



Note que: $\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\, d^3\mathbf{r} = \delta_{ij}$ e $\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r}-\mathbf{R})\, d^3\mathbf{r} \approx 0$ se $\mathbf{R} \neq \vec{0}$

mas: $$\int \phi_i^*(\mathbf{r})\Delta V(\mathbf{r})\phi_j(\mathbf{r}-\mathbf{R})\, d^3\mathbf{r} \neq 0$$

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

Logo, para i=j a expressão

$$\epsilon_j \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'} \int \phi_j^*(\mathbf{r})\, \phi_j(\mathbf{r}-\mathbf{R}')\, d^3\mathbf{r} + \int \phi_j^*(\mathbf{r})\, \Delta V(\mathbf{r})\phi_j(\mathbf{r}-\mathbf{R}')\, d^3\mathbf{r} = E_j(\mathbf{q}) \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'} \int \phi_j^*(\mathbf{r})\, \phi_j(\mathbf{r}-\mathbf{R}')\, d^3\mathbf{r}$$

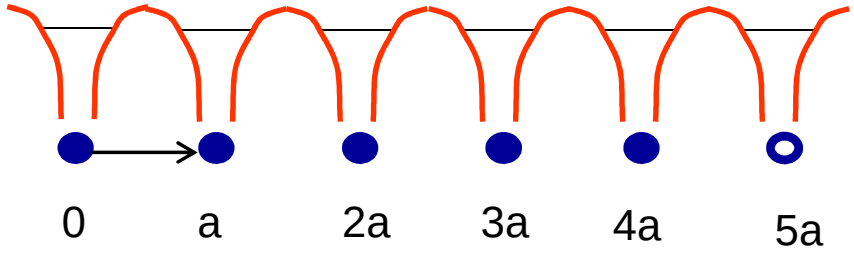
Simplifica para:

$$\boxed{E_j(\mathbf{q}) = \epsilon_j + \sum_{\mathbf{R}'} e^{i\mathbf{q}\cdot\mathbf{R}'} \int \phi_j^*(\mathbf{r})\, \Delta V(\mathbf{r})\phi_j(\mathbf{r}-\mathbf{R}')\, d^3\mathbf{r}}$$

Modelo 1D com 1 orbital (1 banda).

- Caso 1D com 1orbital por sítio:

$$E(q) = \epsilon_0 + \sum_n e^{inqa} \int \phi^*(x)\ \Delta V(x) \phi(x - na)\ dx$$



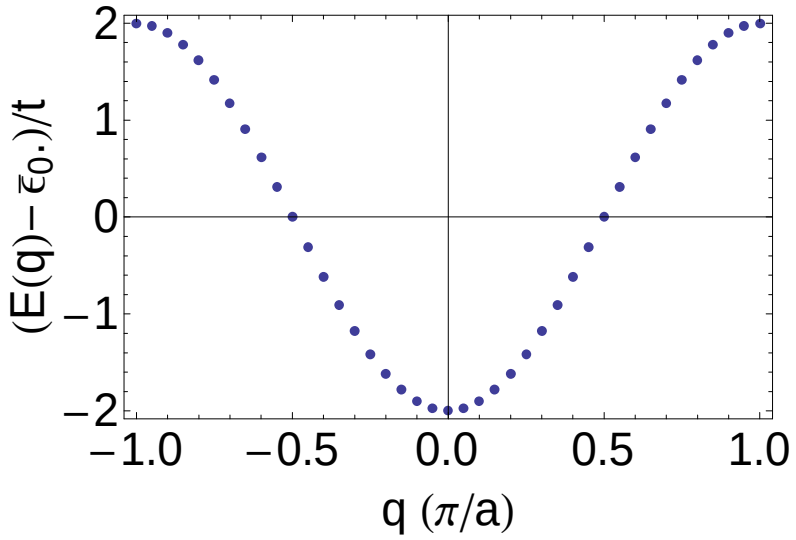
- Aproximação adicional: apenas n ±1 contribuem para as integrais (“1os vizinhos”).

- Definimos:

$$\bar{\epsilon}_0 = \epsilon_0 + \int \phi^*(x)\ \Delta V(x) \phi(x)\ dx \qquad \text{e} \qquad t = -\int \phi^*(x)\ \Delta V(x) \phi(x \pm a)\ dx$$

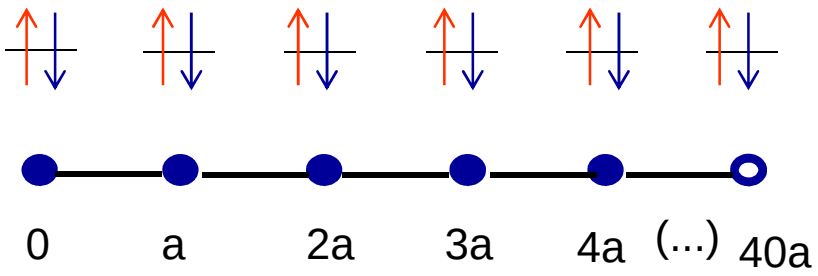
O resultado é a dispersão de tight-binding:

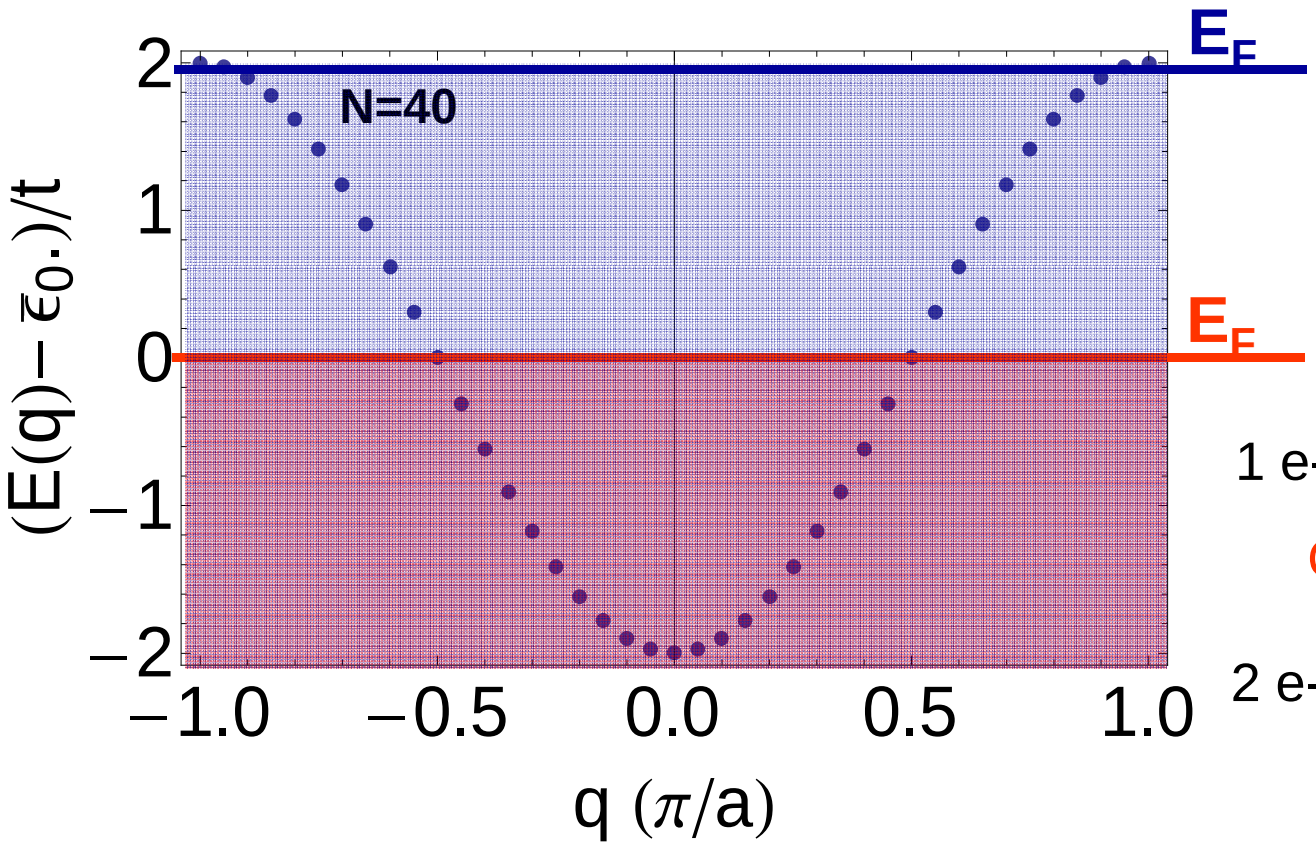
$$E(q) = \bar{\epsilon}_0 - 2t \cos(qa)$$



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