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Two-dimensional (2D) materials

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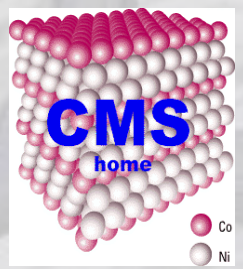

FOM

a crash course in solid state electronic structure theory

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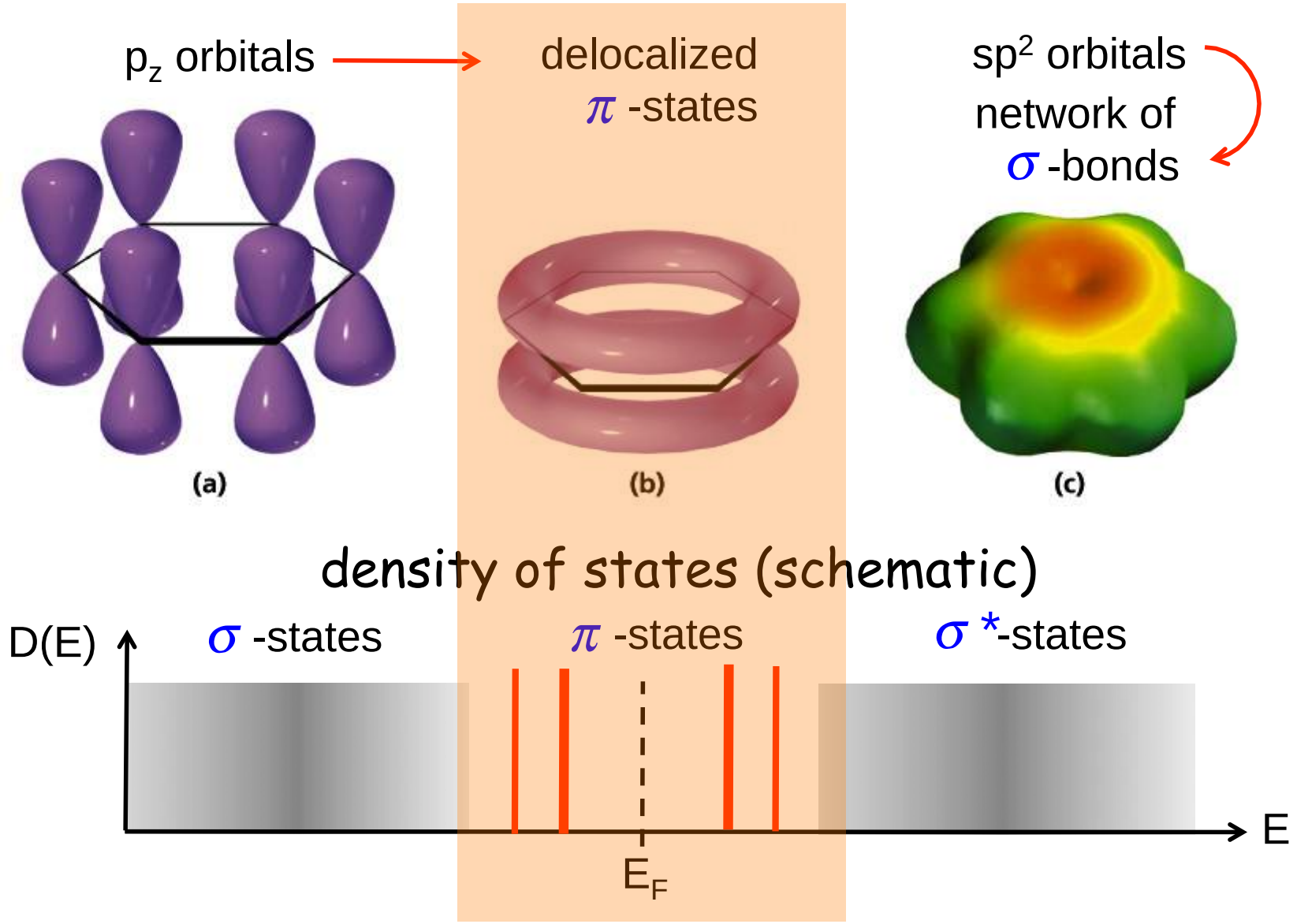
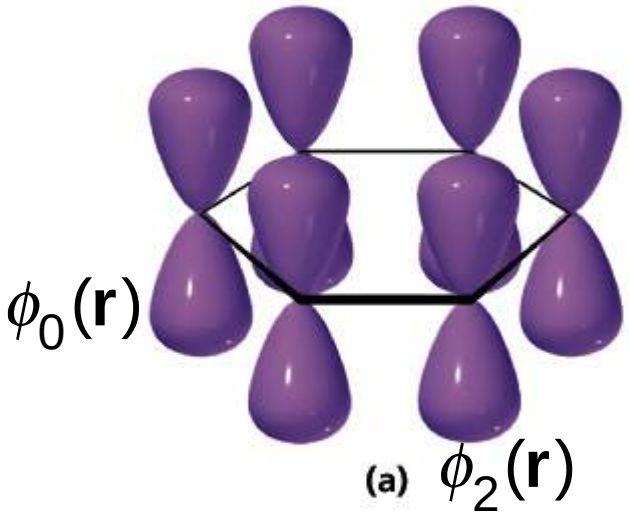
The benzene molecule

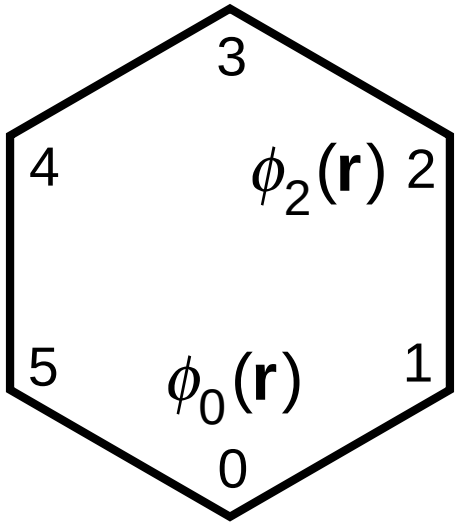


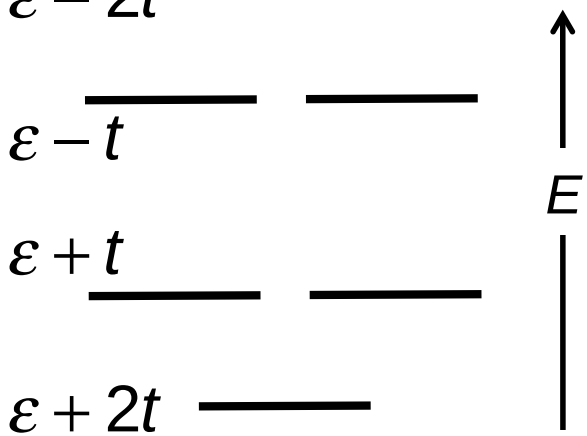
The benzene molecule: Hückel for π-states

$$\Psi_m(\mathbf{r}) = \sum_{n=0}^{5} c_n \phi_n(\mathbf{r})$$

eigenvalues







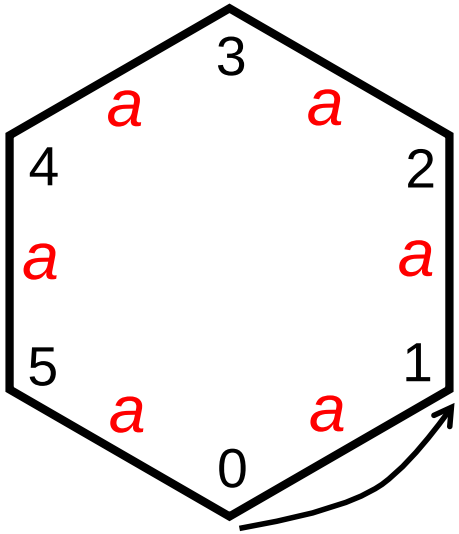
$$\hat{H}\Psi_m(\mathbf{r}) = E_m \Psi_m(\mathbf{r}) \rightarrow \underline{H}\,\underline{c}_m = E_m \underline{c}_m$$

6 X 6 problem

$$\left[\underline{H}\right]_{nn} = \left\langle \phi_n \middle| \hat{H} \middle| \phi_n \right\rangle \equiv \varepsilon \qquad \left[\underline{H}\right]_{nn\pm1} = \left\langle \phi_n \middle| \hat{H} \middle| \phi_{n\pm1} \right\rangle \equiv t$$

$$\left[\underline{H}\right]_{np} = 0; p \neq n, n \pm 1$$

Hückel for π-states: the solid state way



basis set transformation

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{6}} \sum_{n=0}^{5} e^{ikR_n}\, \phi_n(\mathbf{r}) \begin{cases} R_n = na; n = 0,\ldots,5 \\ k = m\frac{2\pi}{6a}; m = 0,\ldots,5 \end{cases}$$

$$[U]_{kn} = \frac{1}{\sqrt{6}} e^{ikR_n}$$ is a unitary transformation

$$\langle \psi_{k'} | \psi_k \rangle = \delta_{k'k}$$

Hamiltonian becomes diagonal

$$[\underline{H}]_{k'k} = \langle \psi_{k'} | \hat{H} | \psi_k \rangle = \delta_{k'k} \left(\varepsilon + 2t\cos(ka) \right)$$

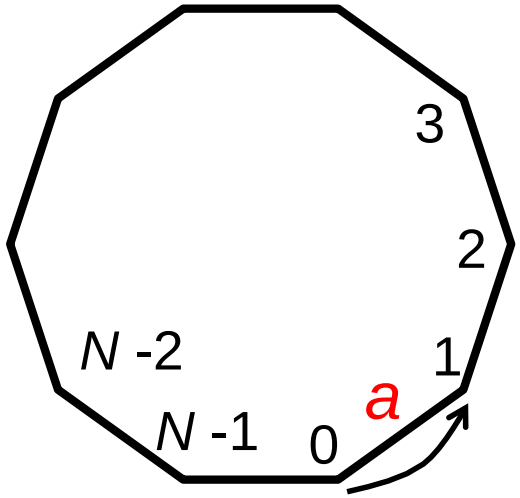
eigenvalues

$$E_k = \varepsilon + 2t\cos(ka)$$

eigenstates

$$\psi_k(\mathbf{r})$$ "Bloch states"

solid state way: works for any ring



basis set transformation

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{ikR_n}\, \phi_n(\mathbf{r}) \begin{cases} R_n = na; n = 0,\ldots,N-1 \\ k = m\frac{2\pi}{Na}; m = 0,\ldots,N-1 \end{cases}$$

$$[U]_{kn} = \frac{1}{\sqrt{N}} e^{ikR_n}$$ is a unitary transformation

$$\langle \psi_{k'} | \psi_k \rangle = \delta_{k'k}$$

Hamiltonian becomes diagonal

$$[\underline{H}]_{k'k} = \langle \psi_{k'} | \hat{H} | \psi_k \rangle = \delta_{k'k} \left(\varepsilon + 2t\cos(ka) \right)$$

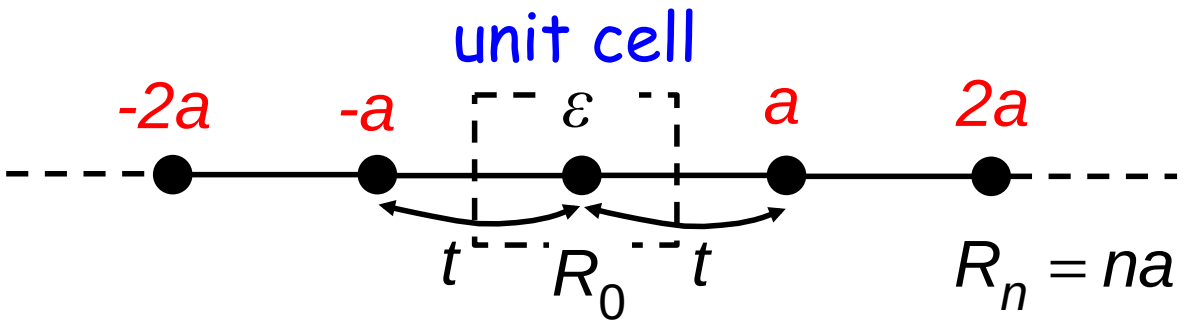
eigenvalues

$$E_k = \varepsilon + 2t\cos(ka)$$

eigenstates

$\psi_k(\mathbf{r})$ "Bloch states"

my first band structure: 1D periodic lattice



Born-von Karman boundary condition

$$R_{n+N} = R_n$$

ring-like topology

Bloch states

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N} e^{ikR_n}\, \phi_n(\mathbf{r}) \qquad k = m\,\Delta k; \quad \Delta k = \frac{2\pi}{Na}$$

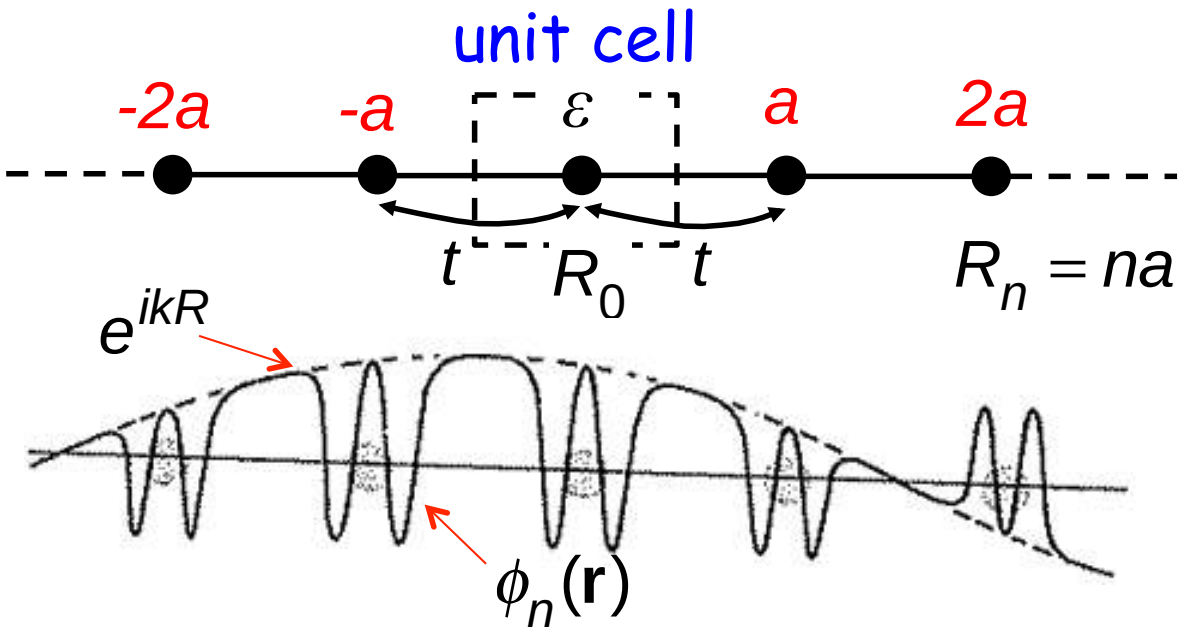
eigenvalues $E_k = \varepsilon + 2t\cos(ka)$

are periodic in k $\quad E_{k+N\,\Delta k} = E_k \qquad \psi_{k+N\,\Delta k}(\mathbf{r}) = \psi_k(\mathbf{r})$

interval containing all information $\quad k \in \left(-\frac{\pi}{a}; \frac{\pi}{a}\right]$

"Brillouin zone"

my first band structure: 1D periodic lattice



Bloch states are waves

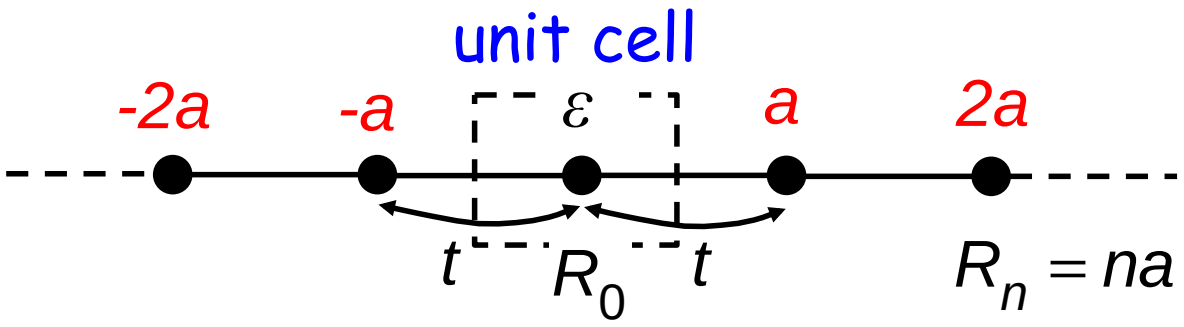
$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n=0}^{N} e^{ikR_n}\, \phi_n(\mathbf{r})$$

"dispersion relation" $E_k = \hbar\omega_k = \varepsilon + 2t\cos(ka)$

group velocity of electron waves $v_g = \dfrac{d\omega_k}{dk}$

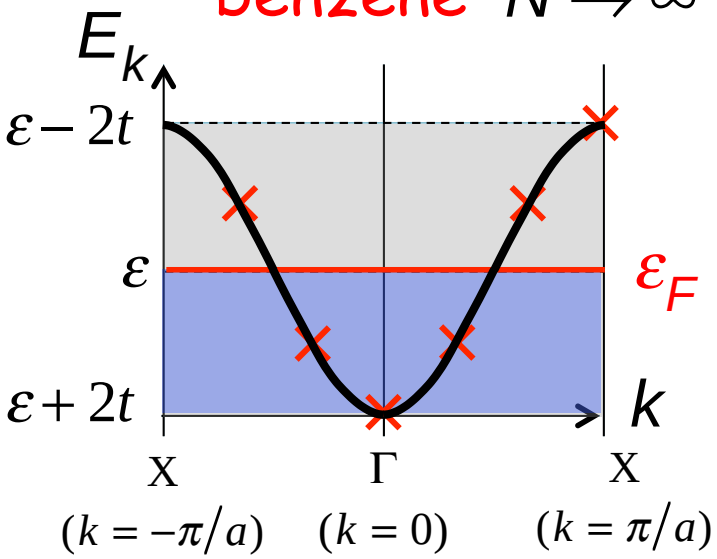
QM particle wave duality $p = \hbar k$ ⇒ electric and heat conduction

my first band structure: 1D periodic lattice



eigenvalues $E_k = \varepsilon + 2t\cos(ka)$ $\quad k \in \left(-\frac{\pi}{a};\frac{\pi}{a}\right]$

benzene $N \to \infty$



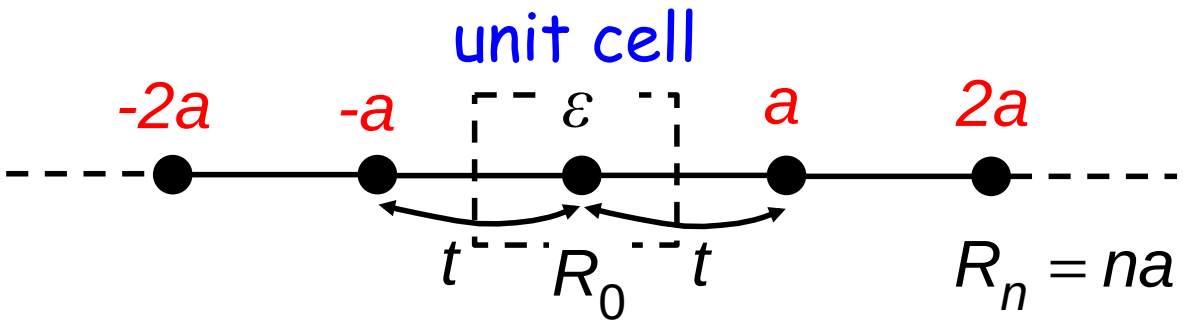
(energy) band

filled states

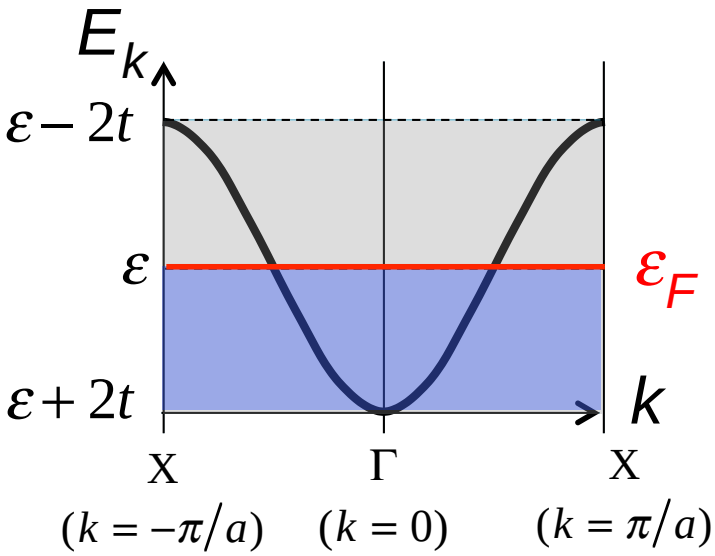
Fermi energy = energy of highest filled state

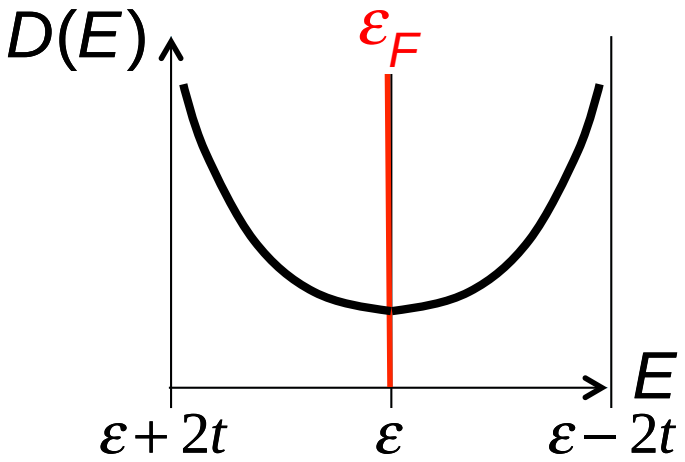
Fermi energy cuts through a band -> a metal !!

my first band structure: 1D periodic lattice



density of states: number of energy levels per unit energy

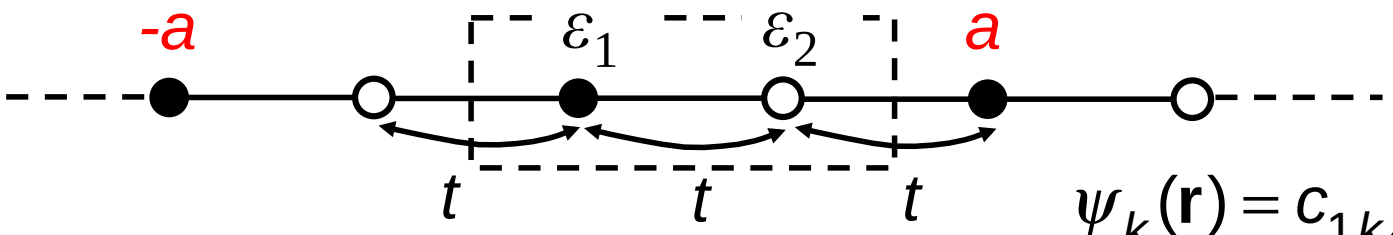




total energy $$E_{tot} = 2\sum_{k}^{occ} E_k = \int_{-\infty}^{\varepsilon_F} E\, D(E)\, dE$$

my second band structure: a semiconductor

unit cell: atoms 1,2 $\varepsilon_1 < \varepsilon_2$



Bloch state

$$\psi_k(\mathbf{r}) = c_{1,k}\chi_{1,k}(\mathbf{r}) + c_{2,k}\chi_{2,k}(\mathbf{r})$$

Bloch orbitals

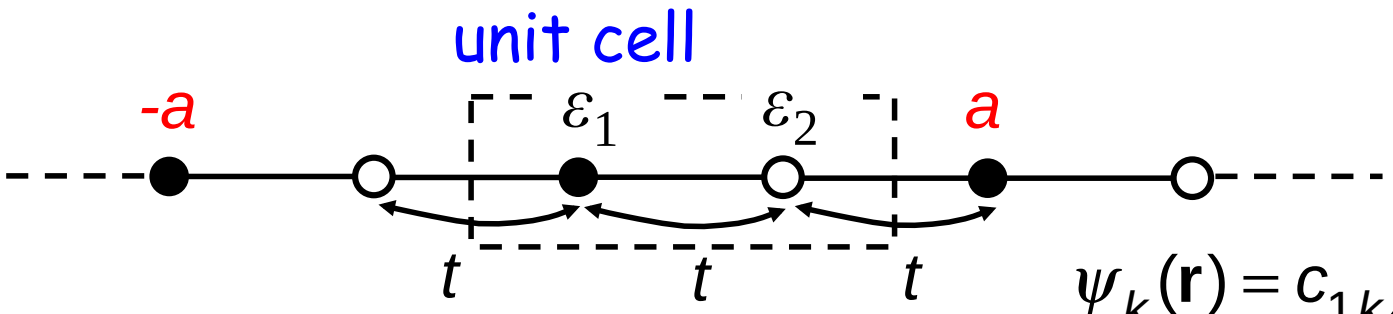
$$\chi_{1,k}(\mathbf{r}) = \sum_{n=0}^{N} e^{ikR_n}\,\phi_{1,n}(\mathbf{r}) \qquad \chi_{2,k}(\mathbf{r}) = \sum_{n=0}^{N} e^{ikR_n}\,\phi_{2,n}(\mathbf{r})$$

Hamiltonian matrix

$$\underline{H}_k = \begin{bmatrix} \langle\phi_{1,0}|\hat{H}|\chi_{1,k}\rangle & \langle\phi_{1,0}|\hat{H}|\chi_{2,k}\rangle \\ \langle\phi_{2,0}|\hat{H}|\chi_{1,k}\rangle & \langle\phi_{2,0}|\hat{H}|\chi_{2,k}\rangle \end{bmatrix} = \begin{bmatrix} \varepsilon_1 & t\left(1+e^{-ika}\right) \\ t\left(1+e^{ika}\right) & \varepsilon_2 \end{bmatrix}$$

Bloch vector $\underline{c}_k = \begin{bmatrix} \langle\phi_{1,0}|\psi_k\rangle \\ \langle\phi_{2,0}|\psi_k\rangle \end{bmatrix} = \begin{bmatrix} c_{1,k} \\ c_{2,k} \end{bmatrix}$

my second band structure: a semiconductor



$$\psi_k(\mathbf{r}) = c_{1,k}\chi_{1,k}(\mathbf{r}) + c_{2,k}\chi_{2,k}(\mathbf{r})$$

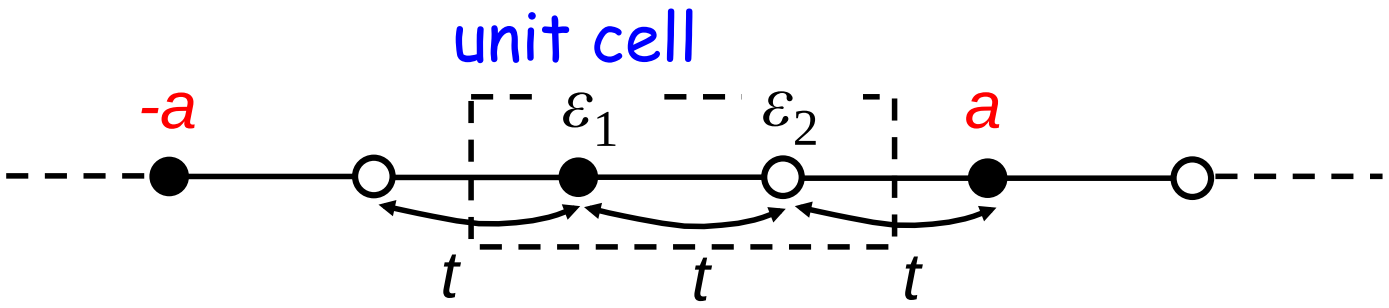
Hückel

$$\underline{H}_k \underline{c}_k = E_k \underline{c}_k \rightarrow \begin{bmatrix} \varepsilon_1 & t_k \\ t_k^* & \varepsilon_2 \end{bmatrix} \begin{bmatrix} c_{1,k} \\ c_{2,k} \end{bmatrix} = E_k \begin{bmatrix} c_{1,k} \\ c_{2,k} \end{bmatrix} \qquad t_k = t\left(1 + e^{-ika}\right)$$

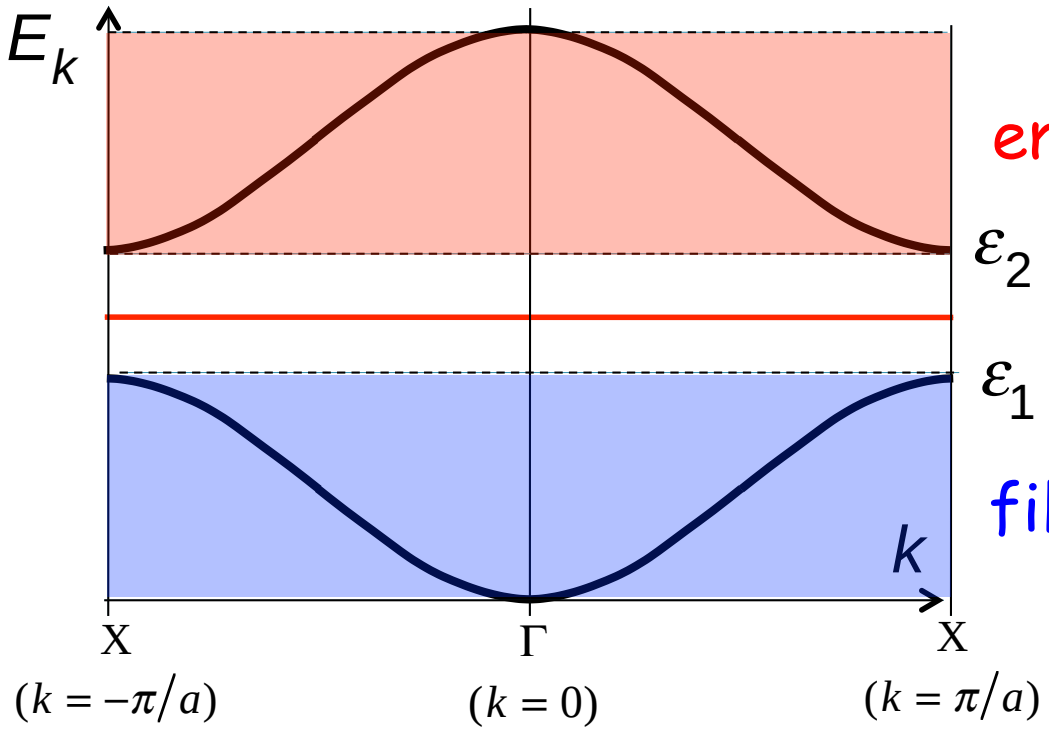
eigenvalues $$E_k^{\pm} = \frac{1}{2}\left(\varepsilon_1 + \varepsilon_2\right) \pm \left[\frac{1}{4}\left(\varepsilon_1 - \varepsilon_2\right)^2 + \left|t_k\right|^2\right]^{\frac{1}{2}}$$

$$\left|t_k\right|^2 = 4t^2 \cos^2\left(\frac{ka}{2}\right)$$

my second band structure: a semiconductor



eigenvalues $E = \frac{1}{2}\left(\varepsilon_1 + \varepsilon_2\right) \pm \left[\frac{1}{4}\left(\varepsilon_1 - \varepsilon_2\right)^2 + 4t^2 \cos^2\left(\frac{ka}{2}\right)\right]^{\frac{1}{2}}$



ε_F
Fermi energy

Fermi energy in band gap-> an insulator/semiconductor !!