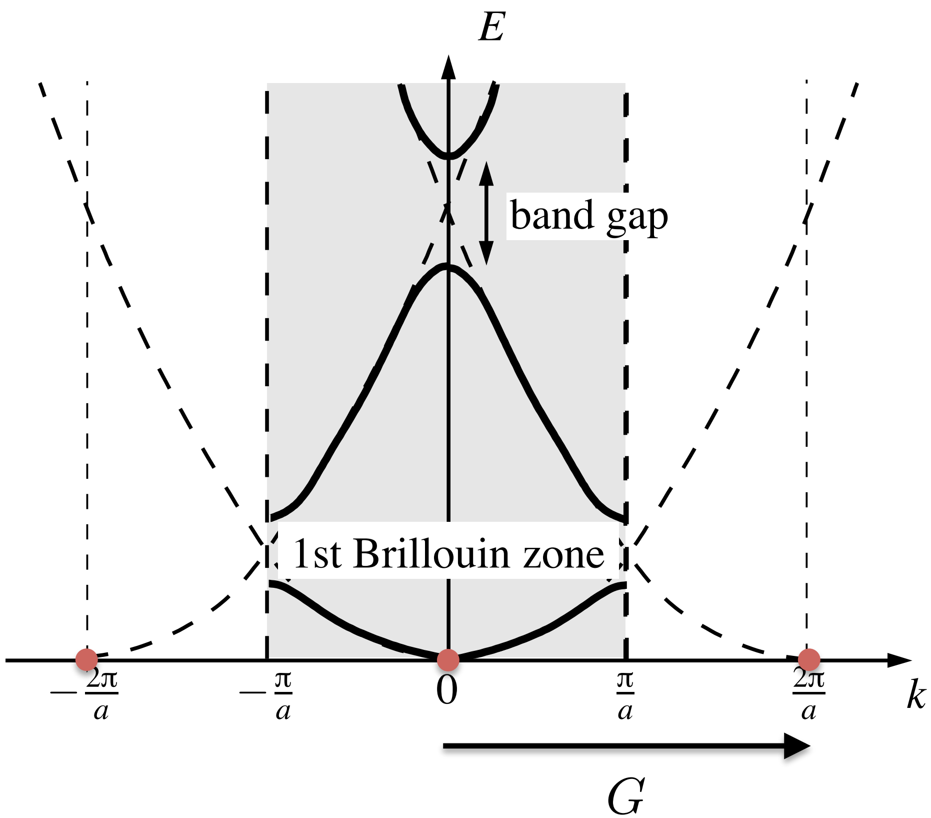
nearly free electron approximation

Bloch equation

$$\left(\frac{(\hat{\vec{p}} + \hbar\vec{k})^2}{2m} + V(\hat{\vec{r}})\right) u_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} u_{\vec{k}}(\vec{r})$$



periodic potential

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

periodic Bloch function

$$u_{\vec{k}}(\vec{r}) \stackrel{\rightarrow}{=} \sum_{\vec{G}} c_{\vec{G}} e^{-i\vec{G}\cdot\vec{r}},$$

$$\left(\frac{\hbar^2}{2m}(\vec{k} - \vec{G})^2 - \epsilon_{\vec{k}}\right) c_{\vec{G}} + \sum_{\vec{G}'} V_{\vec{G}'-\vec{G}} c_{\vec{G}'} = 0$$

tight-binding approximation

starting point: atomic limit

$$\mathcal{H}_a(\vec{R})\phi_n(\vec{r}-\vec{R}) = \epsilon_n \phi_n(\vec{r}-\vec{R})$$

atom at position $\vec{R}$

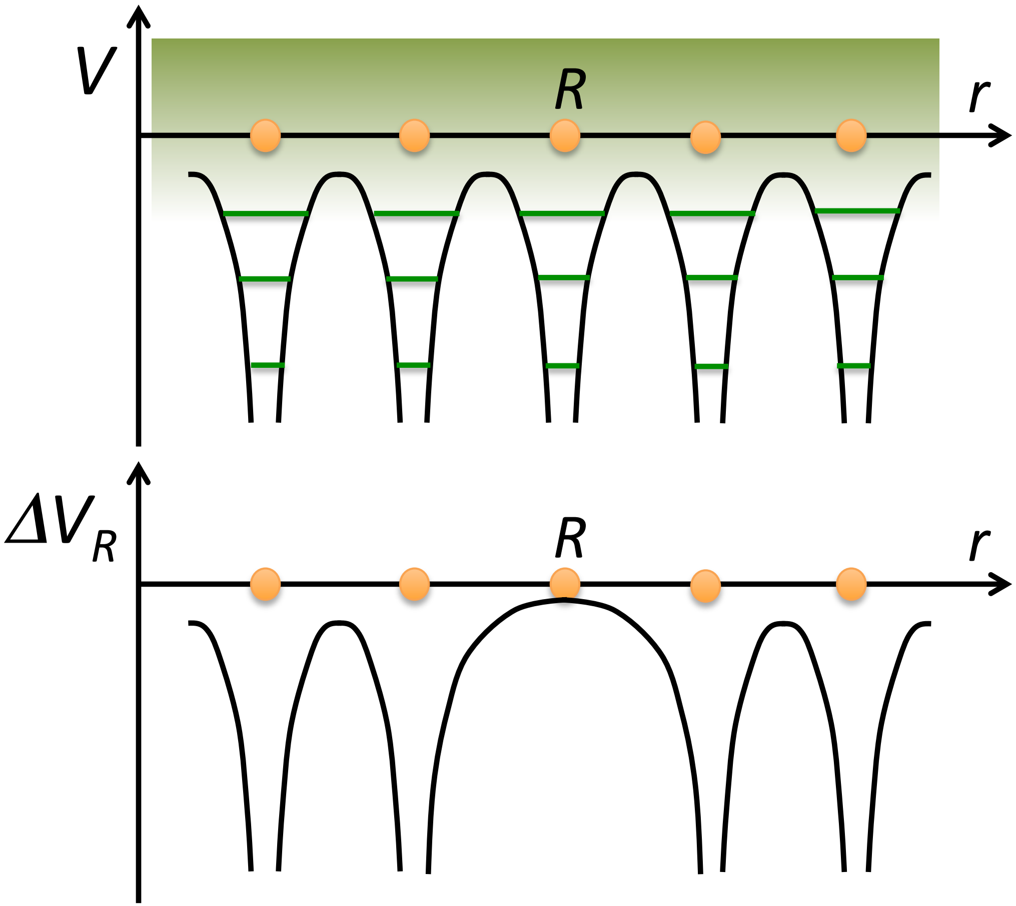
$$\mathcal{H}_a(\vec{R}) = \frac{\hat{\vec{p}}^2}{2m} + V_a(\vec{r}-\vec{R})$$

regular array of atoms

$$\mathcal{H} = \frac{\hat{\vec{p}}^2}{2m} + \sum_{\vec{R}_j} V_a(\vec{r}-\vec{R}_j)$$

$$= \mathcal{H}_a(\vec{R}) + \Delta V_{\vec{R}}(\vec{r})$$

$$\Delta V_{\vec{R}_j}(\vec{r}) = \sum_{\vec{R}_{j'} \neq \vec{R}} V_a(\vec{r}-\vec{R}_{j'})$$



Linear combination of atomic orbitals (LCAO)

$$\psi_{\tilde{n}\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_j} e^{i\vec{k}\cdot\vec{R}_j} \phi_{\tilde{n}}(\vec{r} - \vec{R}_j)$$

Bloch function

norm:
$$\langle 1 \rangle_{\tilde{n}\tilde{n}'}(\vec{k}) = \int d^3r \psi_{\tilde{n}\vec{k}}(\vec{r})^* \psi_{\tilde{n}'\vec{k}}(\vec{r}) = \frac{1}{N} \sum_{\vec{R}_j, \vec{R}_{j'}} \int d^3r e^{i\vec{k}\cdot(\vec{R}_{j'} - \vec{R}_j)} \phi^*_{\tilde{n}}(\vec{r} - \vec{R}_j) \phi_{\tilde{n}'}(\vec{r} - \vec{R}_{j'})$$

$$= \sum_{\vec{R}_j} \int d^3r e^{-i\vec{k}\cdot\vec{R}_j} \phi^*_{\tilde{n}}(\vec{r} - \vec{R}_j) \phi_{\tilde{n}'}(\vec{r})$$

$$= \delta_{\tilde{n}\tilde{n}'} + \sum_{\vec{R}_j \neq 0} e^{-i\vec{k}\cdot\vec{R}_j} \alpha_{\tilde{n}\tilde{n}'}(\vec{R}_j) \qquad \alpha_{nn'}(\vec{R}) \ll 1$$

Hamiltonian:

$$\langle \mathcal{H} \rangle_{\tilde{n}\tilde{n}'}(\vec{k}) = \frac{1}{N} \sum_{\vec{R}_j, \vec{R}_{j'}} \int d^3r e^{i\vec{k}\cdot(\vec{R}_{j'} - \vec{R}_j)} \phi^*_{\tilde{n}}(\vec{r} - \vec{R}_j) \{H_a(\vec{R}_{j'}) + \Delta V_{\vec{R}_{j'}}(\vec{r})\} \phi_{\tilde{n}'}(\vec{r} - \vec{R}_{j'})$$

$$= E_{\tilde{n}'} \langle 1 \rangle_{\tilde{n}\tilde{n}'}(\vec{k}) + \Delta E_{\tilde{n}\tilde{n}'} + \sum_{\vec{R}_j \neq 0} e^{-i\vec{k}\cdot\vec{R}_j} \gamma_{\tilde{n}\tilde{n}'}(\vec{R}_j)$$

$$\Delta E_{\tilde{n}\tilde{n}'} = \int d^3r \phi^*_{\tilde{n}}(\vec{r}) \Delta V_{\vec{R}_{j'}=0}(\vec{r}) \phi_{\tilde{n}'}(\vec{r}) \qquad \gamma_{\tilde{n}\tilde{n}'}(\vec{R}_j) = \int d^3r \phi^*_{\tilde{n}}(\vec{r} - \vec{R}_j) \Delta V_{\vec{R}_{j'}=0}(\vec{r}) \phi_{\tilde{n}'}(\vec{r})$$

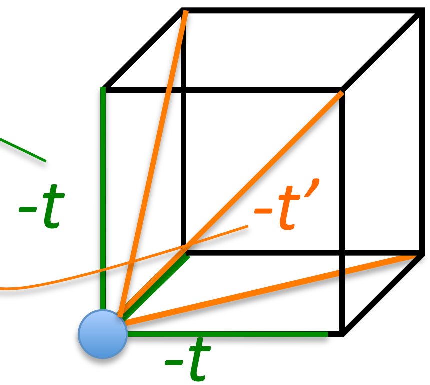
tight-binding approximation

energy spectrum $$det\left[\langle\mathcal{H}\rangle_{\tilde{n}\tilde{n}'}(\vec{k})-\epsilon_{\vec{k}}\langle 1\rangle_{\tilde{n}\tilde{n}'}(\vec{k})\right]=0$$

band structure of s-orbitals in simple cubic lattice

$$\phi_s(\vec{r})=\phi_s(r)$$

$$\gamma_{ss}(\vec{R}_j)=\begin{cases}-t & \vec{R}_j \text{ nearest neighbors}\\ -t' & \vec{R}_j \text{ next-nearest neighbors}\end{cases}$$



$$\epsilon_{\vec{k}}=E_s+\Delta E_s-t\sum_{\vec{R}_j}^{n.n.}e^{-i\vec{k}\cdot\vec{R}_j}-t'\sum_{\vec{R}_j}^{n.n.n.}e^{-i\vec{k}\cdot\vec{R}_j}$$

$$=E_s+\Delta E_s-2t\{\cos(k_xa)+\cos(k_ya)+\cos(k_za)\}$$

$$-4t'[\cos(k_xa)\cos(k_ya)+\cos(k_ya)\cos(k_za)+\cos(k_za)\cos(k_xa)\}$$

tight-binding approximation

band structure of p-orbitals in simple cubic lattice

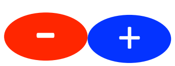
$$\phi_x(\vec{r}) = x\varphi(r), \; \phi_y(\vec{r}) = y\varphi(r), \; \phi_z(\vec{r}) = z\varphi(r)$$

nearest neighbors

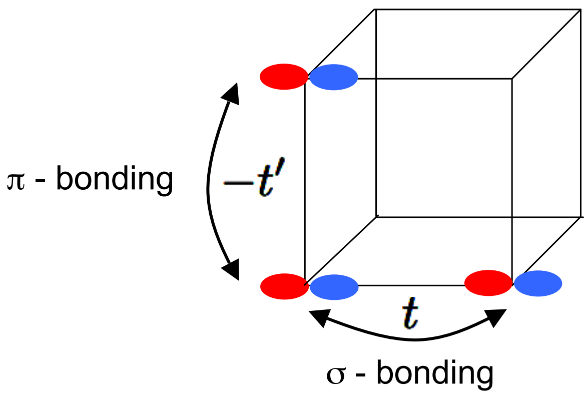
next- nearest neighbors

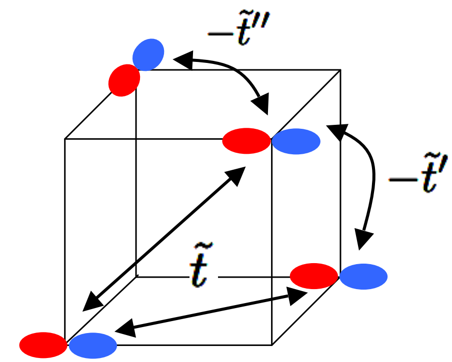
Important:

phase structure
of wave function

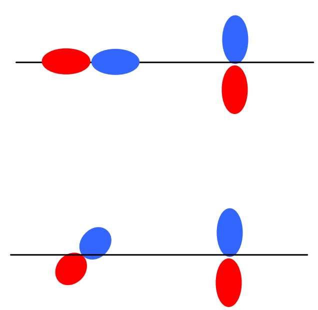


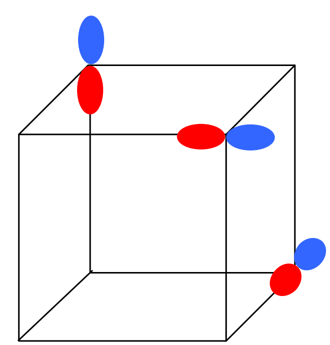
p-orbital





no coupling





tight-binding approximation

band structure of p-orbitals in simple cubic lattice

$$\langle \mathcal{H} \rangle_{\tilde{n}\tilde{n}'} = \begin{pmatrix} E_x(\vec{k}) & -4\tilde{t}'' \sin(k_x a) \sin(k_y a) & -4\tilde{t}'' \sin(k_x a) \sin(k_z a) \\ -4\tilde{t}'' \sin(k_x a) \sin(k_y a) & E_y(\vec{k}) & -4\tilde{t}'' \sin(k_y a) \sin(k_z a) \\ -4\tilde{t}'' \sin(k_x a) \sin(k_z a) & -4\tilde{t}'' \sin(k_y a) \sin(k_z a) & E_z(\vec{k}) \end{pmatrix}$$

$$E_x(\vec{k}) = E_p + \Delta E_p + 2t \cos(k_x a) - 2t' (\cos(k_y a) + \cos(k_z a))$$

$$+ 4\tilde{t} \cos(k_x a)(\cos(k_y a) + \cos(k_z a)) - 4\tilde{t}' \cos(k_y a) \cos(k_z a)$$

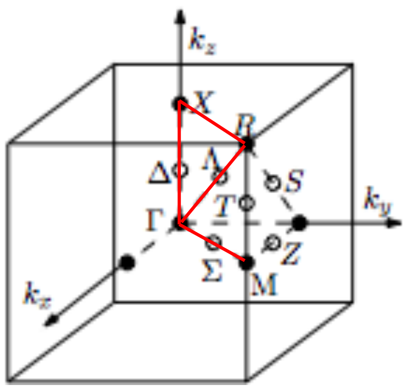
$\vec{k} \cdot \vec{p}$ - approximation at Γ-point (k=0)

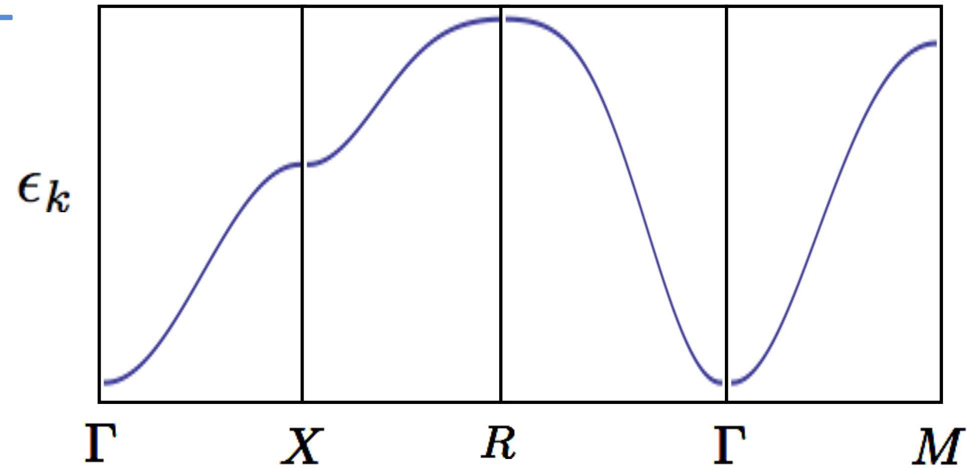
$$\langle \mathcal{H} \rangle_{\tilde{n}\tilde{n}'} = E_\Gamma + \begin{pmatrix} Ak_x^2 + B(k_y^2 + k_z^2) & Ck_x k_y & Ck_x k_z \\ Ck_x k_y & Ak_y^2 + B(k_z^2 + k_x^2) & Ck_y k_z \\ Ck_x k_z & Ck_y k_z & Ak_z^2 + B(k_x^2 + k_y^2) \end{pmatrix}$$

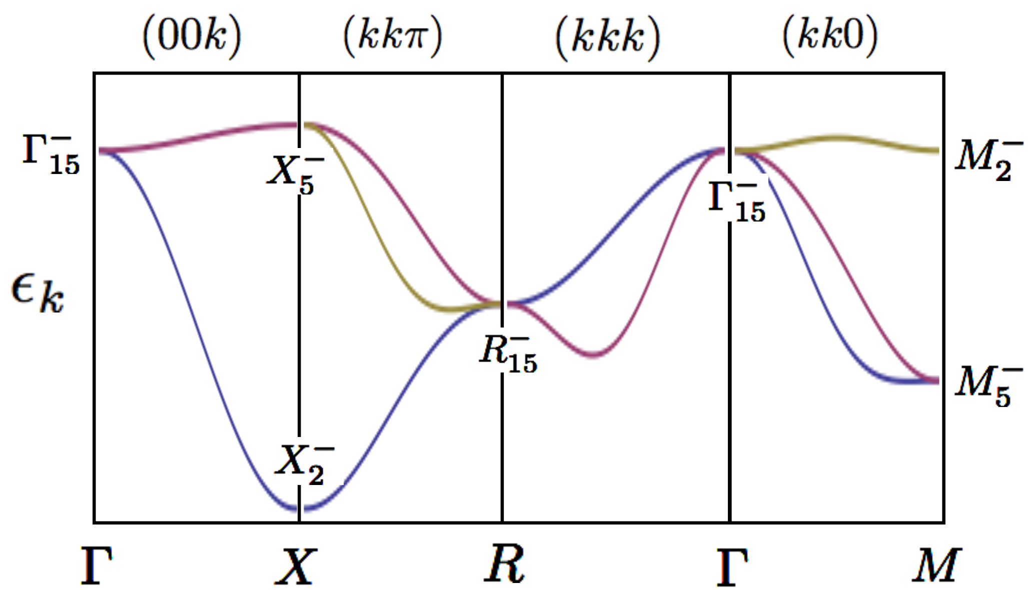
energy bands in 1st BZ

s-orbitals

$t' = 0.2t$







p-orbitals

$t' = 0.2t$ $\quad \tilde{t}' = 0.05t$

$\tilde{t} = 0.1t$ $\quad \tilde{t}'' = 0.15t$