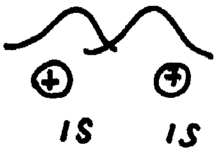
Lect 7: tight-binding method

§: bonds v.s. bands

↗ Pauling

H_2



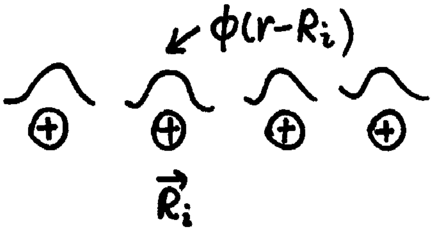
strong potential

atomic orbitals 1S, 2S, 2P, ····

in the lattice, orbitals from different atoms overlap such that electrons can hop.

bands — plane wave basis works better for weak periodical lattice
metal

bonds — strong potential, — suitable for insulator, or metal/insulator tranition.



we consider the space spanned by the atomic orbits $\phi(\vec r-\vec R_i)$ $i=1, \cdots N$

$$\psi(r) = \sum_{R_i} e^{ikR_i}\,\phi(r-\vec R_i)$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \sum_i V(\vec r-\vec R_i) = \underbrace{-\frac{\hbar^2\nabla^2}{2m} + V(\vec r-\vec R_i)}_{H_{at}} + \Delta V(\vec r-\vec R_i)$$

$$H\psi(r) = \sum_{R_i} e^{ikR_i}\,(H_{at}+\Delta V)\,\phi(\vec r-\vec R_i) = \mathcal{E}\sum_{R_i} e^{ikR_i}\phi(\vec r-\vec R_i) + \sum_{R_i} e^{ikR_i}\,\Delta V(i)\phi(\vec r-\vec R_i)$$

$$= \mathcal{E}(k)\sum_{R_i} e^{ikR_i}\,\phi(\vec r-\vec R_i)$$

$$\Rightarrow (\mathcal{E}(k)-\mathcal{E})\sum_{R_i} e^{ikR_i}\,\phi(\vec r-\vec R_i) = \sum_{R_i} e^{ikR_i}\,\Delta V(i)\,\phi(\vec r-\vec R_i)$$

$$(\mathcal{E}(k)-\mathcal{E})\sum_{R_i} e^{ikR_i}\int dr\,\phi^*(\vec r-R_j)\,\phi(r-\vec R_i) = \sum_{R_i} e^{ikR_i}\int dr\,\phi^*(\vec r-R_j)\,\Delta V(i)\,\phi(\vec r-\vec R_i)$$

shift $R_i \to R_i - R_j$

$$(\mathcal{E}(k) - \mathcal{E})\, e^{ikR_j} \sum_R \underset{e^{ik\vec{R}}}{\int dr\, \phi^*(\vec{r})\, \phi(r-\vec{R})} = e^{ikR_j} \sum_R \int dr\, e^{ik\vec{R}}\, \phi^*(\vec{r})\, \Delta V(\vec{r}-\vec{R})\, \phi(\vec{r}-\vec{R})$$

$$\Rightarrow (\mathcal{E}(k) - \mathcal{E}) \left[1 + \sum_{R \neq 0} \alpha(R)\, e^{i\vec{k}\cdot\vec{R}} \right] = \underset{\sum_R e^{i\vec{k}\cdot\vec{R}}}{\int dr\, \phi^*(r)\, \Delta V(\vec{r}-\vec{R})\, \phi(\vec{r}-\vec{R})}$$

$$= \sum_R e^{i\vec{k}\cdot\vec{R}} \int dr\, \phi^*(\vec{r}+\vec{R})\, \Delta V(\vec{r})\, \phi(r)$$

$$\Rightarrow \mathcal{E}(k) - \mathcal{E} = \frac{\int dr\, \phi^*(\vec{r})\, \Delta V(\vec{r})\, \phi(r) + \sum_{R \neq 0} \underline{\int dr\, \phi^*(\vec{r}+\vec{R})\, \Delta V(\vec{r})\, \phi(\vec{r})}\, e^{i\vec{k}\cdot\vec{R}}}{1 + \sum_{R_i \neq 0} e^{i\vec{k}\cdot\vec{R}_i} \int dr\, \phi^*(\vec{r}+\vec{R}_i)\, \phi(\vec{r})}$$

assume $\int dr\, \phi^*(\vec{r}+\vec{R}_i)\, \phi(\vec{r}) = 0$, (very small

$$\Rightarrow \mathcal{E}(k) = \mathcal{E} + \underbrace{\int dr\, \Delta V(r)\, |\phi(r)|^2} + \sum_{R \neq 0} e^{i\vec{k}\cdot\vec{R}} \underbrace{\int dr\, \phi^*(\vec{r}+\vec{R})\, \Delta V(r)\, \phi(\vec{r}}$$

$\beta \nearrow$ shift due to other sites

$-\gamma(R)$: hopping integr

$$\gamma(R) = \int dr\, \phi^*(\vec{r}+\vec{R})\, \Delta V(r)\, \phi(r)$$

$$\gamma(-R) = \int dr\, \phi^*(\vec{r}-\vec{R})\, \Delta V(r)\, \phi(\vec{r}) = \int dr\, \phi^*(-\vec{r}-\vec{R})\, \Delta V(-\vec{r})\, \phi(-\vec{r})$$

$= \gamma(R)$ if inversion symmetry

$$\Rightarrow \boxed{\mathcal{E}(k) = \mathcal{E} - \beta - \sum_{\vec{R} \neq 0} \cos \vec{k}\cdot\vec{R}\ \gamma(\vec{R})}$$

§: second quantization form

$$t_{ij} = \gamma(\vec{R}_i - \vec{R}_j)$$

$$H = -\sum_{ij} t_{ij}\, C_i^\dagger C_j$$

$$\cdot \quad C_i = \frac{1}{\sqrt{N}} \sum e^{i\vec{k}\cdot\vec{R}_i}\, C_{\vec{k}}$$

$$\Rightarrow H = -\frac{1}{N}\sum_{ij}\sum_{kk'} e^{-i\vec{k}\cdot\vec{R}_i}\, e^{i\vec{k}'\cdot R_j}\, t_{ij}\, C_k^\dagger C_{k'}$$

$$= -\frac{1}{N}\sum_{i}\sum_{kk'} e^{-i(k-k')\cdot R_i} \sum_{R_j} e^{i\vec{k}'\cdot(\vec{R}_j-\vec{R}_i)}\, t_{ij}\, C_k^\dagger C_{k'}$$

$$= -\frac{1}{N}\sum_{kk'} C_k^\dagger C_{k'} \left(\sum_i e^{-i(k-k')\cdot R_i}\right) \sum_{\vec{R}} e^{i\vec{k}'\cdot\vec{R}}\, t(\vec{R}).$$

$$= -\sum_{kk'} \delta_{KK'}\, C_k^\dagger C_{k'} \sum_{R'} e^{i\vec{k}'\cdot\vec{R}}\, \overset{\frown}{t(\vec{R})}$$

$$= -\sum_{k} \left(\sum_{R} t(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}\right) C_k^\dagger C_k$$

$$\Rightarrow \mathcal{E}(k) = -\sum_{R} t(\vec{R})\, e^{i\vec{k}\cdot\vec{R}} \xrightarrow[\substack{nn \\ \text{Cubic lattice}}]{} -2t \sum_{\vec{\delta}=x,y,z} \cos \vec{k}\cdot\vec{\delta}$$

- Wannier wave function

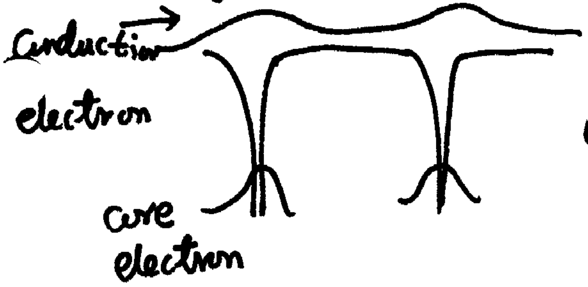
$$\varphi_i(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{k\in BZ} e^{i\vec{k}\cdot\vec{R}_i}\, \psi_{\vec{k}}(\vec{r}) \leftarrow$$

very close to atomic orbit func.

— discreate Fourier transform. $\langle \varphi_i(\vec{r}) \mid \varphi_j(\vec{r}) \rangle = \delta_{ij}$

orthogonal

§ orthogonal plane-wave (OPW)



the ionic potential is very sharp. we need to use a lot of plane basis because $V(\vec{G})$ has a lot of high momentum component

If we do so, certainly we can get all the spectra and eigenfunc, which include the core electrons. But we are not interested in core electrons, which are localized. The outer shell bands are very delocalized, we don't need so much component.

we design

$$\phi_k = e^{i\vec{k}\cdot\vec{r}} + \sum_c b_c \psi_k^c(r)$$

to be determined

core wavefunction

$$\psi_k^c(r) = \sum_{R_i} e^{i\vec{k}\cdot R_i} \psi(\vec{r}-\vec{R}_i)$$

and require

$$\int dr\, \phi_k^*(r)\psi_k^c(r) = 0 \Rightarrow b_c = -\int dr\, \psi_k^{c*}(r)\, e^{i\vec{k}\cdot\vec{r}}$$

using this basis of ϕ_k, the matrix element

$$V'(G-G') = \int \phi^*_{k+G}(r)\, V(r)\, \phi_{k+G'}(r)\, dr$$

decays much faster than $V(G-G')$

§ pseudo-potential

conside the exact wavefunction $\psi_k(\vec{r})$, which satisfies

$$H\psi_k^* = \varepsilon_k \psi_k .$$

We write the plane wave part as $\phi_k(r)$

$$\psi_k(r) = \phi_k(r) - \left[\sum_c \int dr' \psi_k^{c*}(r')\, \phi_k(r')\right] \psi_k^c(r) \Rightarrow \int dr\, \psi_k^*(r)\, \psi_k^c(r) = 0$$

$$\Rightarrow H\psi_k(r) = H\phi_k(r) - \sum_c \left(\int dr' \psi_k^{*c}(r')\, \phi_k(r')\right) H\psi_k^c(r)$$

$$= \varepsilon_k \left[\phi_k(r) - \sum_c \int dr' \psi_k^{*c}(r')\, \phi_k(r')) \psi_k^c(r) \right]$$

$$H\psi_k^c(r) = \varepsilon_k^c \psi_k^c$$

$$\Rightarrow H\phi_k(r) + \sum_c \underbrace{(\varepsilon_k - \varepsilon_k^c)\left[\int dr' \psi_k^{*c}(r')\phi_k(r')\right] \psi_k^c(r)}_{\text{pseudo-potential}}$$

$$= \varepsilon_k \phi_k$$

define $V^R \phi_k(r) = \sum_c (\varepsilon_k - \varepsilon_k^c)\left\{\int dr' \psi_k^{*c}(r')\, \phi_k(r')\right\} \psi_k^c(r)$

replace ϕ by ψ

no-local operater

$$\Rightarrow (\psi, V^R\psi) = \sum_c (\varepsilon_k - \varepsilon_k^c) \int dr\, \psi_k^c(r)\, \psi_k^*(r) \int dr'\, \psi_k^{*c}(r')\, \psi_k(r')$$

$$= \sum_c (\varepsilon_k - \varepsilon_k^c) \left| \int dr\, \psi_k^{*c}\, \psi \right|^2 > 0$$

partially compensate the negative core.