© **Brillouin Zone**: Wigner-Seitz cell of the reciprocal lattice

in 1d: •⟷• . $b = \frac{2\pi}{a}$; WS cell: $\left[-\frac{b}{2}, \frac{b}{2}\right] = \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$

BZ = 1st BZ = all points that are closest to a given lattice point.

n^{th} BZ: n^{th} closest to origin.

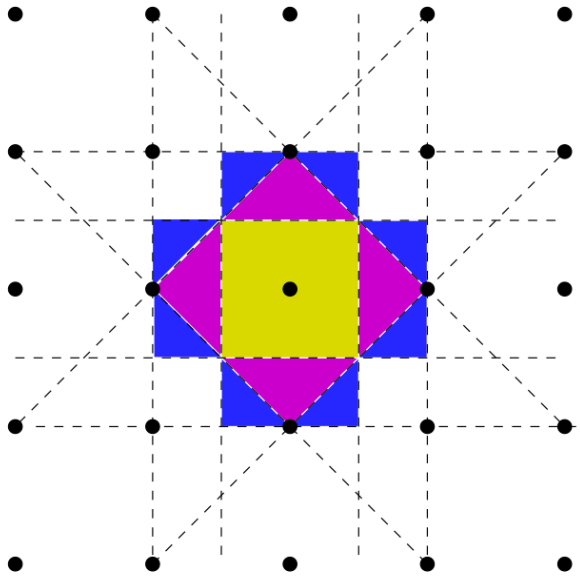


Figure 28: The Brillouin zones for a 2d square lattice. The first is shown in yellow, the second in pink, the third in blue.

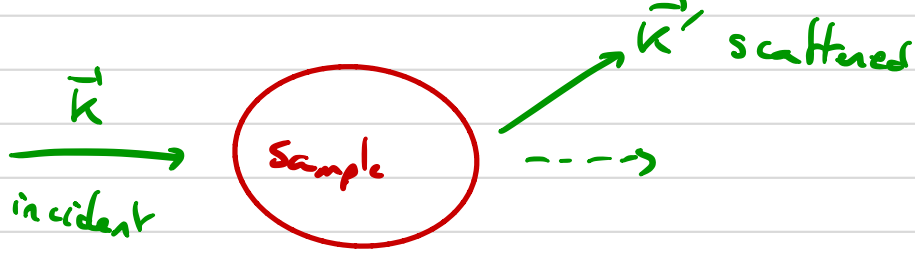
As in 1d, conserved momentum $\in$ 1st BZ.

Reduced zone scheme: higher BZ's are mapped back to the 1st one using $\vec{b}$ vectors.

Crystallographic notation : BZ are 3D for real materials. Choose paths through special points ("Γ", M, R ...)

(III) Wave scattering by crystals

How do we know about crystalline structure?



X-ray, neutrons, e^- etc...

Plane waves see the sample as potential $V(\vec{r})$

Fermi's Golden Rule (rate) $\Gamma_{\vec{k}\to\vec{k}'} = \frac{2\pi}{\hbar} |\langle \vec{k}'|V|\vec{k}\rangle|^2 \times \delta(E_{\vec{k}} - E_{\vec{k}'})$

↳ elastic scattering $|\vec{k}| = |\vec{k}'|$

with $\langle \vec{k}|V|\vec{k}'\rangle = \int d\vec{x}\, d\vec{x}'\, \langle \vec{k}'|\vec{x}'\rangle V(\vec{x}) \underbrace{\delta(\vec{x}-\vec{x}')}_{\langle \vec{x}'|\vec{x}\rangle} \langle \vec{x}|\vec{k}\rangle$

$= \frac{1}{L^3} \int d\vec{x}\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{x}} V(\vec{x}) = FT(V(\vec{x}))$

we already saw:

$$\langle \vec{k}' | V | \vec{k} \rangle = \frac{1}{L^3} \int_{\text{unit cell}} dx^3 \, e^{-i(\vec{k}-\vec{k}')\cdot\vec{x}} \, V(\vec{x}) \times \underbrace{\Delta(\vec{k}-\vec{k}')}_{\sum_{\vec{R}\in\Lambda} e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}}}$$

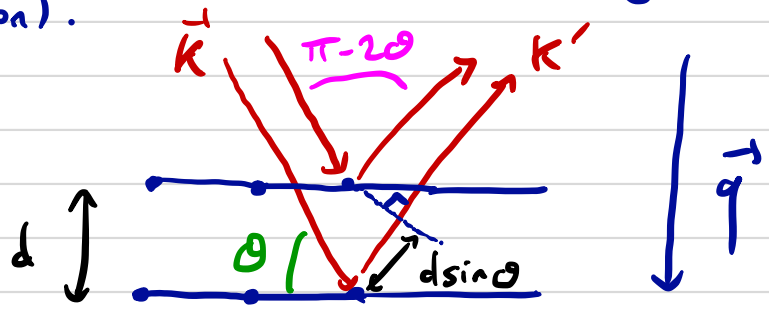
$$= V^* \sum_{\vec{q}\in\Lambda^*} \delta(\vec{k}-\vec{k}'-\vec{q})$$

$$\boxed{\vec{k}-\vec{k}' = \vec{q}} \quad \text{with } \vec{q} \in \Lambda^* \text{ reciprocal vector}$$

Laue condition = crystal momentum conservation

Solutions to this eq aren't generic (for a given $\vec{k}$, chances are there's no solution).

Diffraction picture



$$(\vec{k}-\vec{k}')^2 = q^2 = 2k^2(1-\underbrace{\cos(\pi-2\theta)}_{\cos 2\theta}) = 4k^2\sin^2\theta$$

$$\Rightarrow \quad q = 2k\sin\theta$$

Bragg planes: $\vec{\pi} \in \Lambda$ such that $\vec{\pi}\cdot\vec{q} = 2\pi n$

(recall $e^{i\vec{\pi}\cdot\vec{q}} = 1$) (planes normal to $\vec{q}$)

d = distance between plane $= 2\pi/q$

Wavelength: $\lambda = \frac{2\pi}{k} \Rightarrow \lambda = 2d\sin\theta$

Repeat for $n\vec{q}$: $\boxed{n\lambda = 2d\sin\theta}$ Bragg condition

$\Leftrightarrow$ constructive interferences $n\lambda$ = extra distance (see sketch last page)

Scattering off Bragg planes. Also, $\lambda \sim$ atomic separation $\sim a$

$\Rightarrow$ X-ray

Structure factor: $S(\vec{q}) = \int_T d\vec{x}\, e^{-i\vec{q}\cdot\vec{x}} V(\vec{x})$

(scattering amplitude)

labelled by $\vec{q} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$

(n_1, n_2, n_3)

$V(\vec{x}) = \sum_{j,\text{atoms}} V(\vec{x} - \vec{x}_j)$

↑ form factor

neutrons: $\sim b_j \cdot \delta(\vec{x} - \vec{x}_j)$

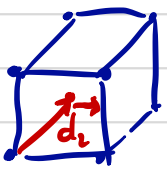
X-ray: scatter off e^-

$V(\vec{x}) \sim e^-$ density

In general, we write: $S_{n_1 n_2 n_3} = \sum_{j \in \text{unit cell}} f_j \cdot e^{-i\vec{q}\cdot\vec{x}_j}$

Example: Think of BCC lattice as cubic lattice of size a with two basis vectors: $\vec{d}_1 = \vec{0}$

$\vec{d}_2 = \frac{a}{2}\begin{pmatrix}1\\1\\1\end{pmatrix}$



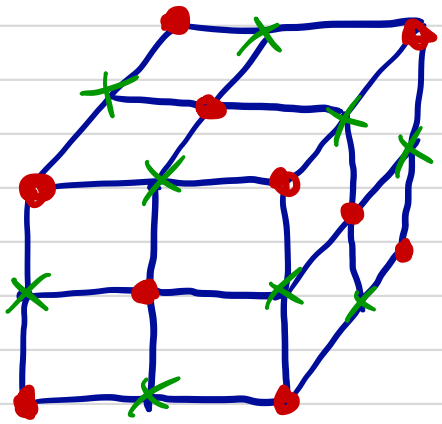
$f_1 = f_2$ (identical atoms)

$$S(\vec{q}) = \beta\left(e^{-i\vec{q}\cdot\vec{d}_1} + e^{-i\vec{q}\cdot\vec{d}_2}\right) = \beta\left(1 + (-1)^{\sum_i n_i}\right)$$

$\vec{q} = \frac{2\pi}{a}\begin{vmatrix} n_1 \\ n_2 \\ n_3 \end{vmatrix}$ for square lattice

$$S(\vec{q}) = \begin{cases} 2 & \text{if } \sum_i n_i \text{ even} \\ 0 & \text{if } \dots \text{ odd} \end{cases}$$

→ Half of the points in Λ^* don't contribute



→ FCC lattice!

That's indeed the reciprocal lattice of a BCC lattice

(IV) Band Theory

We're finally ready to generalize all our results to dimension $d > 1$.

(a) Bloch's theorem : $V(\vec{x} + \vec{n}) = V(\vec{x}) \quad \forall \vec{n} \in \Lambda$

Eigenstates :

$$\boxed{\psi_{\vec{k}}(\vec{x}) = u_{\vec{k}}(\vec{x})\, e^{i\vec{k}\cdot\vec{x}}}$$

$u_{\vec{k}}(\vec{x} + \vec{n}) = u_{\vec{k}}(\vec{x})$

$\vec{n} \in \Lambda$

Proof: Translation operators: $T_{\vec{\pi}} T_{\vec{\pi}'} = T_{\vec{\pi}+\vec{\pi}'}$

$[H, T_{\vec{\pi}}] = 0 \Rightarrow$ label ψ (eigenstate) by eigenvalue $e^{i\theta_{\vec{\pi}}}$ of $T_{\vec{\pi}}$

$$e^{i\theta_{\vec{\pi}}} e^{i\theta_{\vec{\pi}'}} = e^{i\theta_{\vec{\pi}+\vec{\pi}'}}$$

$$T_{\vec{a}_j} \psi(\vec{x}) = \psi(\vec{x}+\vec{a}_j) = e^{i\theta_j} \psi(\vec{x})$$

$$T_{\vec{\pi}} \psi(\vec{x}) = \psi(\vec{x}+\vec{\pi}) = e^{i\sum_j n_j \theta_j} \psi(\vec{x})$$

$\vec{\pi} = \sum_{j=1}^{d} n_j \vec{a}_j$

$\vec{K}\cdot\vec{\pi}$ where $\vec{K}\cdot\vec{a}_i = \theta_i$

$$\Rightarrow \quad T_{\vec{\pi}} \psi_{\vec{K}}(\vec{x}) = e^{i\vec{K}\cdot\vec{\pi}} \psi_{\vec{K}}(\vec{x})$$

Now $u_{\vec{K}} \equiv e^{-i\vec{K}\cdot\vec{x}} \psi_{\vec{K}}(\vec{x})$

$$u_{\vec{K}}(\vec{x}+\vec{\pi}) = e^{-i\vec{K}\cdot\vec{\pi}} e^{-i\vec{K}\cdot\vec{x}} \psi_{\vec{K}}(\vec{x}+\vec{\pi}) = u_{\vec{K}}(\vec{x}) \checkmark$$

$e^{i\vec{K}\cdot\vec{\pi}} \psi_{\vec{K}}(\vec{x})$

Crystal momentum: defined up to $\vec{q} \in \Lambda^*$

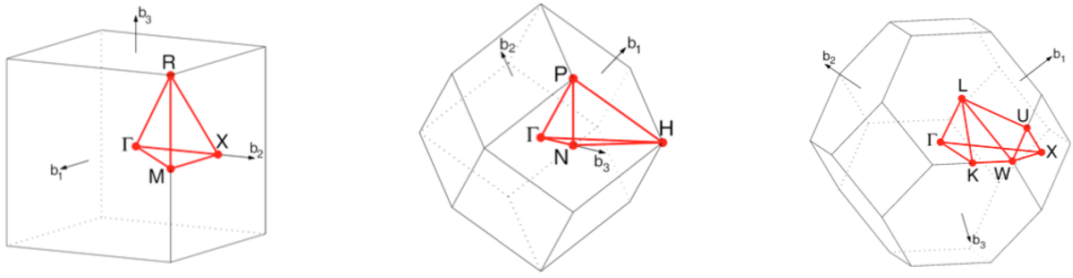
$$\psi_{\vec{K}+\vec{q}}(\vec{x}) = e^{+i\vec{K}\cdot\vec{x}} \underbrace{e^{-i\vec{q}\cdot\vec{x}} u_{\vec{K}+\vec{q}}(\vec{x})}_{\tilde{u}_{\vec{K}}(\vec{x})}$$

$\tilde{u}_{\vec{K}}(\vec{x})$ also obeys $\tilde{u}_{\vec{K}}(\vec{x}+\vec{\pi}) = \tilde{u}_{\vec{K}}(\vec{x})$ $\vec{\pi} \in \Lambda$ since $e^{i\vec{q}\cdot\vec{\pi}} = 1$

as in 1d, we can choose $\vec{K} \in$ 1st BZ, and label levels by bands ("reduced zone scheme"): $\psi_{\vec{K},n}$

n: band index

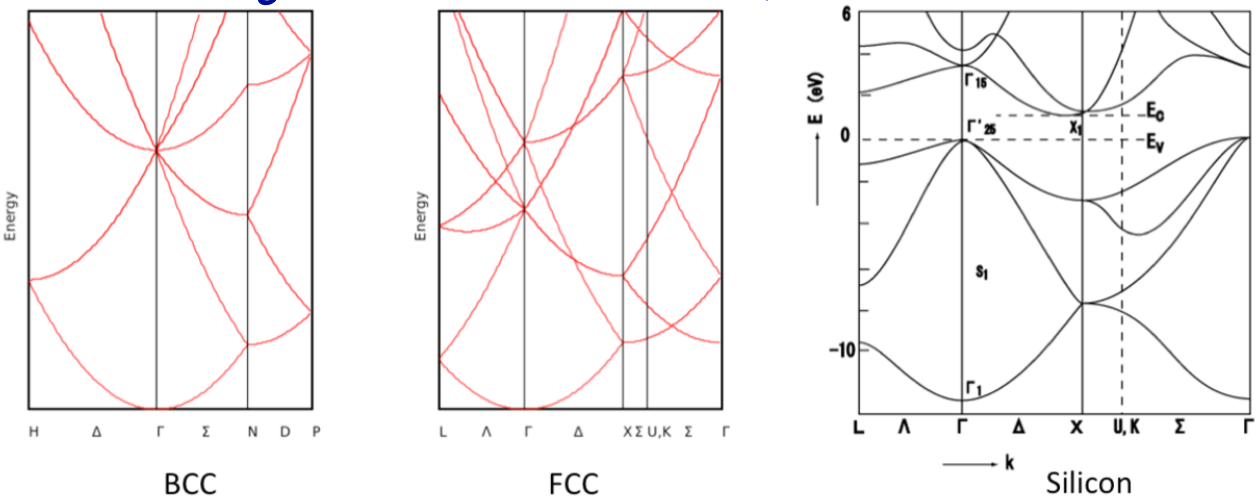
or take $\vec{k} \in \mathbb{R}^d$ (extended zone scheme), $\vec{k}$'s that differ by $\vec{q} \in \Lambda^*$ have the same crystal momenta.



Cubic BCC FCC

E_0 spectrum

$E_0 = \frac{\hbar^2 k^2}{2m}$



BCC FCC Silicon

$E_{\vec{k}}$

(e) Nearly free electrons

Similar to 1d case. Start with $H_0 = \frac{p^2}{2m}$, $E_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$

$$\langle \vec{x} | \vec{k} \rangle = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{x}}$$

Then perturb with $V(\vec{x}) = V(\vec{x} + \vec{n})$

$\vec{n} \in \Lambda$

Matrix elements: $\langle \vec{k}|V(\vec{x})|\vec{k}'\rangle = \frac{1}{V}\int d^3\vec{x}\, e^{i(\vec{k}'-\vec{k}).\vec{x}} V(\vec{x})$

Non vanishing only if $k-\vec{k}' = \vec{q} \in \Lambda^*$: $V(\vec{x}) = \sum_{\vec{q}\in\Lambda^*} e^{i\vec{q}.\vec{x}} \tilde{V}_{\vec{q}}$

$|\vec{k}\rangle \xrightarrow[\text{scatter}]{} |\vec{k}-\vec{q}\rangle$

This is basically Bloch's theorem again.

$\psi^0_{\vec{k}} = \frac{1}{\sqrt{V}} e^{i\vec{k}.\vec{x}} \longrightarrow \psi_{\vec{k}}(\vec{x}) = \sum_{\vec{q}\in\Lambda^*} e^{i(\vec{k}-\vec{q}).\vec{x}} C_{\vec{k}-\vec{q}}$

$= e^{i\vec{k}.\vec{x}} \underbrace{\sum_{\vec{q}\in\Lambda^*} e^{-i\vec{q}.\vec{x}} C_{\vec{k}-\vec{q}}}_{U_k(\vec{x})}$

Low momentum : $|\vec{k}\rangle$ and $|\vec{k}+\vec{q}\rangle$ have very $\neq$ energies

small corrections from 2nd order perturbation theory

Near edges of BZ : $E_0(\vec{k}) = E_0(\vec{k}+\vec{q})$ (small denominators)

$\Rightarrow \quad k^2 = (\vec{k}+\vec{q})^2 \quad \Rightarrow \quad q^2 + 2\vec{k}.\vec{q} = 0$

$\Rightarrow \boxed{\vec{k} = -\vec{q}/2 + \vec{k}_\perp}$ with $\vec{k}_\perp . \vec{q} = 0$

Perpendicular bisector of origin and point $-\vec{q} \in \Lambda^*$

$\Rightarrow$ edge of the BZ ! (Wigner-Seitz cell)

as in 1d, V opens up a gap using degenerate perturbation theory.

How many states in the BZ?

For an infinite lattice, k continuous. What if we have N lattice sites?

$$\vec{n} = \sum_i n_i \vec{a}_i \qquad 0 \le n_i < N_i \;; \qquad N = N_1 N_2 N_3$$

Total volume: VN with $V = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|$

PBC: $\psi_{\vec{k}}(\vec{x} + N_i \vec{a}_i) = \psi_{\vec{k}}(\vec{x}) \qquad i = 1,2,3$ ("Born-von Karman")

$\psi_{\vec{k}}(\vec{x}) = e^{i\vec{k}\cdot\vec{x}} u_{\vec{k}}(\vec{x})$ and $u_{\vec{k}}(\vec{x} + \vec{a}_i) = u_{\vec{k}}(\vec{x}) \Rightarrow e^{i N_i \vec{k}\cdot\vec{a}_i} = 1$

$$\Rightarrow \quad \vec{k} = \sum_i \frac{m_i}{N_i} \vec{b}_i \qquad (\text{recall: } \vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij})$$

$$m_i \in \mathbb{Z}$$

$\vec{k}$ quantized, as expected, labelled $|k\rangle \{m_1, m_2, m_3\}$

Each state occupies a volume: $\dfrac{|\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)|}{N_1 N_2 N_3} = \dfrac{V^*}{N}$

$\Rightarrow$ **# states in BZ = N**

(c) Wannier functions: Pick energy band: $\psi_k(\vec{x}) = e^{i\vec{k}\cdot\vec{x}} u_{\vec{k}}(\vec{x})$

$$W_{\vec{n}}(\vec{x}) = \frac{1}{\sqrt{N}} \sum_{\vec{k} \in BZ} e^{-i\vec{k}\cdot\vec{n}} \psi_{\vec{k}}(\vec{x})$$

Basis of functions localized near $\vec{n} \in \Lambda$

$$w_{\vec{\pi}+\vec{\pi}'}(\vec{x}+\vec{\pi}') = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{\pi}} e^{-i\vec{k}\cdot\vec{\pi}'} \underbrace{\psi_{\vec{k}}(\vec{x}+\vec{\pi}')}_{e^{i\vec{k}\cdot\vec{x}}\, e^{i\vec{k}\cdot\vec{\pi}'}\, u_{\vec{k}}(\vec{x})}$$

$$= w_{\vec{\pi}}(\vec{x})$$

$$\Rightarrow \quad w_{\vec{\pi}}(\vec{x}) = w(\vec{x}-\vec{\pi})$$

Inverse: $$\psi_{\vec{k}}(\vec{x}) = \frac{1}{\sqrt{N}} \sum_{\vec{\pi}\in\Lambda} e^{i\vec{k}\cdot\vec{\pi}}\, w(\vec{x}-\vec{\pi})$$

Orthogonality: $$\int d^3\vec{x}\; w(\vec{x}-\vec{\pi})\, w(\vec{x}-\vec{\pi}') = \frac{1}{N}\int d^3\vec{x} \sum_{\vec{k},\vec{k}'} e^{i\vec{k}'\cdot\vec{\pi}' - i\vec{k}\cdot\vec{\pi}}$$

$$\psi^*_{\vec{k}'}(\vec{x})\,\psi_{\vec{k}}(\vec{x}) = \frac{1}{N}\sum_{\vec{\pi}} e^{i\vec{k}(\vec{\pi}'-\vec{\pi})} = \delta_{\vec{\pi},\vec{\pi}'}$$

(d) Tight-Binding model in 3d

As in 1d, assume e^- live on sites $\vec{\pi}\in\Lambda$

$$H = \sum_{\vec{\pi}\in\Lambda} E_0 |\vec{\pi}\rangle\langle\vec{\pi}| - \sum_{\langle\vec{\pi},\vec{\pi}'\rangle} t_{\vec{\pi}'-\vec{\pi}} \left(|\vec{\pi}'\rangle\langle\vec{\pi}| + \text{h.c.} \right)$$

($|\vec{\pi}'\rangle\langle\vec{\pi}|$ + h.c.)

$$= \sum_{\vec{\pi}\in\Lambda} \left[E_0 |\vec{\pi}\rangle\langle\vec{\pi}| - \sum_{\vec{a}} t_{\vec{a}} |\vec{\pi}\rangle\langle\vec{\pi}+\vec{a}| \right]$$

↖ lattice vectors connecting $\vec{\pi}$ to its neighbours

6 terms for cubic lattice

$$\left(t_{\vec{a}} = t_{-\vec{a}} \right)$$

$$= t$$

Eigenstates: $|\psi_{\vec{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{n} \in \Lambda} e^{i\vec{k}\cdot\vec{n}} |\vec{n}\rangle$

$E_{\vec{k}} = E_0 - \sum_{\vec{a}} t\, e^{i\vec{k}\cdot\vec{a}}$ (delocalized!)

$\sum_{\vec{a}}$ include $-\vec{a}$, sum over all neighbors

ex: cubic lattice: $\vec{a} = \begin{pmatrix}\pm 1\\0\\0\end{pmatrix}, \begin{pmatrix}0\\\pm 1\\0\end{pmatrix}, \begin{pmatrix}0\\0\\\pm 1\end{pmatrix}$

$$\Rightarrow \boxed{E_{\vec{k}} = E_0 - 2t\left(\cos k_x a + \cos k_y a + \cos k_z a\right)}$$

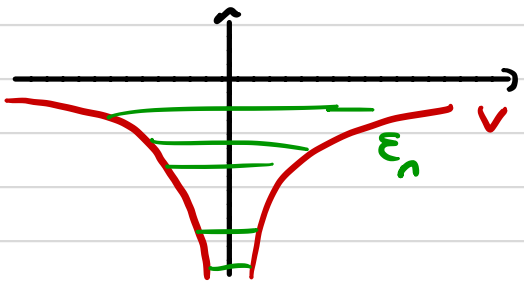
Bandwidth: $\Delta E = 12\, t$.

ⓔ Derivation of the tight-binding model, LCAO

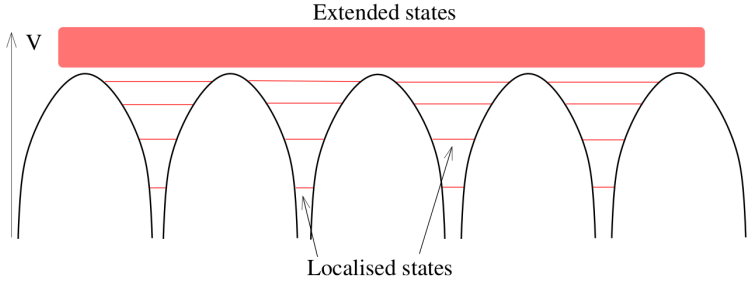
Single atom $H_{atom} = \frac{p^2}{2m} + V_{atom}(\vec{x})$

$\vec{x}$: for an e^- orbiting this atom

$H_{atom}\, \phi_n(\vec{x}) = \varepsilon_n\, \phi_n(\vec{x})$,



lattice: $V_{lattice}(\vec{x}) = \sum_{\vec{n} \in \Lambda} V_{atom}(\vec{x} - \vec{n})$



- Let's assume we have a single valence e^- with localized wave functions $\phi(\vec{x})$, energy ε.

We want to diagonalize $H = \frac{p^2}{2m} + V_{lattice}(\vec{x})$

- Let's guess a good Bloch state:

$$|\psi_k(\vec{x})\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{n}\in\Lambda} e^{i\vec{k}\cdot\vec{n}}\, \phi(\vec{x}-\vec{n})$$

$\phi(\vec{x}-\vec{n})$: ~ Wannier functions BUT $\phi(\vec{x})$ on $\neq$ sites not orthogonal.

(Satisfies $\psi_k(\vec{x}+\vec{n}) = e^{i\vec{k}\cdot\vec{n}}\,\psi_k(\vec{n})$)

Overlap very important! $\int \neq \delta(\vec{n}-\vec{n}')$

We have: $\langle\psi_k|\psi_k\rangle = \frac{1}{N}\sum_{\vec{n},\vec{n}'} e^{i\vec{k}\cdot(\vec{n}'-\vec{n})} \underbrace{\int d^3\vec{x}\, \phi^*(\vec{x}-\vec{n})\,\phi(\vec{x}-\vec{n}')}_{\int d^3x\, \phi^*(\vec{x}-\vec{n}+\vec{n}')\,\phi(\vec{x})}$

$$= \sum_{\vec{n}} e^{-i\vec{k}\cdot\vec{n}} \int d^3\vec{x}\, \phi^*(\vec{x}-\vec{n})\,\phi(\vec{x})$$

$\int$ overlap of wave functions separated by $\vec{n}$

$$= 1 + \sum_{\substack{\vec{n}\neq 0 \\ \vec{n}\in\Lambda}} e^{-i\vec{k}\cdot\vec{n}}\, \alpha(\vec{n})$$

$$\langle\psi_k|H|\psi_k\rangle = \varepsilon\langle\psi_k|\psi_k\rangle + \sum_{\vec{n}\in\Lambda} e^{-i\vec{k}\cdot\vec{n}} \underbrace{\int d^3\vec{x}\, \phi^*(\vec{x}-\vec{n})\,\Delta V(\vec{x})\,\phi(\vec{x})}_{\int d^3\vec{x}\, \phi^*(\vec{x})\,\Delta V(\vec{x})\,\phi(\vec{x})}$$

$H = H_{atom} + \Delta V$

$\Delta V = \sum_{\vec{n}\neq\vec{0}} V_{atom}(\vec{x}-\vec{n})$

$$= \varepsilon\langle\psi_k|\psi_k\rangle + \Delta\varepsilon + \sum_{\vec{n}\neq 0} e^{-i\vec{k}\cdot\vec{n}}\,\gamma(\vec{n})$$

Energy $E_{\vec{k}} = \frac{\langle \psi_{\vec{k}} | H | \psi_{\vec{k}} \rangle}{\langle \psi_{\vec{k}} | \psi_{\vec{k}} \rangle} = \varepsilon + \frac{\Delta\varepsilon + \sum_{\vec{n}\neq 0} e^{-i\vec{k}\cdot\vec{n}} \gamma(\vec{n})}{1 + \sum_{\vec{n}\neq 0} e^{-i\vec{k}\cdot\vec{n}} \alpha(\vec{n})}$

$\gamma \ll 1$
$\alpha \ll 1$

$$\simeq \varepsilon + \Delta\varepsilon + \sum_{\vec{n}\neq\vec{0}} e^{-i\vec{k}\cdot\vec{n}} \left(\gamma(\vec{n}) - \alpha(\vec{n})\Delta\varepsilon \right)$$

Example s-orbitals : $\phi(\vec{n}) = \phi(n)$, and ϕ real.

Also assume α, γ only sizable for nearest neighbors.

$$\alpha(\vec{n}) = \int d^3\vec{x}\, \phi(\vec{x}-\vec{n})\,\phi(\vec{x}) = \alpha(-\vec{n})$$

$\gamma(\vec{n}) = \gamma(-\vec{n})$ too if $V(\vec{n}) = V(-\vec{n})$ ("inversion symmetry")

$\vec{n} = \pm\vec{a}$ only

$$E_k = \varepsilon + \Delta\varepsilon + e^{-i\vec{k}\cdot\vec{a}} \left(\gamma_{\vec{a}} - \alpha_{\vec{a}}\Delta\varepsilon \right) + e^{+i\vec{k}\cdot\vec{a}} \left(\gamma_{-\vec{a}} - \alpha_{-\vec{a}}\Delta\varepsilon \right)$$

$\varepsilon + \Delta\varepsilon = E_0$; $\gamma_{\vec{a}} - \alpha_{\vec{a}}\Delta\varepsilon = -t_{\vec{a}}$

$$= E_0 - \sum_{\vec{a}} \cos(\vec{k}\cdot\vec{a})\, t_{\vec{a}}$$

- Good approximation if this band doesn't mix with lower energy bound states.

Linear combination of atomic orbitals (LCAO)

More energy levels? Approximate solution as :

$$\psi_{\vec{k}}(\vec{x}) = \frac{1}{\sqrt{N}} \sum_{\vec{n}\in\Lambda} e^{+i\vec{k}\cdot\vec{n}} \sum_{n} c_n \phi_n(\vec{x}-\vec{n})$$

Linear Combination of Atomic orbitals

ϕ_n: energy ε_n for Hatom

Variational ansatz, minimize $E_{\vec{k}} = \dfrac{\langle\psi_k|H|\psi_k\rangle}{\langle\psi_k|\psi_k\rangle}$

$$\langle\psi_k|\psi_k\rangle = \sum_{\vec{n}\in\Lambda} \sum_{n,n'} c_{n'}^* c_n e^{-i\vec{k}\cdot\vec{n}} \underbrace{\int d^3\vec{x}\, \phi_{n'}(\vec{x}-\vec{n})\phi_n(\vec{x})}_{\alpha_{n,n'}(\vec{n})}$$

(don't isolate $\vec{n}=\vec{0}$ term as before!)

$$\langle\psi_k|H|\psi_k\rangle = \sum_{\vec{n}\in\Lambda} \sum_{n,n'} c_{n'}^* c_n e^{-i\vec{k}\cdot\vec{n}} \int d^3\vec{x}\, \phi_{n'}^*(\vec{x}-\vec{n})\,(H_{atom}+\Delta V)\,\phi_n(\vec{x})$$

$$= \sum_{\vec{n}\in\Lambda} \sum_{n,n'} c_{n'}^* c_n e^{-i\vec{k}\cdot\vec{n}} \left(\varepsilon_n \alpha_{n,n'}(\vec{n}) + \gamma_{n,n'}(\vec{n})\right)$$

$$\frac{\partial E_{\vec{k}}}{\partial c_{n'}^*} = \frac{1}{\langle\psi_k|\psi_k\rangle} \frac{\partial\langle\psi_k|H|\psi_k\rangle}{\partial c_{n'}^*} - \frac{E_k}{\langle\psi_k|\psi_k\rangle} \frac{\partial\langle\psi_k|\psi_k\rangle}{\partial c_{n'}^*} = 0$$

$$\Rightarrow \sum_{n} \underbrace{\left[\sum_{\vec{n}\in\Lambda} e^{-i\vec{k}\cdot\vec{n}} \left(\gamma_{n,n'}(\vec{n}) + (\varepsilon_n - E_k)\,\alpha_{n,n'}(\vec{n})\right)\right]}_{M_{n,n'}(\vec{k})\text{ : matrix}} c_n = 0$$

c_n: eigenvector with 0 eigenvalue

$$\Rightarrow \boxed{\det \hat{M}(\vec{k}) = 0}$$

$p \times p$ matrix with p orbitals

$\rightarrow$ solution: p bands $E_n(\vec{k})$, $n = 1, \ldots, p$