# MSE 423 Fall 2024 – Week 9

# Bloch by Bloch



# Last week

$\alpha = \langle p_{z_i} | \hat{H} | p_{z_i} \rangle$ $\beta = \langle p_{z_i} | \hat{H} | p_{z_{i\pm1}} \rangle$

$N_2 / O_2$ $\pi / \sigma$

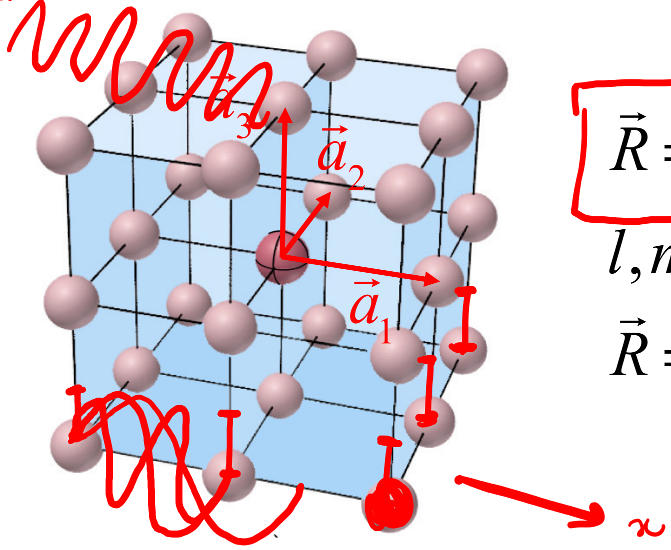
- Homonuclear diatomic levels
- Empirical tight binding/Hückel model
- Energy levels and molecular orbitals of benzene
- Symmetry to classify solutions (e.g. in benzene)
- Solutions and spectra in rings
- Symmetry operations, group theory
- Translational symmetry, Bravais lattices
- ~~A~~ crystal as a Bravais lattice + basis $\{\vec{R}\}$ $l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$
- Primitive, conventional, Wigner-Seitz unit cell

$\boxed{14}$ BANDWIDTH $4\beta$

# Reciprocal lattice (I)

- Let's start with a Bravais lattice, defined in terms of its primitive lattice vectors…

$Ae^{i(\vec{G}\cdot\vec{r})}$




$$\boxed{\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3}$$

$l, m, n$ integer numbers

$$\vec{R} = (l, m, n)$$

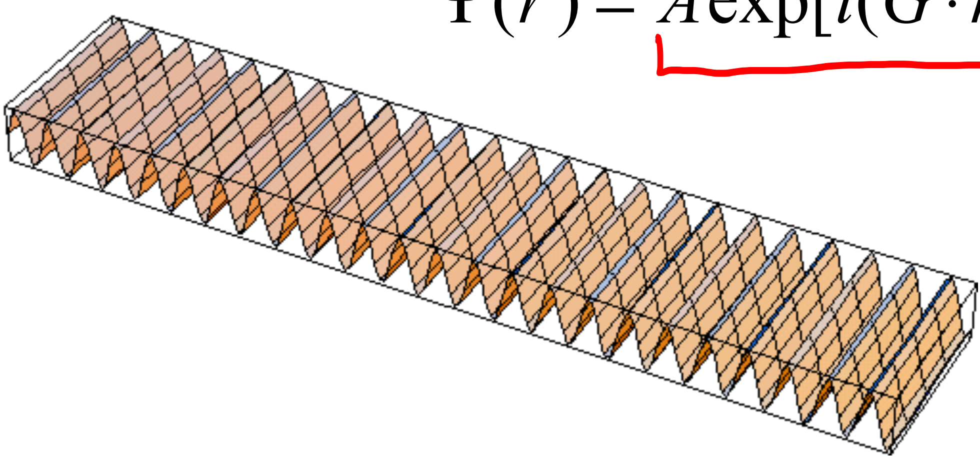


# Reciprocal lattice (II)

- …and then let's take a plane wave

WAVE VECTOR

$$\Psi(\vec{r}) = \underbrace{A\exp[i(\vec{G}\cdot\vec{r})]}$$



# Reciprocal lattice (III)

- What are the wavevectors for which our plane wave has the same amplitude at all lattice points ?

FOR A GENERIC $\vec{R}$

$$\boxed{\exp[i(\vec{G}\cdot\vec{r})] = \exp[i(\vec{G}\cdot(\vec{r}+\vec{R}))]}$$

$$\exp[i(\vec{G}\cdot\vec{R})] = 1$$

$$\exp[i(\vec{G}\cdot(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3))] = 1$$

$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$

$\vec{a}_1, \vec{a}_2$ and $\vec{a}_3$ define the primitive unit cell

$$e^{i(\vec{G}\cdot\vec{R})} = 1 \qquad \underbrace{\vec{G}\cdot\vec{R}} = 2\pi n = -4\pi, -2\pi, 0, 2\pi, 4\pi$$



# Reciprocal lattice (IV)

$\vec{G}\cdot\vec{R} = 2\pi n$

$(h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3)\cdot(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3) = 2\pi hl + 2\pi im + 2\pi jn = 2\pi$ TIMES AN INTEGER

$\boxed{\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}}$ n integer is satisfied by

$\underbrace{\vec{G} = h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3}$ with $h, i, j$ integers,

provided $\vec{b}_1 = 2\pi\dfrac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$ $\quad \vec{b}_2 = 2\pi\dfrac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$ $\quad \vec{b}_3 = 2\pi\dfrac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$

$= \vec{a}_2\cdot(\vec{a}_3\times\vec{a}_1) = \vec{a}_3\cdot(\vec{a}_1\times\vec{a}_2) = V$

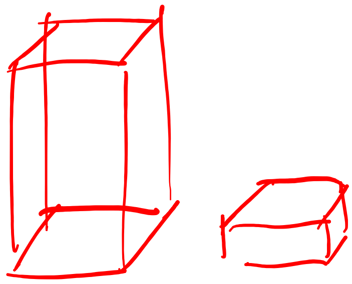
$\vec{G} = (h, i, j)$ are the reciprocal-lattice vectors

$\vec{G}\cdot\vec{R} = 2\pi n \Rightarrow e^{i(\vec{G}\cdot\vec{R})} = 1$

# Examples of reciprocal lattices

| Direct lattice | Reciprocal lattice |
|---|---|
| Simple cubic | Simple cubic |
| FCC $\longrightarrow$ | BCC |
| BCC $\longrightarrow$ | FCC |
| Orthorhombic | Orthorhombic |

$$\boxed{\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}}$$





# Brillouin zones

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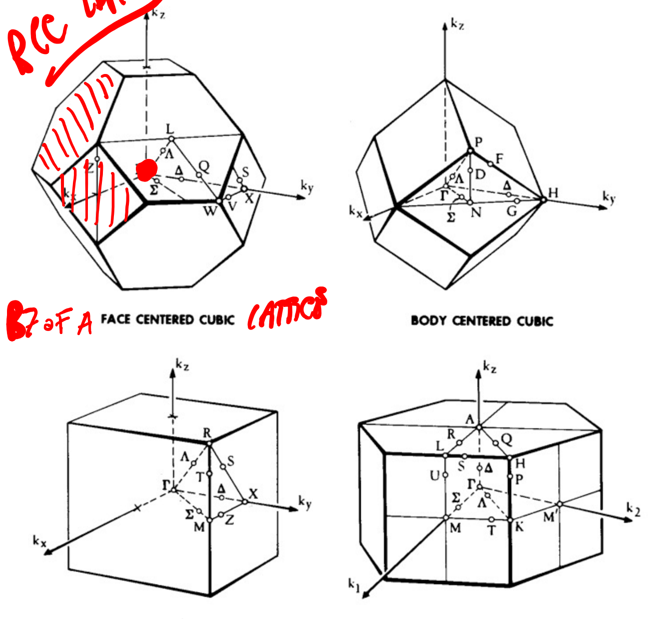


Brillouin zones are the Wigner-Seitz unit cells of the reciprocal lattice

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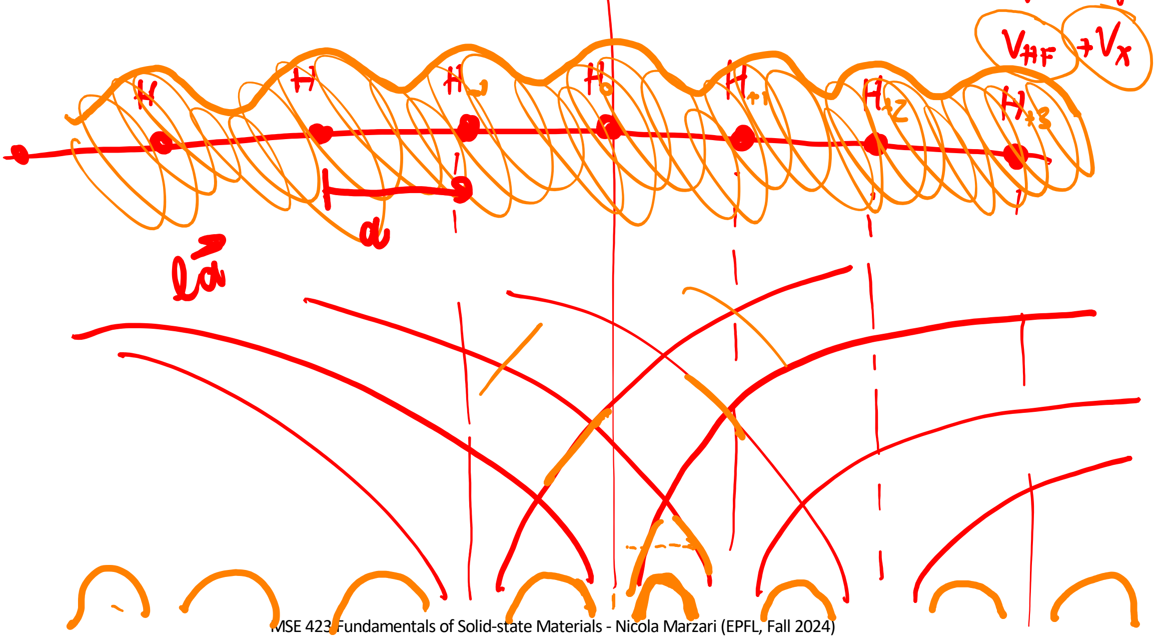
BCC RECIPROCAL LATTICE

https://www.materialscloud.org/work/tools/seekpath

# Hamiltonian in a periodic potential

$V_H = -\frac{1}{r}$ $\quad V_{EXT}(\vec{r}) = -\sum_{i=1}^{\infty} \frac{1}{|\vec{r}-\vec{R}_{H_i}|}$ $\quad V_{EXT} + \sum_{ij} \frac{1}{|\vec{r}_i-\vec{r}_j|}$






# Periodic potential

LATTICE TRANSLATION OPERATOR $\quad \hat{T}_{\vec{R}}\, f(\vec{r}) \Rightarrow f(\vec{r}+\vec{R})$

$$[\hat{H}_{CRYSTAL}, \hat{T}_{\vec{R}}] = 0$$

$$\hat{H}_c \hat{T}_{\vec{R}} = \hat{T}_R \hat{H}_c$$

$$\hat{T}_R \hat{H}_c(\vec{r}) f(\vec{r})$$

$$\hat{T}_R (\hat{H}_c(\vec{r}) f(\vec{r})) = \hat{H}_c(\vec{r}+\vec{R}) f(\vec{r}+\vec{R})$$

$$= \hat{H}_c(\vec{r}) f(\vec{r}+\vec{R})$$

$$= \hat{H}_c(\vec{r}) \hat{T}_R f(\vec{r})$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2024)

# Bloch Theorem

The one-particle effective Hamiltonian $\hat{H}$ in a periodic lattice commutes with the lattice-translation operator $\hat{T}_{\mathrm{R}}$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

EIGENSTATES OF A PERIODIC HAM.

u PERIODIC FUNC. • PLANE WAVE MODULATED

$$\boxed{[\,\hat{H},\,\hat{T}_{\mathrm{R}}\,] = 0} \Rightarrow \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}}$$

$\mathbf{k} \in 1^{st}$ BZ.

- n, k are the quantum numbers (band index and crystal QUASI momentum), u is periodic
- From two requirements: a translation can't change the charge density, and two translations must be equivalent to one that is the sum of the two



# Bloch Theorem

$$\begin{cases} \hat{H}\psi = \varepsilon\psi \\ \hat{T}_{\vec{R}}\,\psi = c(\vec{R})\,\psi \end{cases}$$

CHARGE DENSITY DOES NOT CHANGE UPON TRANSLATION

$$\|\psi(\vec{r})\|^2 \Rightarrow \|c(\vec{R})\psi(\vec{r})\|^2 \Rightarrow \|c(\vec{R})\|^2 = 1$$

I STATEMENT

$$\hat{T}_{\vec{R}}\,\hat{T}_{\vec{R}'}\,\psi(\vec{r}) = \hat{T}_{\vec{R}}\,\psi(\vec{r}+\vec{R}') = \psi(\vec{r}+\vec{R}'+\vec{R})$$

$$\hat{T}_{\vec{R}}\,\hat{T}_{\vec{R}'} = \hat{T}_{\vec{R}'}\,\hat{T}_{\vec{R}} = \hat{T}_{\vec{R}+\vec{R}'} \Rightarrow \underbrace{c(\vec{R})\,c(\vec{R}') = c(\vec{R}+\vec{R}')}_{\text{II STATEMENT}}$$

# Bloch Theorem

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\hat{T}_{a_1}\psi = c(\vec{a}_1)\psi \quad \dots \quad \hat{T}_{a_2}\psi = c(\vec{a}_2)\psi \dots$$

$$c(\vec{a}_1) = e^{i2\pi x_1}$$

$$c(\vec{a}_2) = e^{i2\pi x_2}$$

$$c(\vec{a}_3) = e^{i2\pi x_3}$$

$$c(\vec{R}) = c(\underbrace{\vec{a}_1+\vec{a}_1+\vec{a}_1+\vec{a}_1 \dots}_{n_1 \text{ TIMES}} \underbrace{\vec{a}_2+\vec{a}_2+\vec{a}_2 \dots}_{n_2 \text{ TIMES}} + \underbrace{\vec{a}_3+\vec{a}_3+\vec{a}_3 \dots}_{n_3 \text{ TIMES}}) =$$

$$= c(a_1)^{n_1}\, c(a_2)^{n_2}\, c(a_3)^{n_3} = e^{i2\pi(n_1x_1+n_2x_2+n_3x_3)}$$



# Bloch Theorem

$$\boxed{c(\vec{R})} = e^{i2\pi(x_1n_1+x_2n_2+x_3n_3)}$$

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\vec{k} = x_1\vec{b}_1 + x_2\vec{b}_2 + x_3\vec{b}_3$$

$$= \boxed{e^{i\vec{k}\cdot\vec{R}}}$$

$$\hat{T}_{\vec{R}}\psi(\vec{r}) = \psi(\vec{r}+\vec{R}) = \underbrace{e^{i\vec{k}\cdot\vec{R}}}_{\text{PHASE FACTOR}}\psi(\vec{r})$$

BLOCH IN 2nd FORM.

# Bloch Theorem (in two equiv forms)

$$\Psi_{\vec{k}}\left(\vec{r}+\vec{R}\right)=\exp\left(i\vec{k}\cdot\vec{R}\right)\Psi_{\vec{k}}\left(\vec{r}\right)$$

$\psi_k(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}$ is periodic

$$\psi_k(\vec{r}+\vec{R})\, e^{-i\vec{k}\cdot(\vec{r}+\vec{R})} = \cancel{e^{i\vec{k}\cdot\vec{R}}}\, \psi_k(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}\, \cancel{e^{-i\vec{k}\cdot\vec{R}}}$$

$$\psi_k(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}} = u_k(\vec{r}) \Rightarrow \psi_k(\vec{r}) = u_k(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}$$



# Bloch Theorem (in two equiv forms)

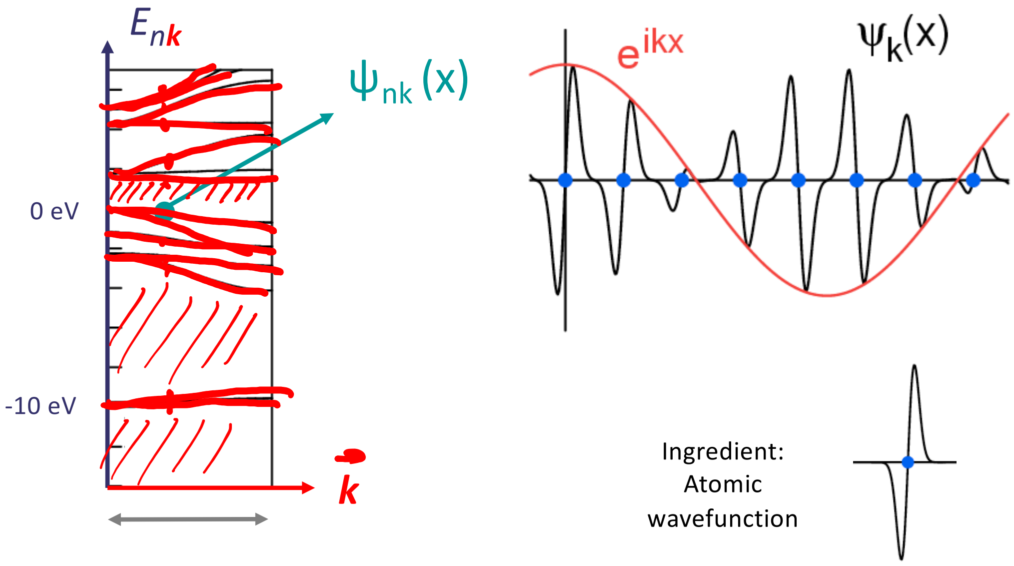
$\vec{k}+\vec{G}_i$

$$\Psi_{\vec{k}}\left(\vec{r}+\vec{R}\right)=\exp\left(\underline{i\vec{k}\cdot\vec{R}}\right)\Psi_{\vec{k}}\left(\vec{r}\right)$$

$$\Psi_{\vec{k}}\left(\vec{r}\right)=\exp\left(i\vec{k}\cdot\vec{r}\right)u_{\vec{k}}\left(\vec{r}\right)$$

# Bloch Theorem

## Bloch wavefunction






$\langle e^{i\vec{k}\cdot\vec{r}} | -\frac{1}{2}\nabla^2 | e^{i\vec{k}\cdot\vec{r}} \rangle$

# From extended to primitive

$\frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$

$\varepsilon = \frac{1}{2} k^2$