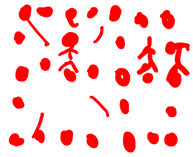
MSE 423 Fall 2025 – Week 9

Bloch by Bloch

Last week

- Homonuclear diatomic levels
- Empirical tight binding/Hückel model
- Energy levels and molecular orbitals of benzene
- Symmetry operations, group theory
- Symmetry to classify solutions (e.g. in benzene)
- Solutions and spectra in rings
- Translational symmetry, Bravais lattices
- A crystal as a Bravais lattice + basis

Bravais Lattices



- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.

$$\boxed{\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \quad \text{l,m and n integers}}$$

$$\vec{a}_1, \vec{a}_2 \text{ and } \vec{a}_3 \text{ primitive lattice vectors}$$ (~~NOT~~ LINEARLY INDEPENDENT)

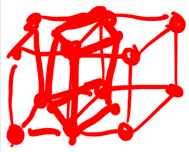
- 14 Bravais lattices exist in 3 dimensions (1848)
- M. L. Frankenheimer in 1842 thought they were 15. So, so naïve…

4 Lattice types

BODY CENTERED

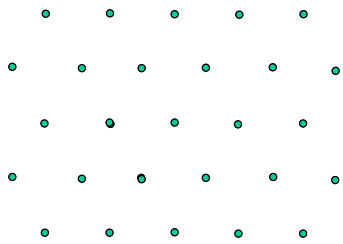
7 Crystal classes

14 Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

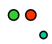


$a(\frac{1}{2},\frac{1}{2},0)$
$a(\frac{1}{2},0,\frac{1}{2})$
$a(0,\frac{1}{2},\frac{1}{2})$

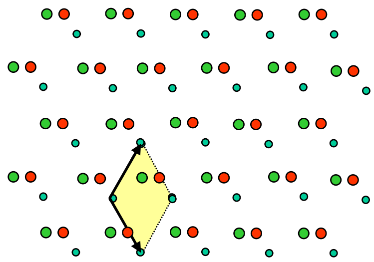
Crystal Structure = Lattice + Basis



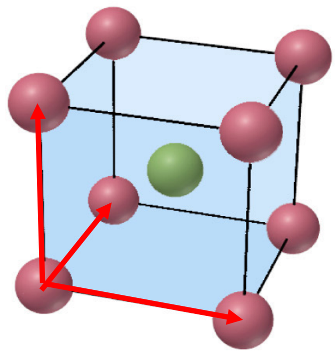
Lattice



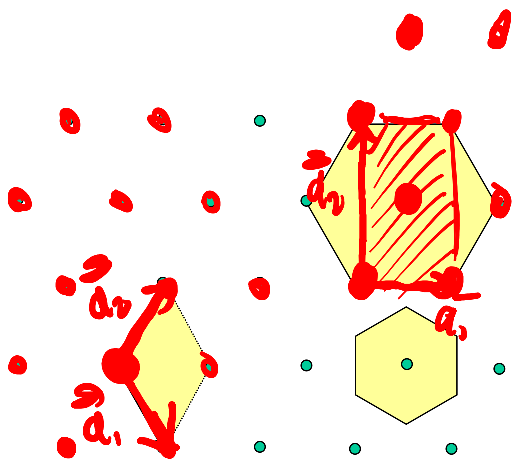
Basis

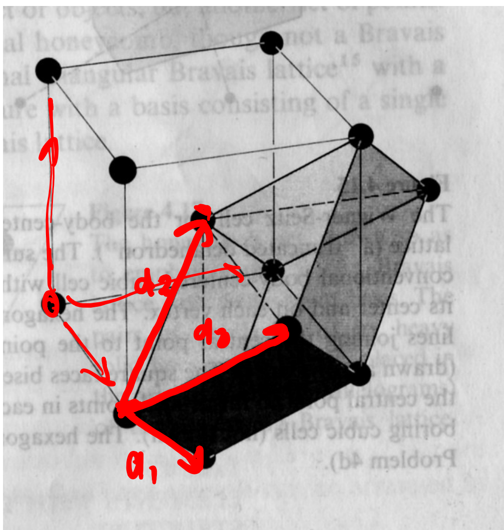


Crystal Structure = Lattice + basis



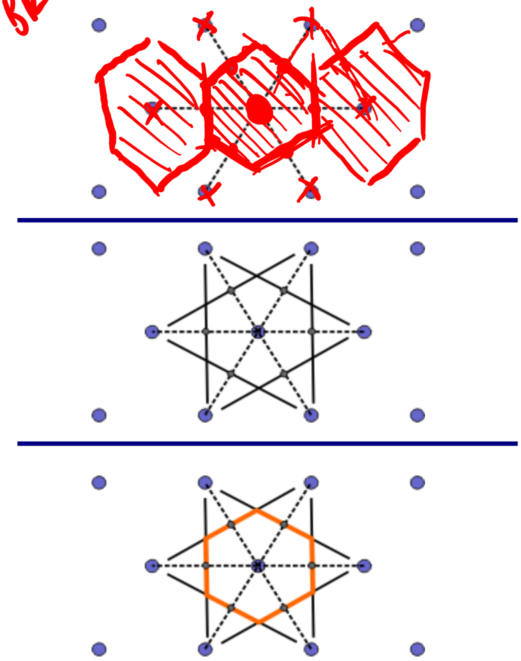
Primitive unit cell and conventional unit cell



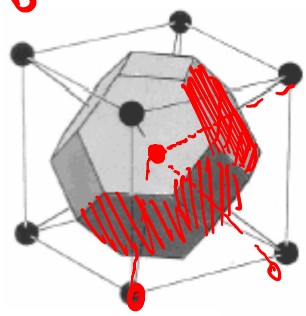


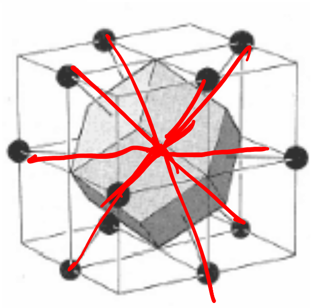
Wigner-Seitz cell

BR LATT RO.



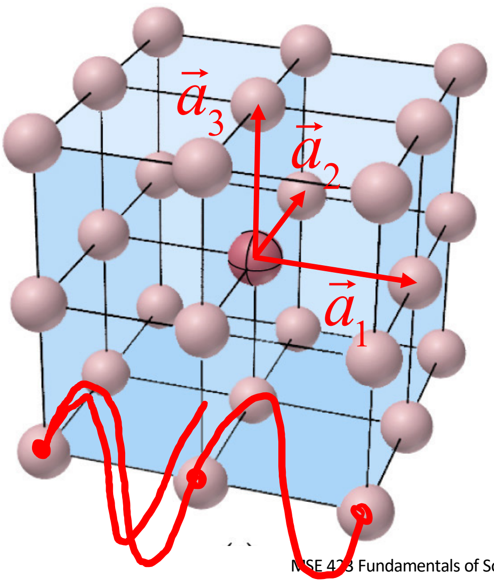
BCC





Reciprocal lattice (I)

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



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

l, m, n integer numbers

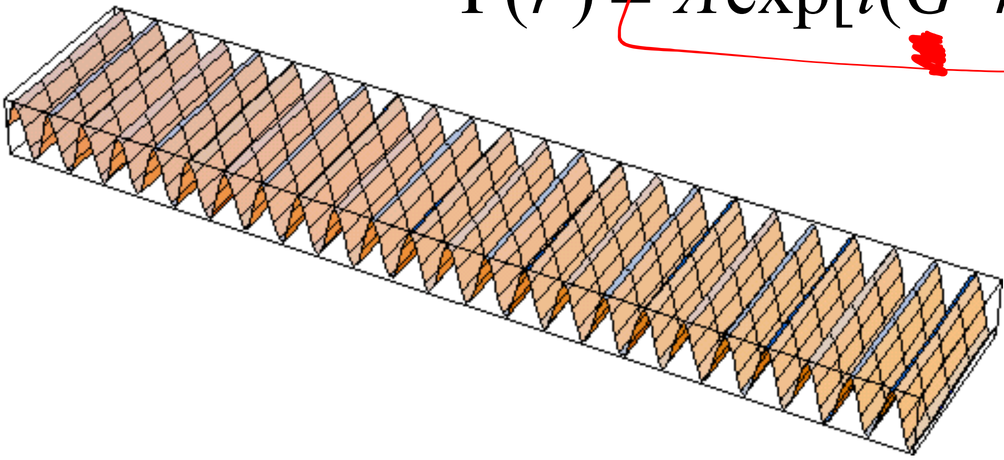
$$\vec{R} = (l, m, n)$$

Reciprocal lattice (II)

$\vec{R}$

- …and then let's take a plane wave

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



Reciprocal lattice (III)

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

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

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

FOR WHICH $\vec{G}$ THIS EQUALITY HOLDS ?

Reciprocal lattice (IV)

$\vec{G} \cdot \vec{R} = (h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3)\cdot(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3) =$

$= hl\,\vec{b}_1 \cdot \vec{a}_1 + hm\,\cancel{\vec{b}_1 \cdot \vec{a}_2} \ldots$

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

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

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

→ V PRIMITIVE CELL

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

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

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

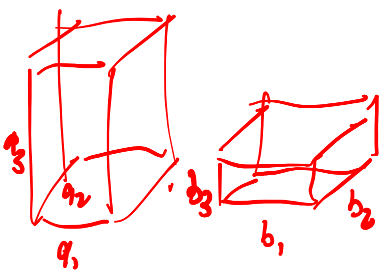
Examples of reciprocal lattices

$\vec{a}_1 = a(1,0,0)$

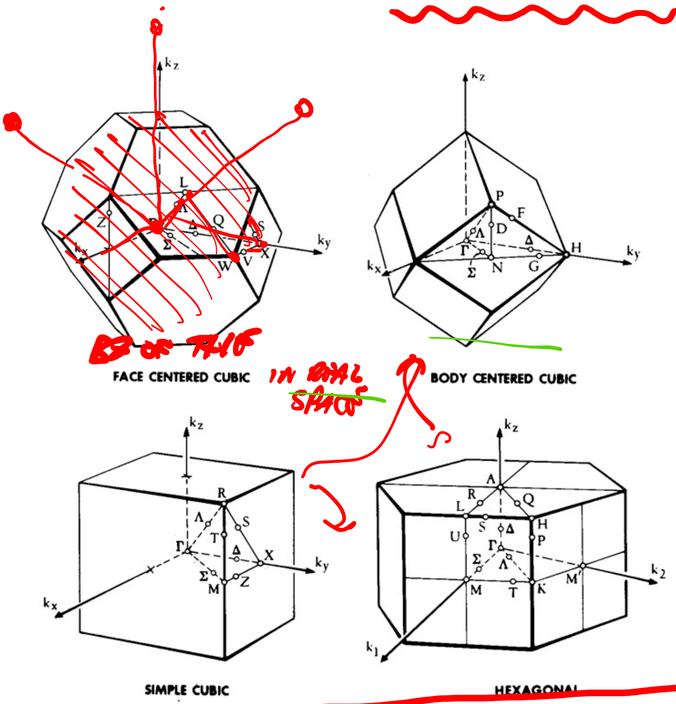
$\vec{a}_2 = a(0,1,0)$

Direct lattice	Reciprocal lattice
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
Orthorhombic	Orthorhombic

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



Brillouin zones = W-S PRIM. CELL OF REC. LATT.



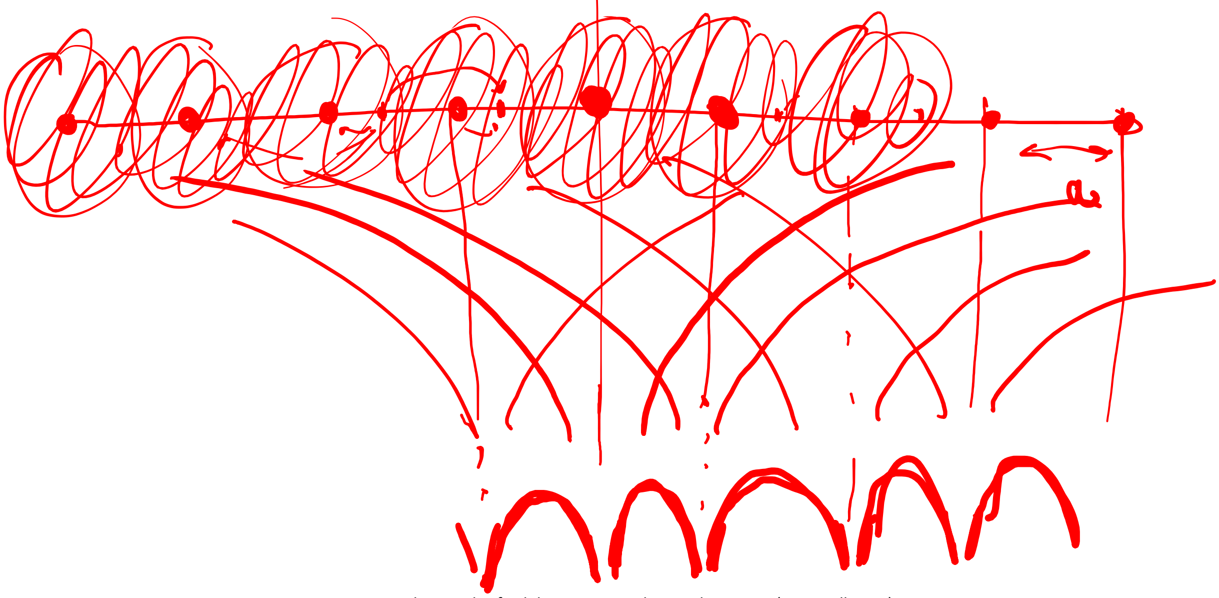
Brillouin zones are the Wigner-Seitz unit cells of the reciprocal lattice

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

Hamiltonian in a periodic potential

PRX

$$V_{EXP}(\vec{r}) = -\sum_i \frac{1}{|\vec{r}-\vec{R}_i|}$$



Periodic potential

LATTICE TRANSL. OPERATORS $\hat{T}_{\vec{R}} f(\vec{r}) = f(\vec{r} + \vec{R})$

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

$$\hat{H}_{cr} \hat{T}_{\vec{R}} = \hat{T}_{\vec{R}} \hat{H}_{cr} \quad -\nabla^2 + V(\vec{r})$$

$$\hat{T}_{\vec{R}} \hat{H}_{cr}(\vec{r}) f(\vec{r}) = \hat{H}(\vec{r}+\vec{R}) f(\vec{r}+\vec{R}) =$$

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

$$= \hat{H}(\vec{r}) \hat{T}_{\vec{R}} f(\vec{r})$$

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:

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

- n, k are the quantum numbers (band index and crystal 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

$\hat{H}\psi = \varepsilon\psi$

$\hat{T}_{\vec R}\psi = c_{\vec R}\psi \qquad c_{\vec R} = c(\vec R)$

CHARGE DENSITY K PERIODIC

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

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

$$\hat{T}_{\vec R}\hat{T}_{\vec R'} = \hat{T}_{\vec R'}\hat{T}_{\vec R} = \hat{T}_{\vec R+\vec R'} \qquad \hat{T}_{\vec R}\hat{T}_{\vec R'}\psi = \hat{T}_{\vec R+\vec R'}\psi$$

$$c(\vec R)c(\vec R') = c(\vec R+\vec R')$$

Bloch Theorem

$$\vec R = n_1\vec a_1 + n_2\vec a_2 + n_3\vec a_3$$

$\hat{T}_{\vec a_1}\psi = c(\vec a_1)\psi \qquad \hat{T}_{\vec a_2}\psi = c(\vec a_2)\psi \ldots$

$c(\vec a_1) = e^{i2\pi x_1} \qquad c(\vec a_2) = e^{i2\pi x_2} \qquad c(\vec a_3) = e^{i2\pi x_3}$

$$c(\vec R) = c(n_1\vec a_1 + n_2\vec a_2 + n_3\vec a_3) =$$

$$= c(\underbrace{\vec a_1+\vec a_1+\vec a_1+\ldots}_{n_1} + \underbrace{\vec a_2+\vec a_2}_{n_2} + \underbrace{\vec a_3+\vec a_3+\vec a_3}_{n_3}\ldots) =$$

$$= \underbrace{c(\vec a_1)\cdot c(\vec a_1)\ldots}_{n_1}\ \underbrace{c(\vec a_2)\,c(\vec a_2)\ldots}_{n_2}\ \underbrace{c(\vec a_3)\,c(\vec a_3)\ldots}_{n_3\ \text{TIMES}}$$

Bloch Theorem

$$c(\vec{R}) = [c(\vec{a}_1)]^{n_1} [c(\vec{a}_2)]^{n_2} [c(\vec{a}_3)]^{n_3}$$

$$\underbrace{c(\vec{a}_1)}_{e^{i2\pi x_1}} \quad e^{i2\pi x_2} \quad e^{i2\pi x_3}$$

$$= e^{i2\pi x_1 n_1} \cdot e^{i2\pi x_2 n_2} \cdot e^{i2\pi x_3 n_3}$$

$$= e^{i2\pi(x_1 n_1 + x_2 n_2 + x_3 n_3)}$$

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

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

$$\hat{T}_R[\psi(\vec{r})] = \psi(\vec{r}+\vec{R}) = c(\vec{R})\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r})$$

$$\vec{k}\cdot\vec{R} = (x_1\vec{b}_1 + \ldots\ldots) \cdot (n_1\vec{a}_1 + \ldots\ldots)$$

BLOCH TH. IN 2ND FORM.

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

Bloch Theorem (in two equiv forms)

BLOCH IN 2ND FORM.

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

$\psi_{\vec{k}}(\vec{r})e^{-i\vec{k}\cdot\vec{r}}$ IS PERIODIC.

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

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

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

BLOCH IN 1ST FORM

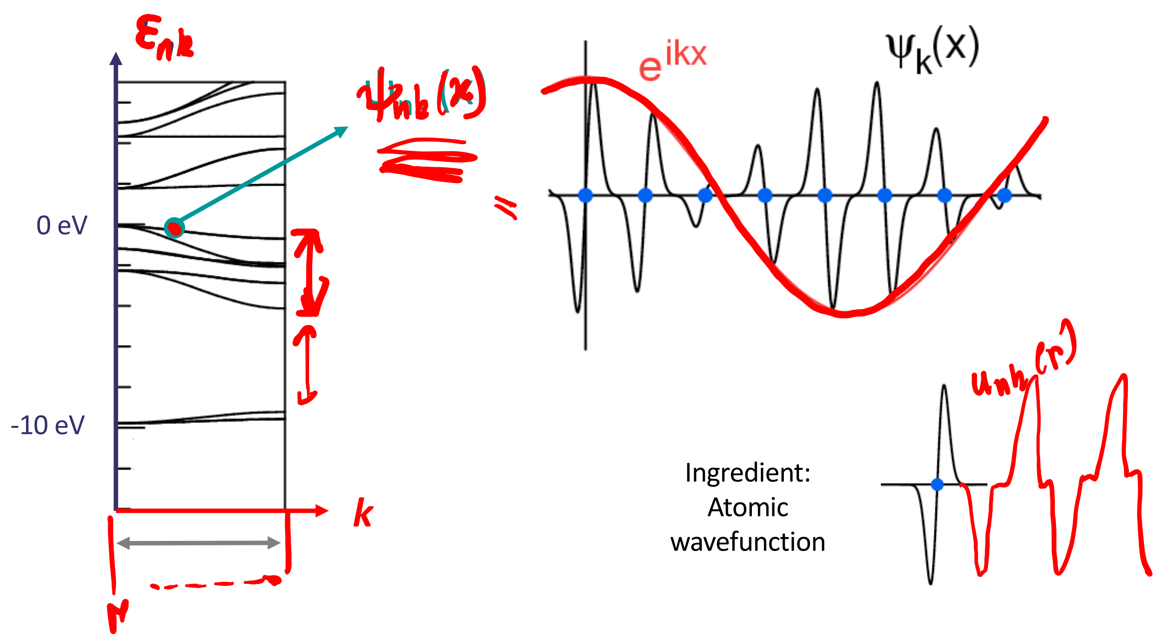
Bloch Theorem (in two equiv forms)

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

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

Bloch Theorem

Bloch wavefunction



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

From extended to primitive