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Solid State Physics

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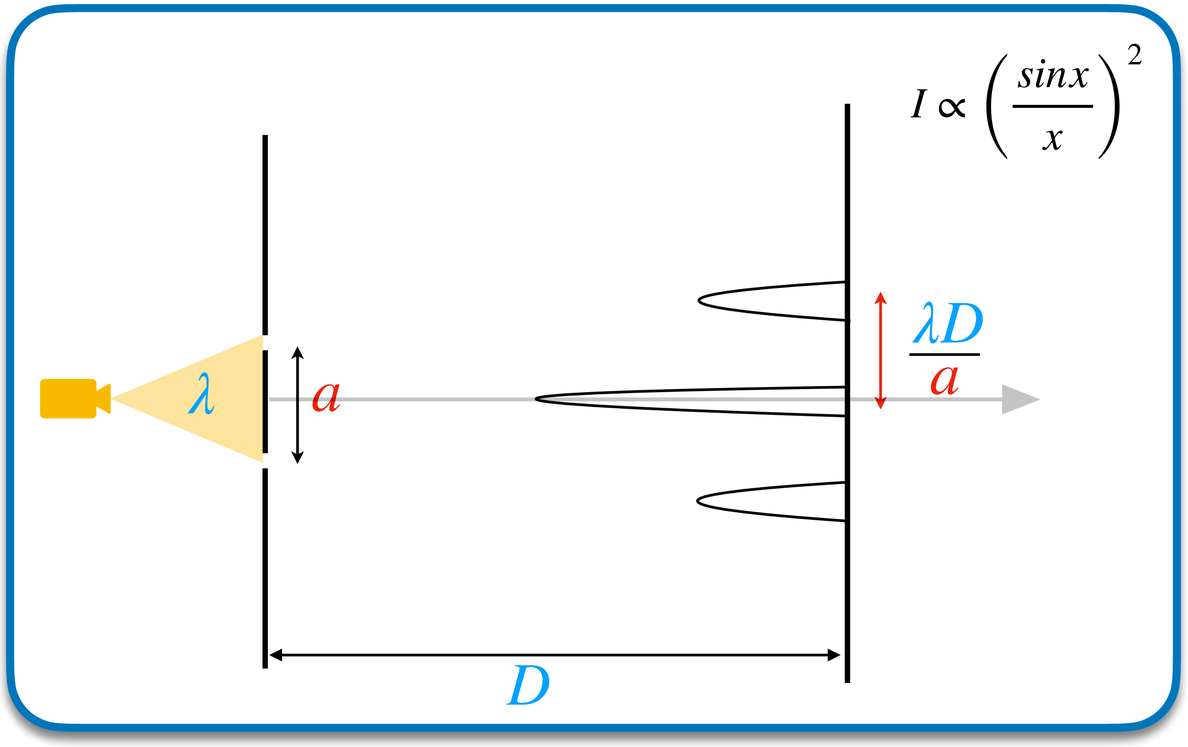
Objective : description of electrons in a PERIODIC system

periodicity	Fourier transform
k points	reciprocal space
gap	Brillouin zone

Outline

Introduction : double-slit experiment

$a \rightarrow 1/a$



$a \rightarrow 1/a$

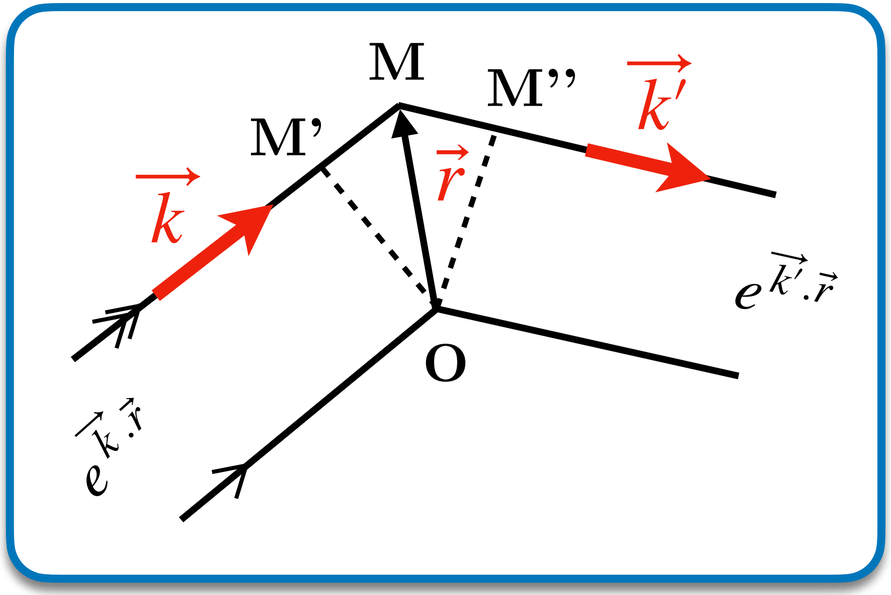
***conjugation* relation**

$x \rightarrow \frac{d}{dx}$

$\hat{x} \rightarrow \hat{p}_x = -i\hbar\frac{d}{dx}$

$\Delta x \,.\, \Delta p_x \sim \hbar$

Diffracted amplitude for elastic scattering



$$\| \vec{k} \| = \| \vec{k'} \|$$

path difference $\delta_{2/1}$ **evaluation :**

$$\delta_{2/1} = \mathrm{M'M} + \mathrm{MM''}$$

$$\delta_{2/1} = \frac{\lambda}{2\pi} \vec{k} \,.\, \vec{r} - \frac{\lambda}{2\pi} \vec{k'} \,.\, \vec{r}$$

diffracted amplitude :

$$F = \int d\vec{r}\; n(\vec{r})\; e^{-i \Delta\vec{k} \,.\, \vec{r}}$$

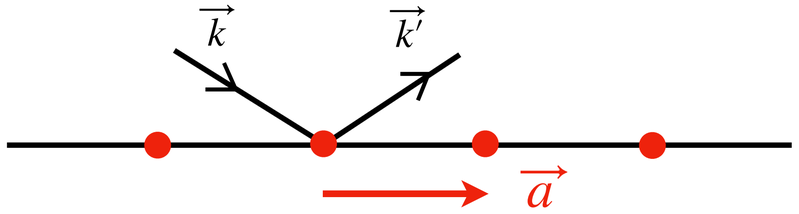
phase factor

$$\Delta\vec{k} = \vec{k'} - \vec{k}$$

density

Exercise : X-Ray diffraction

N **diffracting centers**

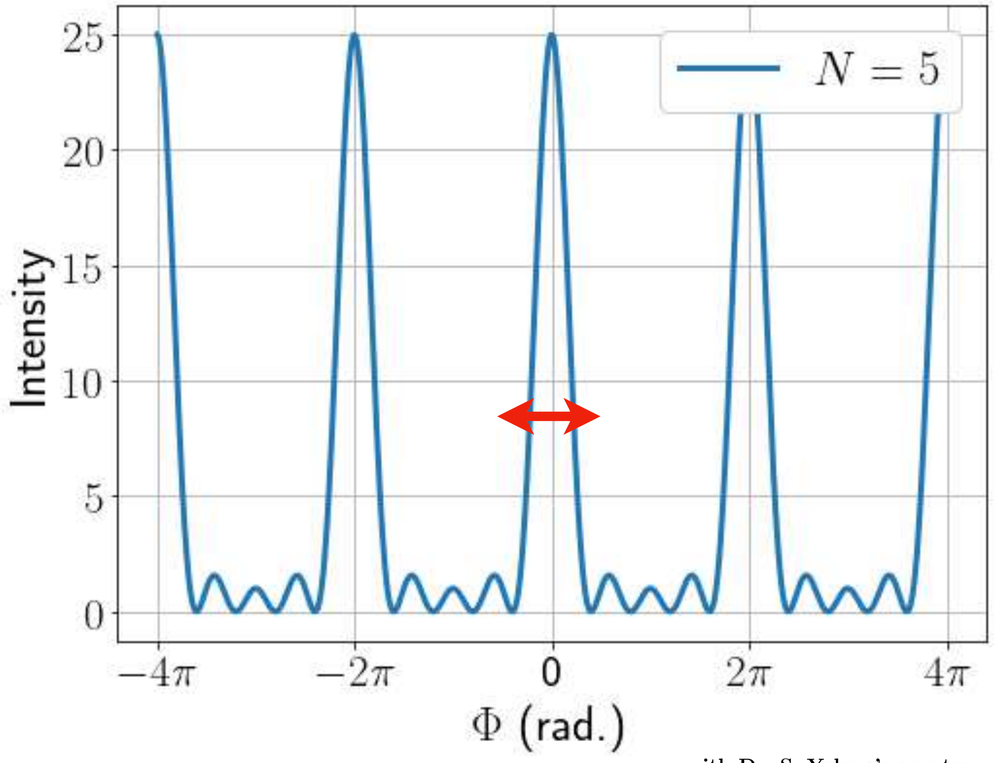


phase factor $\Phi = \Delta\vec{k} \,.\, \vec{a}$

$$F = \sum_{n=0}^{N-1} e^{-i\left(\Delta\vec{k} \,.\, n\vec{a}\right)} = \frac{1 - e^{-iN\Phi}}{1 - e^{-i\Phi}} = e^{i(N-1)\frac{\Phi}{2}} \frac{\sin\frac{N\Phi}{2}}{\sin\frac{\Phi}{2}}$$

Exercise : X-Ray diffraction

$$FF^* = \left(\frac{\sin \frac{N\Phi}{2}}{\sin \frac{\Phi}{2}} \right)^2$$



with Dr. S. Yalouz's courtesy

- **maxima** $\Delta \vec{k} \,.\, \vec{a} = 2\pi m$ $\quad \Delta k = m\frac{2\pi}{a} \quad m \in \mathbb{Z}$

Bragg condition

- **intensity maxima** $FF^* = N^2$

- **peaks width** $\propto 1/N$ → **large crystals for *resolution***

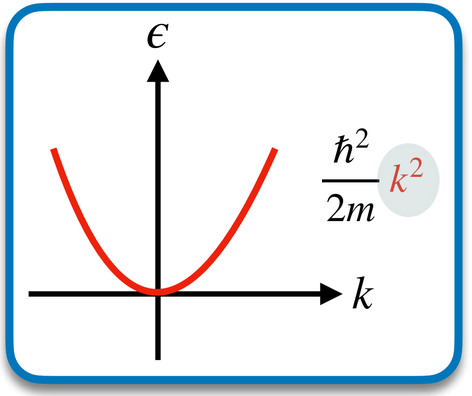
$a \longrightarrow 1/a$

''from free electrons to nearly-free electrons''

1. FREE ELECTRON

$V(x) = 0 \quad \forall x$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\varphi(x) = \epsilon \,.\, \varphi(x)$$



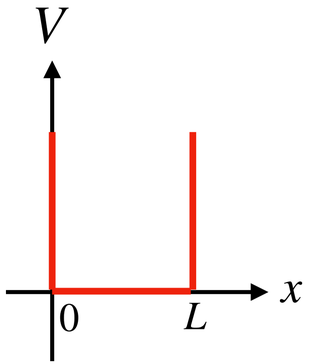
$\varphi(x) = e^{\pm ikx}$

plane-waves

plane-waves cannot describe a physical state normalization !

$k \longrightarrow p_x = \hbar k$ is perfectly defined

2. ELECTRON IN BOX



$$\begin{cases} V(0) = V(L) = \infty \\ V(x) = 0 \qquad \text{elsewhere} \end{cases}$$

$$\varphi_n(x) = \mathrm{A}\sin\left(\frac{2\pi}{\lambda_n}x\right) \qquad \frac{n\lambda_n}{2} = L$$

constraints ⟶ **quantization**

$$k_n = \frac{2\pi}{\lambda_n} = \frac{n\pi}{L} \qquad \epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

Definition : the *Fermi level* is the energy of the highest occupied level

example : N electrons, 2 electrons per level

$$n_F = \frac{N}{2} \qquad \epsilon_F = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2$$

perturbation scheme from a free-electron picture

3. NEARLY-FREE ELECTRON

$\hat{H} = \hat{H}_0$ zeroth-order plane-waves $\varphi_{\pm}(x) = e^{\pm ikx}$ $\epsilon(k) = \dfrac{\hbar^2 k^2}{2m}$

$\hat{H} = \hat{H}_0 + \hat{P}$ presence of nuclei

Bragg condition : $\Delta k = 2k = m\dfrac{2\pi}{a}$

$k = \pm\dfrac{\pi}{a},\ \pm\dfrac{2\pi}{a}\cdots$

Bragg reflected standing waves are generated

$$\psi_{\pm}(x) = \frac{e^{ikx} \pm e^{-ikx}}{\sqrt{2}}$$

energies of these standing waves ?

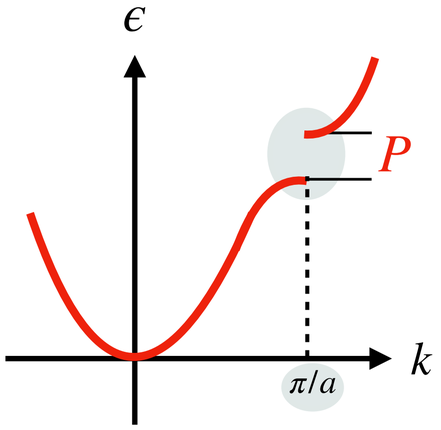
PERIODICITY of the potential $\hat{H} = \hat{H}_0 + \hat{P}$

$P(x) = P\cos\left(\frac{2\pi}{a}x\right)$ *a*-periodic potential

$$E_{\pm} = \epsilon(\pi/a) + \langle\psi_{\pm}|\hat{P}|\psi_{\pm}\rangle$$

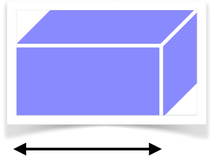
$$\Delta E = E_+ - E_- = \int_0^a dx \left(|\psi_+(x)|^2 - |\psi_-(x)|^2 \right) P(x)$$

$$\Delta E = P$$



Born-Von Kármán boundary conditions

PERIODICITY ?

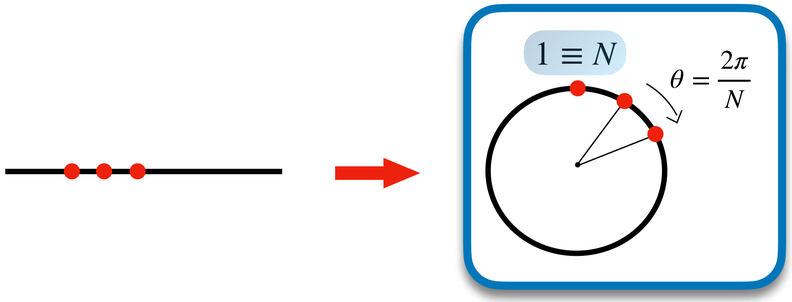


crystal = finite-size system

$L \sim \mu m$

inter-atomic distance $a \sim$ Å

$\sim N = 10^4$ atoms



$$\Psi\left(\vec{r} + N_i \vec{a_i}\right) = \Psi\left(\vec{r}\right) \qquad i = 1 - 3$$

Born-Von Kármán boundary conditions

Periodicities : direct and reciprocal spaces

Physical and Practical periodicities

$n(\vec{r}+\vec{R}) = n(\vec{r})$ $\qquad \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \qquad n_i \in \mathbb{Z}$

Definition : $\vec{a}_i$ are the *direct space* vectors

$$\vec{b}_3 = 2\pi\frac{\vec{a}_1 \times \vec{a}_2}{V_c} \qquad V_c = \vec{a}_1 . \left(\vec{a}_2 \times \vec{a}_3\right)$$

$\vec{b}_2$ and $\vec{b}_3$ similarly

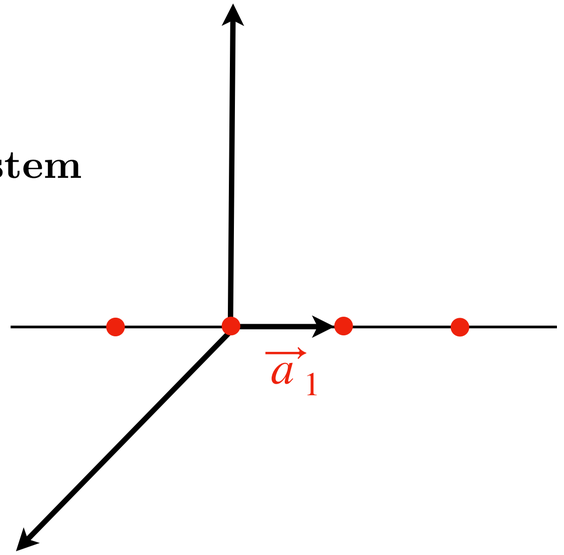
Definition : $\vec{b}_j$ are the *reciprocal space* vectors $\mathbb{R}^{-3}$

$$\vec{K} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3 \qquad m_i \in \mathbb{Z}$$

Fourier decomposition : $n(\vec{r}) = \sum_{\vec{K}} n_K \, e^{i\vec{K}.\vec{r}}$

Periodicity in 1D system ?

example **: 1D system**



direct space $\mathbb{R}^3$

$\vec{a}_i \cdot \vec{a}_j = \delta_{ij} \qquad \vec{a}_1 \cdot \vec{a}_j = \delta_{ij}$

$\left|\vec{a}_1\right| = a$

$\left|\vec{a}_2\right| \gg a$ **and** $\left|\vec{a}_3\right| \gg a$

reciprocal space $\mathbb{R}^{-3}$

$$\left|\vec{b}_1\right| = \frac{2\pi}{a}$$

Definition **:** $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ **Brillouin zone**

Physical and Practical periodicities

Born-Von Kármán boundary conditions : $\Psi\left(\vec{r}+N_i\vec{a_i}\right)=\Psi\left(\vec{r}\right) \qquad i=1-3$

$$\vec{q}=m_1\frac{\vec{b}_1}{N_1}+m_2\frac{\vec{b}_2}{N_2}+m_3\frac{\vec{b}_3}{N_3}$$

$$\vec{b}_3=2\pi\frac{\vec{a}_1\times\vec{a}_2}{V_c}$$

Fourier decomposition : $\Psi(\vec{r})=\sum_{\vec{q}} c_q\, e^{i\vec{q}.\vec{r}}$

Consequences : Bloch Theorem

Physical ***and*** ***Practical*** **periodicities**

$$U(\vec{r}) = \sum_{\vec{K}} U_K \, e^{i\vec{K}.\vec{r}} \qquad \Psi(\vec{r}) = \sum_{\vec{q}} c_q \, e^{i\vec{q}.\vec{r}}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{U} \qquad \hat{H}\Psi(\vec{r}) = \epsilon\Psi(\vec{r})$$

Exercise : $$\sum_q e^{i\vec{q}\vec{r}} \left\{ \left(\frac{\hbar^2 q^2}{2m} - \epsilon \right) c_q + \sum_K U_K c_{q-K} \right\} = 0$$

$$\left(\frac{\hbar^2}{2m} \left(\vec{k} - \vec{K'} \right)^2 - \epsilon \right) c_{k-K'} + \sum_K U_{K'-K} c_{k-K} = 0$$

Schrödinger equation !

for a given $\vec{k}$ in the Brillouin zone : $c_k, c_{k-K}, c_{k-K'} \ldots$ **are coupled**

$$\Psi(\vec{r}) = \sum_{\vec{K}} c_{k-K} \, e^{i(\vec{k}-\vec{K}).\vec{r}}$$

$\vec{K} \in \mathbb{R}^{-3}$

Consequences : Bloch theorem

$$\Psi\left(\vec{r}\right) = \sum_{\vec{K}} c_{k-K}\, e^{i(\vec{k}-\vec{K}).\vec{r}} = e^{i\vec{k}.\vec{r}} \sum_{\vec{K}} c_{k-K}\, e^{-i\vec{K}.\vec{r}} = e^{i\vec{k}.\vec{r}}\,.\,u_k\left(\vec{r}\right)$$

$$\text{with} \qquad u_k\left(\vec{r}\right) = \sum_{\vec{K}} c_{k-K}\, e^{-i\vec{K}.\vec{r}}$$

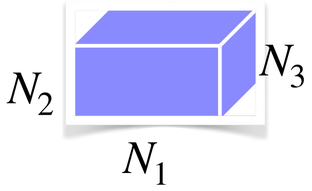
Exercise : check that $u_k\left(\vec{r}+\vec{R}\right) = u_k\left(\vec{r}\right)$

$$\Psi\left(\vec{r}+\vec{R}\right) = e^{i\vec{k}.\vec{R}}\,.\,\Psi\left(\vec{r}\right) \quad \rightarrow \quad n\left(\vec{r}+\vec{R}\right) = n\left(\vec{r}\right)$$

Bloch theorem

$$\Psi_k\left(\vec{r}\right) = e^{i\vec{k}.\vec{r}}\,.\,u_k\left(\vec{r}\right) \quad u_k \text{ being } \vec{R} \text{ periodic}$$

Consequence of Bloch theorem



$N_1 \times N_2 \times N_3$ **unit cells**

$$\Psi(\vec{r} + N_i\vec{a_i}) = \Psi(\vec{r}) = e^{iN_i\vec{k}.\vec{a_i}} . \Psi(\vec{r})$$

Bloch theorem

BVK

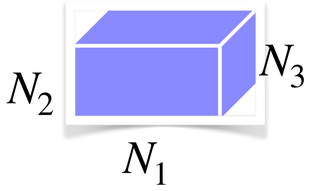
$$e^{iN_i\vec{k}.\vec{a_i}} = 1$$

$$\vec{k} = \sum_{i=1}^{3} x_i \vec{b}_i \qquad \vec{b}_i \in \mathbb{R}^{-3} \qquad \vec{k} . \vec{a}_i = 2\pi x_i$$

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

$$e^{2\pi i x_i N_i} = 1 \qquad x_i = \frac{m_i}{N_i} \qquad m_i \in \mathbb{Z}$$

Consequence of Bloch theorem



$N_1 \times N_2 \times N_3$ **unit cells**

$$\vec{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \vec{b}_i$$

- **elementary volume in the reciprocal space :** $\Delta \vec{k} = \frac{\vec{b}_1}{N_1} . \left(\frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3} \right)$
- **volume in the reciprocal space :** $V = \vec{b}_1 . \left(\vec{b}_2 \times \vec{b}_3 \right)$

number of k **points = number of unit cells**

Band structure of a solid

$\Psi_k(\vec{r}) = e^{i\vec{k}.\vec{r}}.u_k(\vec{r})$ **in the Schrödinger equation :**

$$\begin{cases} \hat{H}u_k(\vec{r}) = \left(\frac{\hbar^2}{2m}\left(-i\vec{\nabla} + \vec{k}\right)^2 + U(\vec{r})\right)u_k(\vec{r}) = \epsilon_k u_k(\vec{r}) \\ u_k\left(\vec{r} + \vec{R}\right) = u_k(\vec{r}) \end{cases}$$

→ u_{nk} and ϵ_{nk}

boundary conditions

this is the *band structure* of the solid

Exercise : check that $\vec{k} \to \vec{k} + \vec{K}$ the spectrum remains identical

Preliminary conclusions

PERIODICITY

cf. *symmetries* in molecules

- **reciprocal space** $\mathbb{R}^{-3}$

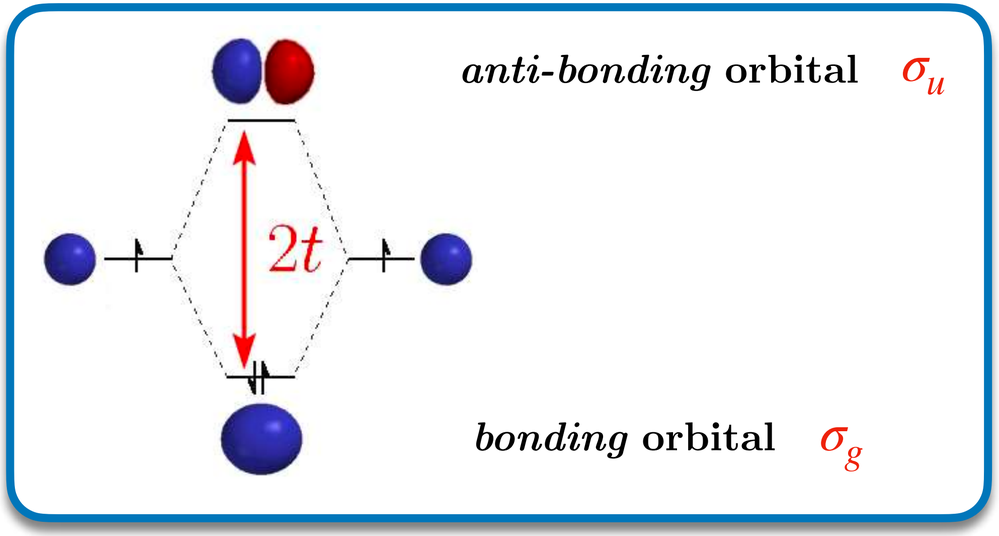
  Brillouin zone $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ **Fourier transform**

- **band gap opening** $\pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \ldots$ **Bragg reflection**

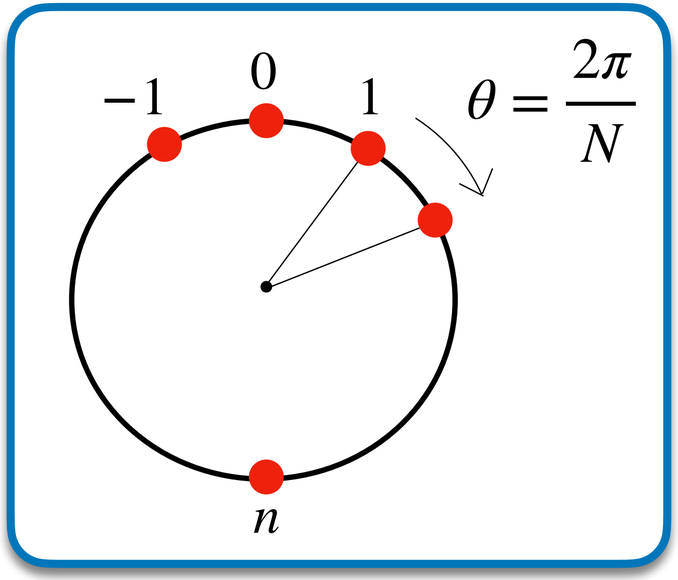
- $\Psi_k(\vec{r}) = e^{i\vec{k}.\vec{r}}.u_k(\vec{r})$ u_k **being** $\overrightarrow{R}$ **periodic** **Bloch theorem**

''from atoms to large molecules''

brief reminder H_2 in a minimal atomic orbitals basis set



Starting picture : $N \gg 1$ atoms regularly spaced



symmetry point group C_{2n}

BVK conditions !

$N = 2n$ **atomic orbitals** $\left\{ |\varphi_0\rangle \, , \, |\varphi_{\pm 1}\rangle \, , \, |\varphi_{\pm 2}\rangle \, , \, \ldots \, , \, |\varphi_{\pm(n-1)}\rangle \, , \, |\varphi_n\rangle \right\}$

simplicity !

$$\Gamma_{2n} = \bigoplus_{l=-n+1}^{n} \Gamma_l$$

irreducible **representations of the**

C_{2n} *symmetry point group*

Bloch function

basis set : $\left\{ |\varphi_0\rangle \ , \ |\varphi_{\pm 1}\rangle \ , \ |\varphi_{\pm 2}\rangle \ , \ \ldots \ , \ |\varphi_{\pm(n-1)}\rangle \ , \ |\varphi_n\rangle \right\}$

$$|\Phi_l\rangle = \frac{1}{\sqrt{2n}} \sum_{m=-n+1}^{n} \exp\left(\frac{2i\pi ml}{2n}\right) |\varphi_m\rangle$$

Setting $k = \dfrac{2\pi}{Na} l$ $\qquad l = 0 \ , \ \pm 1 \ , \ \pm 2 \ , \ \ldots \ , \ n$ ← $N \gg 1$ **values**

number of k **points = number of cells**

2π **is the length of the circle**

Na **is the length of the chain**

with $\vec{r}_m = m\vec{a}$

$$|\Phi_k\rangle = \frac{1}{\sqrt{2n}} \sum_{m=-n+1}^{n} e^{i\vec{k}.\vec{r}_m} |\varphi_m\rangle$$

Definition **:** Φ_k **are the** *Bloch orbitals*

Note **:** k **varies almost continuously in** $\left[-\dfrac{\pi}{a}, \dfrac{\pi}{a}\right]$

from translational periodicity : $\varphi_m(\vec{r}) = \varphi_0(\vec{r} - \vec{r}_m)$ **(Hint : check for** $\vec{r} = \vec{r}_m$ **)**

$$\Phi_k\left(\vec{r}\right) = \frac{1}{\sqrt{2n}} \sum_{m=-n+1}^{n} e^{i\vec{k}.\vec{r}_m} . \varphi_m\left(\vec{r}\right) = \frac{1}{\sqrt{2n}} \sum_{m=-n+1}^{n} e^{i\vec{k}.\vec{r}_m} . \varphi_0\left(\vec{r} - \vec{r}_m\right)$$

$$= e^{i\vec{k}.\vec{r}} \underbrace{\frac{1}{\sqrt{2n}} \sum_{m=-n+1}^{n} e^{-i\vec{k}.\left(\vec{r} - \vec{r}_m\right)} . \varphi_0\left(\vec{r} - \vec{r}_m\right)}_{u_k\left(\vec{r}\right)}$$

Exercise : **check that** u_k **is** a **periodic**

$$\Phi_k\left(\vec{r}\right) = e^{i\vec{k}.\vec{r}} . u_k\left(\vec{r}\right)$$ **Bloch theorem !**

From Bloch orbitals to crystalline orbitals

Theorem : $\langle \Phi_k | \hat{h} | \Phi_{k'} \rangle = 0$ as soon as $k \neq k'$

molecules : $\langle \varphi_\alpha | \hat{h} | \varphi_\beta \rangle = 0$ as soon as $\Gamma_\alpha \neq \Gamma_\beta$

Generalization : M Bloch functions $\left\{ | \Phi_{k,j} \rangle \right\}_{j = 1 - M}$

example : diamond, $2s$, $2p$
$M = 4$

$$| \Psi_k \rangle = \sum_{j=1}^{M} c_{k,j} \, | \Phi_{k,j} \rangle$$

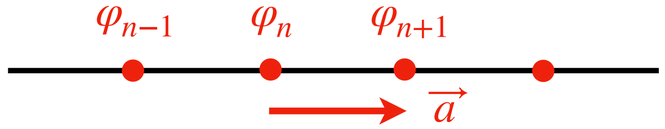
Definition : Ψ_k are the *crystalline orbitals*

analogy : $| MO \rangle = \sum_{j=1}^{M} c_{\alpha,j} \, | SALC_{\alpha,j} \rangle$

***S**ymmetry-**A**dapted **L**inear **C**ombinations*

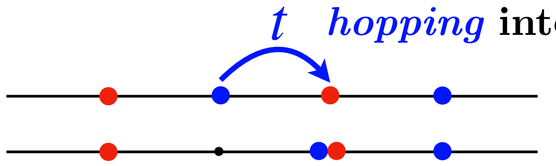
basis sets of the irreducible representations Γ_α

Tight-binding approach to a 1D system



$$\begin{cases} h_{ii} = \alpha \\ h_{ij} = \langle \varphi_i | \hat{h} | \varphi_j \rangle = t \\ \langle \varphi_i | \varphi_j \rangle = \delta_{ij} \end{cases}$$

Hückel !



$\alpha \sim -10$ eV

$t = \beta \sim -1$ eV

chemist's view on such problem :

$$\begin{vmatrix} \ddots & \ddots & 0 & 0 \\ \ddots & \alpha - \epsilon & t & 0 \\ 0 & t & \alpha - \epsilon & \ddots \\ 0 & 0 & \ddots & \ddots \end{vmatrix} = 0$$

secular determinant

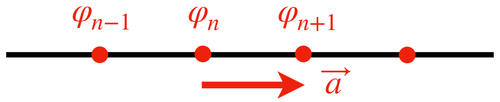
Bloch function construction :

$$|\Phi_k\rangle = \frac{1}{\sqrt{2n}} \sum_m e^{ikma} |\varphi_m\rangle$$

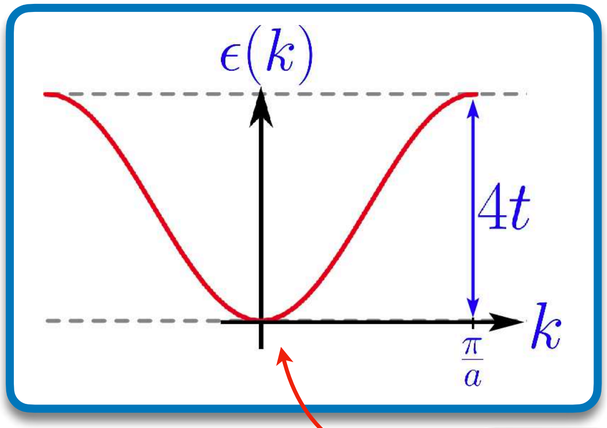
note : crystalline orbitals = Bloch orbitals

Exercise : show that $\epsilon_k = \langle \Phi_k | \hat{h} | \Phi_k \rangle = \alpha + 2t \cos(ka)$

Tight-binding approach to a 1D system



$$\epsilon(k) = \langle \Phi_k | \hat{h} | \Phi_k \rangle = \alpha + 2t\cos(ka)$$



$\epsilon_k \propto k^2$

$|k| \ll \frac{1}{a}$ or $\lambda \gg a$: the electron doesn't ''see'' the ions

Energy calculation : *half-filled* band

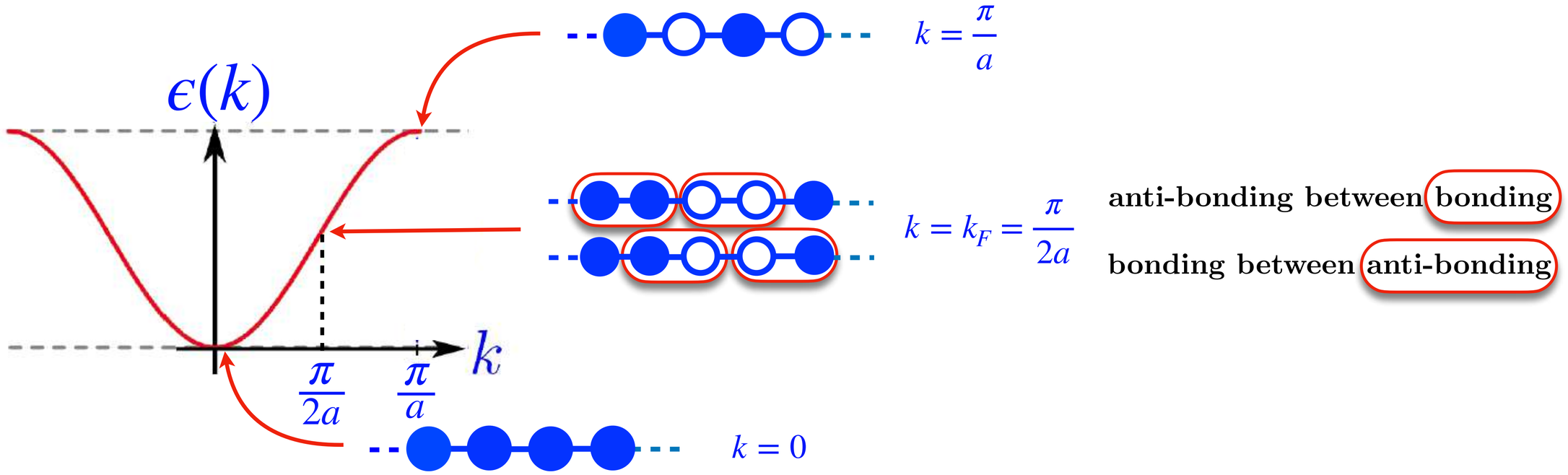
e*xample* : H-atom chain $2n$ **sites** 1e-/site

$$k_F = \frac{2\pi}{Na}\frac{n}{2} = \frac{\pi}{2a}$$

Exercise : $$E = \frac{1}{N}\sum_{j=-n/2+1}^{n/2} 2\left(\alpha + 2t\cos\frac{2\pi j}{N}\right) = \frac{a}{2\pi}\int_{-\pi/2a}^{\pi/2a} 2\left(\alpha + 2t\cos ka\right) dk = \alpha + \frac{4t}{\pi}$$

Back to molecular orbitals

$$|\Phi_k\rangle = \frac{1}{\sqrt{2n}} \sum_m e^{ikma} |\varphi_m\rangle$$



anti-bonding between bonding

bonding between anti-bonding

$$(\mathbf{H})_{2n} \equiv (\mathbf{H}_2)_n$$

chain of *atoms* chain of *dimers*

Peierls instability

metal/insulator transition

PERIODICITY

Physicists and / or Chemists views

- Brillouin zone $\left[-\frac{\pi}{a},\frac{\pi}{a}\right]$
- band structure

Bloch theorem $\Psi_k(\vec{r}) = e^{i\vec{k}.\vec{r}}.u_k(\vec{r})$

importance of plane-waves :

- starting point
- basis set
- reminiscent in Bloch theorem

tight-binding → DFT framework more lectures !