

THE PERIODIC LCAO APPROACH: HOW TO SOLVE THE SCHRÖDINGER EQUATION IN CRYSTALS

Davide Mitoli

University of Torino (Italy)

Jan 26, 2026



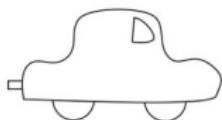
UNIVERSITÀ
DI TORINO

Advanced School on
QUANTUM MODELLING
of Materials with CRYSTAL



MODEL A SYSTEM

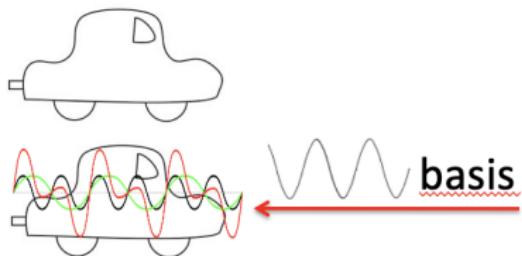
WHAT DOES IT MEAN?



- ☞ basis set of **localized** functions, to describe electrons (AOs)
- ☞ define the energetic contributions in the Hamiltonian, \hat{H} and build up the corresponding **Fock matrix**, F
- ☞ diagonalize such matrix to get
 - eigenvalues $\rightarrow \epsilon_i$
 - eigenvectors $\rightarrow \{c_{\mu i}\} \rightarrow \varphi_i(\mathbf{r})$
 - wavefunction $\rightarrow \Psi(\mathbf{r}) = \hat{A}| \dots \varphi_i \varphi_j \dots |$

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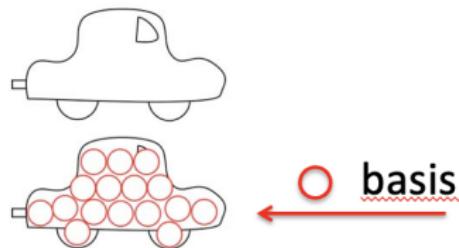
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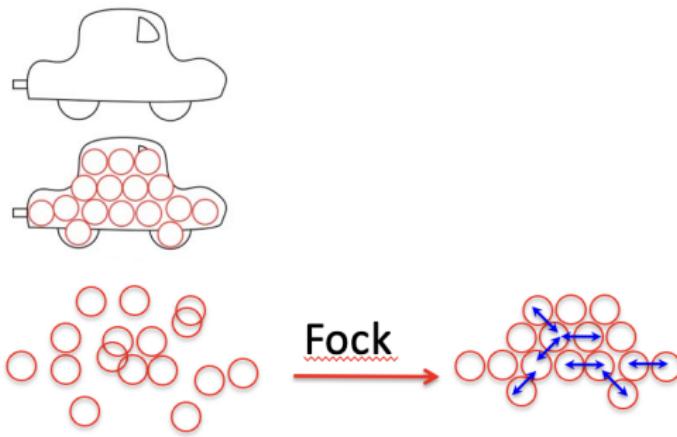
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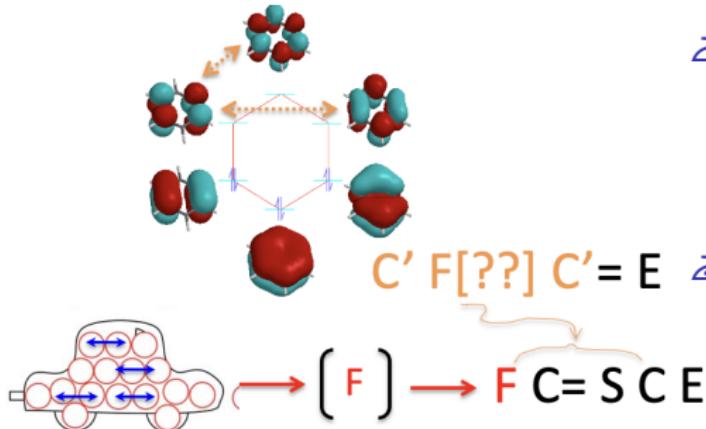
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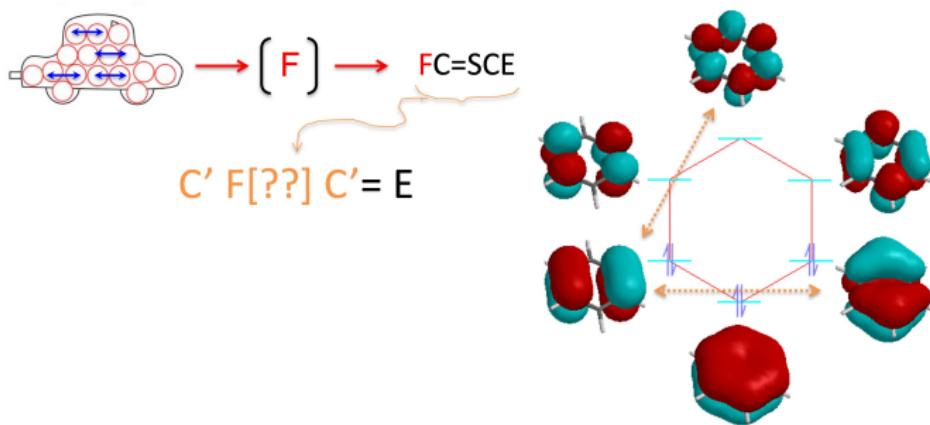


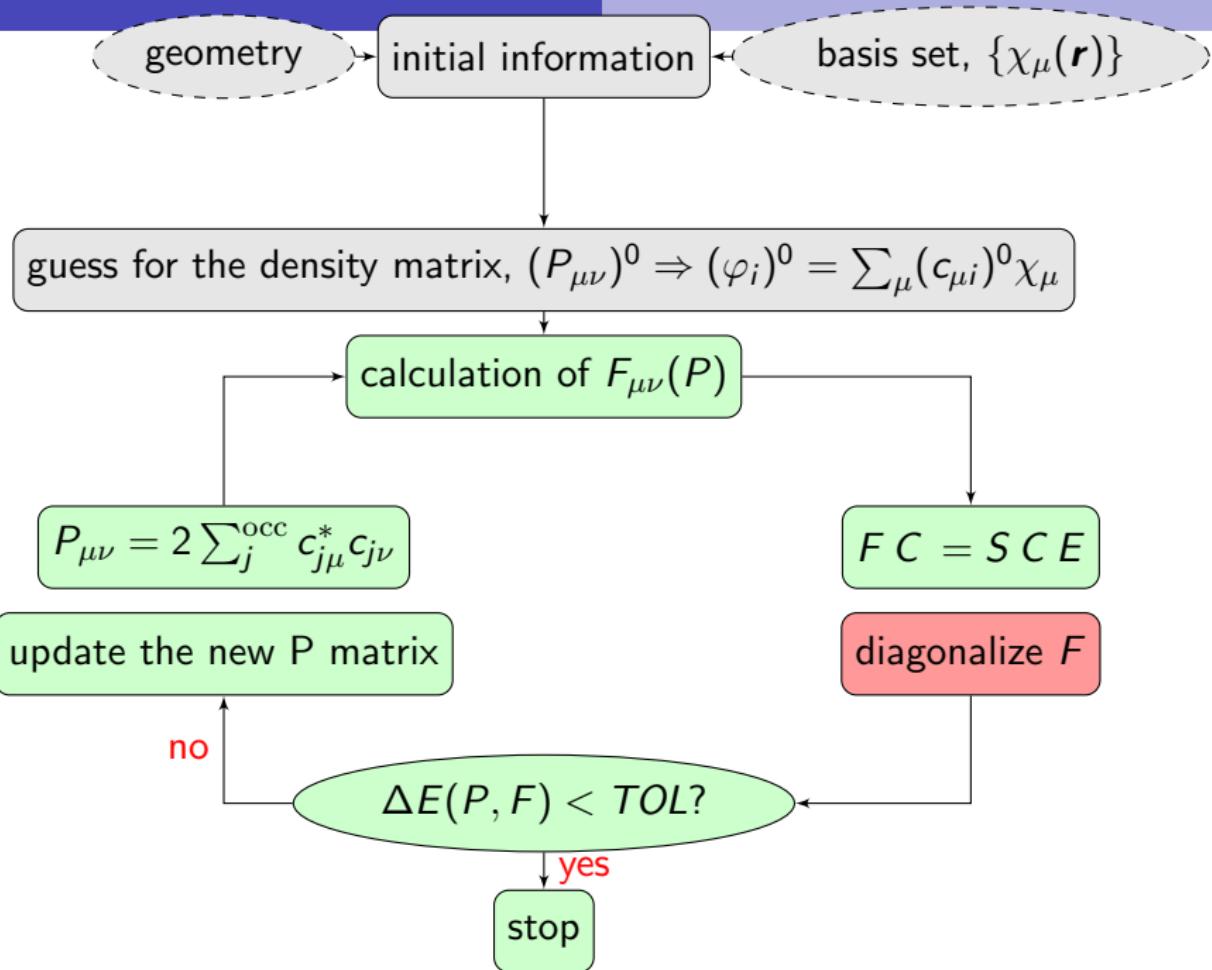
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MODEL A SYSTEM

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Need of a self-consistent field cycle (SCF)





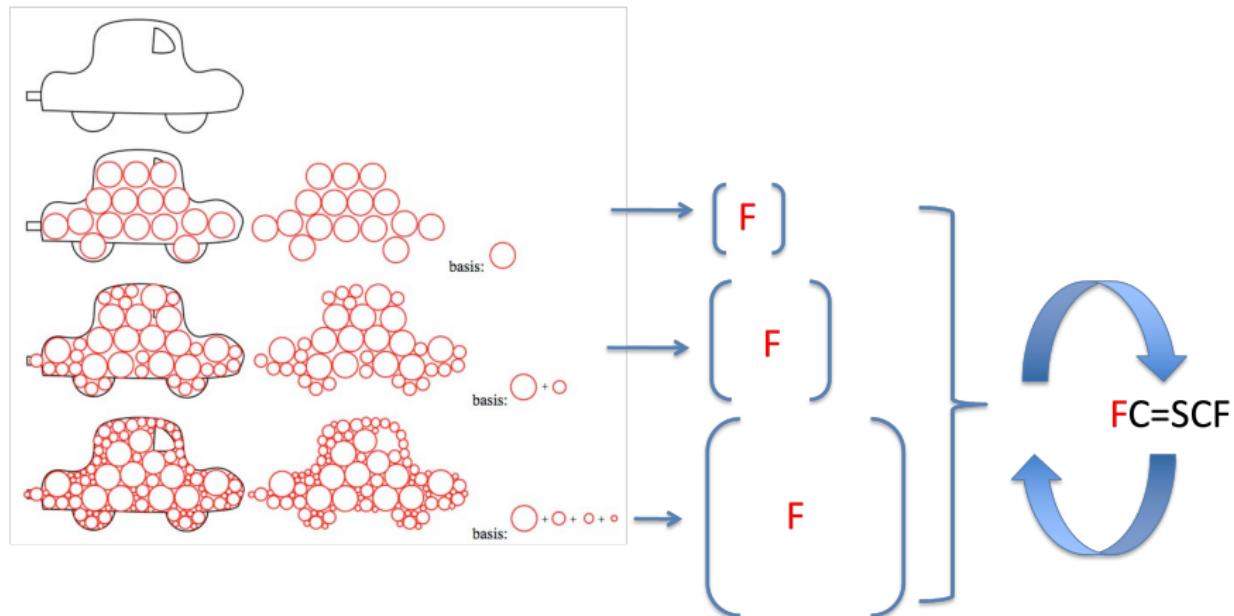
MODEL A MACROSCOPIC SYSTEM?

WHAT DOES IT MEAN?

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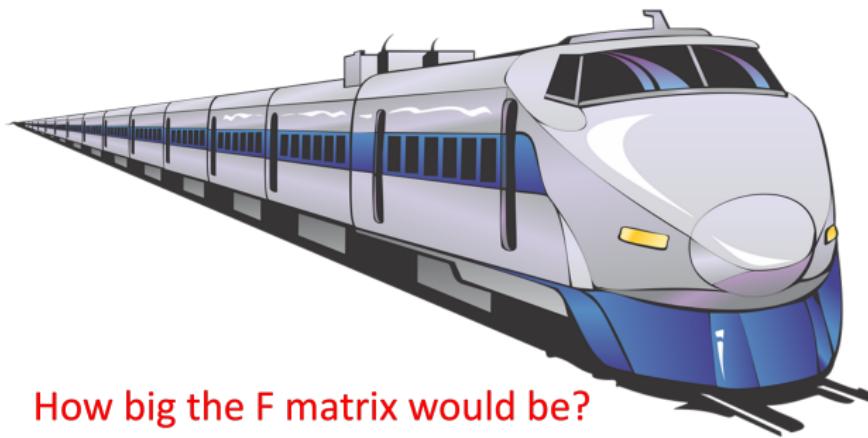
WHAT DOES IT MEAN?

effect of the **basis set**, $\{\chi_\mu(\mathbf{r})\}^M$, on the **Fock matrix dimension**



MODEL A MACROSCOPIC SYSTEM?

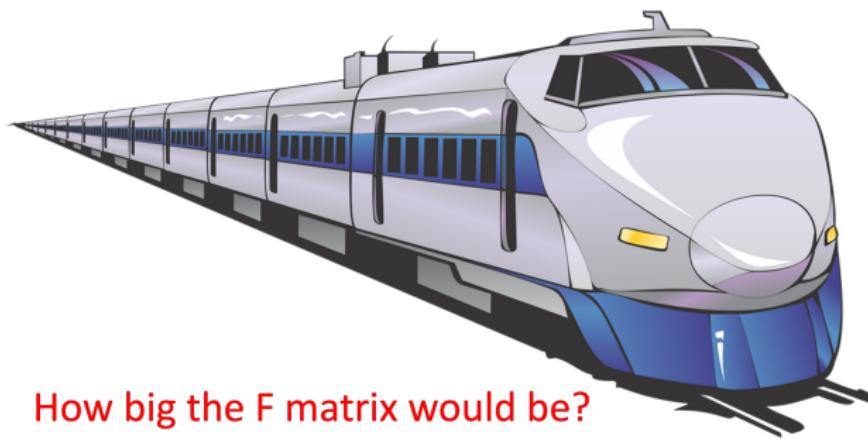
WHAT DOES IT MEAN?



How big the F matrix would be?

MODEL A MACROSCOPIC SYSTEM?

WHAT DOES IT MEAN?



How big the F matrix would be?

IN CONDENSED MATTER, SYMMETRY MATTERS!

...and **must** be exploited at many levels

OUTLINE

- 1 THE PERIODIC MODEL
- 2 SYMMETRY EXPLOITATION IN DIRECT SPACE
- 3 SYMMETRY EXPLOITATION IN RECIPROCAL SPACE
- 4 SCF ITERATIVE PROCEDURE IN SOLIDS

FROM REALITY TO THE MODEL

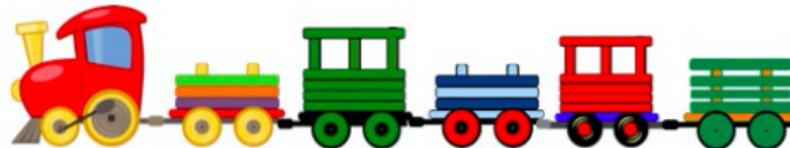
A REAL CRYSTAL

- ⌚ has an ∞ number of atoms and electrons
- ⌚ contains **defects**, i.e. dislocations, vacancies, interstitial and etero atoms, etc.. .
- ⌚ has **surfaces**

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→ Translational invariance and long-range order are almost **never satisfied**



THE MODEL

A MODEL CRYSTAL HAS

- ☺ Translational invariance
- ☺ No surfaces
- ☺ Periodic Boundary conditions

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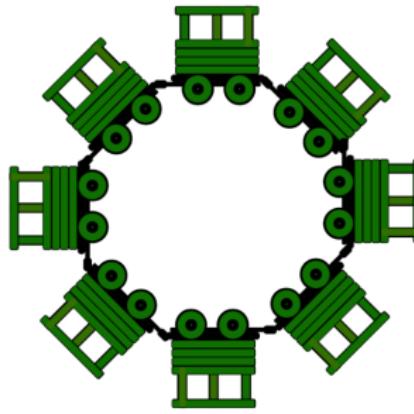
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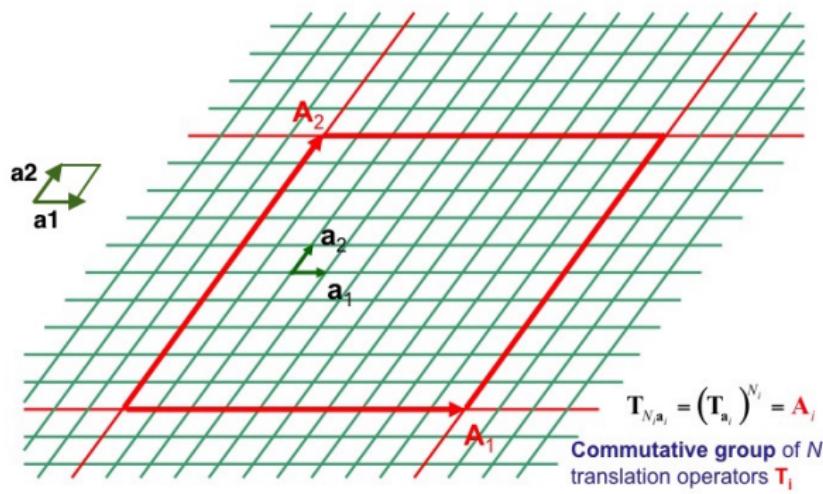
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MODEL OF A PERFECT CRYSTAL

A macro-lattice of $N = N_1 N_2 N_3$ unit cells

- as N is very large and surface effects are negligible in the bulk
- it coincides with the crystallographic model of an infinite array of cells containing the same group of atoms



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1. POINT SYMMETRY

DIRECT SPACE SYMMETRY

Given the space group $\{\hat{R}\}$ and the info on the asymmetric unit:

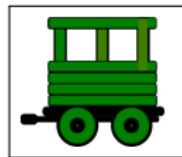
- build up the infinite system
- calculation of the irreducible integrals
- calculation of the irreducible part of the matrices

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Given the space group $\{\hat{R}\}$ and the info on the asymmetric unit:

reducible number of objects



$$\leftarrow \{\hat{R}\}$$

irreducible



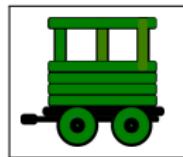
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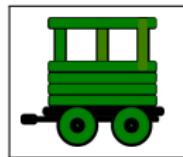
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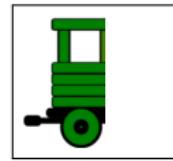
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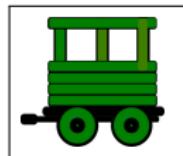
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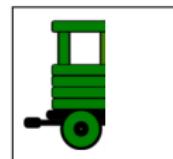
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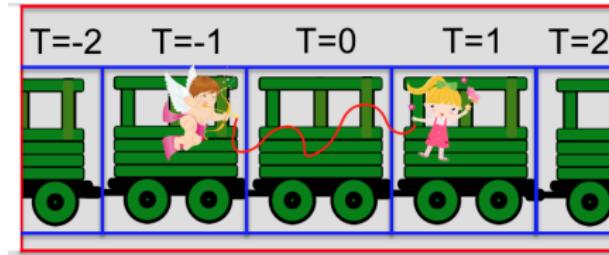


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2. TRANSLATIONAL SYMMETRY

IN DIRECT SPACE

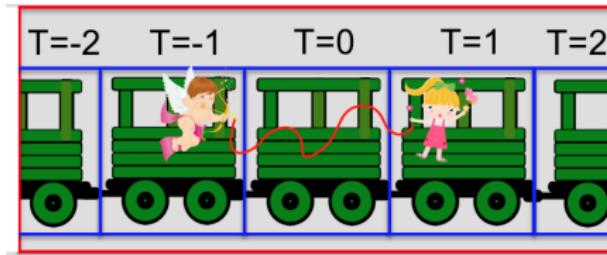
Given the translational invariance of the system



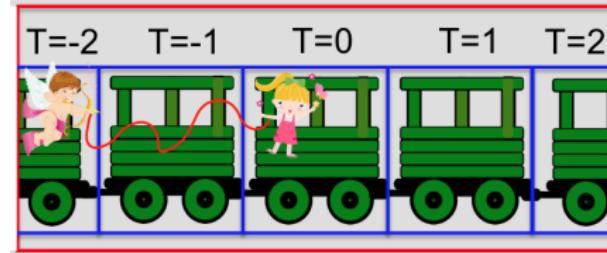
2. TRANSLATIONAL SYMMETRY

IN DIRECT SPACE

Given the translational invariance of the system



→ all the contributions to the Fock matrix are calculated with respect to the reference cell



A CLOSER LOOK AT THE FOCK MATRIX

IN DIRECT SPACE

- Representation in the AO basis set
- a set of M AO: $\{\chi_\mu^0(\mathbf{r})\}^M$ in the reference cell
- dimension of the CRYSTAL: N cells
- Square matrix $N^2 \Rightarrow$ blocks of size M

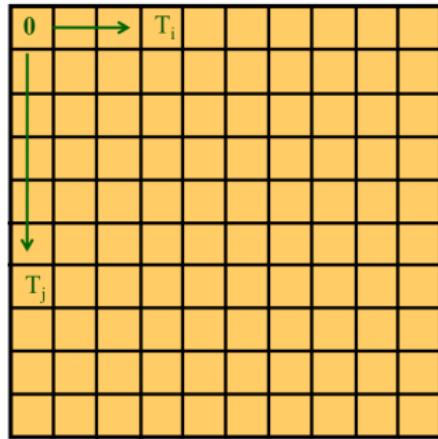
$T=0$


$$\langle \chi_\mu^{\mathbf{T}_i}(\mathbf{r}) | \hat{F} | \chi_\nu^{\mathbf{T}_j}(\mathbf{r}) \rangle = \langle \chi_\mu^0(\mathbf{r}) | \hat{F} | \chi_\nu^{(\mathbf{T}_j - \mathbf{T}_i)}(\mathbf{r}) \rangle \equiv F_{\mu\nu}^{\mathbf{T}_{ji}}$$

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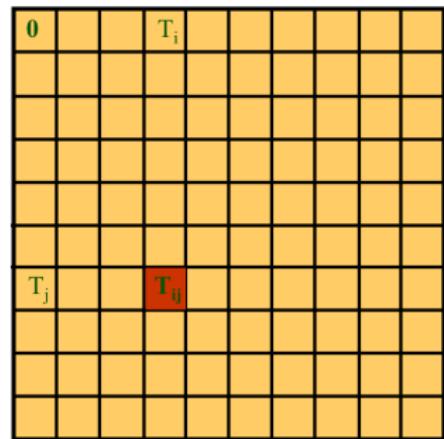


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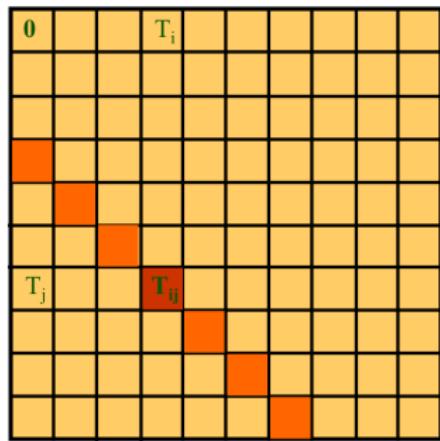


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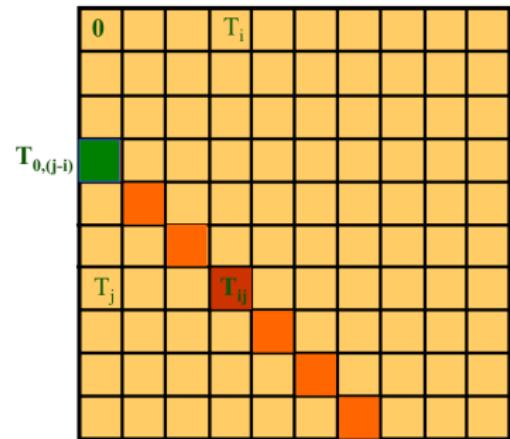


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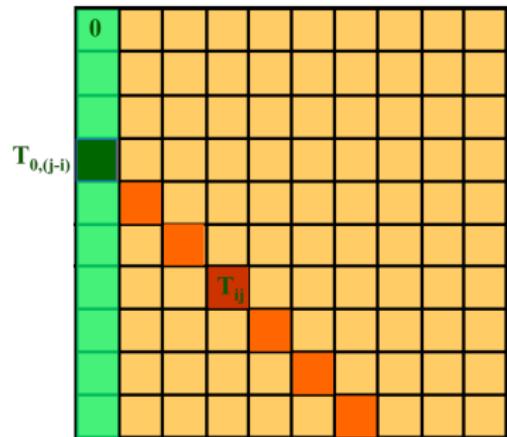


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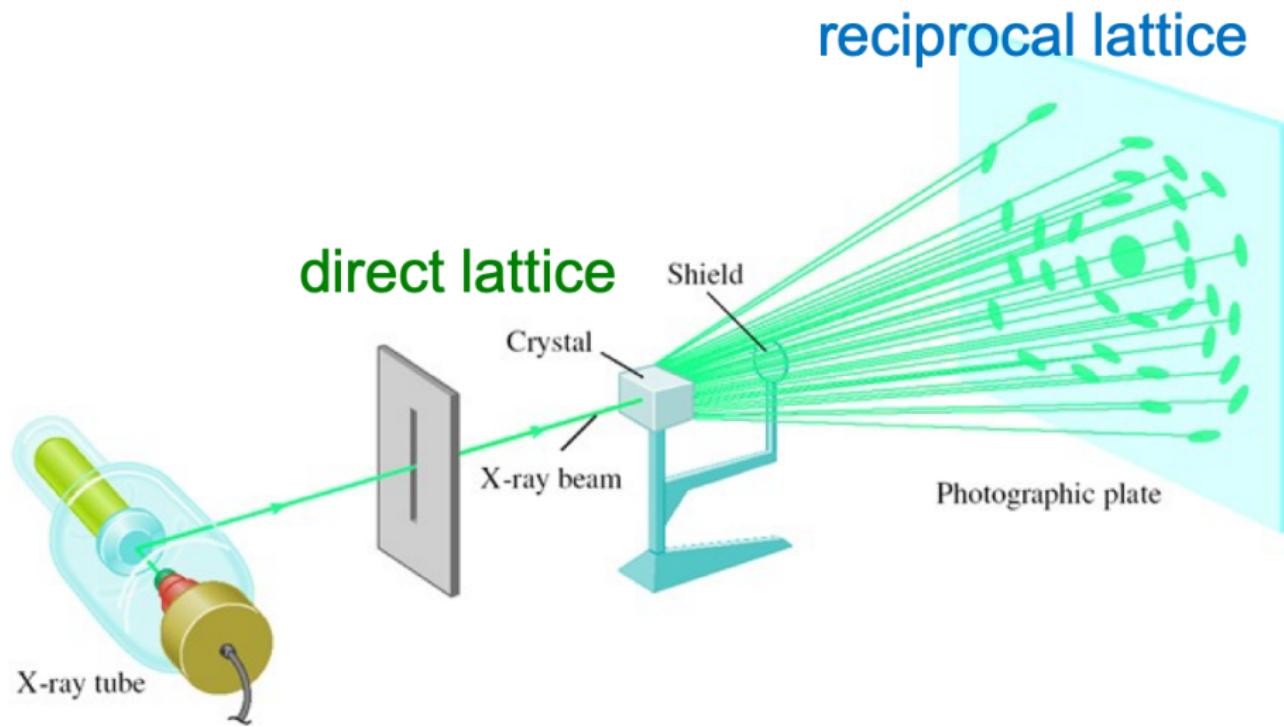


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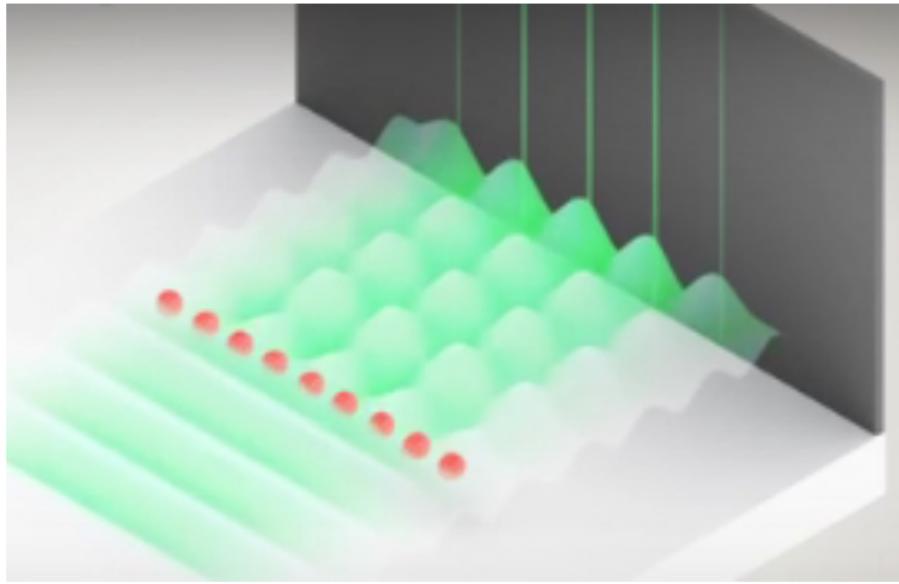
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WORKING BETWEEN TWO LATTICES



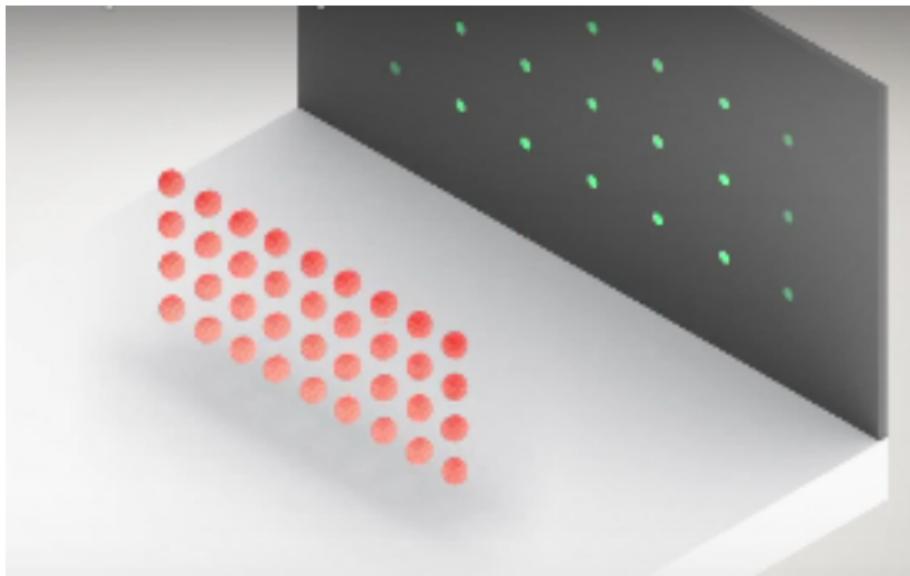
WHAT'S RECIPROCAL LATTICE?

- when X-rays interact with a periodic array of atoms, the pattern observed is a periodic array of lines



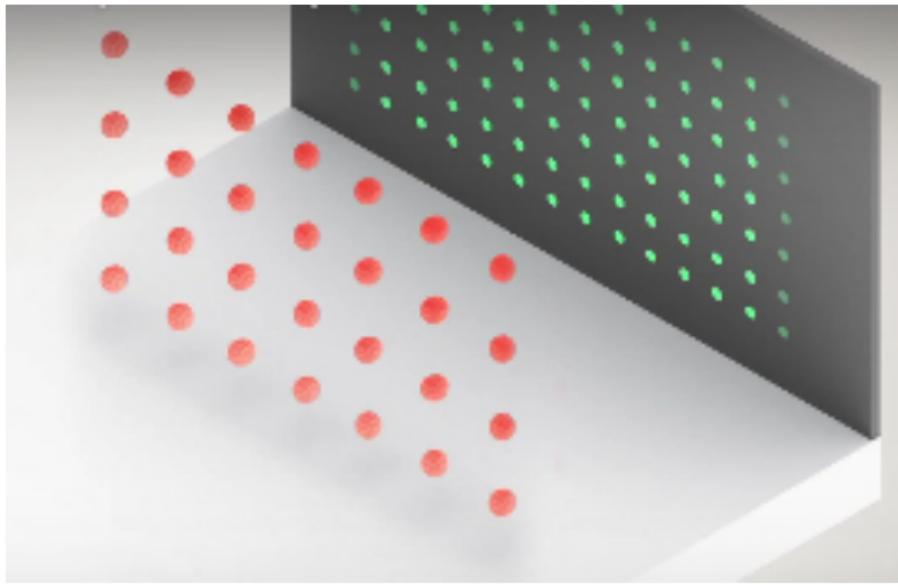
WHAT'S RECIPROCAL LATTICE?

- ☞ for a crystal, the diffraction pattern is a regular array of light spots, arranged in a **reciprocal** lattice



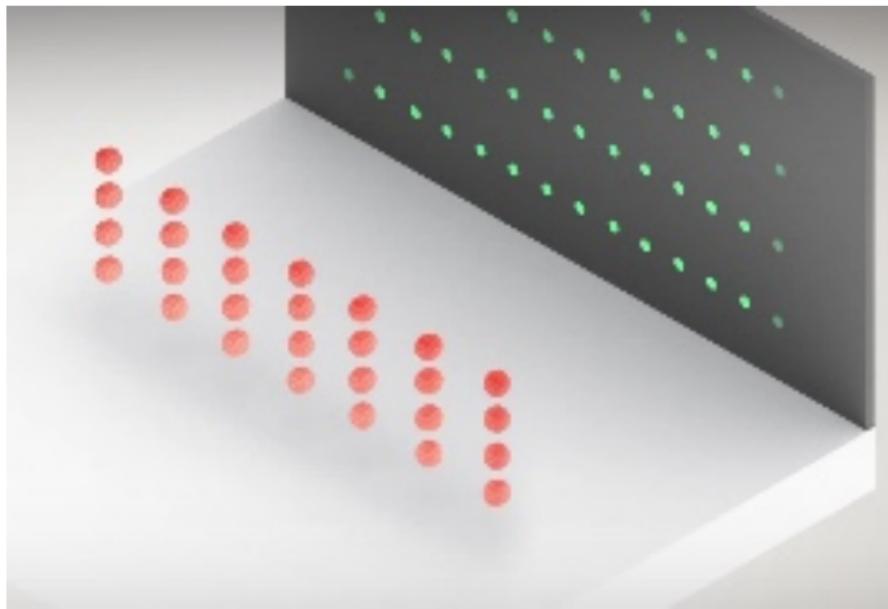
WHAT'S RECIPROCAL LATTICE?

- if atoms are more widely spaced, light spots get closer



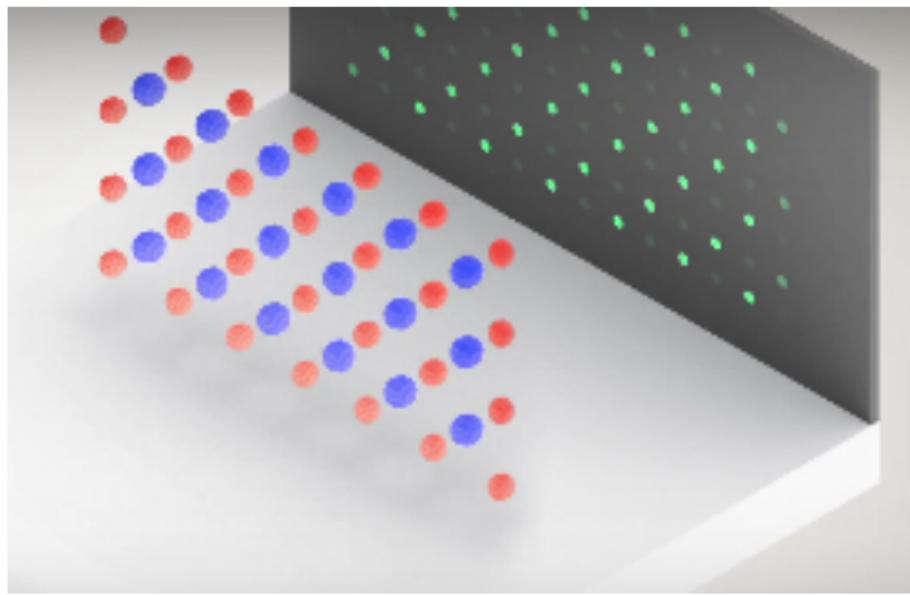
WHAT'S RECIPROCAL LATTICE?

- when atoms get closer, the reciprocal lattice expands



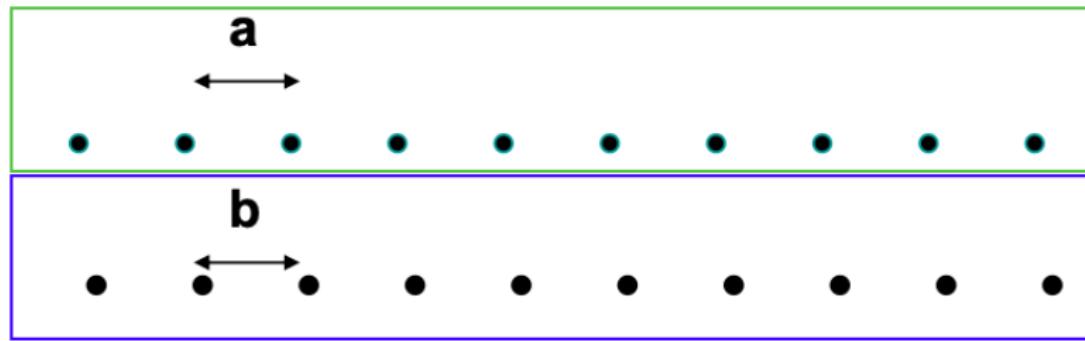
WHAT'S RECIPROCAL LATTICE?

- if other atoms are added, the intensity of the light spots may vary



DIRECT → RECIPROCAL

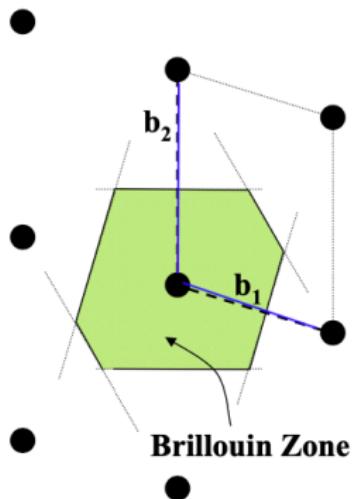
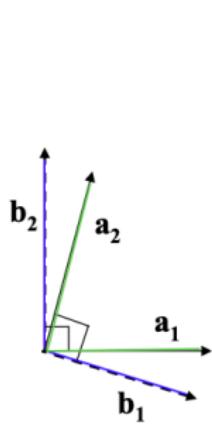
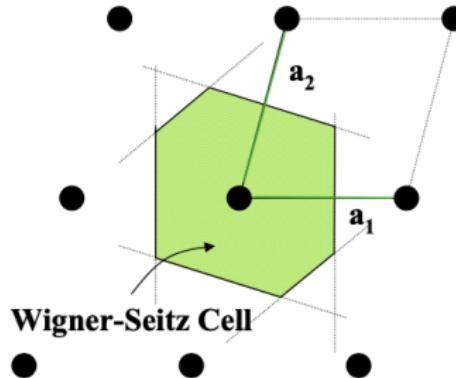
LATTICE IN 1D



$$\mathbf{b} = \frac{2\pi}{\mathbf{a}}$$

DIRECT → RECIPROCAL

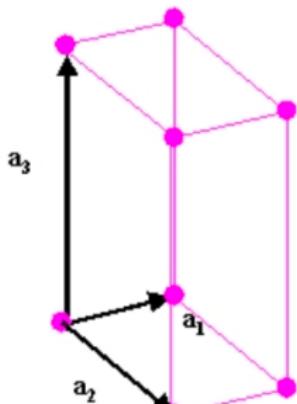
LATTICE IN 2D



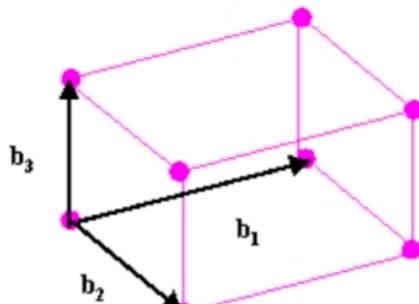
$$\mathbf{b}_i = \frac{2\pi}{a_j} \delta_{ij}$$

DIRECT → RECIPROCAL

LATTICE IN 3D



Simple Orthorhombic Bravais Lattice
with $a_3 > a_2 > a_1$



Reciprocal Lattice
Note: $b_1 > b_2 > b_3$

$$\mathbf{b}_i = \frac{2\pi}{|\mathbf{a}_i(\mathbf{a}_j \times \mathbf{a}_k)|} (\mathbf{a}_j \times \mathbf{a}_k)$$

THE 14 BRAVAIS LATTICE

IN DIRECT SPACE

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	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

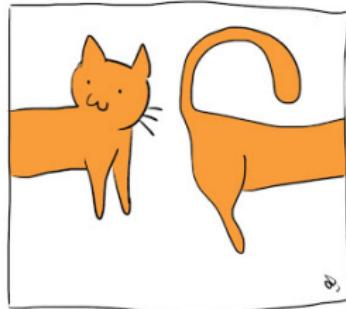
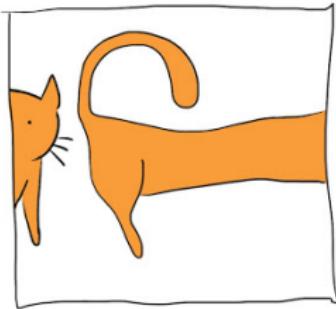
PERIODIC (OR CYCLIC) BOUNDARY CONDITIONS

BORN-VON KARMAN

The Fock matrix diagonalization is still a dreadful task...

- cyclic boundary conditions or Born-Von Karman boundary conditions

PERIODIC BOUNDARY CONDITIONS

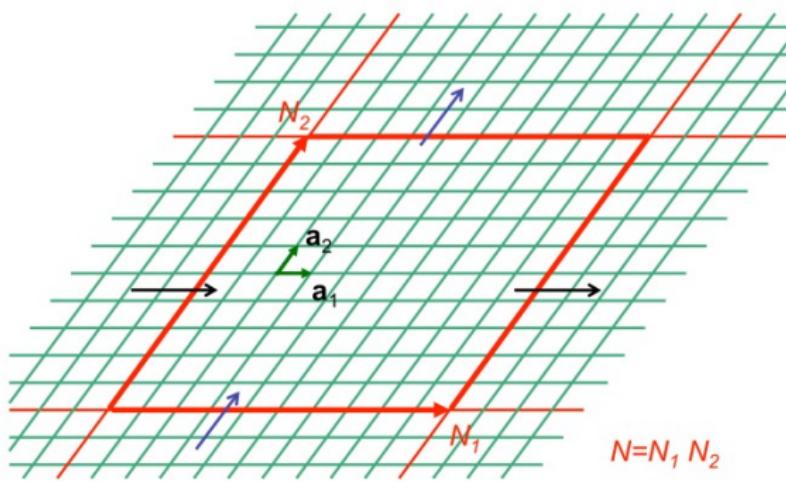


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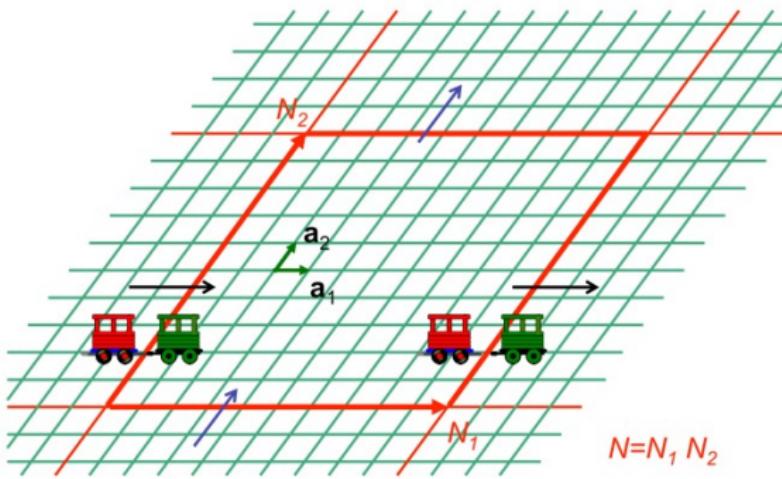
$$N=N_1 N_2$$

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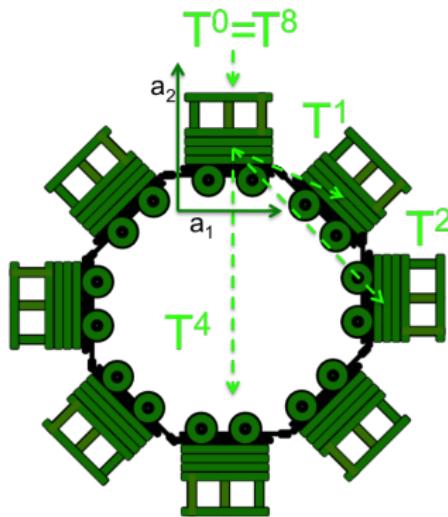
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PERIODIC (OR CYCLIC) BOUNDARY CONDITIONS

A. THE TRANSLATIONAL SYMMETRY GROUP
of the crystal becomes an abelian **CYCLIC** group



PERIODIC (OR CYCLIC) BOUNDARY CONDITIONS

B. THE CHARACTER TABLE IS FOUND

by calculating the $N_{\text{IRREP}} \times N_{\text{SymmOp}}$ roots of the unity

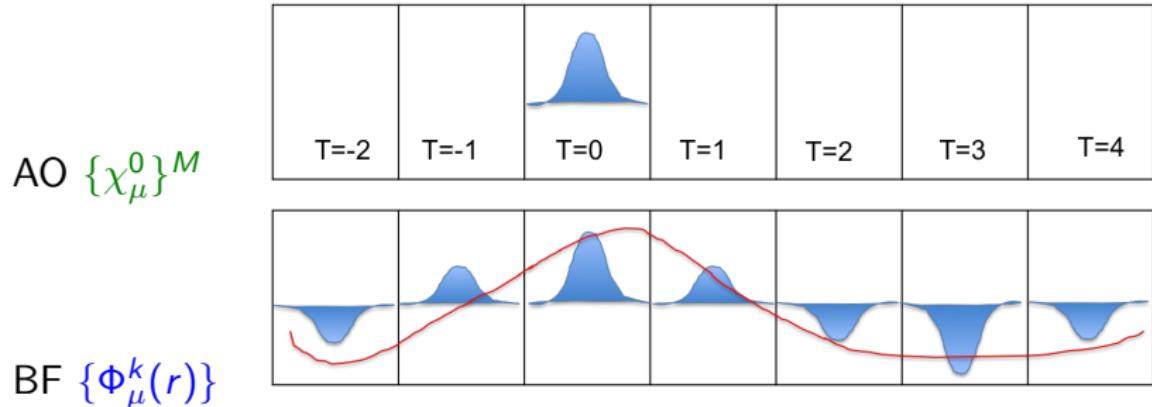
$N_{\text{irrep}} = N_{\text{sym-op}}$	$T_0 = I$	T_i	T_j
k_0	1	1	1
k_1	1	.	.
.	.	.	.
.	.	.	.
k_m	1	$\exp(i K_m T_i)$	$\exp(i K_m T_j)$
.	.	.	.
.	.	.	.
k_n	1	$\exp(i K_n T_i)$	$\exp(i K_n T_j)$

$$N_{\text{SymmOp}}(\hat{T}) \equiv N_{\text{cells}} \equiv N_{\text{Class}} \equiv N_{\text{IRREP}}$$

PERIODIC (OR CYCLIC) BOUNDARY CONDITIONS

C. FOR EACH \mathbf{k} -IRREP A WIGNER OPERATOR, \hat{P}^k , CAN BE DERIVED and applied to the atomic orbitals in the reference cell, $\{\chi_\mu^0\}^M$ to get M Bloch functions, (BF):

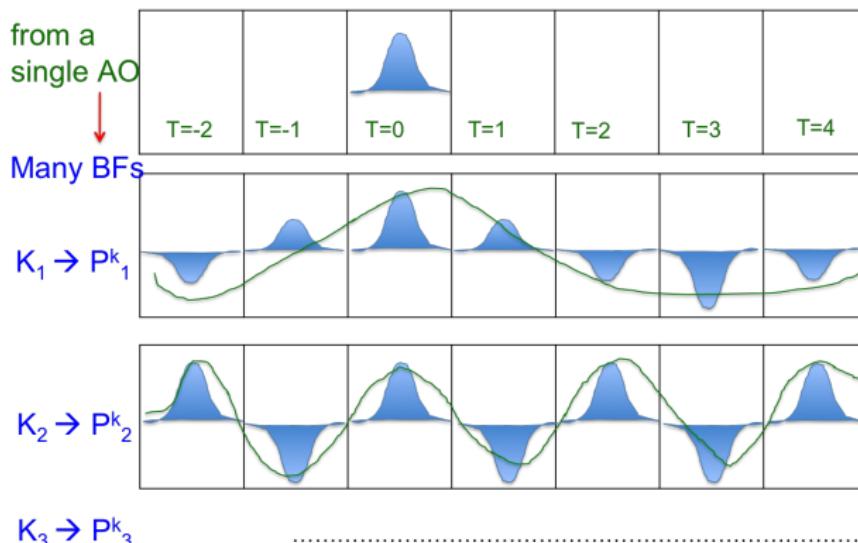
$$\hat{P}^k \chi_\mu^0(\mathbf{r}) = \sum_{\mathbf{T}} \exp[2\pi i (\frac{\mathbf{k}}{N} \cdot \mathbf{T})] \hat{\mathbf{T}} \chi_\mu^0(\mathbf{r}) = \sum_{\mathbf{T}} \exp[i \mathbf{k} \cdot \mathbf{T}] \chi_\mu^T(\mathbf{r}) = \Phi_\mu^k(r)$$



PERIODIC (OR CYCLIC) BOUNDARY CONDITIONS

D. BLOCH FUNCTIONS AS COMBINATION OF ATOMIC ORBITALS

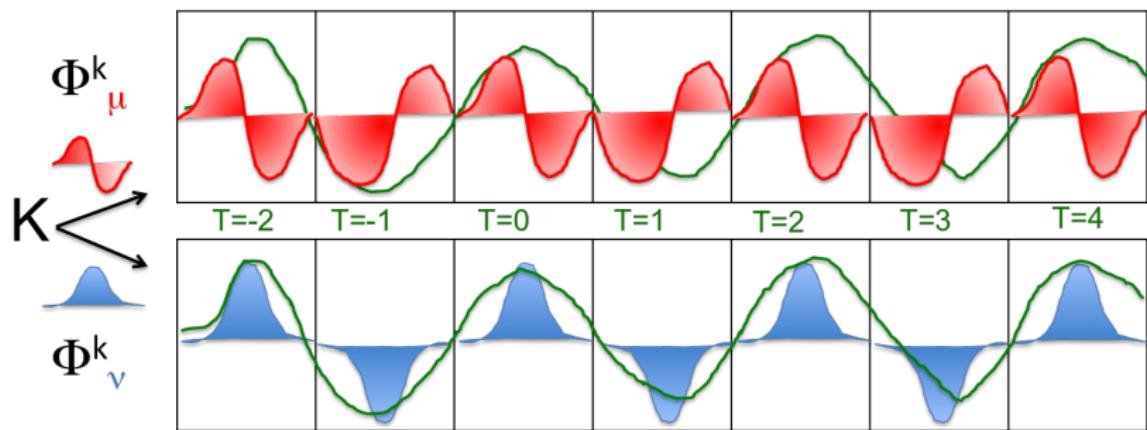
$$\Phi_{\mu}^k(\mathbf{r}) = \hat{P}^k \chi_{\mu}^0(\mathbf{r}) = \sum_{\mathbf{T}} \exp[i\mathbf{k}\cdot\mathbf{T}] \chi_{\mu}^T(\mathbf{r})$$



PERIODIC (OR CYCLIC) BOUNDARY CONDITIONS

E. CRYSTALLINE ORBITALS AS COMBINATION OF BLOCH FUNCTIONS

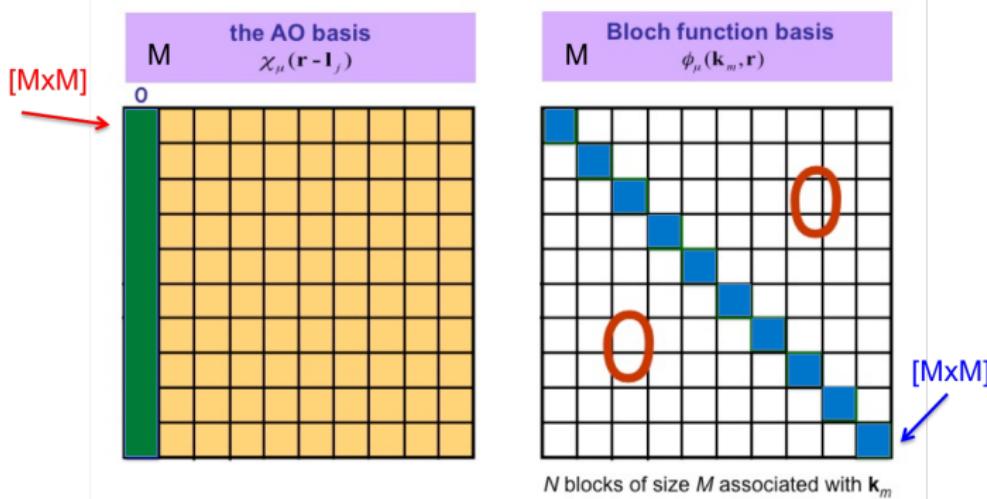
$$\Psi_i^k(\mathbf{r}) = \sum_{\mu} c(\mathbf{k})_{\mu i} \Phi_{\mu}^k(\mathbf{r})$$



CONSEQUENCES OF BLOCH THEOREM

- 1- due to the orthogonality between functions belonging to different IR, elements of the Fock matrix in the **BF basis set** are orthogonal

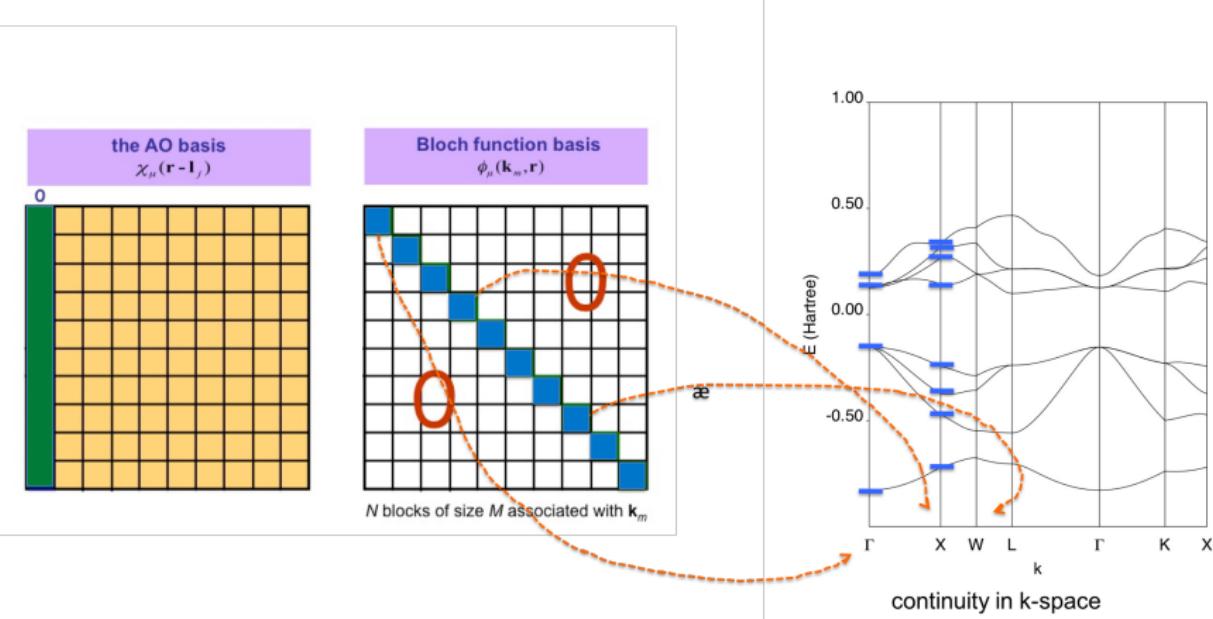
$$F_{\mu\nu}(\mathbf{k}_1, \mathbf{k}_2) = \langle \Phi_\mu^{\mathbf{k}_1}(\mathbf{r}) | \hat{F} | \Phi_\nu^{\mathbf{k}_2}(\mathbf{r}) \rangle = F(\mathbf{k}_1)_{\mu\nu} \delta_{\mathbf{k}_1, \mathbf{k}_2}$$



CONSEQUENCES OF BLOCH THEOREM

2- continuity of the energy in \mathbf{k} -space, $\epsilon_i(\mathbf{k})$:

BAND structure (for a potential with the same periodicity of the lattice) can be found by → interpolation



OUTLINE

- 1 THE PERIODIC MODEL
- 2 SYMMETRY EXPLOITATION IN DIRECT SPACE
- 3 SYMMETRY EXPLOITATION IN RECIPROCAL SPACE
- 4 SCF ITERATIVE PROCEDURE IN SOLIDS

THE PROCEDURE

FROM DIRECT LATTICE, DL TO RECIPROCAL LATTICE, RL

- ① Construction of the ($M^2 \times N$) elements of Fock matrix, $F_{\mu\nu}^T$, in the AOs basis set
- ② Fourier transformation of $F_{\mu\nu}^T$ at every point \mathbf{k} of the Pack-Monkhorst net ($\mathbf{k} \in BZ$)

$$F_{\mu\nu}(\mathbf{k}) = \sum_{\mathbf{T}}^N \exp(i\mathbf{k}\mathbf{T}) F_{\mu\nu}^T$$

- ③ Diagonalization of every M -dimension Fock matrix

$$\mathbb{F}(\mathbf{k})\mathbb{C}(\mathbf{k}) = \mathbb{S}(\mathbf{k})\mathbb{C}(\mathbf{k})\mathbb{E}(\mathbf{k})$$

$$\begin{array}{c} \{c(\mathbf{k})\} \\ \Downarrow \end{array}$$

- ④ In each \mathbf{k} , M crystalline orbitals (CO) $\Psi_j(\mathbf{k}, \mathbf{r})$ and eigenvalues $\epsilon_j(\mathbf{k})$ are obtained:

$$\Psi_j(\mathbf{k}, \mathbf{r}) = \sum_{\mu}^M c_{\mu j}(\mathbf{k}) \Phi_{\mu}^{\mathbf{k}}(\mathbf{r})$$

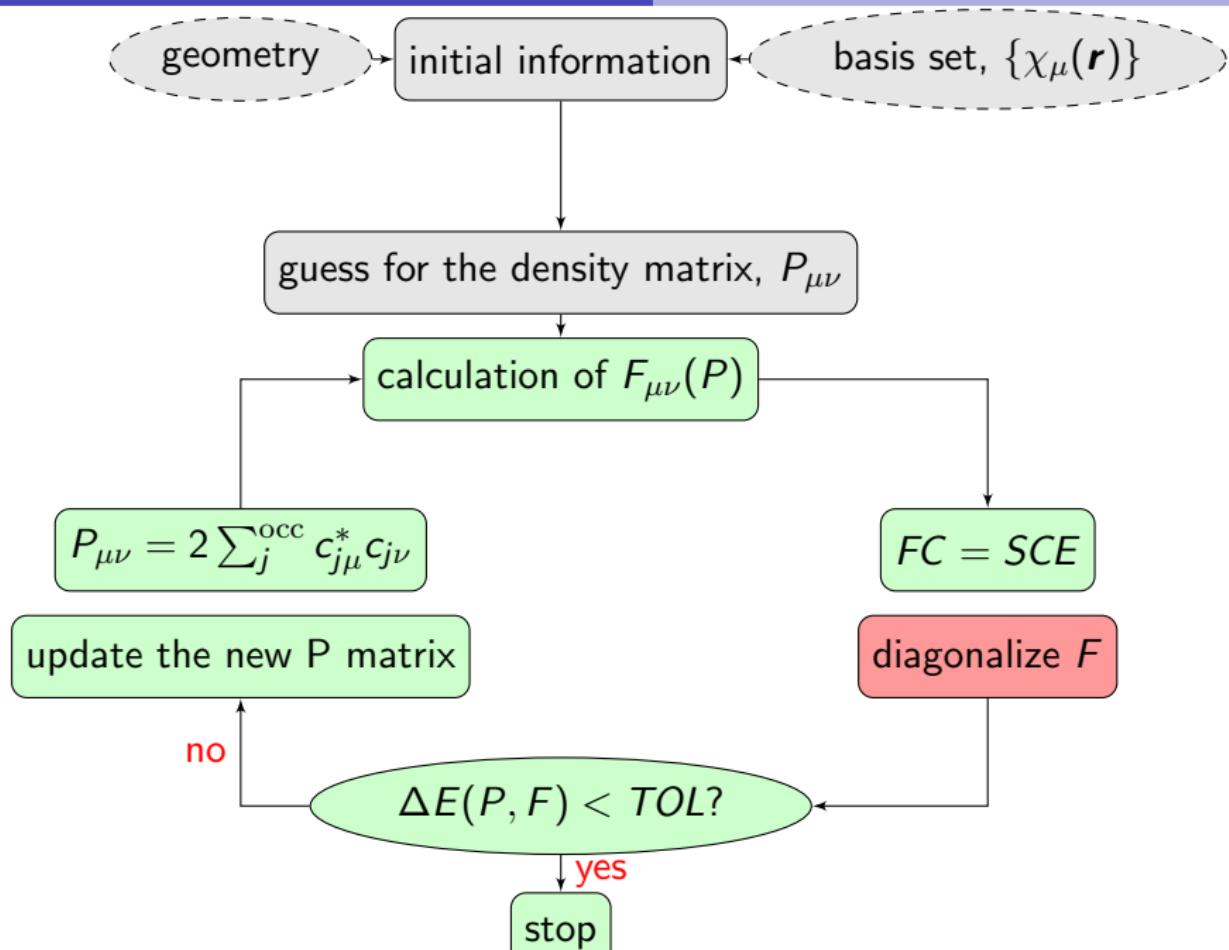
- ⑤ Calculation of the Reciprocal Lattice-density matrix

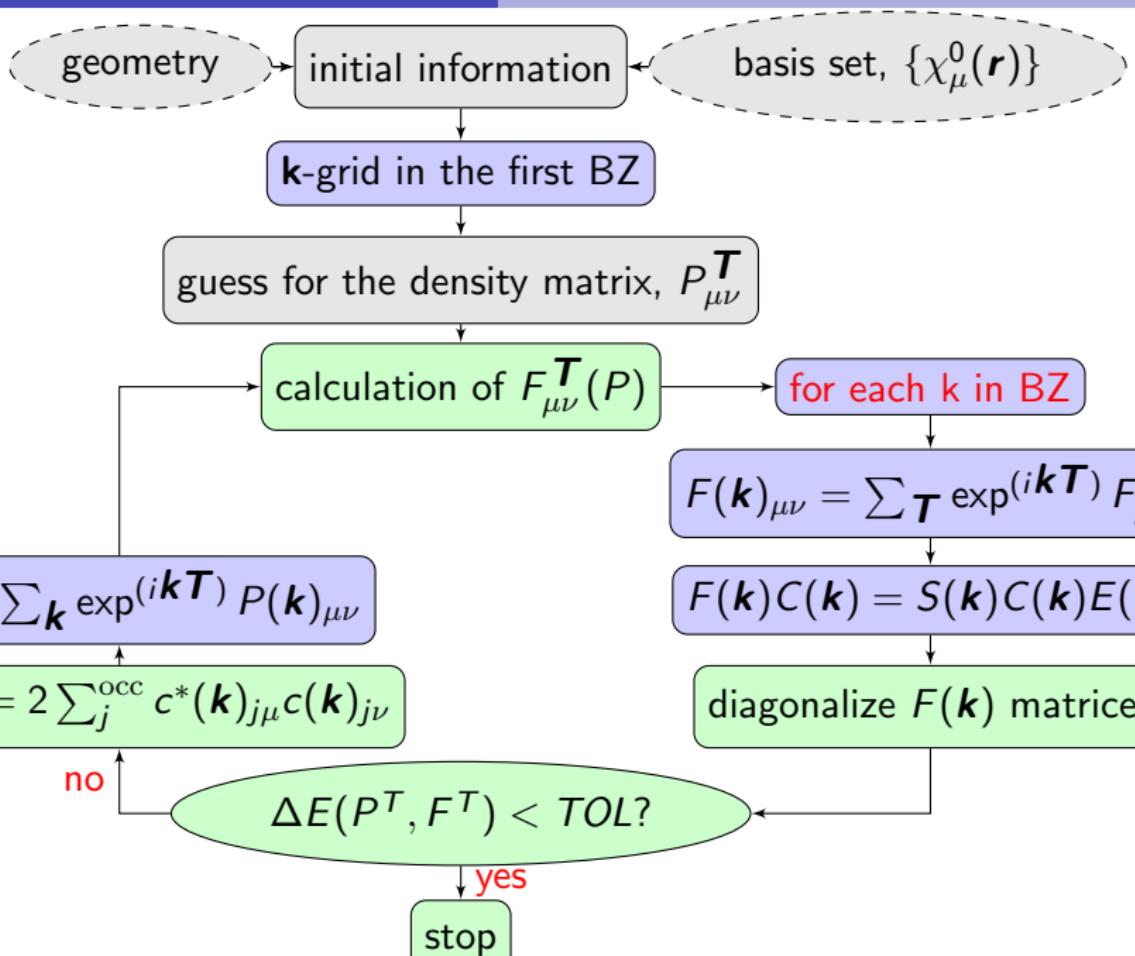
$$P_{\mu\nu}^{\mathbf{k}} = \sum_j c_{\mu j}(\mathbf{k}) c_{\nu j}^*(\mathbf{k})$$

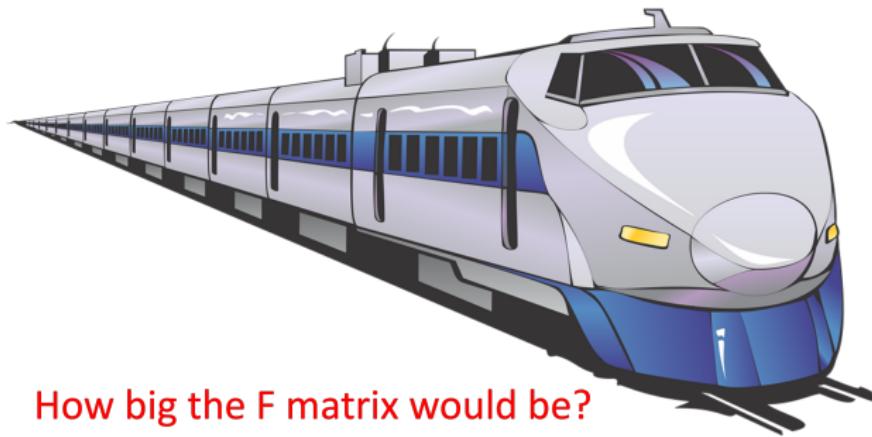
- ⑥ back-Fourier transformation of the density matrix

$$P_{\mu\nu}^T = \sum_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{T}) P_{\mu\nu}^{\mathbf{k}}$$

- ⑦ from $P_{\mu\nu}^T$ to a new $F_{\mu\nu}^T$







How big the F matrix would be?

IT DOESN'T MATTER! ☺☺☺

ACKNOWLEDGMENTS

I would like to thank the whole CRYSTAL group...



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...prof. Silvia Casassa who kindly shared her slides with me...



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...and all of you for your kind attention!