Basic concepts of the electronic models: $E^{(1)}$ reference density and tight-binding parameters
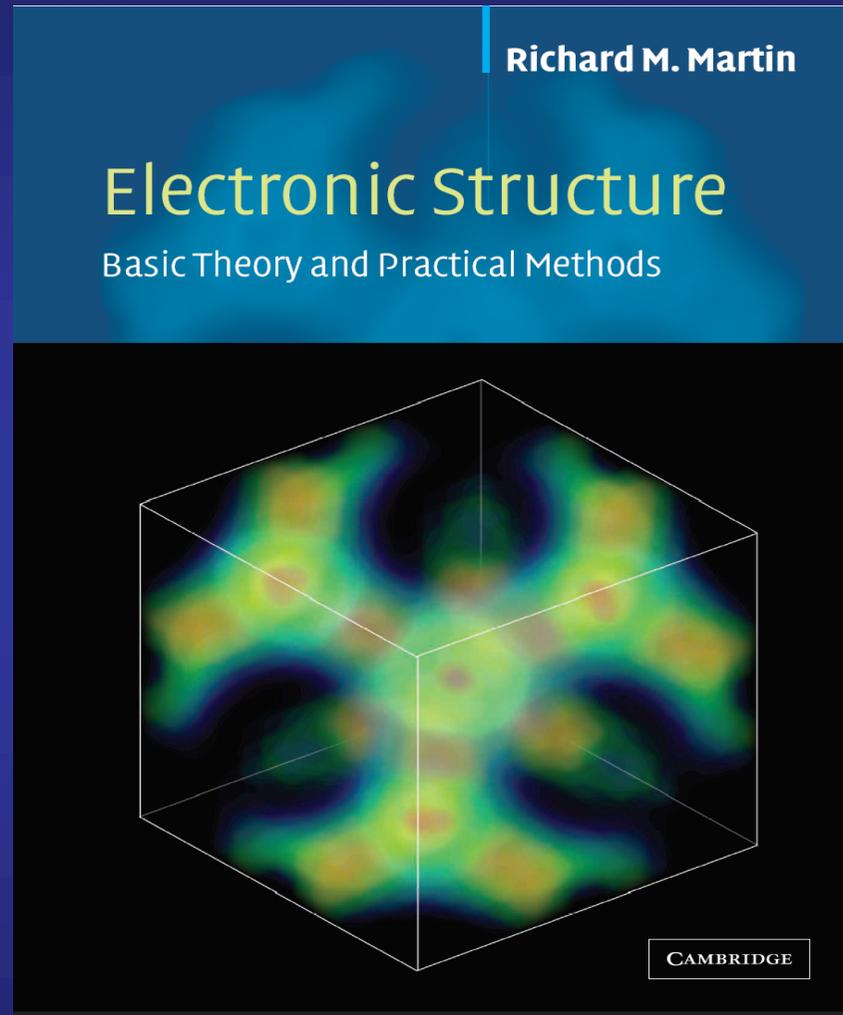
Javier Junquera
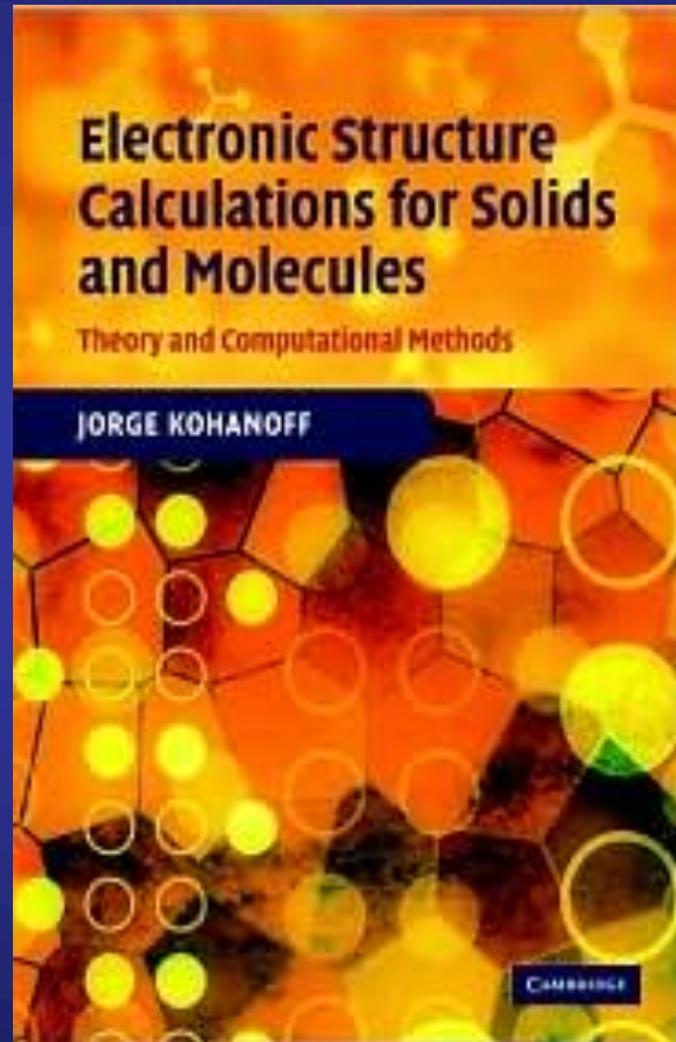
UC

UNIVERSIDAD
DE CANTABRIA

Most important references followed in this lecture

comprehensive review of DFT,
including most relevant references and exercises

ISBN: 0 521 78285 6
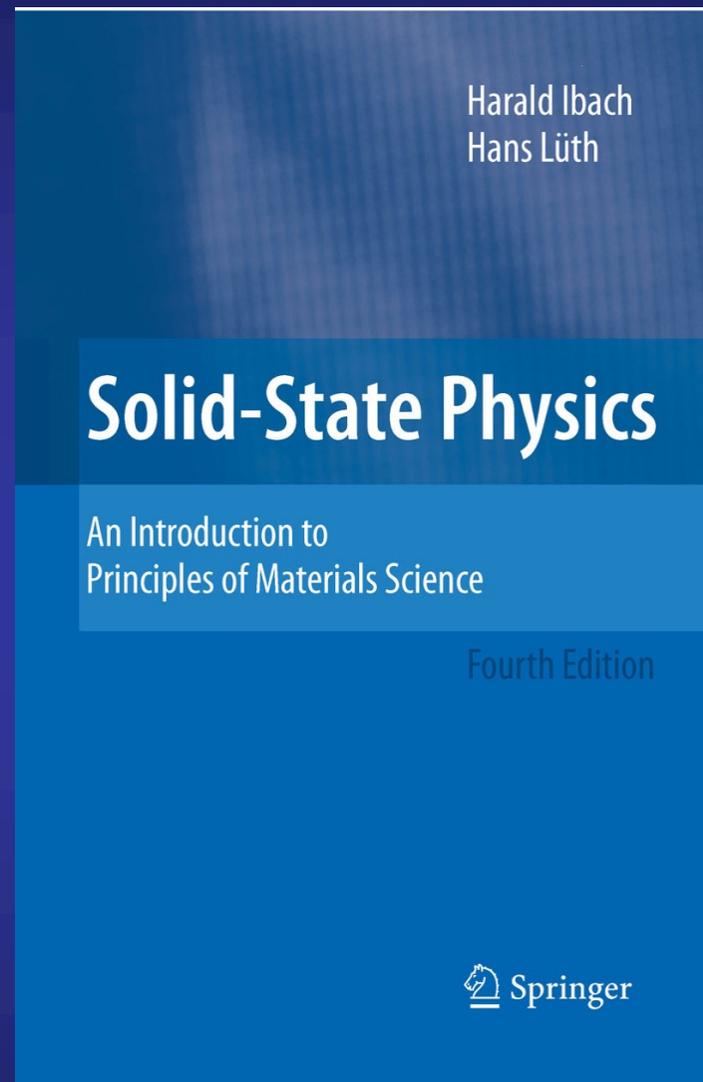
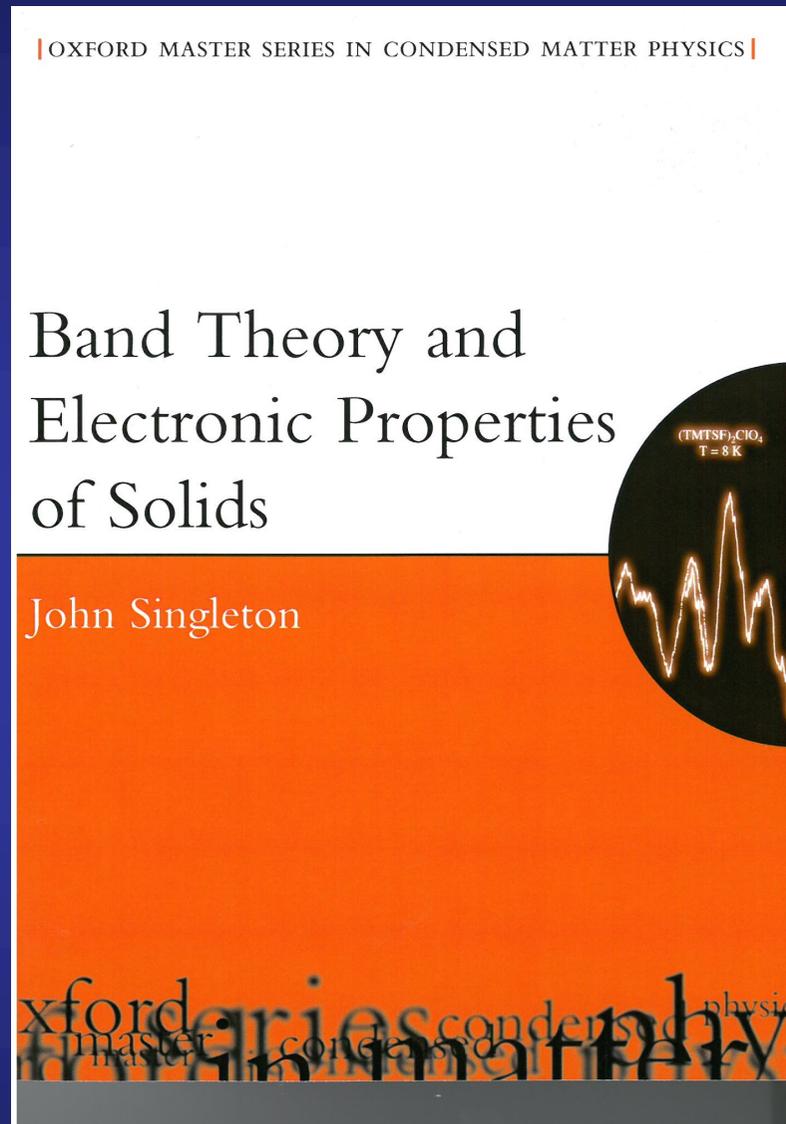# Most important references followed in this lecture

Most important references followed in this lecture

Harald Ibach
Hans Lüth

Solid-State Physics

An Introduction to
Principles of Materials Science

Fourth Edition

Springer

ISBN: 978-3-540-93803-3

Most important references followed in this lecture

OXFORD MASTER SERIES IN CONDENSED MATTER PHYSICS

Band Theory and
Electronic Properties
of Solids

$(TMTSF)_2ClO_4$
$T = 8 K$

John Singleton

Conditions that the simplified method should fulfill

The method should be simple enough to allow for its application to large systems with a reasonable computational effort

The approximations introduced should not be that severe that they modify the physical forces that determine structural and dynamical properties

The approximated wave function should be as unbiased as possible, avoiding the explicit introduction of pre-existent qualitative ideas

The method should account for all chemically active electrons

The tight binding is a method to describe the electronic band structure of solids and molecules

Provides a faithful representation of systems where the electron are localized in chemical bonds of different degrees of covalency
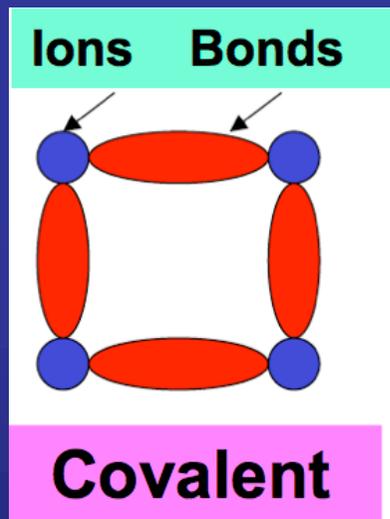
Complementary to the nearly free electron picture, that is a reasonably good approximation of the electronic structure of simple metals
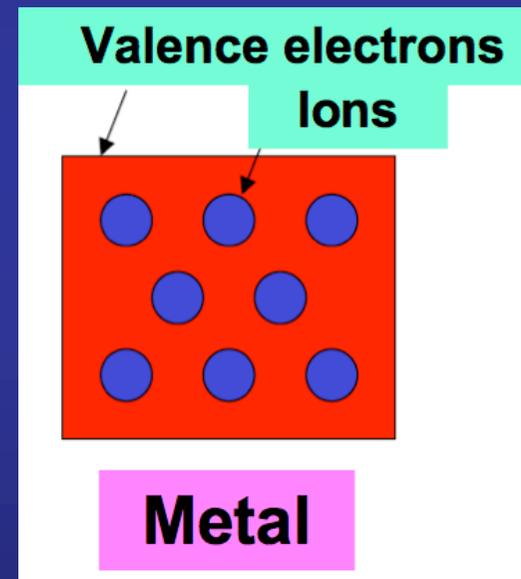
The tight binding is a method to describe the electronic band structure of solids and molecules

Starting point: in a first approximation, the electrons are localized in a single atom, but they have the possibility to jump to neighboring atoms.
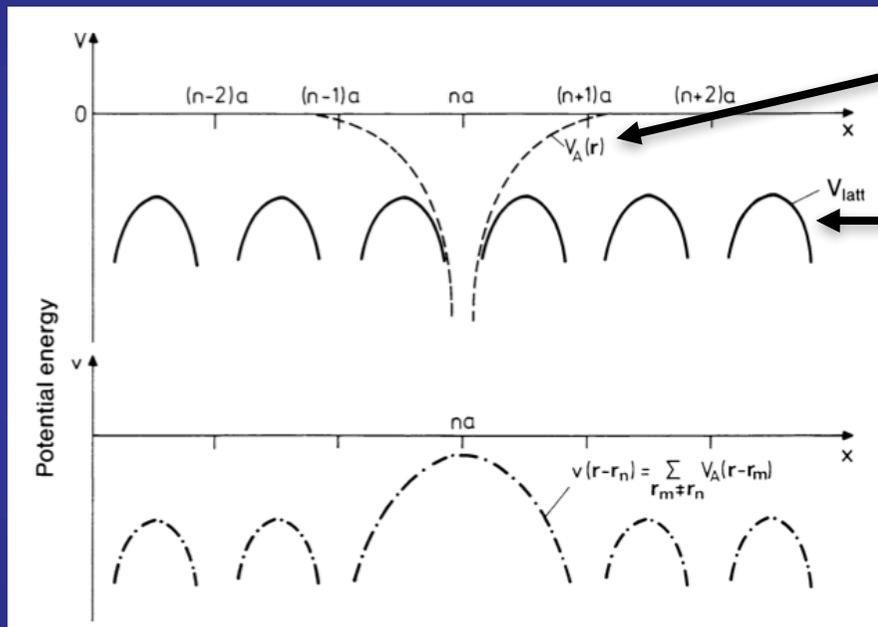
Potential of a free atom

Total lattice potential:
Obtained by summing the potential of a free atom

Perturbation potential around one lattice site:
Difference of the total lattice potential and the atomic potential at that site. The atomic potential around that site is much larger than the one due to the rest of the atoms

The tight binding is a method to describe the electronic band structure of solids and molecules

TB methods range from very basic empirical models to the more sophisticated ab initio schemes, where the Hamiltonian matrix is derived from density functional theory

It should be possible to derive the methodology from a precise starting point (Hartree-Fock or Kohn-Sham) by means of a series of more or less controlled approximations

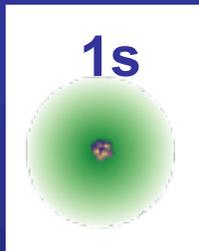# Starting point: the solutions of the Schrödinger equation for the isolated atoms that form the crystal

Assumption of the tight-binding model:
Close to each lattice point, the crystal Hamiltonian $\hat{\mathcal{H}}$
can be approximated by the Hamiltonian of a single atom $\hat{\mathcal{H}}_{\mathrm{at}}$

$$\hat{\mathcal{H}}_{\mathrm{at}}(\vec{r} - \vec{R}_I)\phi_\mu(\vec{r} - \vec{R}_I) = E_\mu \phi_\mu(\vec{r} - \vec{R}_I)$$

$\hat{\mathcal{H}}_{\mathrm{at}}(\vec{r} - \vec{R}_I)$ **is the Hamiltonian for a free atom at the lattice position** $\vec{R}_I$

$\phi_\mu(\vec{r} - \vec{R}_I)$ **is the wavefunction for an electron at energy level** E_μ

1s

The bound levels of $\hat{\mathcal{H}}_{\mathrm{at}}$ are well localized.
$\phi_\mu(\vec{r})$ **are very small a few lattice spacing away**

The set of functions $\phi_\mu(\vec{r})$ **, each associated with an atom in the unit cell at position** $\vec{R}_I$
will form a basis of localized functions

Starting point: the solutions of the Schrödinger equation for the isolated atoms that form the crystal

Assumption of the tight-binding model:
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$\hat{\mathcal{H}}_{\mathrm{at}}(\vec{r} - \vec{R}_I)$ is the Hamiltonian for a free atom at the lattice position $\vec{R}_I$

$\phi_\mu(\vec{r} - \vec{R}_I)$ is the wavefunction for an electron at energy level E_μ

In principle, μ might run over all the atomic orbitals of a given atom: $(1s, 2s, 3d, \ldots)$

We seek solutions for the Schrödinger equation of the entire periodic system

We are now faced with the task of solving the time-independent Schrödinger equation for a single electron under the assumption that the potential $V(\vec{r})$ is periodic

$$\hat{\mathcal{H}}\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$V(\vec{r}) = V(\vec{r} + \vec{T})$$

where $\vec{T}$ represents an arbitrary translation of the three-dimensional periodic lattice

Since the potential is periodic, the solution of the one-electron Schrödinger equation has to comply with the Bloch theorem, i.e. they can be written as the product of a plane wave times a function that has the periodicity of the lattice

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r})$$

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

The eigenfunctions are characterized by two quantum numbers:
- **A discrete index n : the band index**
- **A continuum wave vector $\vec{k}$**

Ansatz: a good approximation for the Bloch eigenfunctions is provided by a linear combination of the atomic orbitals

$$\hat{\mathcal{H}}\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n\vec{k}}(\vec{r})$$

where $\psi_{n\vec{k}}(\vec{r})$ **are the Bloch eigenfunctions that should obey the Bloch theorem**

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r}) \qquad\qquad u_{n\vec{k}}(\vec{r}+\vec{T}) = u_{n\vec{k}}(\vec{r})$$

$$\psi_{n\vec{k}}(\vec{r}) \approx \Phi_{n\vec{k}}(\vec{r}) = \sum_{\mu} c_{\mu n}(\vec{k})\phi_{\mu\vec{k}}(\vec{r})$$

Due to this expansion, in many textbooks the tight-binding approach is also known as the linear combination of atomic orbitals (LCAO) approach

The problem has translated on how to compute:
- the coefficients of the expansion $c_{\mu n}(\vec{k})$
- the discrete set of eigenvalues $E_n(\vec{k})$

Construction of a basis set that satisfies Bloch theorem

The same orbital $\phi_\mu(\vec{r})$ is defined for every atom of the same type in our periodically repeated material

1s   1s   1s   1s...

(n-1)a   na   (n+1)a (n+2)a
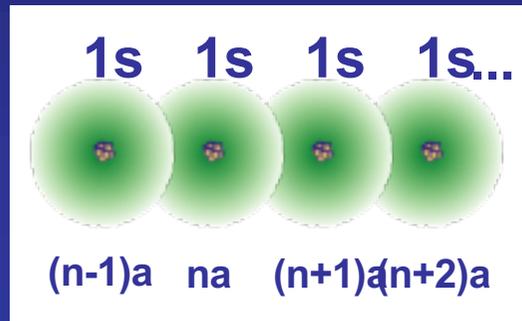
Since the eigenfunctions must comply with the Bloch theorem, it is sensible to define a basis that comply also with the Bloch theorem. For every given $\vec{k}$ -point in the first Brillouin zone, we define

$$\phi_{\mu\vec{k}}(\vec{r}) = A_{\mu\vec{k}} \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} \phi_\mu(\vec{r} - \vec{\tau}_\mu - \vec{T})$$

Exercise 1: Proof that these basis functions verify the Bloch theorem

Exercise 2: Proof that for orthogonal atomic orbitals, then the normalization factor $A_{\mu\vec{k}} = \dfrac{1}{\sqrt{N}}$

Schrödinger equation in a basis of Bloch-like atomic orbitals

Replace the expansion of the eigenfunction

$$\psi_{n\vec{k}}(\vec{r}) \approx \Phi_{n\vec{k}}(\vec{r}) = \sum_{\mu} c_{\mu n}(\vec{k})\phi_{\mu\vec{k}}(\vec{r})$$

In the one-particle Schrödinger equation

$$\hat{\mathcal{H}}\psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n\vec{k}}(\vec{r})$$

We arrive to

$$\sum_{\mu} c_{\mu n}(\vec{k})\hat{\mathcal{H}}\phi_{\mu\vec{k}}(\vec{r}) = E_n(\vec{k})\sum_{\mu} c_{\mu n}(\vec{k})\phi_{\mu\vec{k}}(\vec{r})$$

Multiply at the left by $\phi_{\nu\vec{k}}^{*}(\vec{r})$ **and integrate over all space**

$$\sum_{\mu} c_{\mu n}(\vec{k})\int_{\text{all space}}\phi_{\nu\vec{k}}^{*}(\vec{r})\hat{\mathcal{H}}\phi_{\mu\vec{k}}(\vec{r})d\vec{r} = E_n(\vec{k})\sum_{\mu} c_{\mu n}(\vec{k})\int_{\text{all space}}\phi_{\nu\vec{k}}^{*}(\vec{r})\phi_{\mu\vec{k}}(\vec{r})d\vec{r}$$

Matrix elements of the Hamiltonian in a basis of Bloch-like atomic orbitals

$$\sum_{\mu} c_{\mu n}(\vec{k}) \int_{\text{all space}} \phi^*_{\nu \vec{k}}(\vec{r}) \hat{\mathcal{H}} \phi_{\mu \vec{k}}(\vec{r}) d\vec{r} = E_n(\vec{k}) \sum_{\mu} c_{\mu n}(\vec{k}) \int_{\text{all space}} \phi^*_{\nu \vec{k}}(\vec{r}) \phi_{\mu \vec{k}}(\vec{r}) d\vec{r}$$

This expression can be rewritten as

$$\sum_{\mu} c_{\mu n}(\vec{k}) H_{\nu \mu}(\vec{k}) = E_n(\vec{k}) \sum_{\mu} c_{\mu n}(\vec{k}) S_{\nu \mu}(\vec{k})$$

where

$$H_{\nu \mu}(\vec{k}) = \int_{\text{all space}} \phi^*_{\nu \vec{k}}(\vec{r}) \hat{\mathcal{H}} \phi_{\mu \vec{k}}(\vec{r}) d\vec{r} \qquad S_{\nu \mu}(\vec{k}) = \int_{\text{all space}} \phi^*_{\nu \vec{k}}(\vec{r}) \phi_{\mu \vec{k}}(\vec{r}) d\vec{r}$$

The secular equation takes the form

$$\sum_{\mu} \left[H_{\nu \mu}(\vec{k}) - E_n(\vec{k}) S_{\nu \mu}(\vec{k}) \right] c_{\mu n}(\vec{k}) = 0$$

Matrix elements of the Hamiltonian in a basis of Bloch-like atomic orbitals

The secular equation takes the form

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$$H_{\nu\mu}(\vec{k}) = \int_{\text{all space}} \phi^*_{\nu\vec{k}}(\vec{r}) \hat{\mathcal{H}} \phi_{\mu\vec{k}}(\vec{r}) d\vec{r} \qquad S_{\nu\mu}(\vec{k}) = \int_{\text{all space}} \phi^*_{\nu\vec{k}}(\vec{r}) \phi_{\mu\vec{k}}(\vec{r}) d\vec{r}$$

After some bookeping, we can arrive to the conclusion that the matrix elements of the Hamiltonian and Overlap matrices in $\vec{k}$ space can be computed from the sums of the Hamiltonian and Overlap matrices in real space, modulated by a phase (take it as an exercise)

$$H_{\nu\mu}(\vec{k}) = \langle \phi_\nu(\vec{k}) | \hat{\mathcal{H}} | \phi_\mu(\vec{k}) \rangle = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\nu\mu}(\vec{T})$$

$$S_{\nu\mu}(\vec{k}) = \langle \phi_\nu(\vec{k}) | \phi_\mu(\vec{k}) \rangle = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} S_{\nu\mu}(\vec{T})$$

Since the atomic orbitals are localized, is expected that $H_{\nu\mu}(\vec{T})$ **and** $S_{\nu\mu}(\vec{T})$ **become negligible for large distances** $|\vec{T}|$

The secular equation in matricial form

The secular equation takes the form

$$\sum_{\mu} \left[H_{\nu\mu}(\vec{k}) - E_n(\vec{k}) S_{\nu\mu}(\vec{k}) \right] c_{\mu n}(\vec{k}) = 0$$

Or in matricial notation

$$\left(\quad H(\vec{k}) \quad \right) \left(\quad C_n(\vec{k}) \quad \right) = E_n(\vec{k}) \left(\quad S(\vec{k}) \quad \right) \left(\quad C_n(\vec{k}) \quad \right)$$

$$N \times N \qquad\qquad N \times 1 \qquad\qquad\qquad\qquad N \times N \qquad\qquad N \times 1$$

Where N **is the number of atomic orbitals in the unit cell**

This is a generalized eigenvalue problem.

The secular equation in matricial form

$$\sum_{\mu} \left[H_{\nu\mu}(\vec{k}) - E_n(\vec{k}) S_{\nu\mu}(\vec{k}) \right] c_{\mu n}(\vec{k}) = 0$$

In matricial notation

$$\begin{pmatrix} H(\vec{k}) \end{pmatrix} \begin{pmatrix} C_n(\vec{k}) \end{pmatrix} = E_n(\vec{k}) \begin{pmatrix} S(\vec{k}) \end{pmatrix} \begin{pmatrix} C_n(\vec{k}) \end{pmatrix}$$

$$N \times N \qquad\qquad N \times 1 \qquad\qquad\qquad N \times N \qquad\qquad N \times 1$$

For every $\vec{k}$ -point:

1. **Compute the Hamiltonian and Overlap matrices in $\vec{k}$ -space, from the Hamiltonian and Overlap matrix elements in real space**

$$H_{\nu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\nu\mu}(\vec{T}) \qquad\qquad S_{\nu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} S_{\nu\mu}(\vec{T})$$

2. **Solve the generalized eigenvalue problem (diagonalize the Hamiltonian)**

As a result, there are N eigenvalues (bands), labelled by n , and N -eigenvectors

… Now let us practice with some simple examples: analytical calculations and SCALE-UP simulations

1-D Monoatomic linear chain with only s-orbitals. One atom in the unit cell
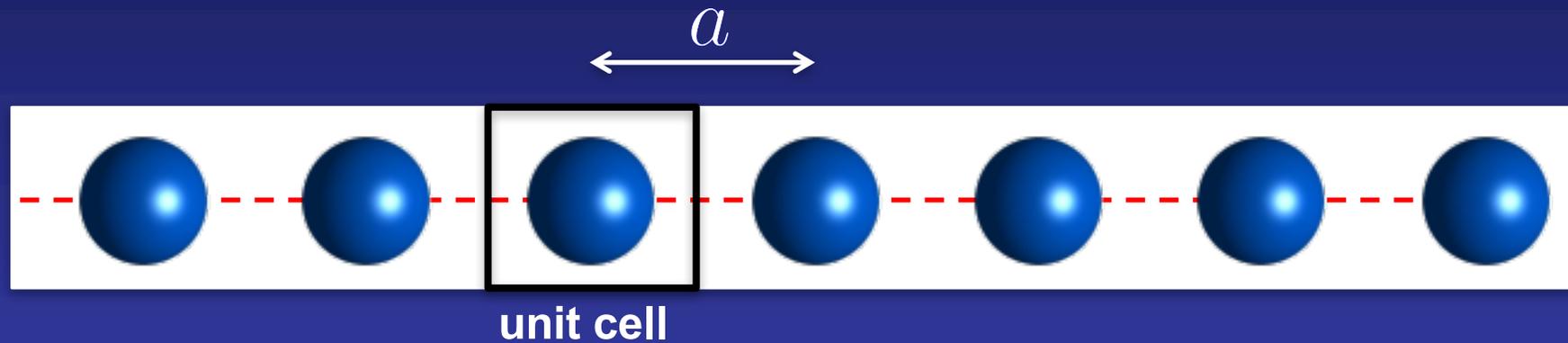
1-D Monoatomic linear chain with only s-orbitals. Two atoms in the unit cell

2-D Monoatomic plane with only s-orbitals

3-D Monoatomic cube with only s-orbitals

2-D CuO_2 plane

... Now let us practice with some simple examples: analytical calculations and SCALE-UP simulations

1-D Monoatomic linear chain with only s-orbitals. One atom in the unit cell

1-D Monoatomic linear chain with only s-orbitals. Two atoms in the unit cell

2-D Monoatomic plane with only s-orbitals

3-D Monoatomic cube with only s-orbitals

2-D CuO_2 plane

Solving the secular equation in a simple case: the linear chain of atoms with only s-orbitals

$$a$$

unit cell

Only one atomic orbital in the unit cell ($N = 1$). Let us denote this orbital (s) $\equiv \mu$

$\Downarrow$

The Hamiltonian and Overlap matrices are just simple real numbers

First approximation: range of interactions

- **Only on-site** $H_{\mu\mu}(\vec{T} = 0) = \alpha$

- **And nearest neigbour approximation** $H_{\mu\mu}(\vec{T} = \pm\vec{a}) = \gamma$

$$H_{\mu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\mu\mu}(\vec{T}) = H_{\mu\mu}(\vec{T} = 0) + e^{i\vec{k}\cdot\vec{a}} H_{\mu\mu}(\vec{T} = \vec{a}) + e^{-i\vec{k}\cdot\vec{a}} H_{\mu\mu}(\vec{T} = -\vec{a})$$

$$= \alpha + 2\gamma \cos(ka)$$

Solving the secular equation in a simple case: the linear chain of atoms with only *s*-orbitals

$$a$$

unit cell

Only one atomic orbital in the unit cell ($N = 1$). Let us denote this orbital (*s*) $\equiv \mu$

$\Downarrow$
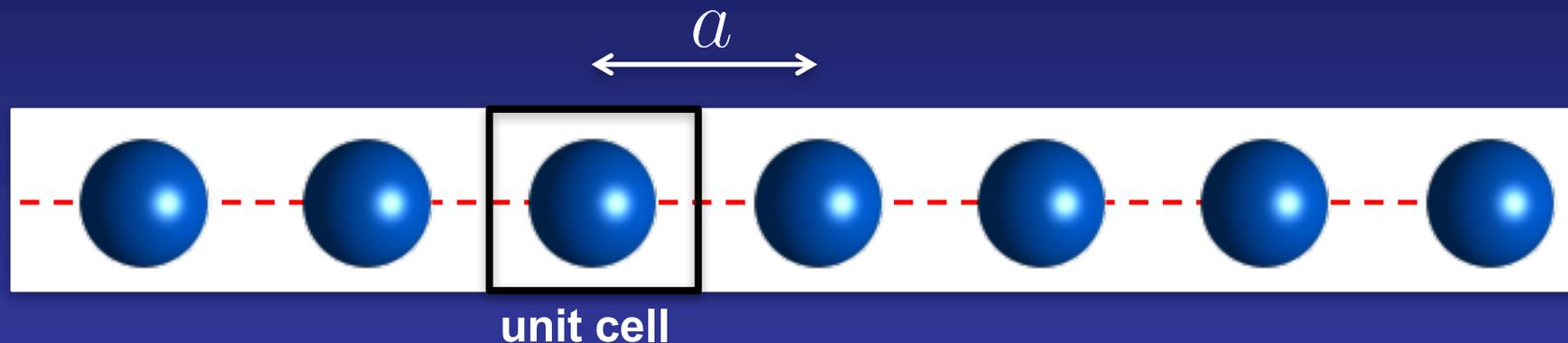
The Hamiltonian and Overlap matrices are just simple real numbers

Second approximation: orthogonal orbitals

If the basis set of atomic orbitals is sufficiently localized, then $\phi_\mu(\vec{r} - \vec{R}_I)$ only has significant values around the atom where it is centered.

To a first approximation, we can retain only the overlap of one orbital with itself, and neglect all the rest of the overlap integrals

$$S_{\nu\mu}(\vec{T}) = \delta_{\nu\mu}\delta_{\vec{T}0} \qquad S_{\nu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} S_{\nu\mu}(\vec{T}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} \delta_{\nu\mu}\delta_{\vec{T}0} = \delta_{\nu\mu}$$

The overlap matrix is diagonal in this approximation.
If we have only one orbitals in the unit cell, the overlap matrix is 1 for all $\vec{k}$

Solving the secular equation in a simple case: the linear chain of atoms with only s-orbitals

unit cell
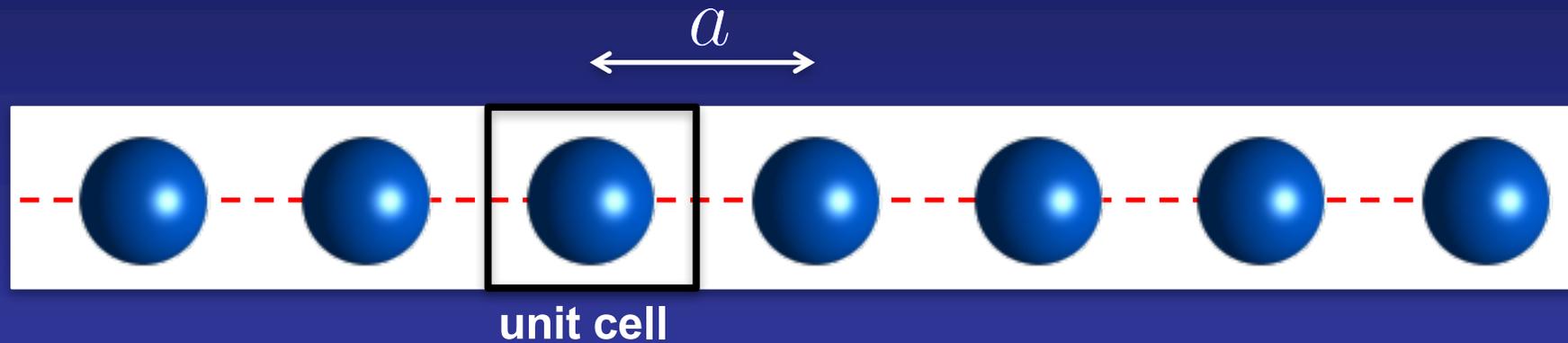
The secular equation for this system is, therefore

$$[\alpha + 2\gamma \cos(ka) - E(k)]\, c(k) = 0$$

Therefore, for a non trivial solution, with $c(k) \neq 0$

$$E(k) = \alpha + 2\gamma \cos(ka)$$

Linear chain of s-orbitals: Input for SCALE-UP


```
<electron_hamiltonian_one>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="0"
        hopc="0"
        gamma="0.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="0"
        hopc="-1"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="0"
        hopc="1"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
</electron_hamiltonian_one>
```

$\gamma_{\mu\mu}(-\vec{T})$

$\gamma_{\mu\mu}(+\vec{T})$

a

α
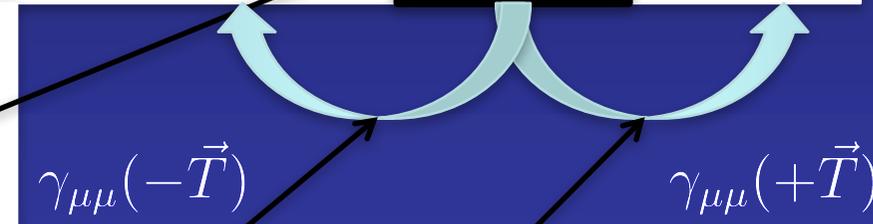
The linear chain of atoms with only *s*-orbitals
Computing the band structure with SCALE-UP

In the input file, select the high-symmetry lines in the Brillouin zone

```
%block band_path
1
30 0.0 0.0 -0.5 0.0 0.0 0.5
%endblock band_path
```

One symmetry line
30 points between (0,0,- π/a) and (0,0, π/a)

Run SCALE-UP

```
$ <your_path_to_scaleup_dir>/bin/scaleup.x < 1d-chain.s.oneatom.fdf > 1d-chain.s.oneatom.out
```

To plot the band structure, you can use some of the utilities

```
python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -bands -file _1d_oneat_tight_binding_FINAL.bands
```
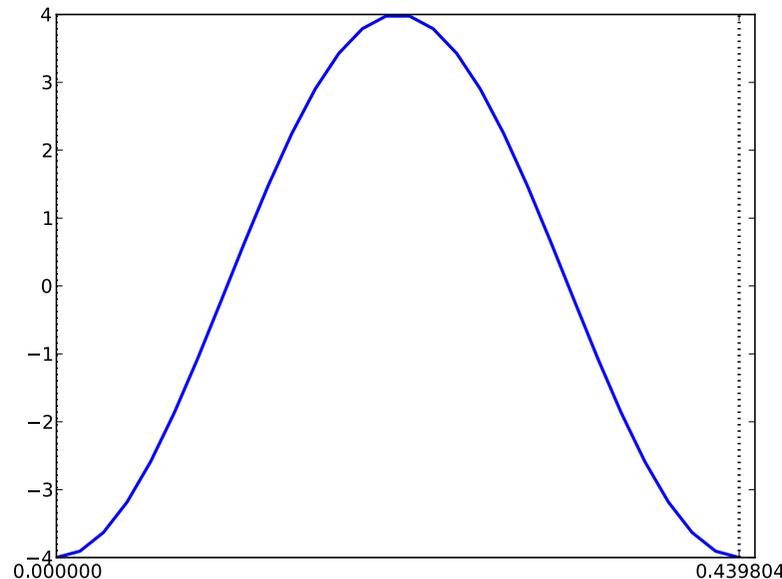
Interpreting the band structure of the linear chain of atoms with only *s*-orbitals
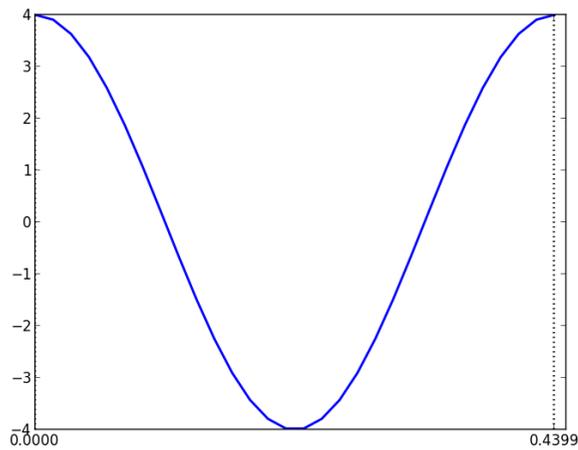
$\lambda = \infty$
$k = 0$
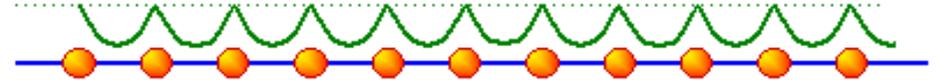
$\lambda = 12a$
$k = (1/6)(\pi/a)$
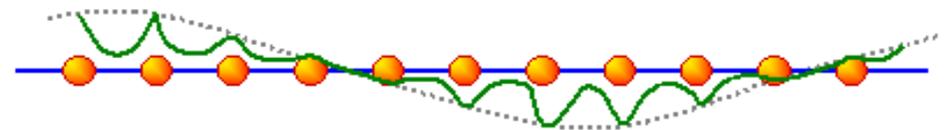
$\lambda = 2a$
$k = \pi/a$
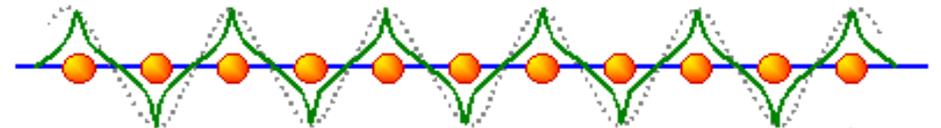
Interpreting the band structure of the linear chain of atoms with only *s*-orbitals

The hopping parameter or transfer integral γ give a direct measure of the width in energy of a band (the bandwidth)
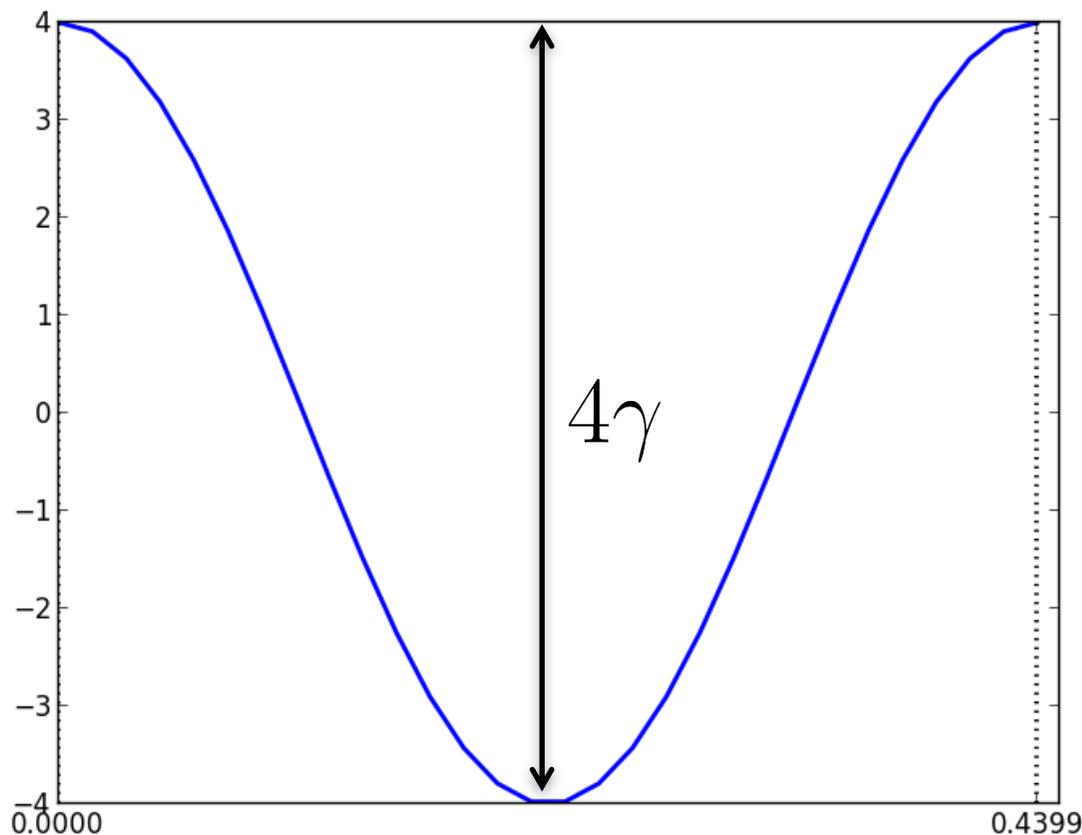
The smaller the hopping parameter γ, the narrower the bands

In the limit case $\gamma \to 0$, i.e. In the case of non-interacting orbitals, the bands would be flat straight lines

Relationship between the hopping parameter and the effective mass

Energy of the one-dimensional tight-binding band

$$E(k) = \alpha + 2\gamma\cos(ka)$$

For a minimum at Γ then

$$\gamma < 0$$

Close to the minimum we can use the approximation for small ka

$$\cos(ka) \approx 1 - \frac{(ka)^2}{2}$$

Replacing in the previous expression

$$E(k) \approx \alpha + 2\gamma - \gamma k^2 a^2$$
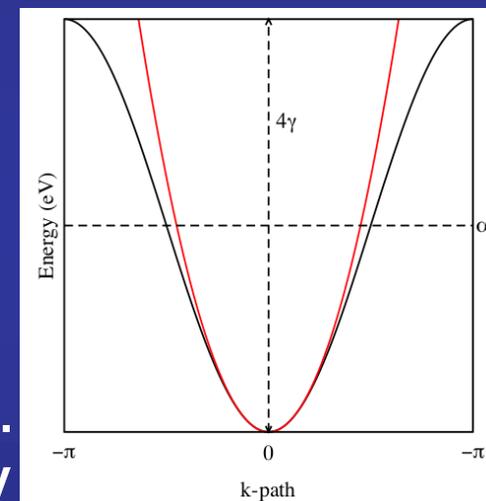
Close to the minima, the bands are approximately parabolic. Close to these points, the electrons can be treated as if they were free, but with an effective mass m^*

General expression

$$E(\vec{k}) \approx E_0 + \frac{\hbar^2}{2m^*}(\vec{k} - \vec{k}_0)^2$$

$\vec{k}_0$ **define the band extremum**

In particular for one-dimensional bands

$$m^* = -\frac{\hbar^2}{2\gamma a^2}$$

Relationship between the hopping parameter and the effective mass

Carriers close to the bottom of a tight-binding band have effective masses which are inversely proportional to the transfer integrals
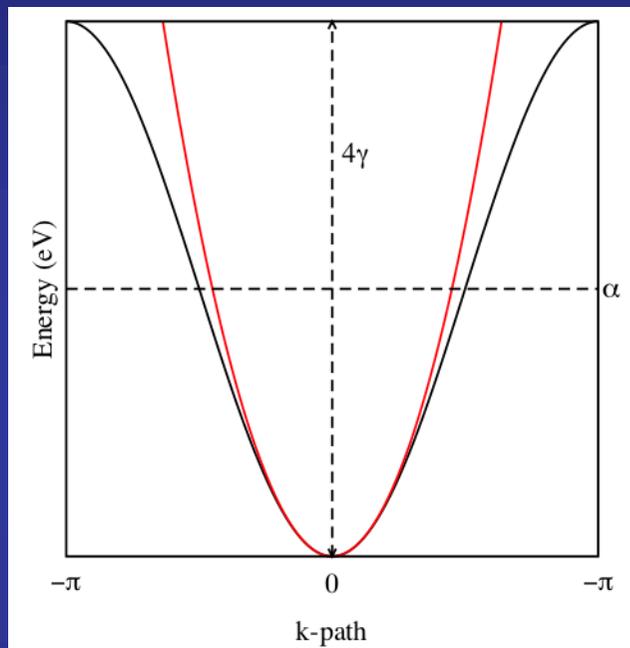
$$m^* = -\frac{\hbar^2}{2\gamma a^2}$$

The effective mass parametrises the ease with which an electron can be accelerated

Small transfer integrals
⇓
Narrow band-widths
⇓
Heavy effective masses
⇓
It is hard to move electrons around

Large transfer integrals
⇓
Large band-widths
⇓
Light effective masses
⇓
It is easy to move electrons around

The linear chain of atoms with only s-orbitals
Computing the density of states with SCALE-UP

In the input file, select the how many $\vec{k}$-points to include in the sampling of the Brillouin zone

```
%block k-sampling
1 1 500
%endblock k-sampling
```

Run SCALE-UP

```
$ <your_path_to_scaleup_dir>/bin/scaleup.x < 1d-chain.s.oneatom.fdf > 1d-chain.s.oneatom.out
```

To plot the density of states (DOS), you can use some of the utilities

```
python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -dos -file _1d_oneat_tight_binding_FINAL.ener
```
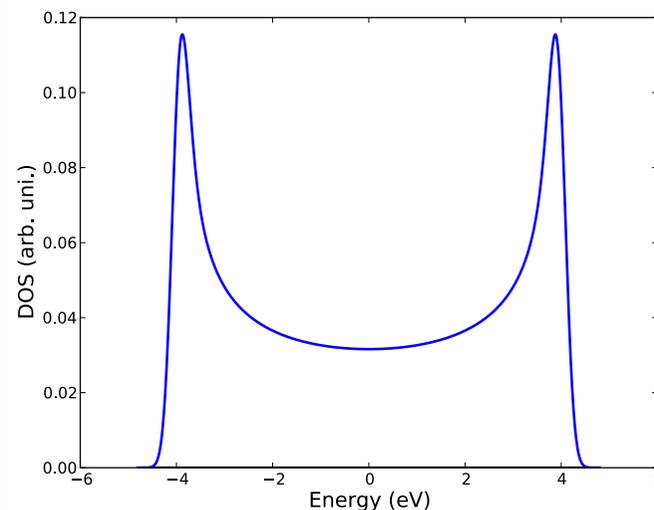
The linear chain of atoms with only s-orbitals
Computing the density of states with SCALE-UP

Convergence with respect the number of $\vec{k}$ -points

In the fdf input

```
! Number of points in the reciprocal space
%block k-sampling
 1 1 2
%endblock k-sampling
```

```
! Number of points in the reciprocal space
%block k-sampling
 1 1 1000
%endblock k-sampling
```

In the output file

```
    Reciprocal lattice
     Sampling:  0  0  2
    Number of k-points:     3
       Point      Kx        Ky        Kz     Weight
           1    0.000     0.000    -0.416    0.250
           2    0.000     0.000     0.000    0.500
           3    0.000     0.000     0.416    0.250
```

```
    Reciprocal lattice
     Sampling:  0   0 1000
    Number of k-points:  1999
       Point      Kx        Ky        Kz     Weight
           1    0.000     0.000    -0.416    0.000
           2    0.000     0.000    -0.415    0.001
    ....
```
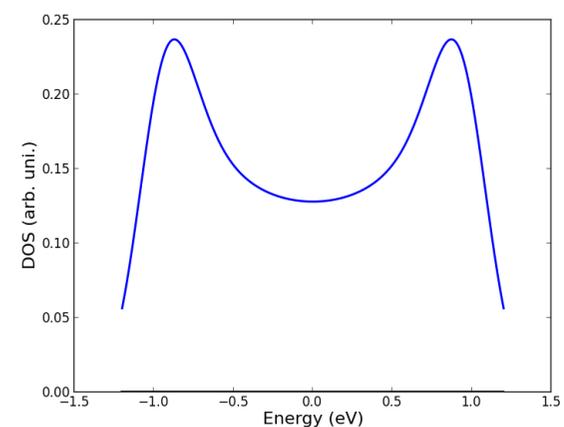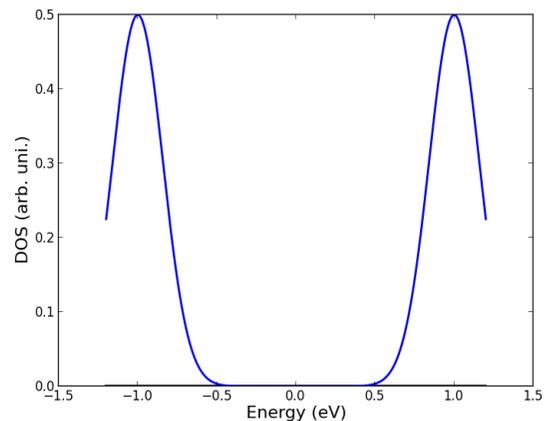
... Now let us practice with some simple examples: analytical calculations and SCALE-UP simulations

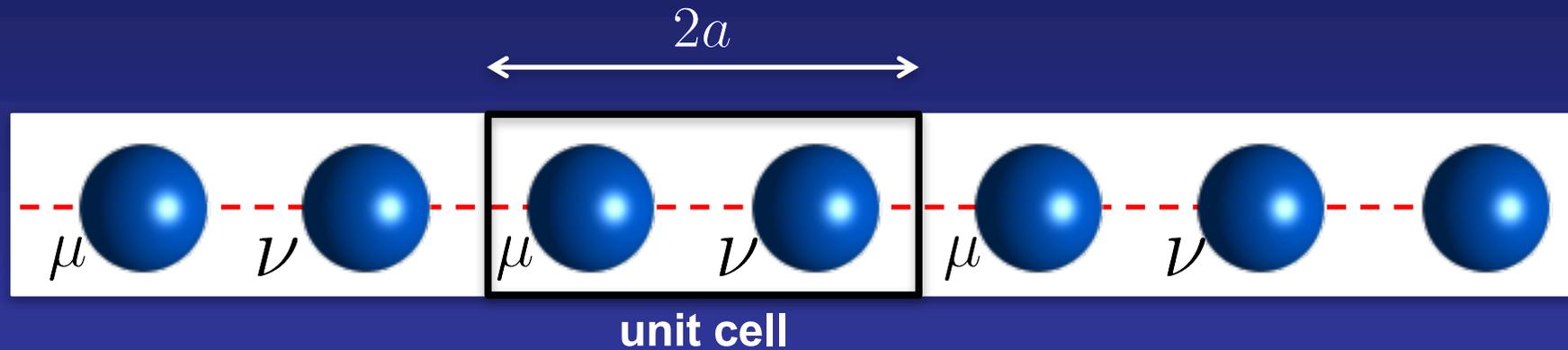1-D Monoatomic linear chain with only s-orbitals. One atom in the unit cell

1-D Monoatomic linear chain with only s-orbitals. Two atoms in the unit cell

2-D Monoatomic plane with only s-orbitals

3-D Monoatomic cube with only s-orbitals

2-D CuO_2 plane

Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

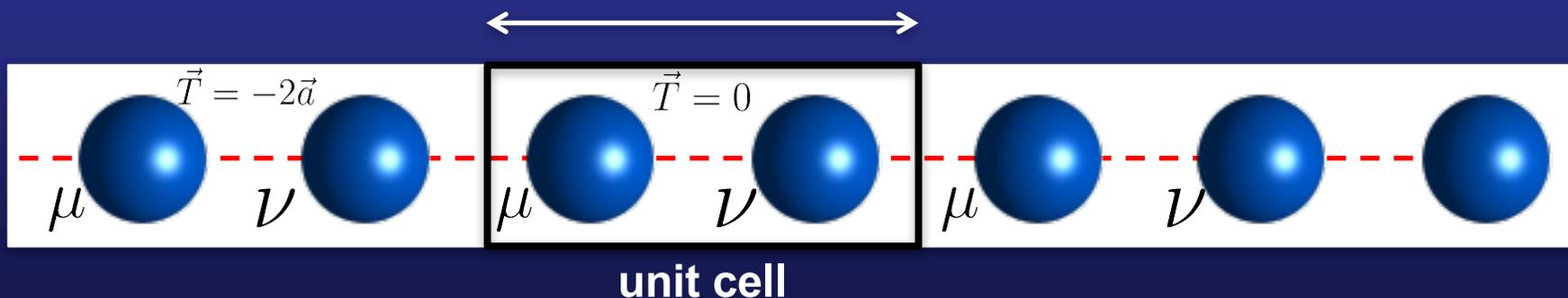

$2a$

μ ν μ ν μ ν

unit cell

Two atomic orbitals in the unit cell ($N = 2$). Let us denote these orbitals (s)$\equiv \mu, \nu$
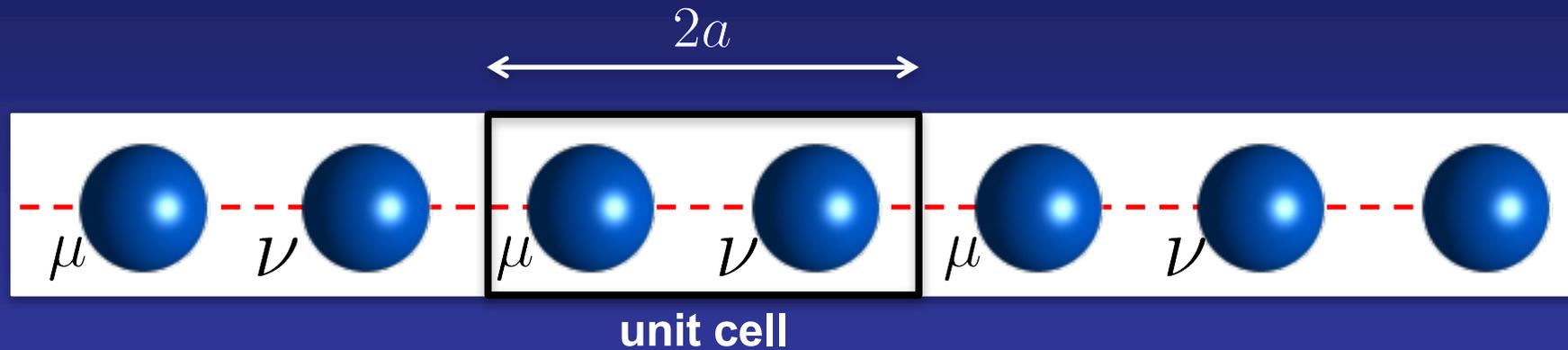
$\Downarrow$

The Hamiltonian and Overlap are (2×2) matrices

Let us compute the diagonal terms of the Hamiltonian, under the assumption of nearest neighbour interaction

The next orbital μ is not a nearest neighbour, so there is only one term in the sum

$$H_{\mu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\mu\mu}(\vec{T}) = H_{\mu\mu}(\vec{T} = 0) = \alpha$$

$$H_{\nu\nu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\nu\nu}(\vec{T}) = H_{\nu\nu}(\vec{T} = 0) = \alpha$$

Solving the secular equation in a simple case: the monoatomic linear chain with only *s*-orbitals

$2a$

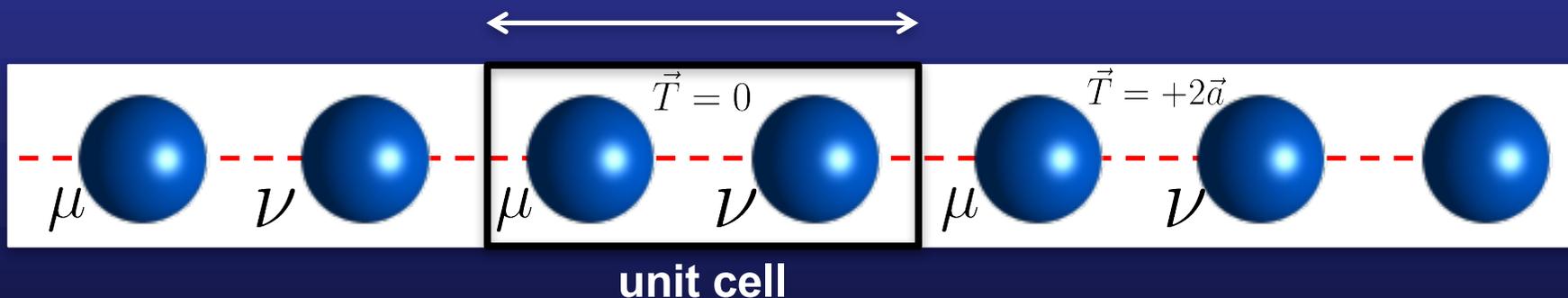μ ν μ ν μ ν

unit cell

Two atomic orbitals in the unit cell ($N = 2$). Let us denote these orbitals (*s*) $\equiv \mu, \nu$
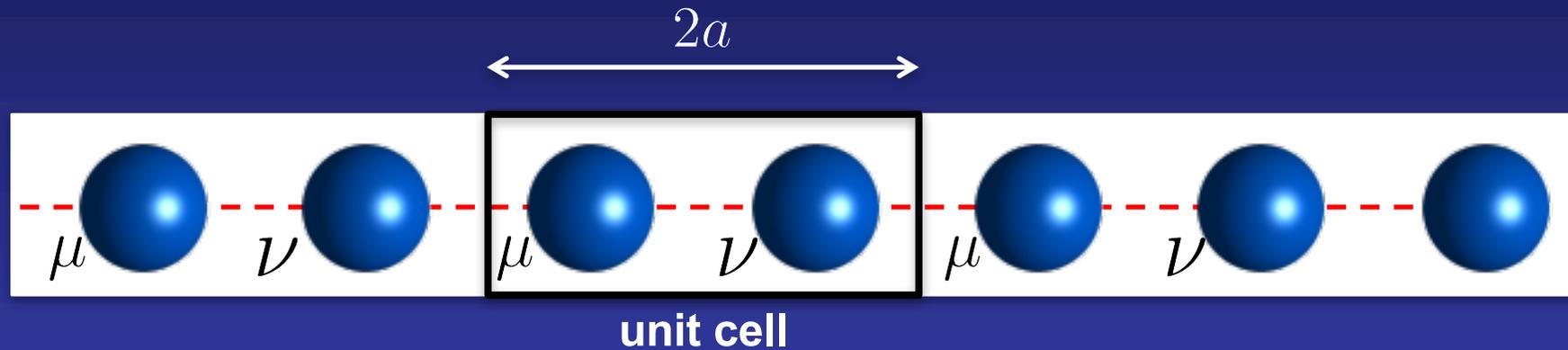
$\Downarrow$

The Hamiltonian and Overlap are (2×2) matrices

Let us compute the off-diagonal terms of the Hamiltonian, under the assumption of nearest neighbour interaction

$$H_{\mu\nu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\mu\nu}(\vec{T}) = H_{\mu\nu}(\vec{T}=0) + e^{-i\vec{k}\cdot 2\vec{a}} H_{\mu\nu}(\vec{T}=-2\vec{a}) = \gamma + e^{-i\vec{k}\cdot 2\vec{a}}\gamma = \gamma\left(1 + e^{-i\vec{k}\cdot 2\vec{a}}\right)$$

$2a$

$\vec{T}=-2\vec{a}$ $\vec{T}=0$

μ ν μ ν μ ν

unit cell

Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

$$2a$$

unit cell

Two atomic orbitals in the unit cell ($N = 2$). Let us denote these orbitals (s)$\equiv \mu, \nu$

$$\Downarrow$$

The Hamiltonian and Overlap are (2×2) matrices

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$$H_{\nu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\nu\mu}(\vec{T}) = H_{\nu\mu}(\vec{T}=0) + e^{i\vec{k}\cdot 2\vec{a}} H_{\nu\mu}(\vec{T}=2\vec{a}) = \gamma + e^{i\vec{k}\cdot 2\vec{a}}\gamma = \gamma\left(1 + e^{i\vec{k}\cdot 2\vec{a}}\right)$$

$$2a$$

$$\vec{T} = 0 \qquad \vec{T} = +2\vec{a}$$

unit cell

Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

$$2a$$

unit cell

Two atomic orbitals in the unit cell ($N = 2$). Let us denote these orbitals (s)$\equiv \mu, \nu$

$\Downarrow$

The Hamiltonian and Overlap are (2×2) matrices

Let us compute the overlap matrix
under the assumption that one orbital only overlaps with itself

$$S_{\nu\mu}(\vec{T}) = \delta_{\nu\mu}\delta_{\vec{T}0} \qquad S_{\nu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} S_{\nu\mu}(\vec{T}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} \delta_{\nu\mu}\delta_{\vec{T}0} = \delta_{\nu\mu}$$

The overlap matrix is diagonal for all $\vec{k}$ in this approximation.

Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

$2a$

μ ν μ ν μ ν

unit cell
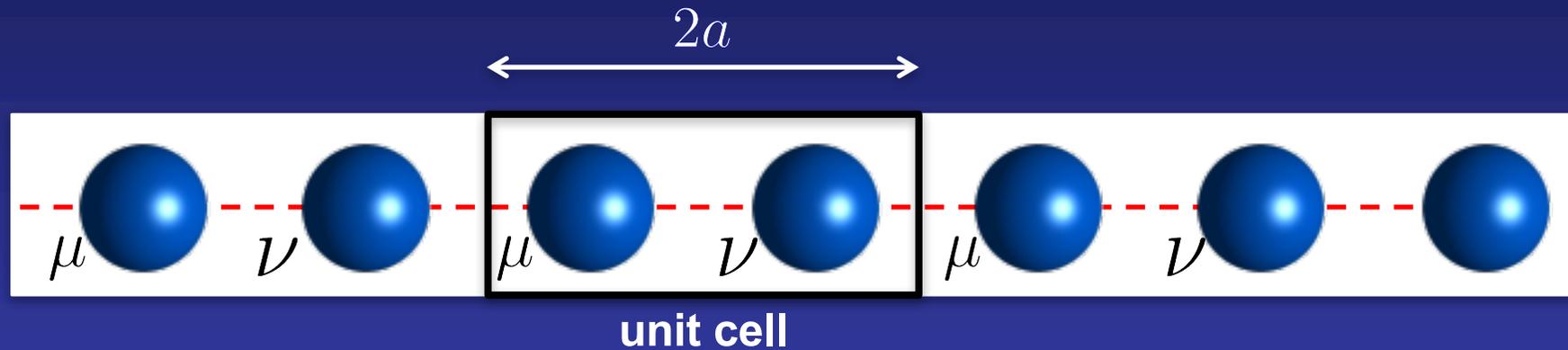
The secular equation to be solved for each $\vec{k}$ -point is

$$
\begin{pmatrix} \alpha & \gamma(1 + e^{-i2\vec{k}\cdot\vec{a}}) \\ \gamma(1 + e^{i2\vec{k}\cdot\vec{a}}) & \alpha \end{pmatrix}
\begin{pmatrix} c_{\mu n}(\vec{k}) \\ c_{\nu n}(\vec{k}) \end{pmatrix}
= E_n(\vec{k})
\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\begin{pmatrix} c_{\mu n}(\vec{k}) \\ c_{\nu n}(\vec{k}) \end{pmatrix}
$$

And the only non-trivial solutions are obtained from the solution of

$$
\det \begin{pmatrix} \alpha - E_n(\vec{k}) & \gamma(1 + e^{-i2\vec{k}\cdot\vec{a}}) \\ \gamma(1 + e^{i2\vec{k}\cdot\vec{a}}) & \alpha - E_n(\vec{k}) \end{pmatrix} = 0
$$

Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

$$\det \begin{pmatrix} \alpha - E_n(\vec{k}) & \gamma(1 + e^{-i2\vec{k}\cdot\vec{a}}) \\ \gamma(1 + e^{i2\vec{k}\cdot\vec{a}}) & \alpha - E_n(\vec{k}) \end{pmatrix} = 0$$
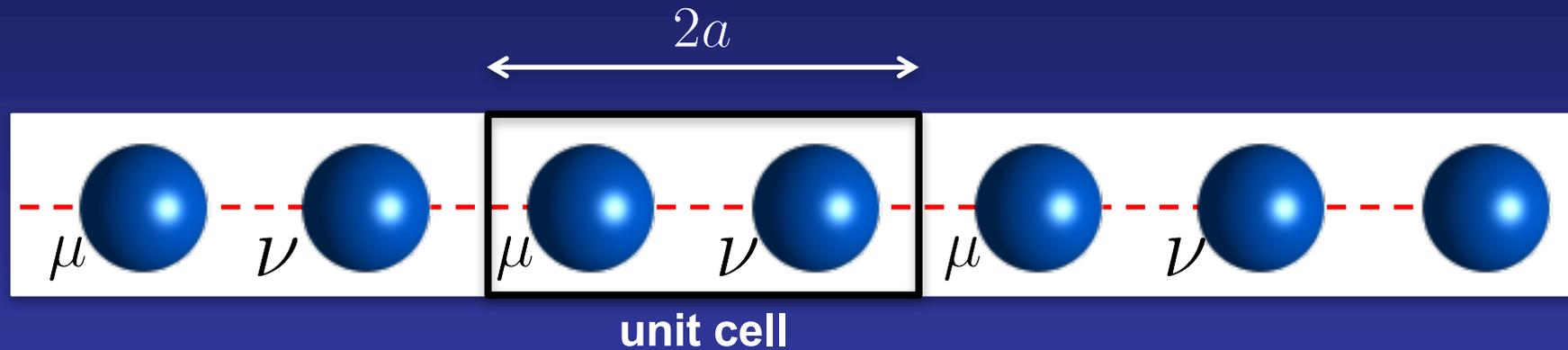
$$\left(\alpha - E_n(\vec{k})\right)^2 - \gamma^2 \left(1 + e^{-i2\vec{k}\cdot\vec{a}}\right)\left(1 + e^{i2\vec{k}\cdot\vec{a}}\right) = 0$$

$$\alpha^2 + E_n^2(\vec{k}) - 2\alpha E_n(\vec{k}) - \gamma^2 - \gamma^2 e^{-i2\vec{k}\cdot\vec{a}} - \gamma^2 e^{i2\vec{k}\cdot\vec{a}} - \gamma^2 = 0$$

$$E_n^2(\vec{k}) - 2\alpha E_n(\vec{k}) + \alpha^2 - 2\gamma^2 - \gamma^2\left(2\cos(2\vec{k}\cdot\vec{a})\right) = 0$$

$$E_n^2(\vec{k}) - 2\alpha E_n(\vec{k}) + \alpha^2 - 2\gamma^2\left(1 + \cos(2\vec{k}\cdot\vec{a})\right) = 0$$

$$E_n(\vec{k}) = \frac{2\alpha \pm \sqrt{4\alpha^2 - 4\left[\alpha^2 - 2\gamma^2\left(1 + \cos(2\vec{k}\cdot\vec{a})\right)\right]}}{2} = \frac{2\alpha \pm \sqrt{8\gamma^2\left(1 + \cos(2\vec{k}\cdot\vec{a})\right)}}{2}$$

$$= \frac{2\alpha \pm 2\gamma\sqrt{2\left(1 + \cos(2\vec{k}\cdot\vec{a})\right)}}{2} = \alpha \pm \gamma\sqrt{2 \times 2\cos^2(\vec{k}\cdot\vec{a})} = \alpha \pm 2\gamma\cos(\vec{k}\cdot\vec{a})$$

Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

$$2a$$

unit cell

And the only non-trivial solutions are obtained from the solution of

$$\det \begin{pmatrix} \alpha - E_n(\vec{k}) & \gamma(1 + e^{-i2\vec{k}\cdot\vec{a}}) \\ \gamma(1 + e^{i2\vec{k}\cdot\vec{a}}) & \alpha - E_n(\vec{k}) \end{pmatrix} = 0$$

$$E_n(\vec{k}) = \alpha \pm 2\gamma \cos(\vec{k} \cdot \vec{a})$$

For every $\vec{k}$ point we have two solutions, but the unit cell where we have to sample has been reduced by half

One atom/unit cell $\left(-\dfrac{\pi}{a}, \dfrac{\pi}{a}\right)$ **Two atoms/unit cell** $\left(-\dfrac{\pi}{2a}, \dfrac{\pi}{2a}\right)$

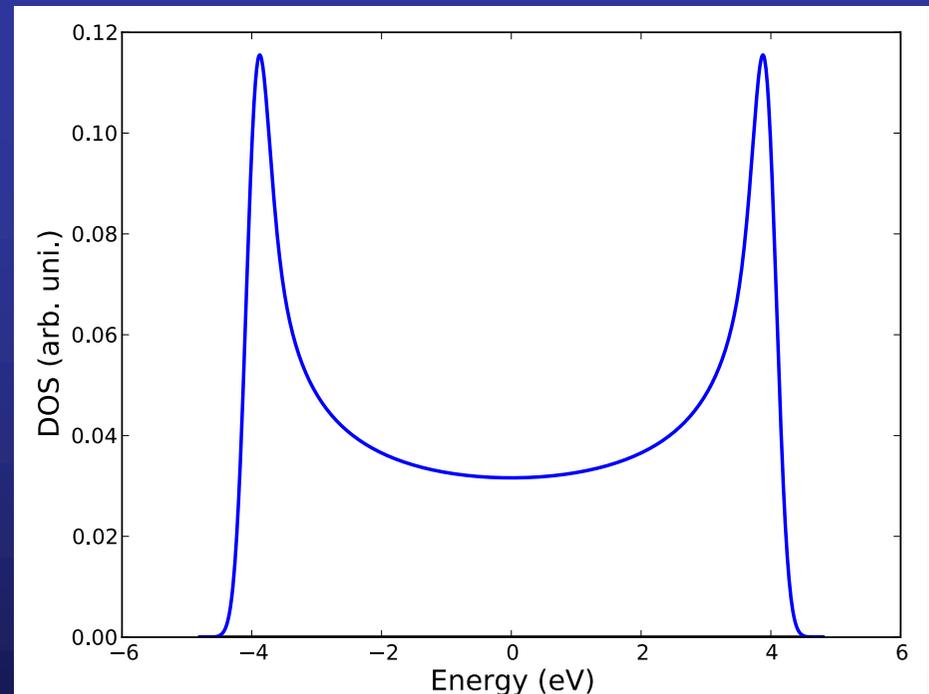# Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

$$2a$$

$$\mu \quad \nu \quad \mu \quad \nu \quad \mu \quad \nu$$

unit cell

And the only non-trivial solutions are obtained from the solution of

$$\det \begin{pmatrix} \alpha - E_n(\vec{k}) & \gamma(1 + e^{-i2\vec{k}\cdot\vec{a}}) \\ \gamma(1 + e^{i2\vec{k}\cdot\vec{a}}) & \alpha - E_n(\vec{k}) \end{pmatrix} = 0$$

$$E_n(\vec{k}) = \alpha \pm 2\gamma \cos(\vec{k} \cdot \vec{a})$$

**For every $\vec{k}$ point we have two solutions,
but the unit cell where we have to sample has been reduced by half**

One atom/unit cell $\left(-\dfrac{\pi}{a}, \dfrac{\pi}{a}\right)$ **Two atoms/unit cell** $\left(-\dfrac{\pi}{2a}, \dfrac{\pi}{2a}\right)$

Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals

Two atoms per unit cell

```
$ <your_path_to_scale_up_dir>/bin/scaleup.x < 1d-chain.s.twoatoms.fdf > 1d-chain.s.twoatoms.out

$ python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -bands -file _1d_twoat_tb_FINAL.bands

$ python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -dos -file _1d_twoat_tb_FINAL.ener
```

Bands
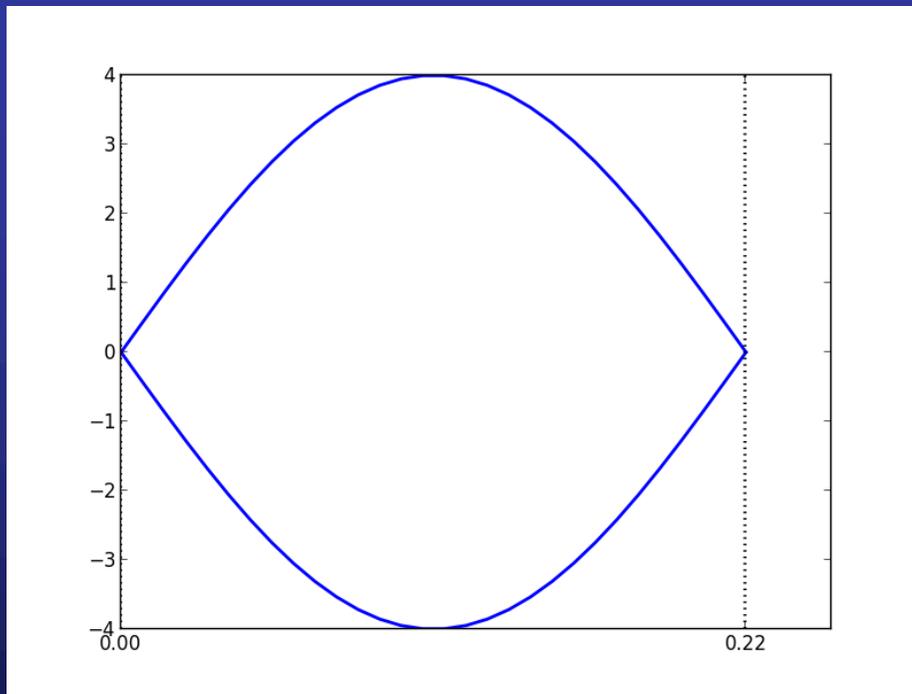
DOS

… Now let us practice with some simple examples: analytical calculations and SCALE-UP simulations

1-D Monoatomic linear chain with only s-orbitals. One atom in the unit cell

1-D Monoatomic linear chain with only s-orbitals. Two atoms in the unit cell

2-D Monoatomic plane with only s-orbitals

3-D Monoatomic cube with only s-orbitals

2-D CuO_2 plane

Solving the secular equation in a simple case: the monoatomic square plane with only s-orbitals

$\vec{a}_y$

$\vec{a}_x$

We keep the previous approximations

Only one atomic orbital in the unit cell ($N = 1$). Let us denote this orbital (s)$\equiv \mu$

$\Downarrow$

The Hamiltonian and Overlap matrices are just simple real numbers

Hamiltonian matrix elements in real space

- Only **on-site** $\qquad H_{\mu\mu}(\vec{T} = 0) = \alpha$

- And **nearest neigbour approximation** $H_{\mu\mu}(\vec{T} = \pm\vec{a}_x) = H_{\mu\mu}(\vec{T} = \pm\vec{a}_y) = \gamma$

Solving the secular equation in a simple case: the monoatomic square plane with only *s*-orbitals
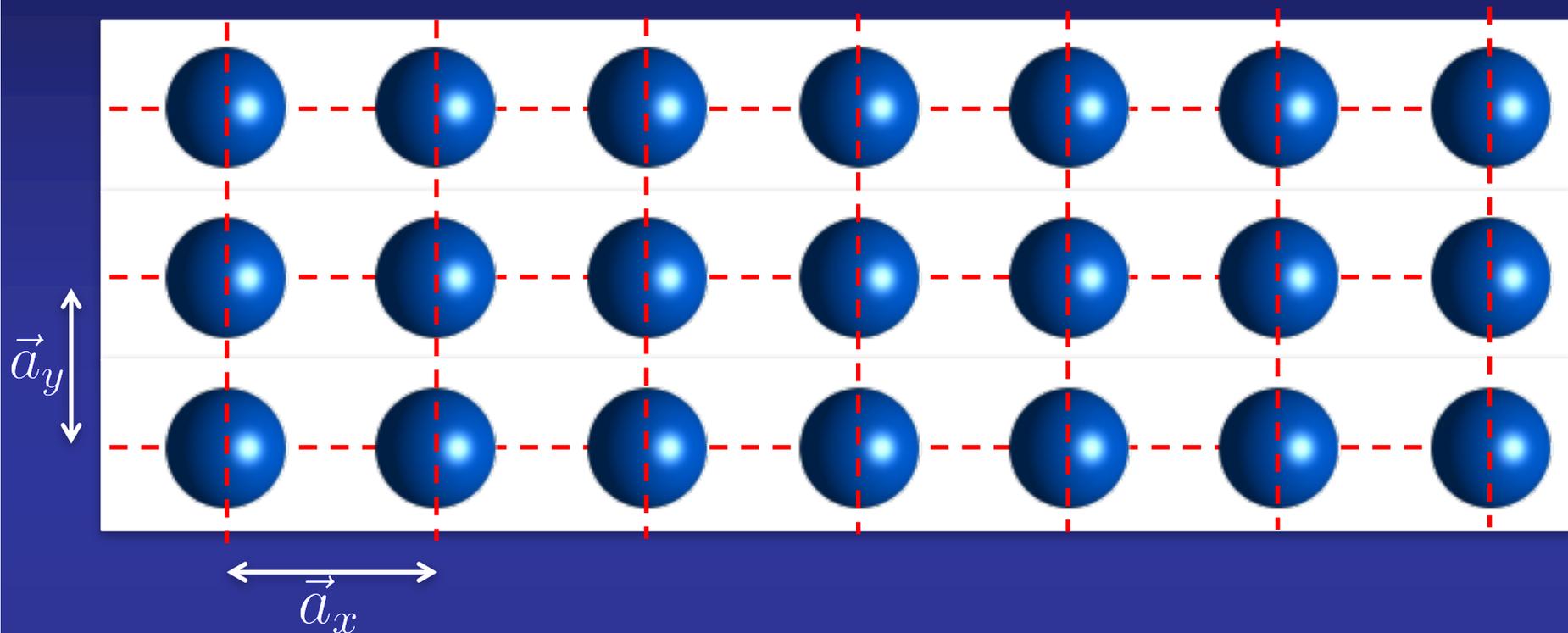
We compute the matrix elements in reciprocal space, as we did before

$$H_{\mu\mu}(\vec{k}) = \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\mu\mu}(\vec{T})$$

$$= H_{\mu\mu}(\vec{T}=0) + e^{i\vec{k}\cdot\vec{a}_x} H_{\mu\mu}(\vec{T}=\vec{a}_x) + e^{-i\vec{k}\cdot\vec{a}_x} H_{\mu\mu}(\vec{T}=-\vec{a}_x) + e^{i\vec{k}\cdot\vec{a}_y} H_{\mu\mu}(\vec{T}=\vec{a}_y) + e^{-i\vec{k}\cdot\vec{a}_y} H_{\mu\mu}(\vec{T}=-\vec{a}_y)$$

$$= \alpha + 2\gamma \left[\cos(k_x a_x) + \cos(k_y a_y) \right]$$

$$S_{\mu\mu}(\vec{k}) = 1$$

Solving the secular equation in a simple case: the monoatomic square plane with only s-orbitals
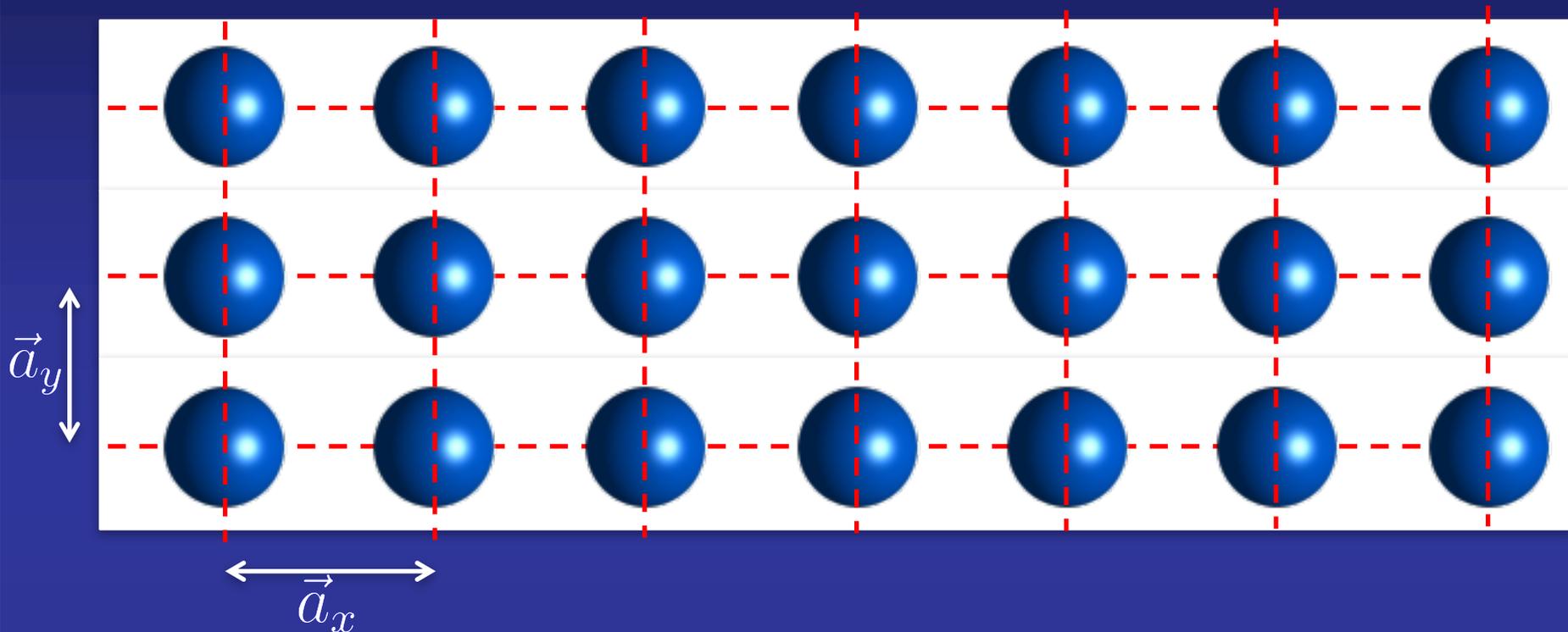
The secular equation for this system is, therefore

$$\left[\alpha + 2\gamma\left[\cos(k_x a_x) + \cos(k_y a_y)\right] - E(\vec{k})\right] c_\mu(\vec{k}) = 0$$

Therefore, for a non trivial solution, with $c(k) \neq 0$

$$E(\vec{k}) = \alpha + 2\gamma\left[\cos(k_x a_x) + \cos(k_y a_y)\right]$$

Solving the secular equation in a simple case: the monoatomic square plane with only *s*-orbitals

Unit cell

$\vec{a}_y$

$\vec{a}_x$

```
%block Supercell
  1 1 1
%endblock Supercell
```
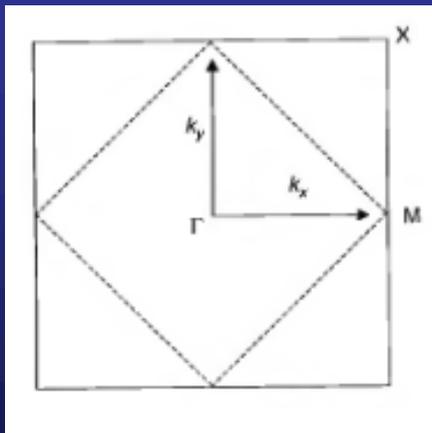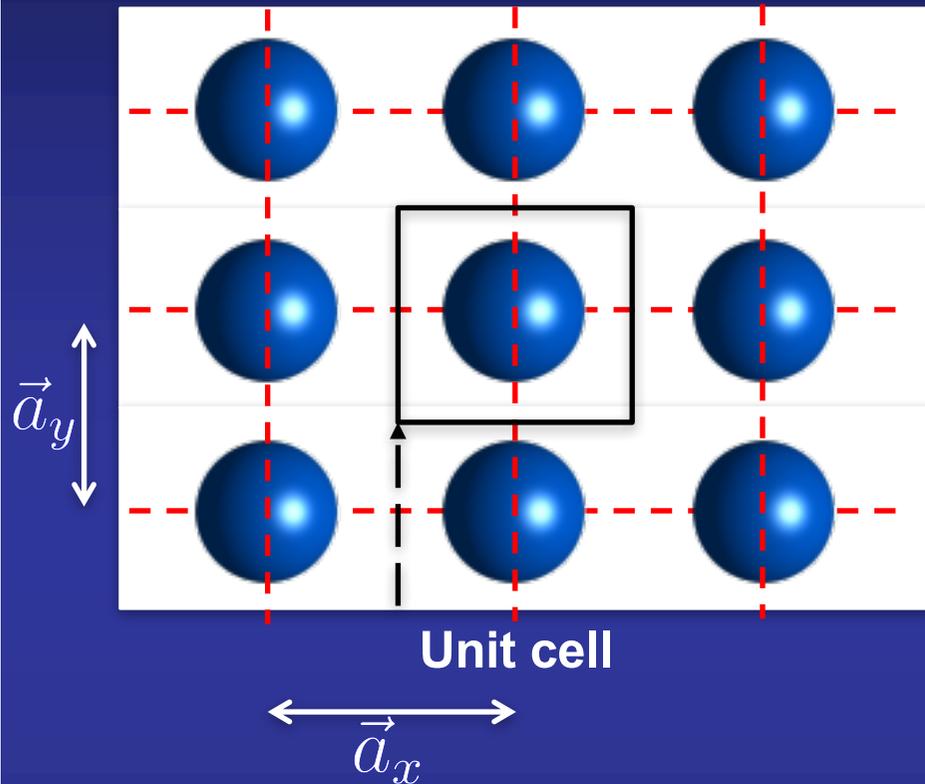
```
%block k-sampling
50 50 1
%endblock k-sampling
```
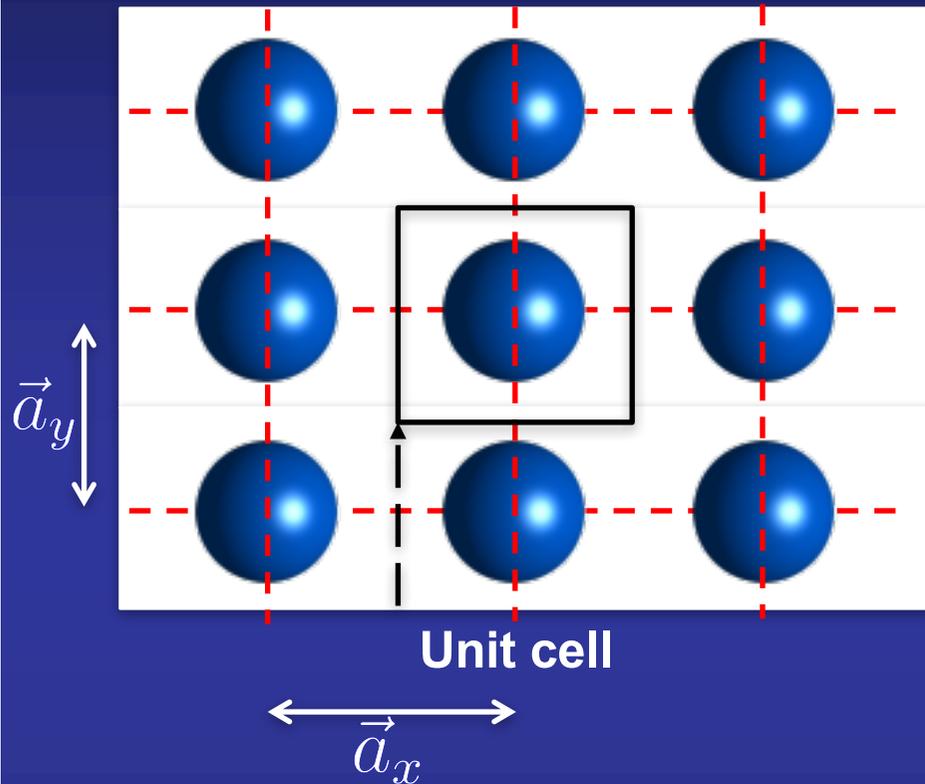
```
%block band_path
3
30 0.0 0.0 0.0 0.5 0.0 0.0
30 0.5 0.0 0.0 0.5 0.5 0.0
30 0.5 0.5 0.0 0.0 0.0 0.0
%endblock band_path

 <unit_cell units="bohrradius">
     5.6700    0.0000    0.0000
     0.0000    5.6700    0.0000
     0.0000    0.0000    7.5600
 </unit_cell>
```

Only one atom in the unit cell

Introducing the tight-binding param in a simple case the monoatomic square plane with only *s*-orbitals

Unit cell

$\vec{a}_y$

$\vec{a}_x$


```
%block Supercell
  1 1 1
%endblock Supercell

%block k-sampling
50 50 1
%endblock k-sampling

%block band_path
3
30 0.0 0.0 0.0 0.5 0.0 0.0
30 0.5 0.0 0.0 0.5 0.5 0.0
30 0.5 0.5 0.0 0.0 0.0 0.0
%endblock band_path

<unit_cell units="bohrradius">
     5.6700    0.0000    0.0000
     0.0000    5.6700    0.0000
     0.0000    0.0000    7.5600
</unit_cell>
```
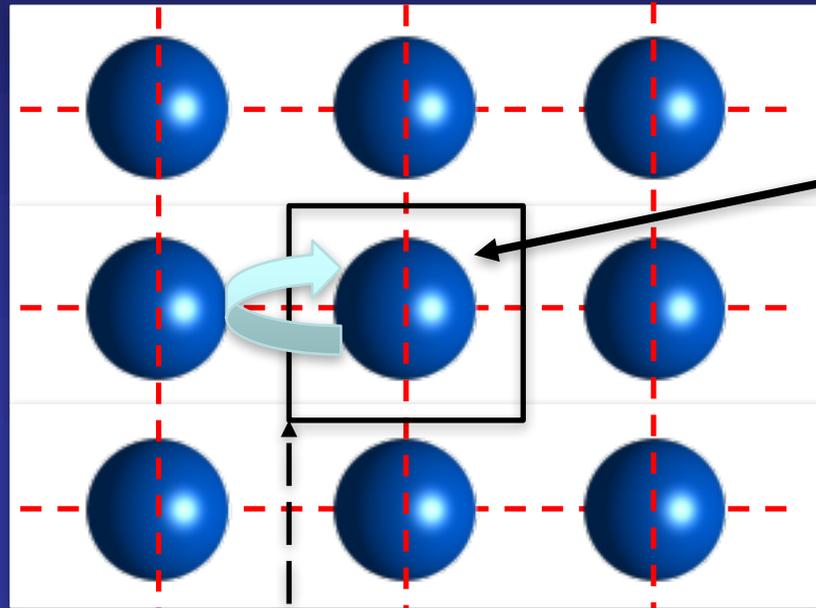
We have to sample now a 2D Brillouin zone

Solving the secular equation in a simple case: the monoatomic square plane with only *s*-orbitals

Unit cell


```
%block Supercell
 1 1 1
%endblock Supercell

%block k-sampling
50 50 1
%endblock k-sampling

%block band_path
3
30 0.0 0.0 0.0 0.5 0.0 0.0
30 0.5 0.0 0.0 0.5 0.5 0.0
30 0.5 0.5 0.0 0.0 0.0 0.0
%endblock band_path

<unit_cell units="bohrradius">
    5.6700    0.0000    0.0000
    0.0000    5.6700    0.0000
    0.0000    0.0000    7.5600
</unit_cell>
```

New path in the high-symmetry BZ to plot the bands

$$\Gamma \to M \to X \to \Gamma$$
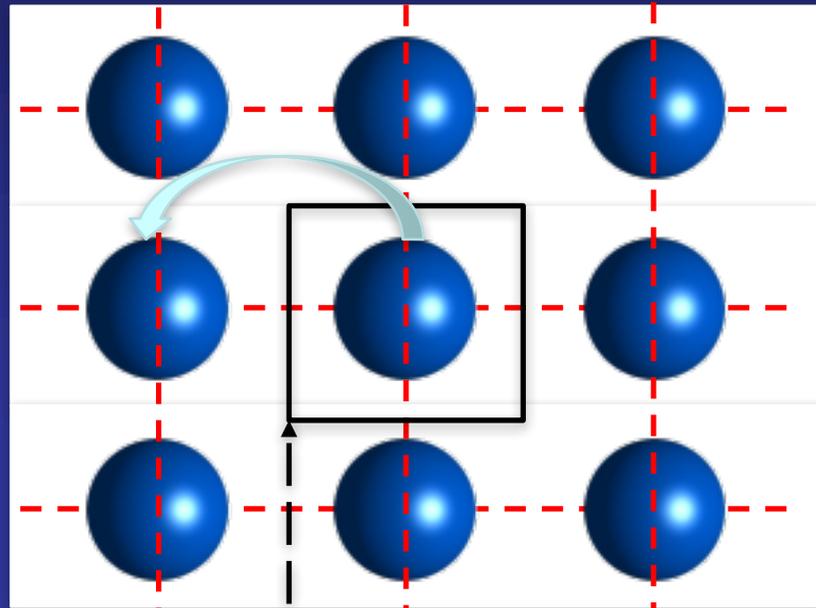
Introducing the tight-binding param in a simple case the monoatomic square plane with only *s*-orbitals

Unit cell

```
<electron_hamiltonian_one>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="0"
        hopc="0"
        gamma="0.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="-1"
        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
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    <interaction_gm
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        orbital_2="1"
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        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
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    <interaction_gm
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        orbital_2="1"
        hopa="0"
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        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
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        orbital_2="1"
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        hopb="1"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
</electron_hamiltonian_one>
```
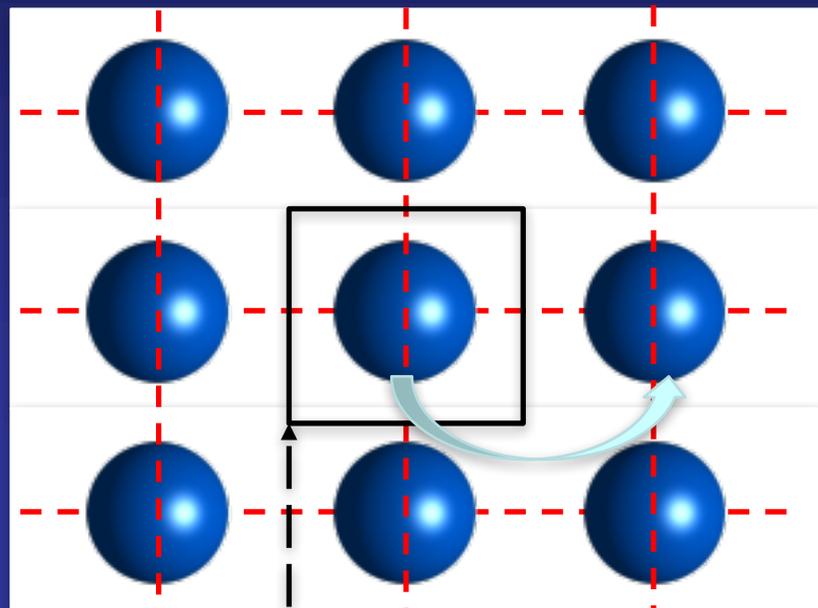
Introducing the tight-binding param in a simple case the monoatomic square plane with only *s*-orbitals

Unit cell

```xml
<electron_hamiltonian_one>
    <interaction_gm
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        hopa="0"
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        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
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        orbital_2="1"
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        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
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        orbital_2="1"
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        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
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        orbital_2="1"
        hopa="0"
        hopb="-1"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
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        hopc="0"
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        ry="0.000"
        rz="0.000">
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</electron_hamiltonian_one>
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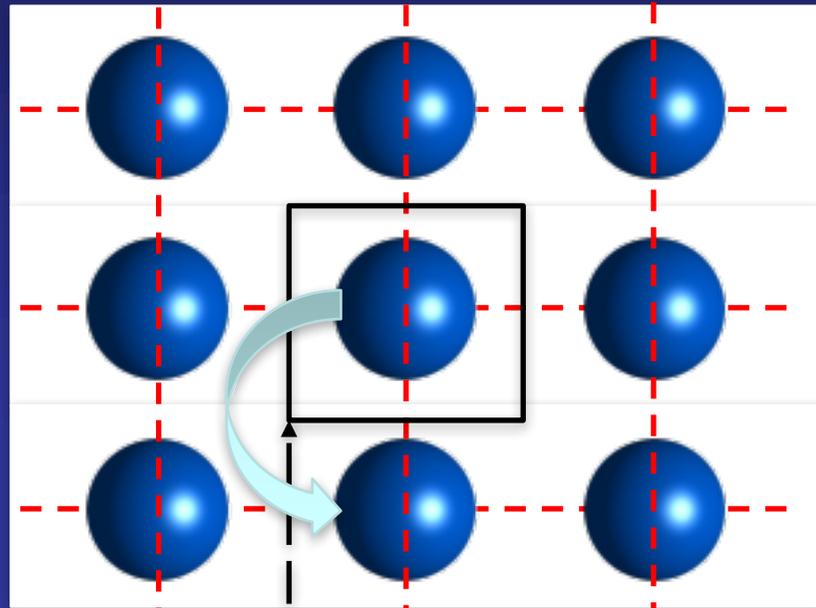
Introducing the tight-binding param in a simple case the monoatomic square plane with only *s*-orbitals

Unit cell

```xml
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        hopb="0"
        hopc="0"
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        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="-1"
        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="1"
        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="-1"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="1"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
</electron_hamiltonian_one>
```
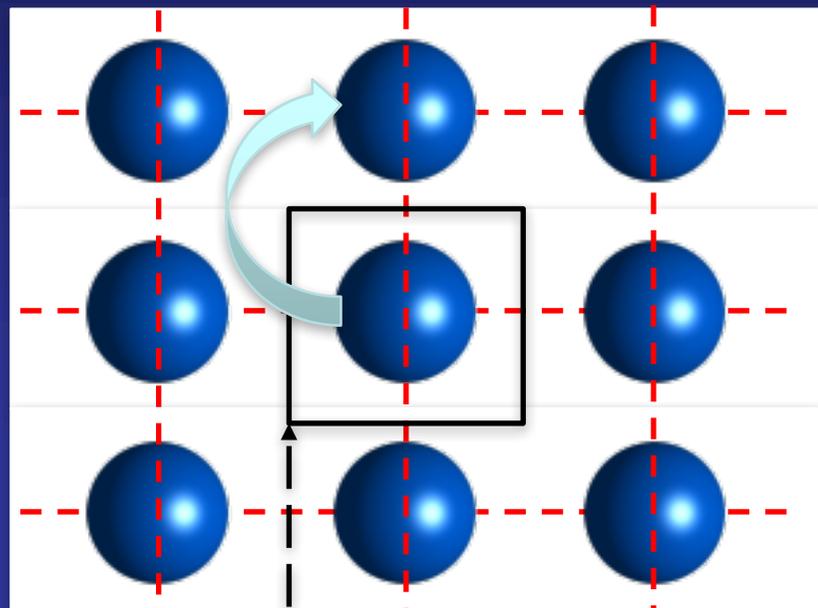
# Introducing the tight-binding param in a simple case the monoatomic square plane with only *s*-orbitals

Unit cell

```
<electron_hamiltonian_one>
    <interaction_gm
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        orbital_2="1"
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        hopb="0"
        hopc="0"
        gamma="0.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="-1"
        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="1"
        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
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        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="1"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
</electron_hamiltonian_one>
```

Introducing the tight-binding param in a simple case the monoatomic square plane with only *s*-orbitals

Unit cell

```xml
<electron_hamiltonian_one>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="0"
        hopc="0"
        gamma="0.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="-1"
        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="1"
        hopb="0"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="-1"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
    <interaction_gm
        orbital_1="1"
        orbital_2="1"
        hopa="0"
        hopb="1"
        hopc="0"
        gamma="2.0000"
        rx="0.000"
        ry="0.000"
        rz="0.000">
    </interaction_gm>
</electron_hamiltonian_one>
```

Running the scale-up code for a simple case the monoatomic square plane with only s-orbitals

```
<your_path_to_scaleup_dir>/bin/scaleup.x < 2d-plane.s.fdf > 2d-plane.s.out
```

Plotting the band structure in a simple case: the monoatomic square plane with only *s*-orbitals

```
python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -bands -file _2d_tight_binding_FINAL.bands
```


$$\Gamma \rightarrow M \rightarrow X \rightarrow \Gamma$$
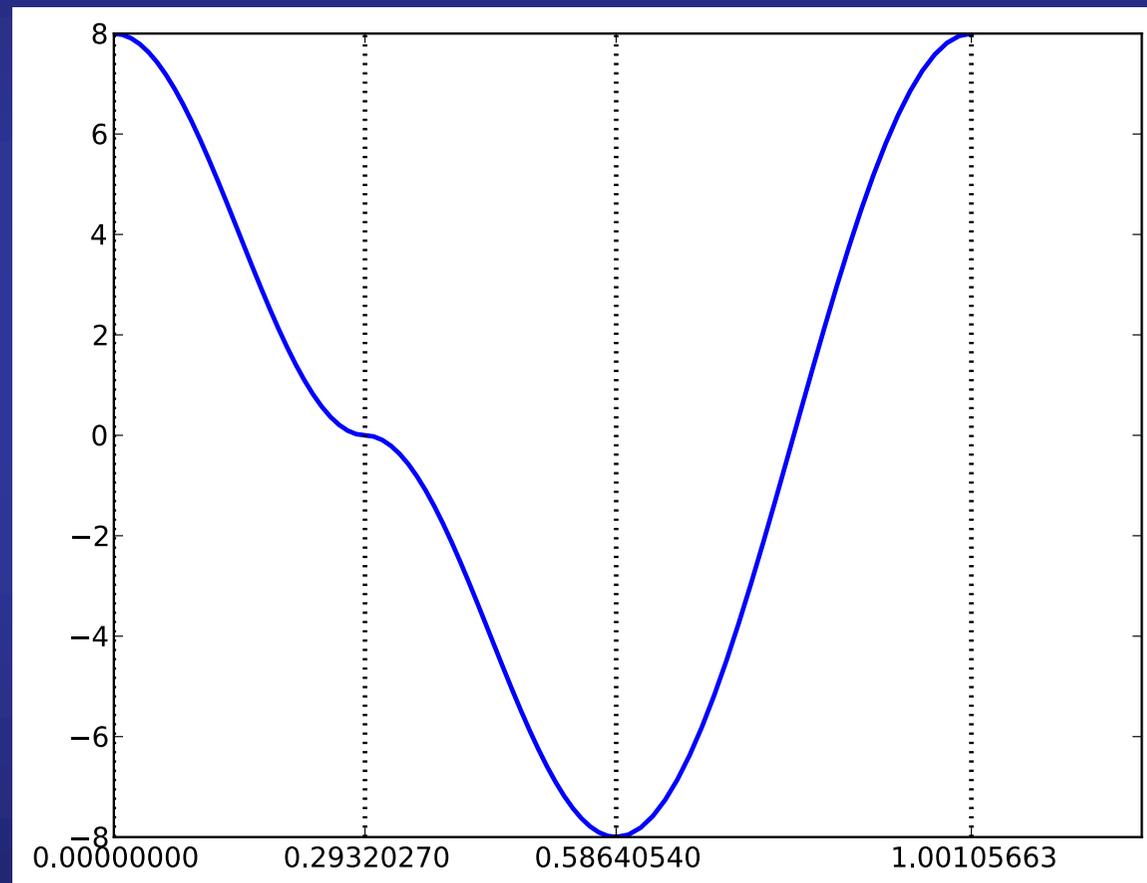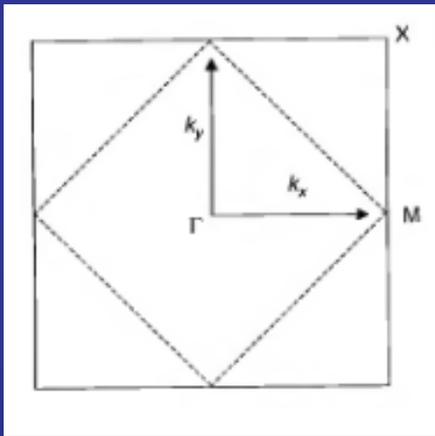
$+4\gamma$

Change in bandwidth

-4γ

Plotting the density of states in a simple case: the monoatomic square plane with only *s*-orbitals

```
python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -dos -file _2d_tight_binding_FINAL.ener
```
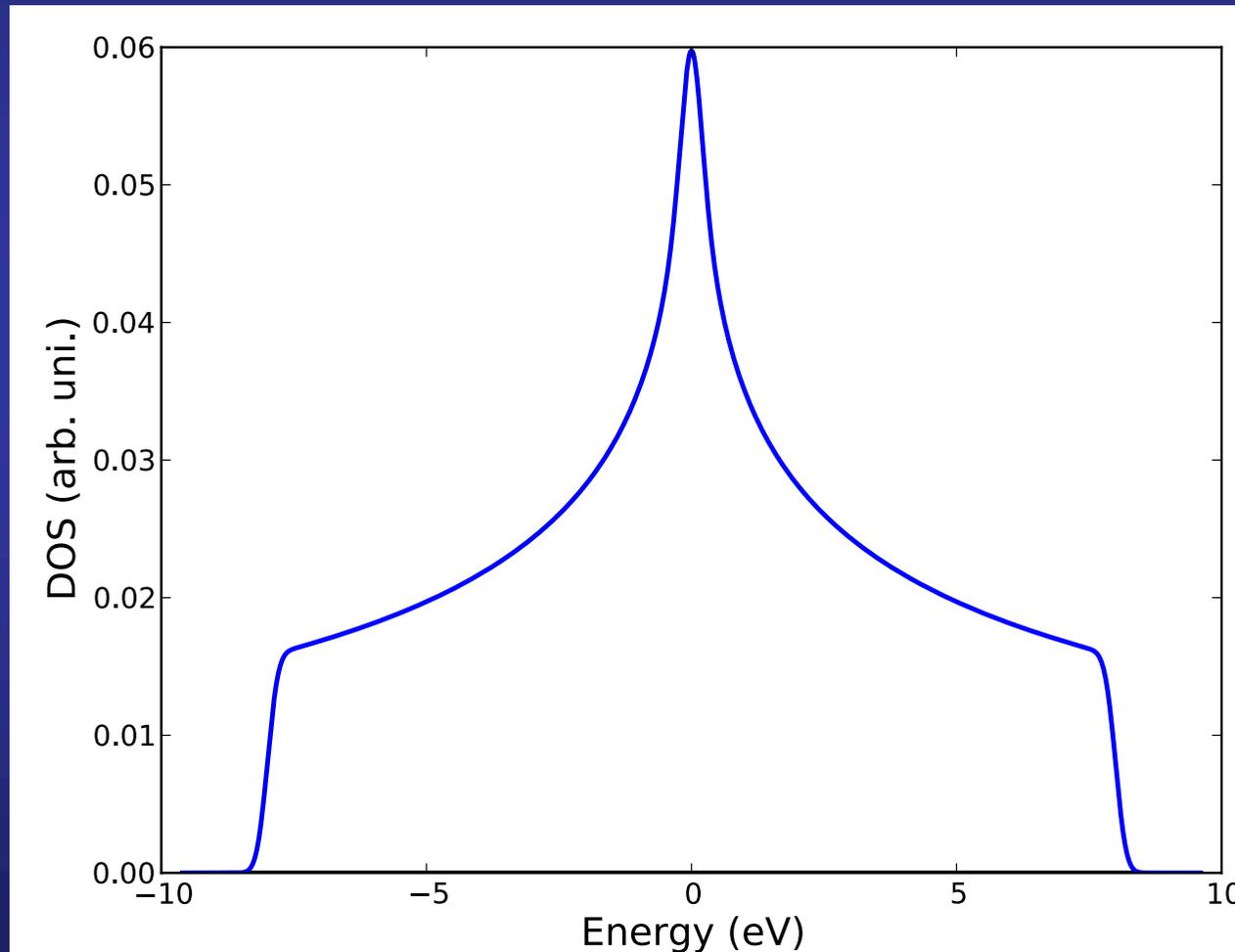
... Now let us practice with some simple examples: analytical calculations and SCALE-UP simulations

1-D Monoatomic linear chain with only s-orbitals. One atom in the unit cell

1-D Monoatomic linear chain with only s-orbitals. Two atoms in the unit cell

2-D Monoatomic plane with only s-orbitals

3-D Monoatomic cube with only s-orbitals

2-D CuO_2 plane

Repeat the exercise for
the monoatomic cube with only *s*-orbitals

```
$ <your_path_to_scale_up_dir>/bin/scaleup.x < 3d-cube.s.fdf > 3d-cube.s.out

python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -bands -file _3d_tight_binding_FINAL.bands

python <your_path_to_scale_up_dir>/scripts/scaleup_utils.py -dos -file _3d_tight_binding_FINAL.ener -width 0.045
```

Band structure
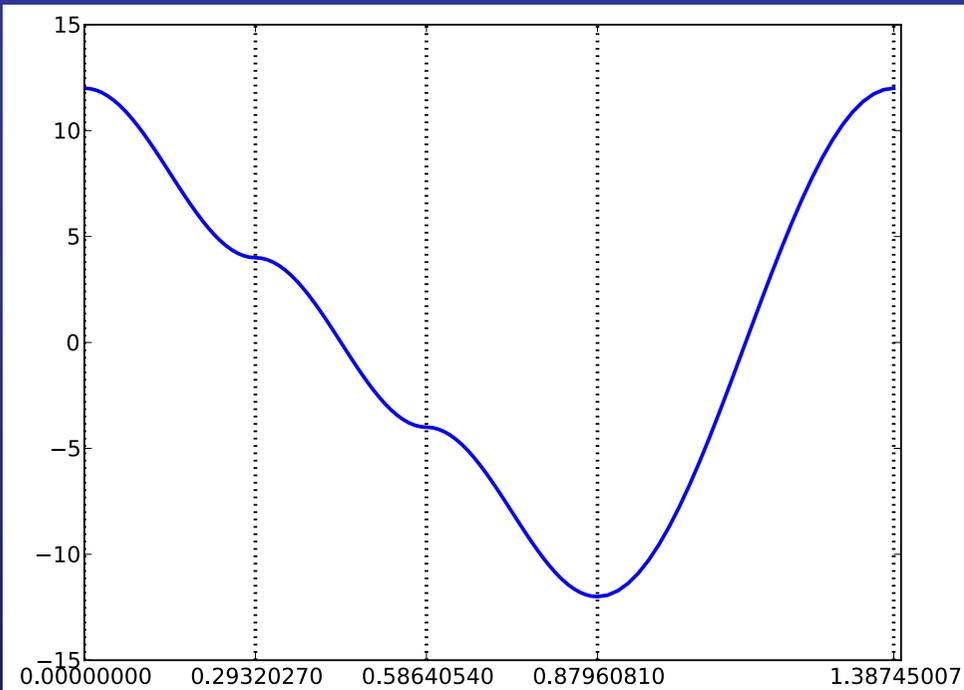
Density Of States
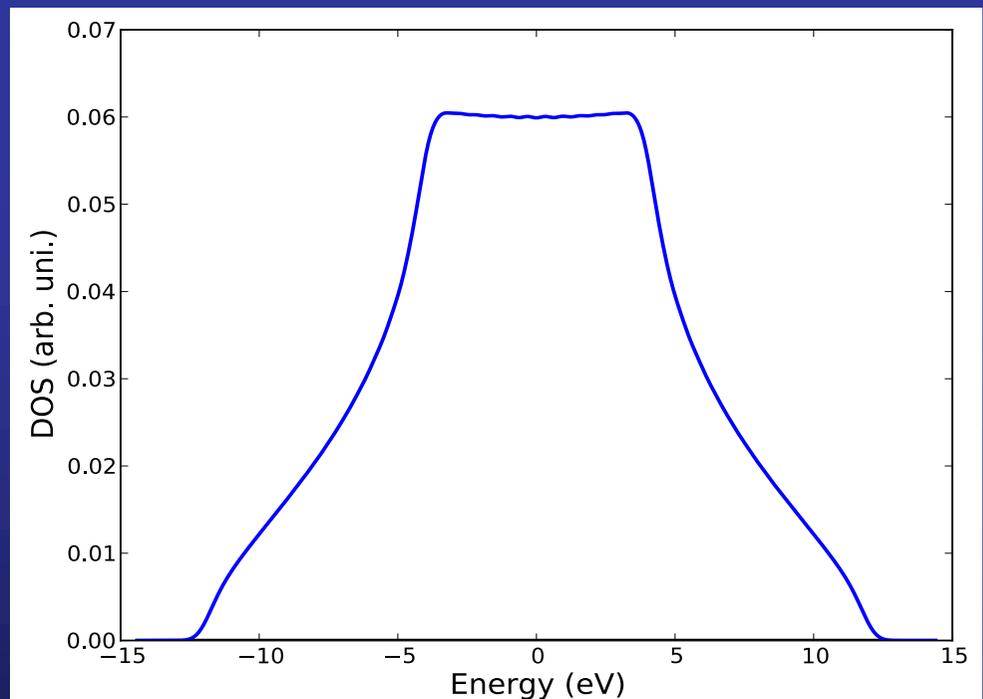
Change in bandwidth to $2 \times \text{dimension} \times (2\gamma)$

... Now let us practice with some simple examples: analytical calculations and SCALE-UP simulations

1-D Monoatomic linear chain with only s-orbitals. One atom in the unit cell

1-D Monoatomic linear chain with only s-orbitals. Two atoms in the unit cell

2-D Monoatomic plane with only s-orbitals

3-D Monoatomic cube with only s-orbitals

2-D CuO_2 plane

Square lattice and CuO$_2$ planes

These kind of planes appear in the bilayers of high-T$_c$ superconductors, such as YBa$_2$Cu$_3$O$_7$

Extensive calculations have shown that the primary electronic states at the Fermi energy are a single band formed from Cu d and O p orbitals
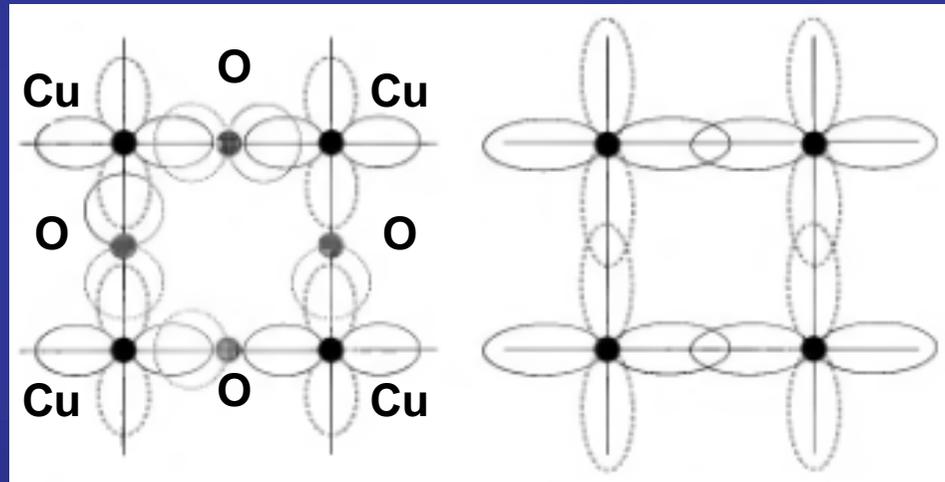
The band has the same symmetry as d_{x2-y2} states centered on each Cu

Square lattice and CuO$_2$ planes: setting up the unit cell

To describe the bands of interest, we need to consider three atoms (one Cooper and two Oxygens) in a square simulation box

```
slab

%block LatticeParameters
 4.0 4.0 4.0 90. 90. 90.
%endblock LatticeParameters

%block Supercell
1 1 1
%endblock Supercell

Types_of_materials    1
Material_1_Number_of_Atoms 3

%block Material_1_Atoms
 1 cooper   0.0   0.0   0.0      63.50   0.0  1
 2 oxigen   0.5   0.0   0.0      16.00   0.0  1
 3 oxigen   0.0   0.5   0.0      16.00   0.0  1
%endblock Material_1_Atoms
```

The material is defined as a slab.
It means that the third lattice vectors will be automatically increased, independently of the value introduced in the LatticeParameters block

The unit cell is a square of 4.00 Å of length

No supercell is made from periodic repetitions of the unit cell

In the unit cell, there is only one kind of material, with three atoms

There are three atoms in the unit cell:
Cu at the origin
One O at the center of the lattice vector along x
One O at the center of the lattice vector along y

Next threee numbers:
Atomic mass
Charge
Number of orbitals considered

Square lattice and CuO$_2$ planes: setting up the basis set

The most important atomic orbitals that will play a role in the basis set will be the Cu d_{x2-y2}, and the O p-orbitals that hybridize with them (the p_x of the first O and the p_y of the second O)
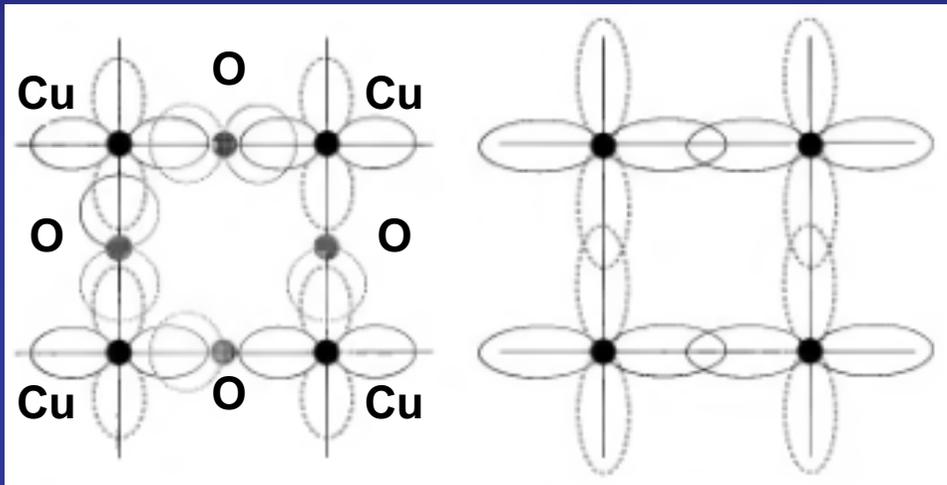

```
%block Material_1_Orbitals
1 1 dx2y2 1. 1.
2 1 px    2. 2.
3 1 py    2. 2.
%endblock Material_1_Orbitals

%block epsilon_inf
10000.0      0.0       0.0
     0.0 10000.0       0.0
     0.0      0.0  10000.0
%endblock epsilon_inf
```

For each atomic orbital within the material, we define
- The atom to which that orbital belongs
- The index of the orbital within the atom
- The label that identifies the orbital
- The reference occupation
- The initial occupation

Occupation of the Cu atom

There are 9 electrons in the d-shell.
Due to crystal field splitting, the energy order of the d-orbitals is

square planar crystal field splitting

There is one unpaired electron in the dx^2-y^2
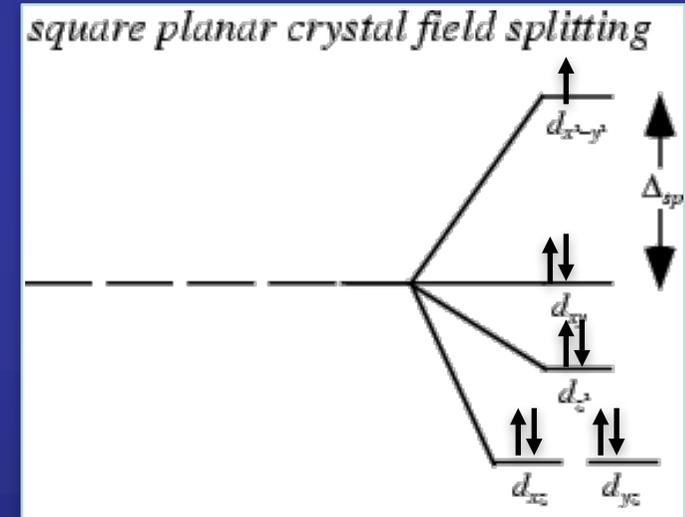
Electronic configuration for neutral Cu:
[Ar] $3d^{10}$ $4s^1$

If it is oxidized, the electronic configuration for Cu^{2+} is:
[Ar] $3d^9$ $4s^0$

Occupation of the O atom

All the p-orbitals of O are occupied with 2 electrons

Electronic configuration for neutral O:
[He] $2s^2\,2p^4$

If it is reduced, the electronic configuration for O^{2-} is:
[He] $2s^2\,2p^6$

Square lattice and CuO$_2$ planes: setting up the self-consistency and the band structure calculation

```
%block k-sampling
 40 40 1
%endblock k-sampling

Totalcharge        0.0
Geometrymode       single-point
MaximumSCFiter     100
SCFthreshold       0.0001
SCFmixing          1.0

%block band_path
3
30 0.0 0.0 0.0 0.5 0.0 0.0
30 0.5 0.0 0.0 0.5 0.5 0.0
30 0.5 0.5 0.0 0.0 0.0 0.0
%endblock band_path
```

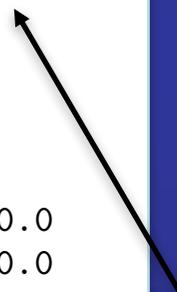**Define the fineness of the Monkhorst-Pack grid**

Define the total charge in the supercell

Define the geometry mode:
Single point: solve for the SCF of the electrons.
Do not perform atomic displacements

Define the Maximum number of SCF steps allowed, the convergence criterion, and the mixing between two consecutive density matrix to speed up the self-consistency
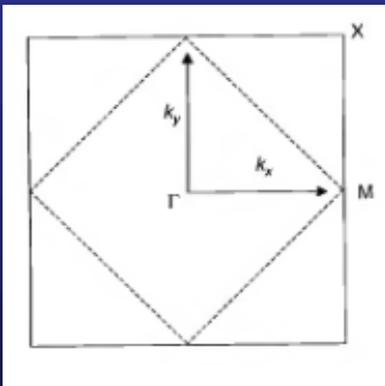
Once SCF is achieved, define the path to plot the bands:
- **30 points between Γ and M**
- **30 points between M and X**
- **30 points between X and Γ**

Square lattice and CuO₂ planes: setting up the interactions

First, set up the on-site interactions


```
!-----------------------------------------------!
! Define the TB interactions                    !
! in the CuO2 plane,                            !
! including the interactions between the        !
! Cu dx2-y2 orbital and the O px and py orbitals!
!-----------------------------------------------!

Number_of_interactions 11

%block Interaction_1
materials 1  1    ! Interaction within material 1
atoms     1  1    ! Interaction within atom 1
orbitals  1  1    ! It is the diagonal element
hop       0 0 0   ! Diagonal element
gamma     2.0000  ! Related to the band's center of mass
%endblock Interaction_1

%block Interaction_2
materials 1  1    ! Interaction within material 1
atoms     2  2    ! Interaction within atom 2
orbitals  1  1    ! It is the diagonal element
hop       0 0 0   ! Diagonal element
gamma    -2.0000  ! Related to the band's center of mass
%endblock Interaction_2

%block Interaction_3
materials 1  1    ! Interaction within material 1
atoms     3  3    ! Interaction within atom 3
orbitals  1  1    ! It is the diagonal element
hop       0 0 0   ! Interaction with the atom on top
gamma    -2.0000  ! Related to the band width
%endblock Interaction_3
```
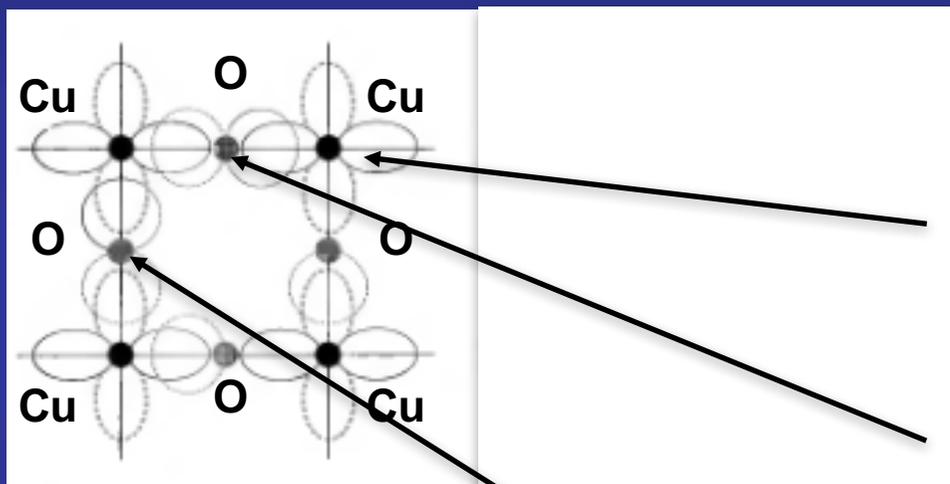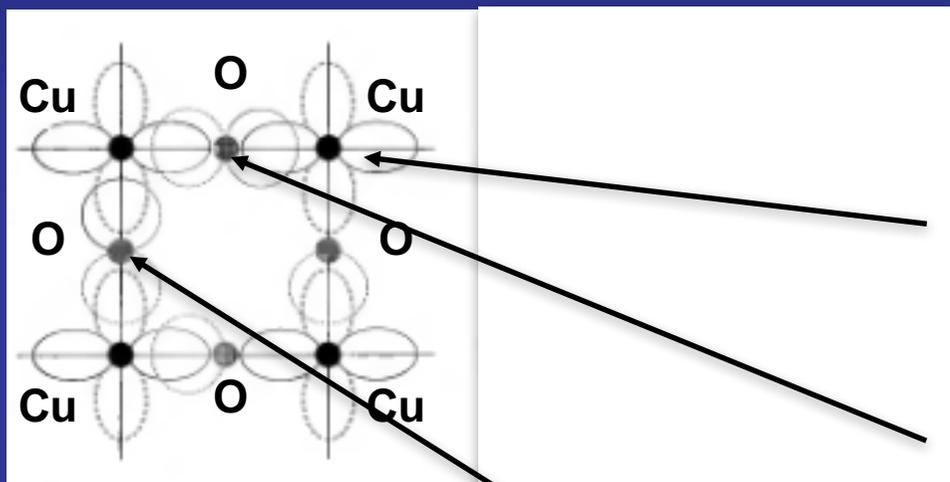
Square lattice and CuO$_2$ planes: setting up the interactions

First, set up the on-site interactions


```
!----------------------------------------------!
! Define the TB interactions                   !
! in the CuO2 plane,                           !
! including the interactions between the       !
! Cu dx2-y2 orbital and the O px and py orbitals!
!----------------------------------------------!

Number_of_interactions 11

%block Interaction_1
materials 1  1    ! Interaction within material 1
atoms     1  1    ! Interaction within atom 1
orbitals  1  1    ! It is the diagonal element
hop       0 0 0   ! Diagonal element
gamma     2.0000  ! Related to the band's center of mass
%endblock Interaction_1

%block Interaction_2
materials 1  1    ! Interaction within material 1
atoms     2  2    ! Interaction within atom 2
orbitals  1  1    ! It is the diagonal element
hop       0 0 0   ! Diagonal element
gamma    -2.0000  ! Related to the band's center of mass
%endblock Interaction_2

%block Interaction_3
materials 1  1    ! Interaction within material 1
atoms     3  3    ! Interaction within atom 3
orbitals  1  1    ! It is the diagonal element
hop       0 0 0   ! Interaction with the atom on top
gamma    -2.0000  ! Related to the band width
%endblock Interaction_3
```

Supplementary information

Empirical tight-binding

If the atoms are sufficiently far appart, electrons in every atom will have the same on-site value of the energy, ε_0 .
This situation can be represented by a model Hamiltonian of the form

$$\hat{\mathcal{H}}_0 = \varepsilon_0 \sum_I |I\rangle\langle I|$$

When the atoms are brought together, we have to conside the possibility of the electrons jumping from one atom to any of its neighbours

$$\hat{\mathcal{H}}_{\mathrm{TB}} = \varepsilon_0 \sum_I |I\rangle\langle I| + t \sum_I \sum_J |I\rangle\langle J|$$

In a model situation, J runs only over the nearest neighbour of I

Hopping or *hopping integral*

The hopping integral

Tight-binding Hamiltonian for a single electron in a molecule

$$\hat{\mathcal{H}}_{\mathrm{TB}} = -\frac{\hbar^2}{2m}\nabla^2 + \sum_{K} v_K(\vec{r} - \vec{R}_K)$$

and propose a linear combination of atomic orbitals for the TB wave function

$$\varphi(\vec{r}) = \sum_{J} C_J \phi_J(\vec{r} - \vec{R}_J)$$

where the ϕ_J are atomic eigenstates

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_J(\vec{r}) \right] \phi_J(\vec{r}) = \varepsilon_0 \phi_J(\vec{r})$$

Replacing the TB wave function into the Schrödinger equation

$$\hat{\mathcal{H}}_{\mathrm{TB}}\varphi(\vec{r}) = \sum_{J} C_J \left[-\frac{\hbar^2}{2m}\nabla^2 + v_J(\vec{r} - \vec{R}_J) + \sum_{K \neq J} C_J v_K(\vec{r} - \vec{R}_K) \right] \phi_J(\vec{r})$$

$$= \varepsilon_0 \sum_{J} C_J \phi_J(\vec{r}) + \sum_{J} C_J \sum_{K \neq J} v_K(\vec{r} - \vec{R}_K)\phi_J(\vec{r})$$