The tight-binding approximation

Javier Junquera

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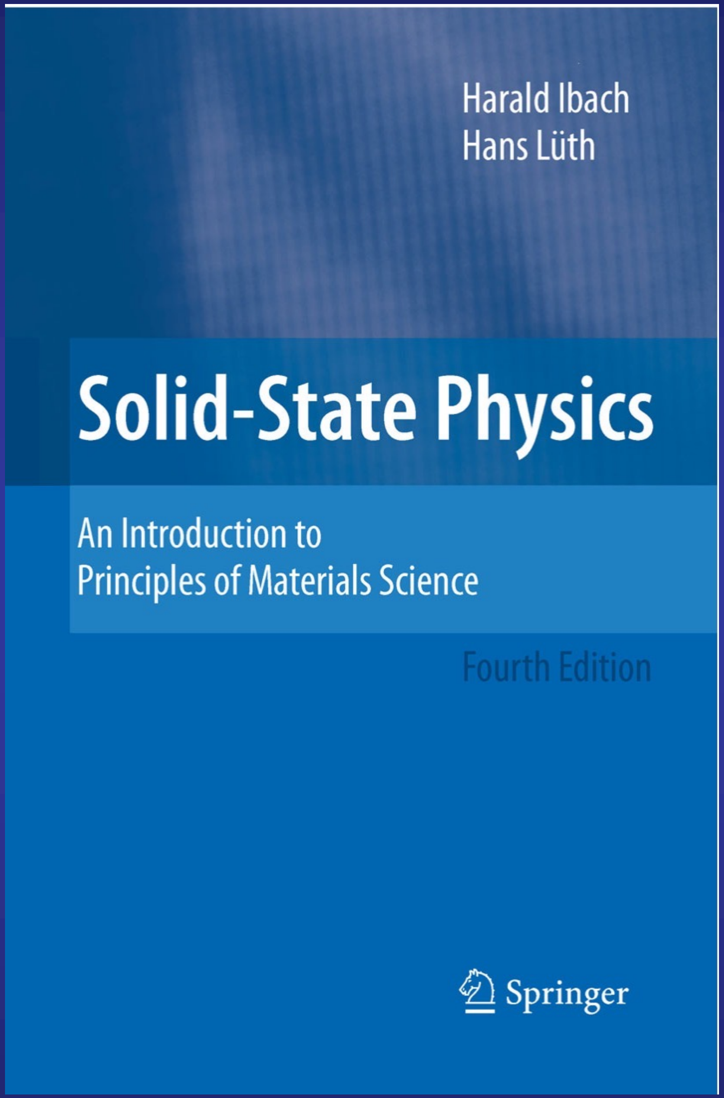
Most important references followed in this lecture



Harald Ibach
Hans Lüth

Solid-State Physics

An Introduction to
Principles of Materials Science

Fourth Edition

Springer

ISBN: 978-3-540-93803-3

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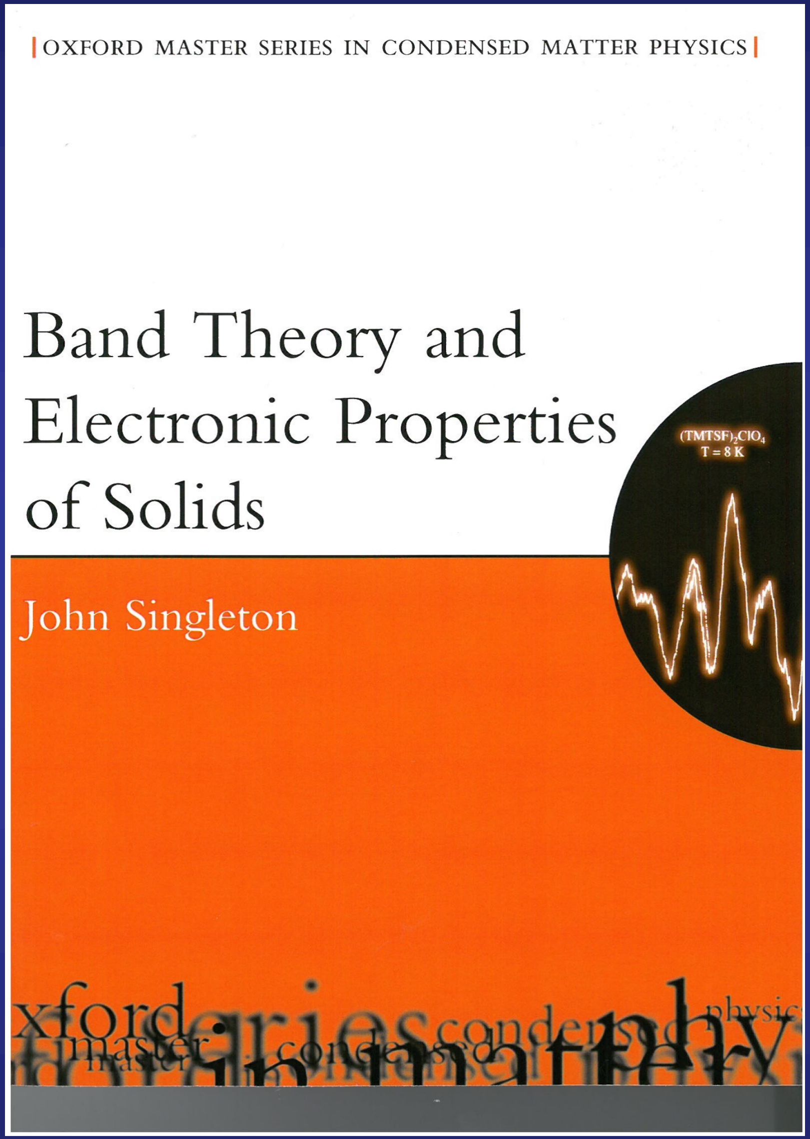


OXFORD MASTER SERIES IN CONDENSED MATTER PHYSICS

Band Theory and Electronic Properties of Solids

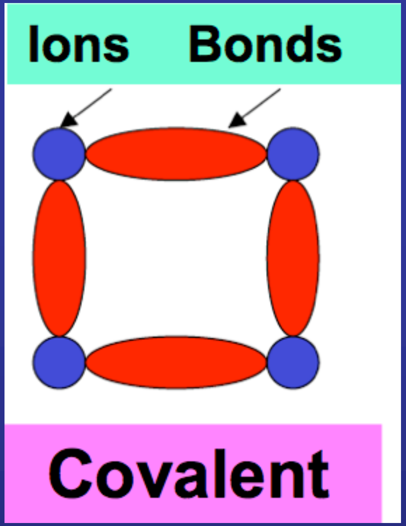
John Singleton

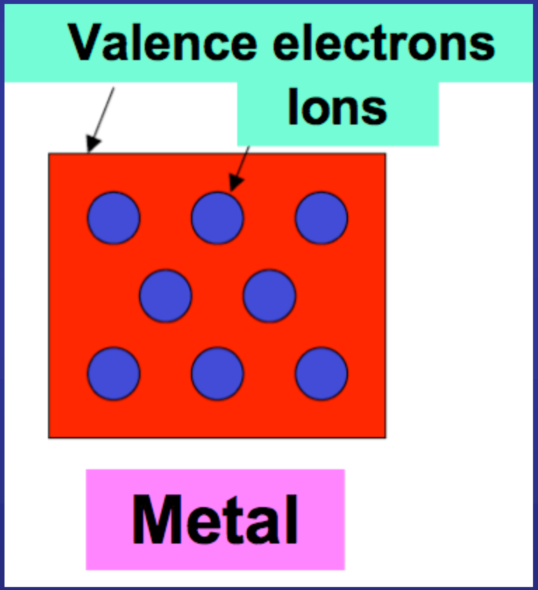
ISBN: 978-0-19-850644-7

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

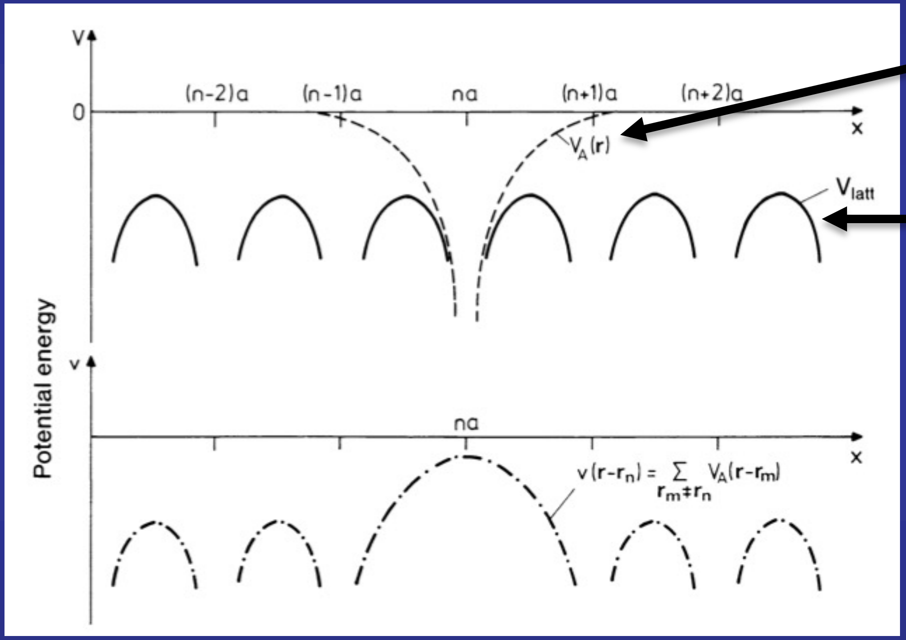




Jorge Kohanoff,
Electronic Structure Calculations for Solids and Molecules (Theory and Computational Methods)
Cambridge University Press, 2006

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

H. Ibach and H. Lüth,
Solid State Physics (An Introduction to Principles of Materials Science)
Springer, 2009

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

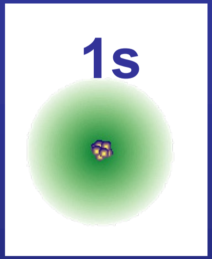
Assumption of the tight-binding model:

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



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

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$\phi_\mu(\vec{r}-\vec{R}_I)$ **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

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

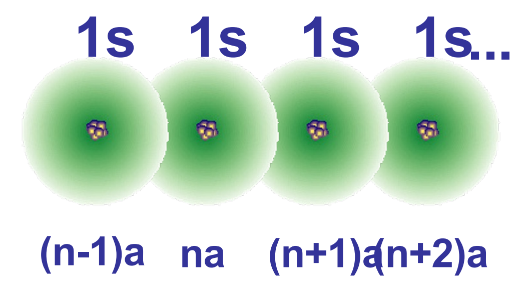
$$\psi_{n\vec{k}}(\vec{r}) \approx \Phi_{n\vec{k}}(\vec{r}) = \sum_{\mu} c_{\mu n}(\vec{k})\phi_{\mu\vec{k}}(\vec{r})$$

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



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 $A_{\mu\vec{k}} = \frac{1}{\sqrt{N}}$

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

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

where

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

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

$$\underbrace{\left(\quad H(\vec{k}) \quad\right)}_{N\times N}\underbrace{\left(\quad C_n(\vec{k}) \quad\right)}_{N\times 1}=E_n(\vec{k})\underbrace{\left(\quad S(\vec{k}) \quad\right)}_{N\times N}\underbrace{\left(\quad C_n(\vec{k}) \quad\right)}_{N\times 1}$$

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

$$\underbrace{\left(\quad H(\vec{k}) \quad \right)}_{N \times N} \underbrace{\left(\quad C_n(\vec{k}) \quad \right)}_{N \times 1} = E_n(\vec{k}) \underbrace{\left(\quad S(\vec{k}) \quad \right)}_{N \times N} \underbrace{\left(\quad C_n(\vec{k}) \quad \right)}_{N \times 1}$$

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**

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

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

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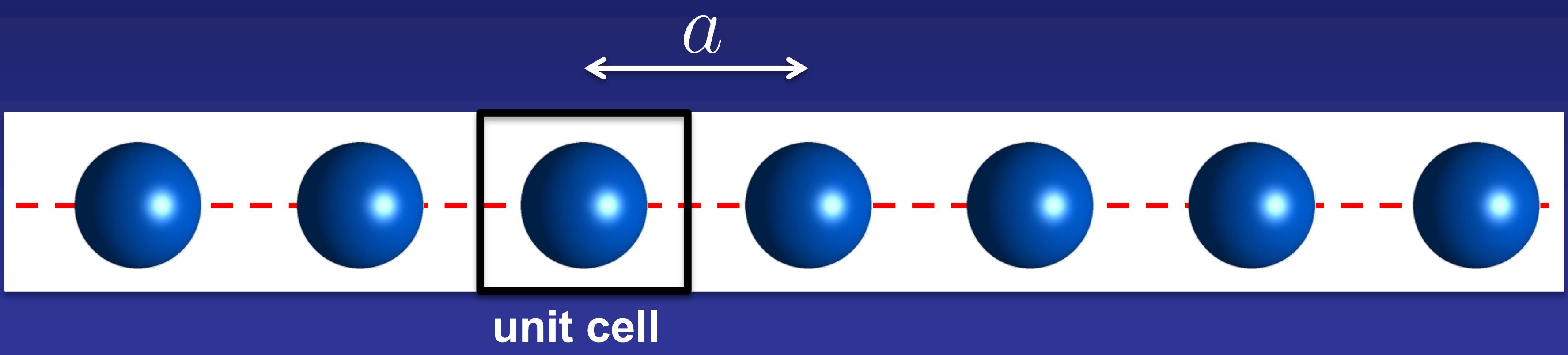
Solving the secular equation in a simple case: the linear chain of atoms with only s-orbitals



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

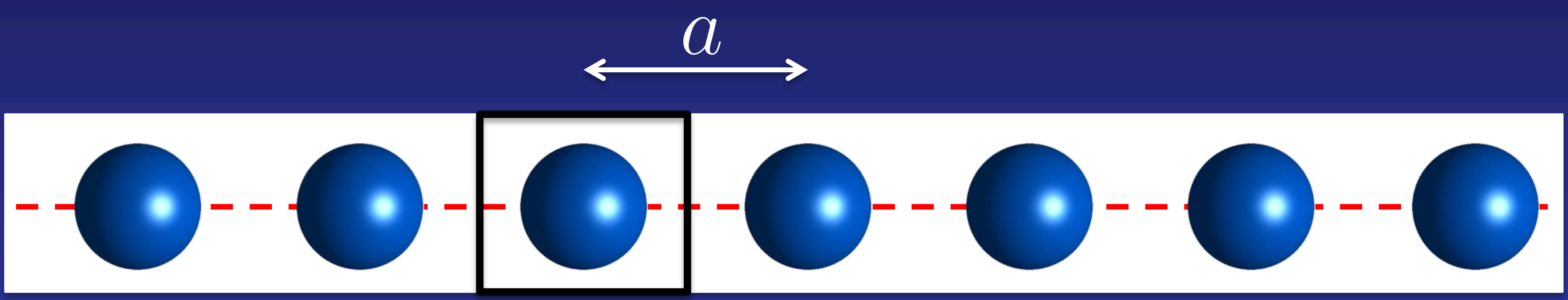
First approximation: range of interactions

- 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



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.

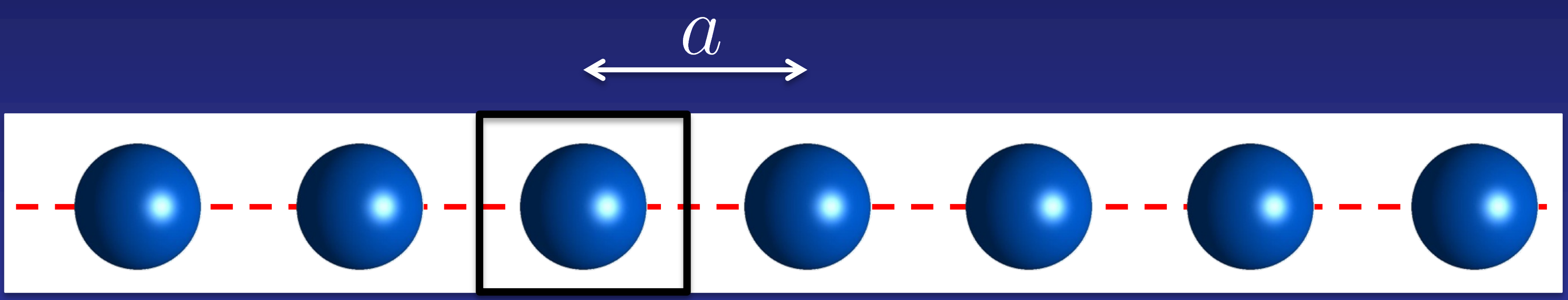
To a first approximation, we can retain only the overlap of one orbital with itself, and neglect all the rest of the overlap integrals

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

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

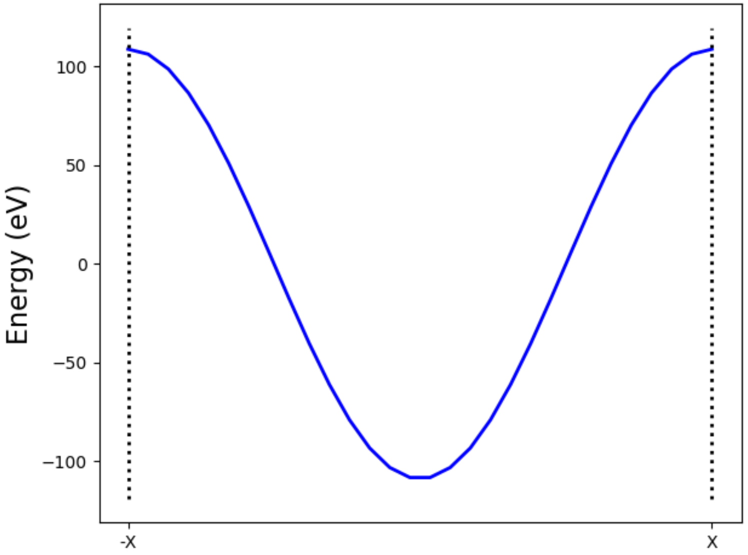
The secular equation for this system is, therefore

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

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

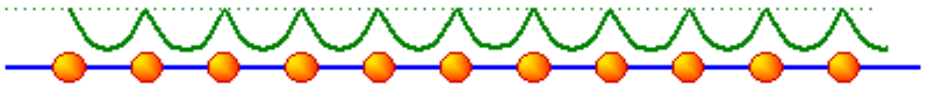
$$E(k) = \alpha + 2\gamma\cos(ka)$$

Interpreting the band structure of the linear chain of atoms with only *s*-orbitals



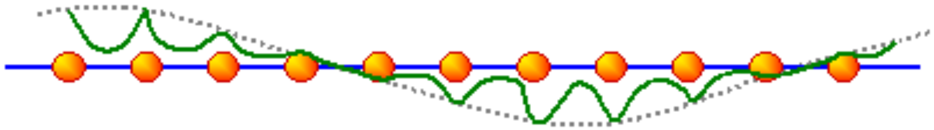
$\lambda = \infty$

$k = 0$



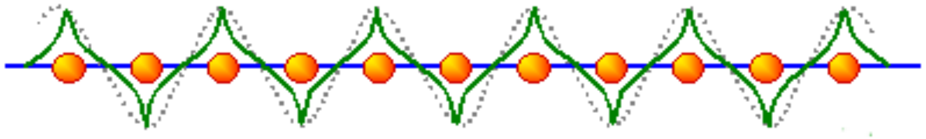
$\lambda = 12a$

$k = (1/6)(\pi/a)$



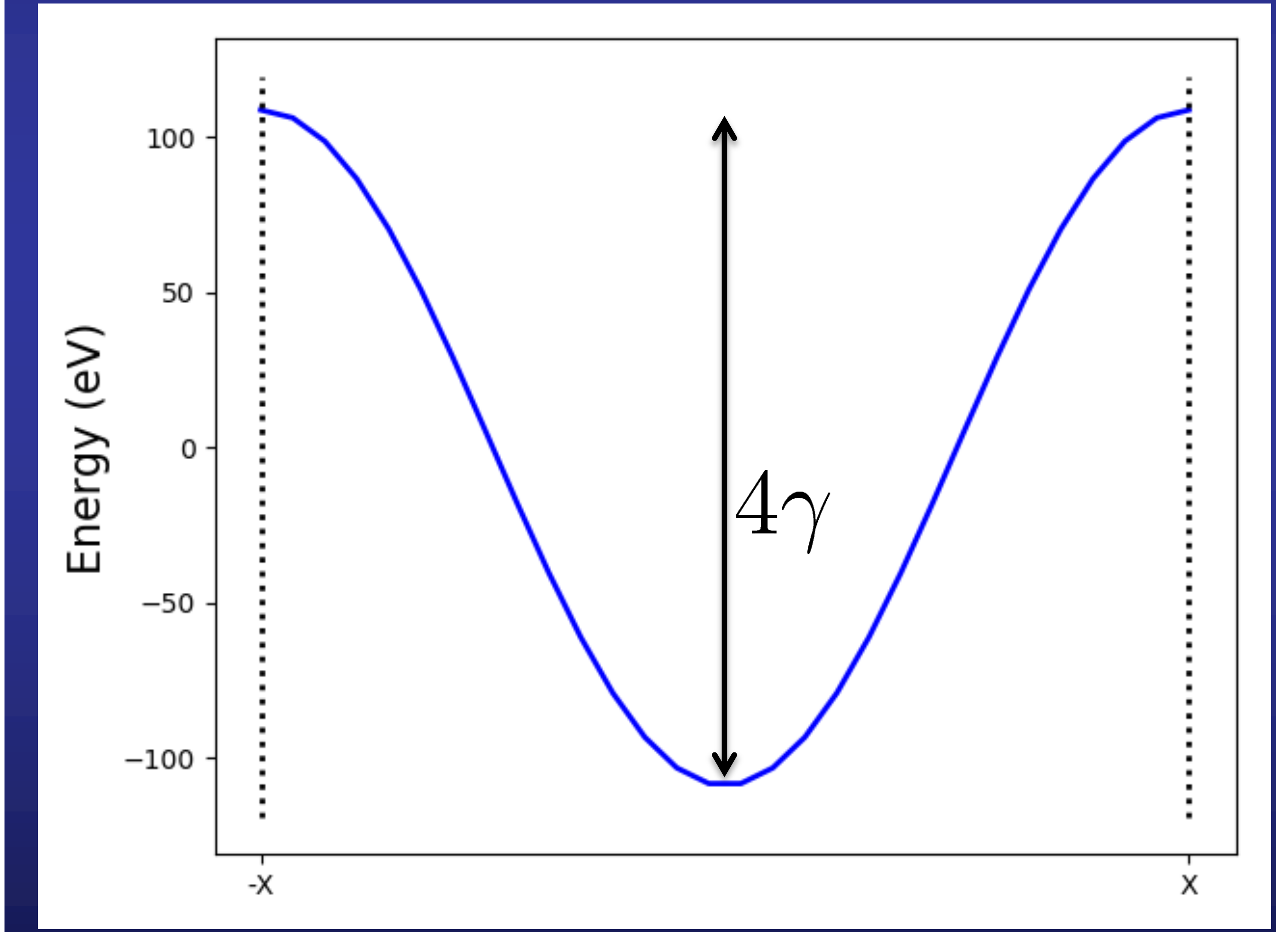
$\lambda = 2a$

$k = \pi/a$



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 $\gamma \rightarrow 0$, 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

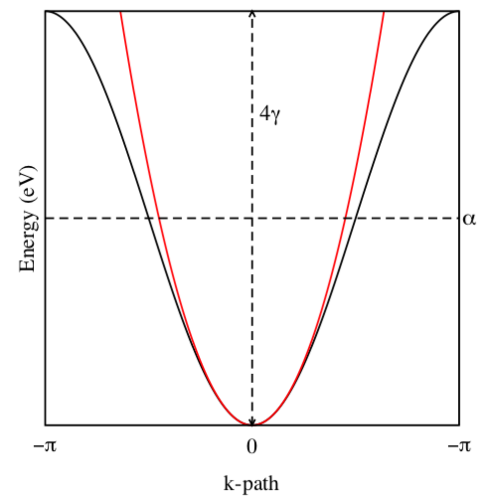
$$\gamma < 0$$

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

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

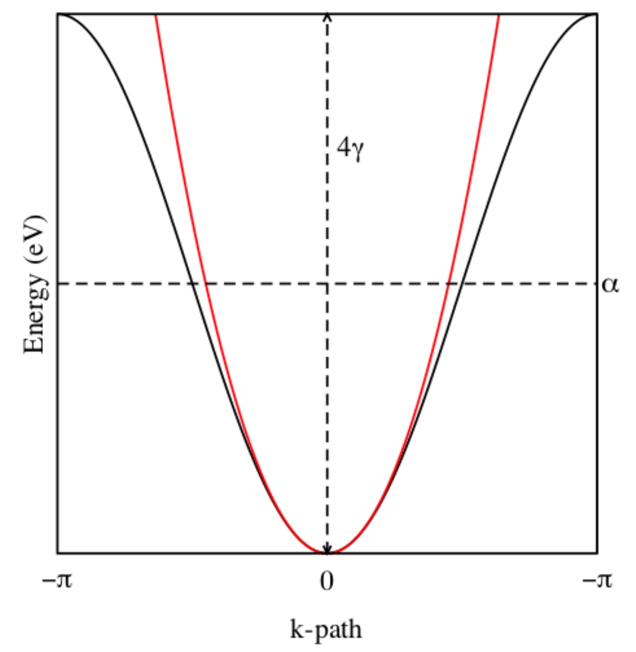
$\vec{k}_0$ **define the band extremum**

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

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

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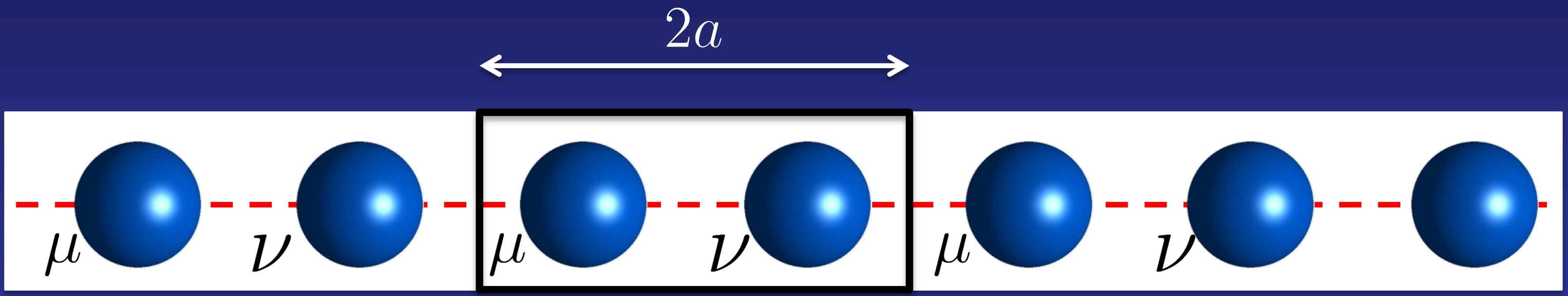
Solving the secular equation in a simple case: the monoatomic linear chain with only s-orbitals



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

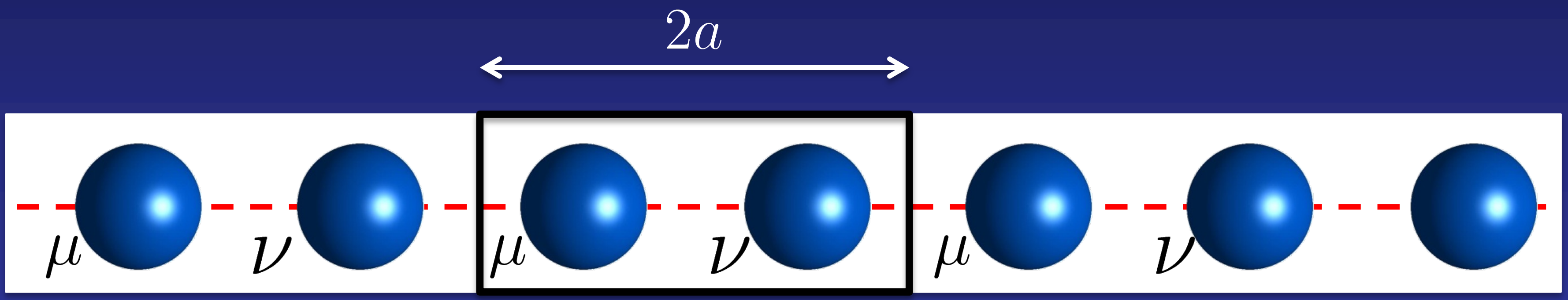
Let us compute the diagonal terms of the Hamiltonian, under the assumption of nearest neighbour interaction

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

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

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

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



unit cell

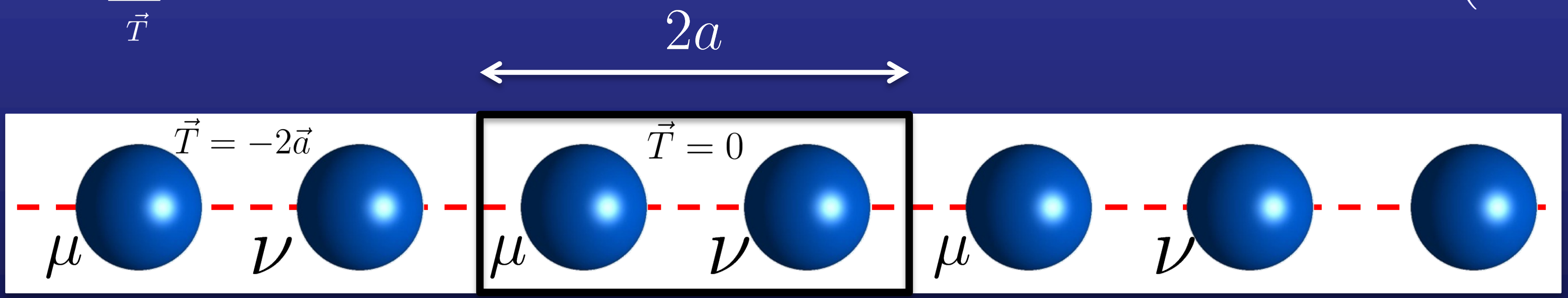
Two atomic orbitals in the unit cell ($N = 2$). Let us denote these orbitals $(s) \equiv \mu, \nu$

$$\Downarrow$$

The Hamiltonian and Overlap are (2×2)matrices

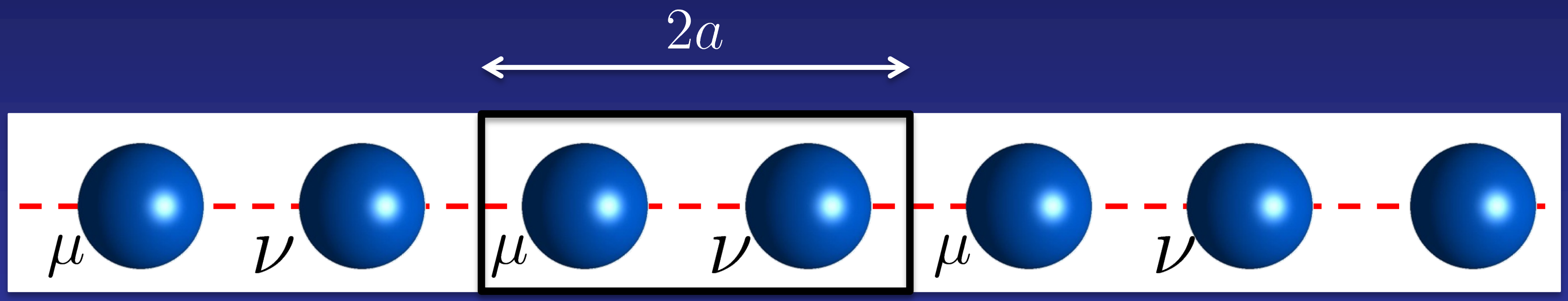
Let us compute the off-diagonal terms of the Hamiltonian, under the assumption of nearest neighbour interaction

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



unit cell

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



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$\Downarrow$

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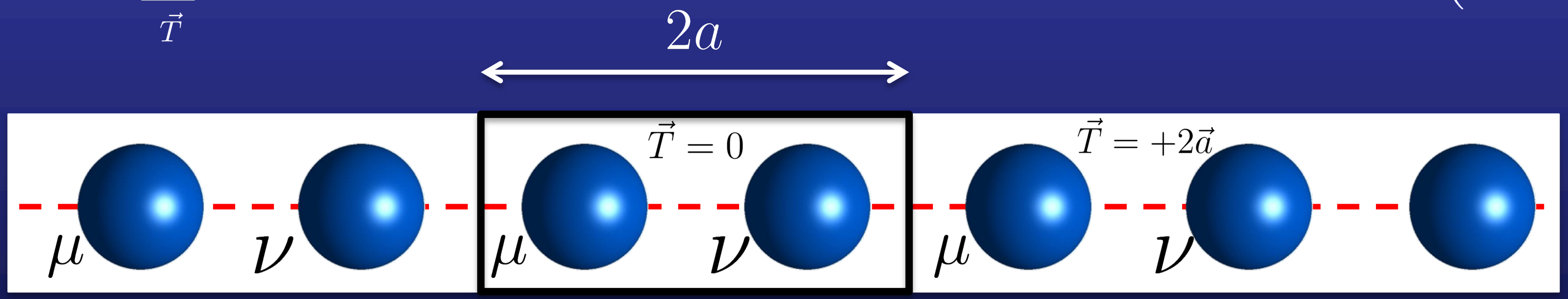
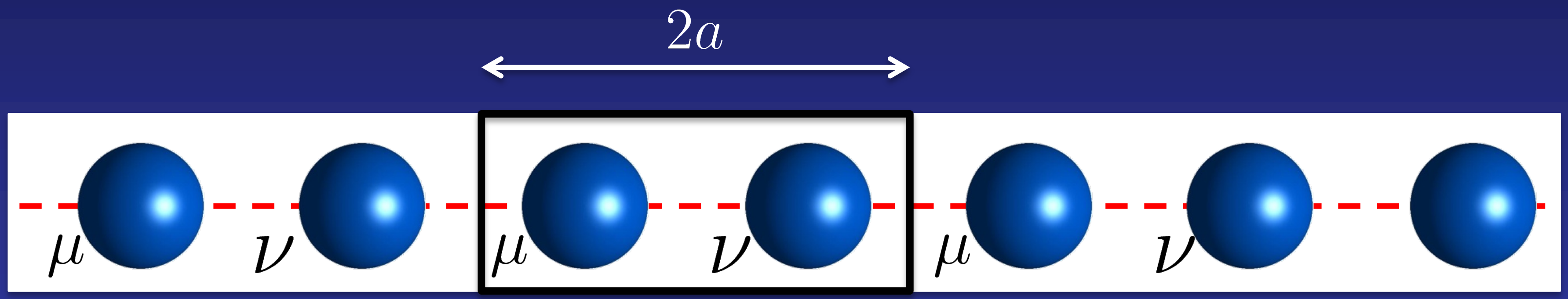


unit cell

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



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.

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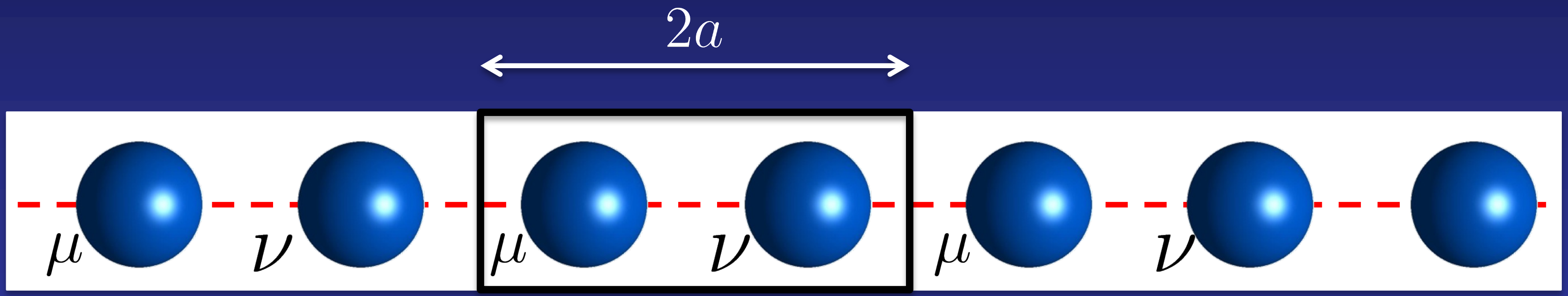

unit cell

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

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

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

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

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

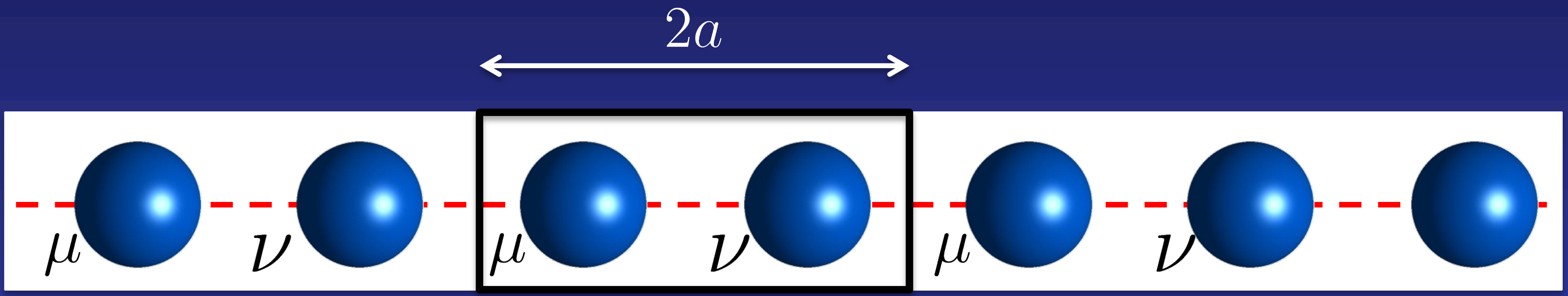
$$E_n^2(\vec{k}) - 2\alpha E_n(\vec{k}) + \alpha^2 - 2\gamma^2 - \gamma^2 \left(2\cos(2\vec{k}\cdot\vec{a})\right) = 0$$

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

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

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

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



unit cell

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

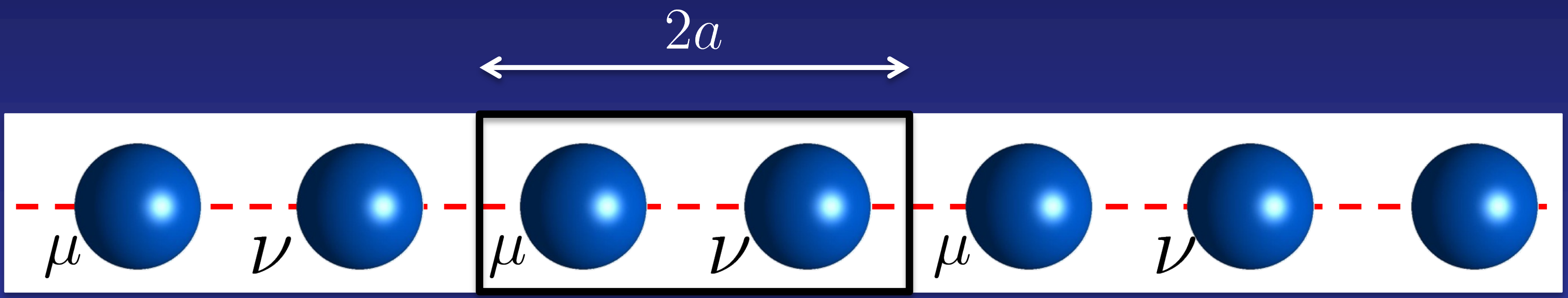
$$\det \begin{pmatrix} \alpha - E_n(\vec{k}) & \gamma(1+e^{-i2\vec{k}\cdot\vec{a}}) \\ \gamma(1+e^{i2\vec{k}\cdot\vec{a}}) & \alpha - E_n(\vec{k}) \end{pmatrix} = 0$$

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

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 $\left(-\frac{\pi}{a}, \frac{\pi}{a}\right)$ Two atoms/unit cell $\left(-\frac{\pi}{2a}, \frac{\pi}{2a}\right)$

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



unit cell

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

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

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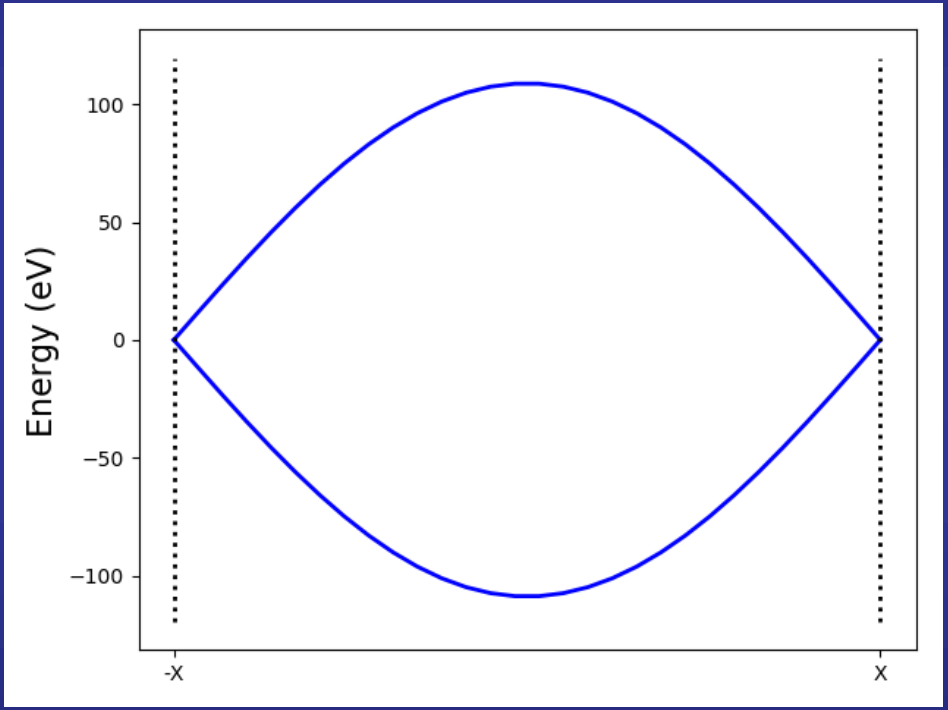
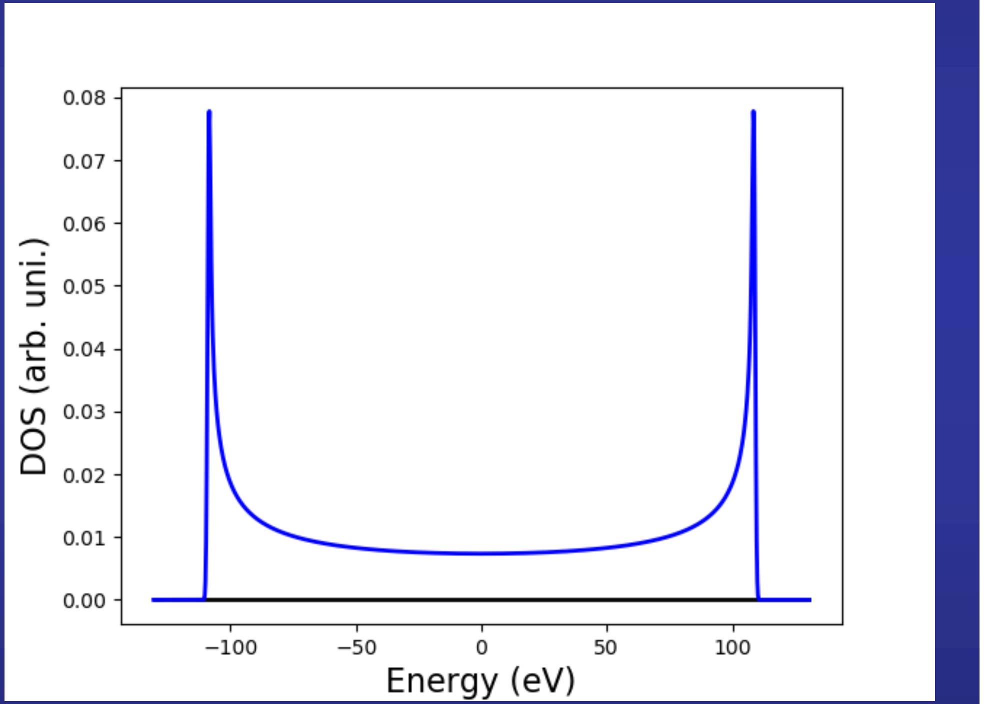
Solving the secular equation in a simple case: the monoatomic linear chain with only *s*-orbitals





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

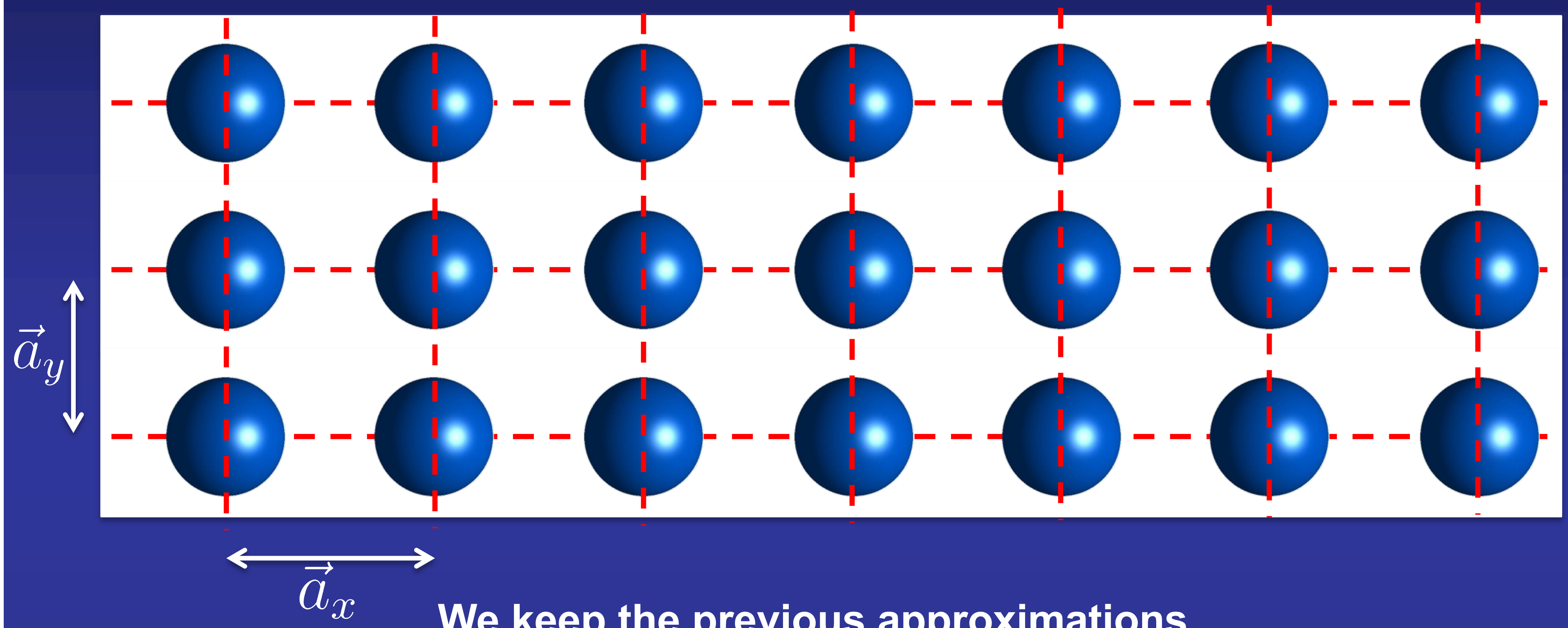
1-D Monoatomic linear chain with only *s*-orbitals. One atom in the unit cell

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

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



We keep the previous approximations

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

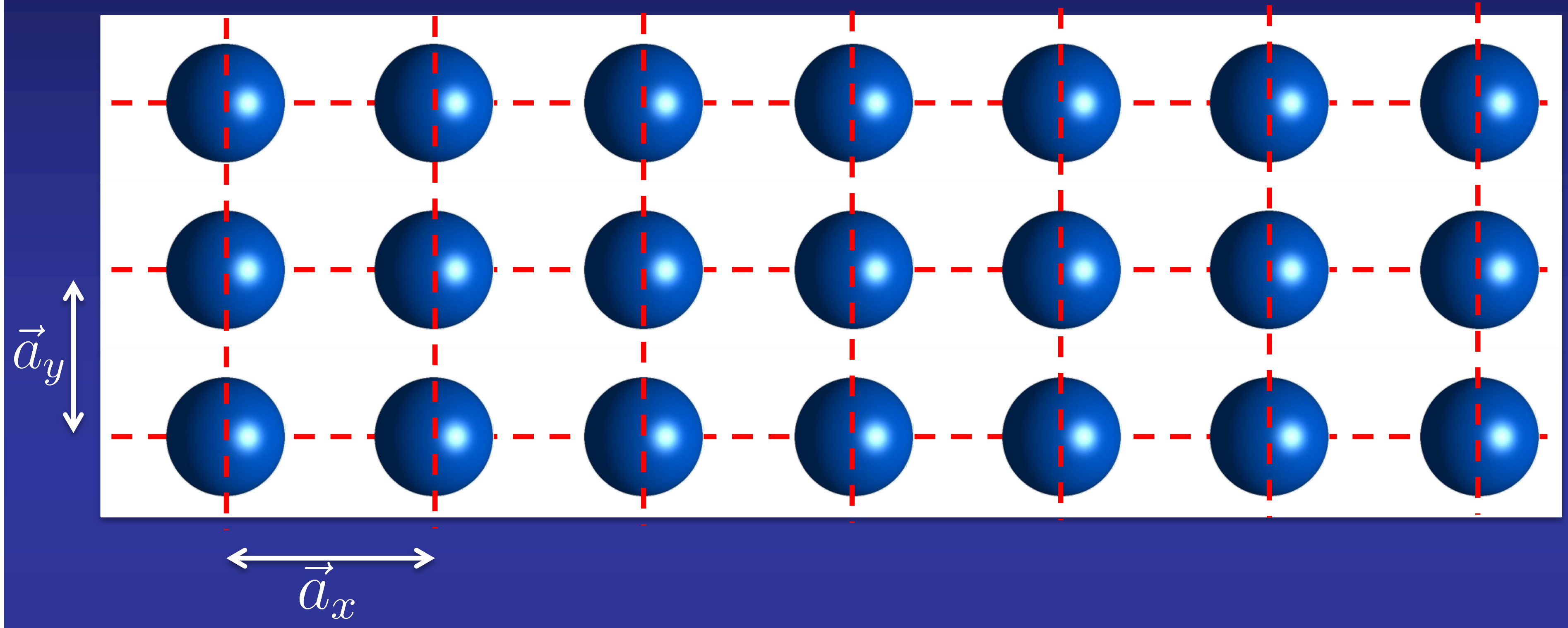
$\Downarrow$

The Hamiltonian and Overlap matrices are just simple real numbers

Hamiltonian matrix elements in real space

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

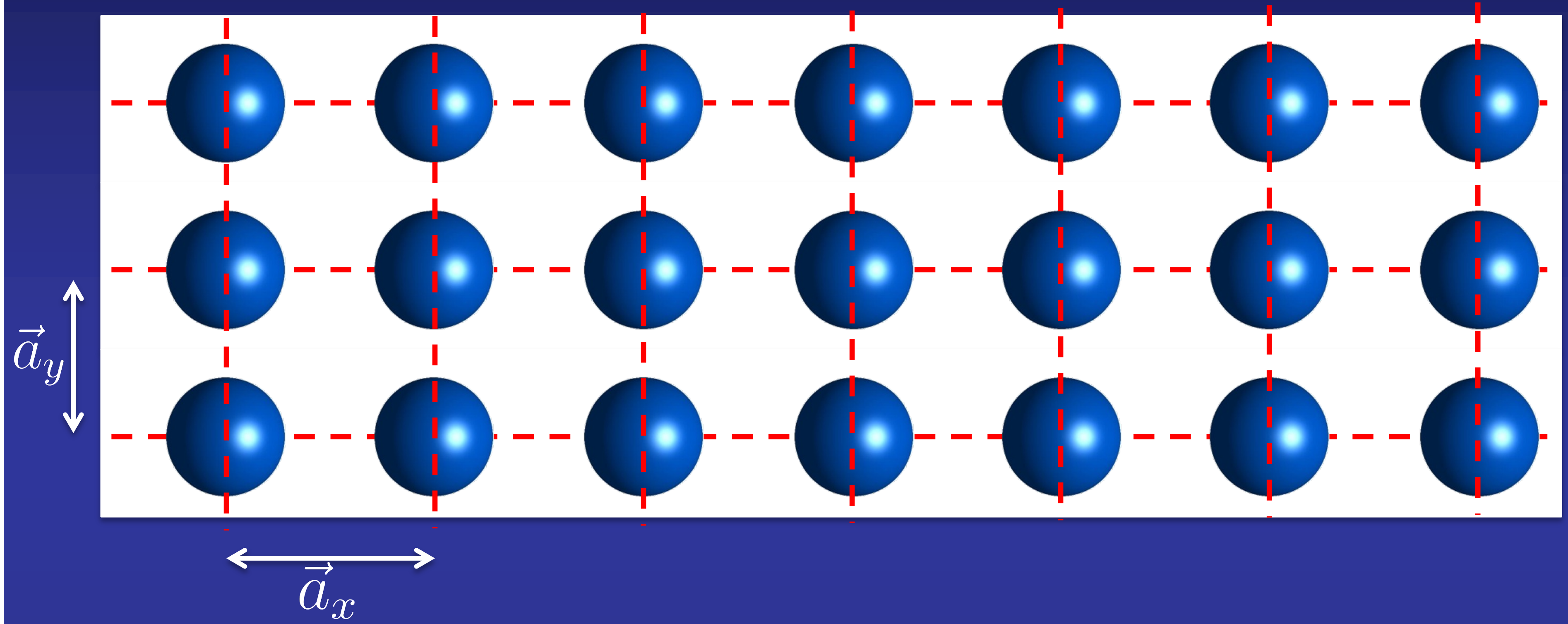


We compute the matrix elements in reciprocal space, as we did before

$$
\begin{aligned}
H_{\mu\mu}(\vec{k}) &= \sum_{\vec{T}} e^{i\vec{k}\cdot\vec{T}} H_{\mu\mu}(\vec{T}) \\
&= H_{\mu\mu}(\vec{T}=0) + e^{i\vec{k}\cdot\vec{a}_x} H_{\mu\mu}(\vec{T}=\vec{a}_x) + e^{-i\vec{k}\cdot\vec{a}_x} H_{\mu\mu}(\vec{T}=-\vec{a}_x) + e^{i\vec{k}\cdot\vec{a}_y} H_{\mu\mu}(\vec{T}=\vec{a}_y) + e^{-i\vec{k}\cdot\vec{a}_y} H_{\mu\mu}(\vec{T}=-\vec{a}_y) \\
&= \alpha + 2\gamma\left[\cos(k_x a_x) + \cos(k_y a_y)\right]
\end{aligned}
$$

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

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



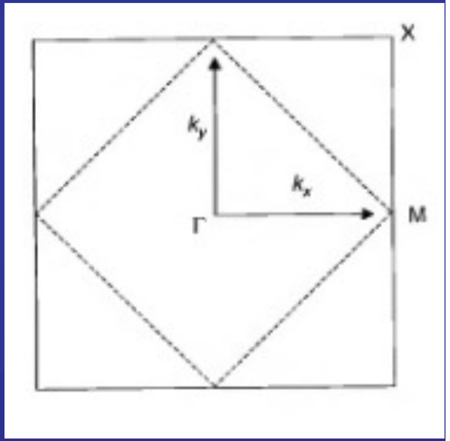
The secular equation for this system is, therefore

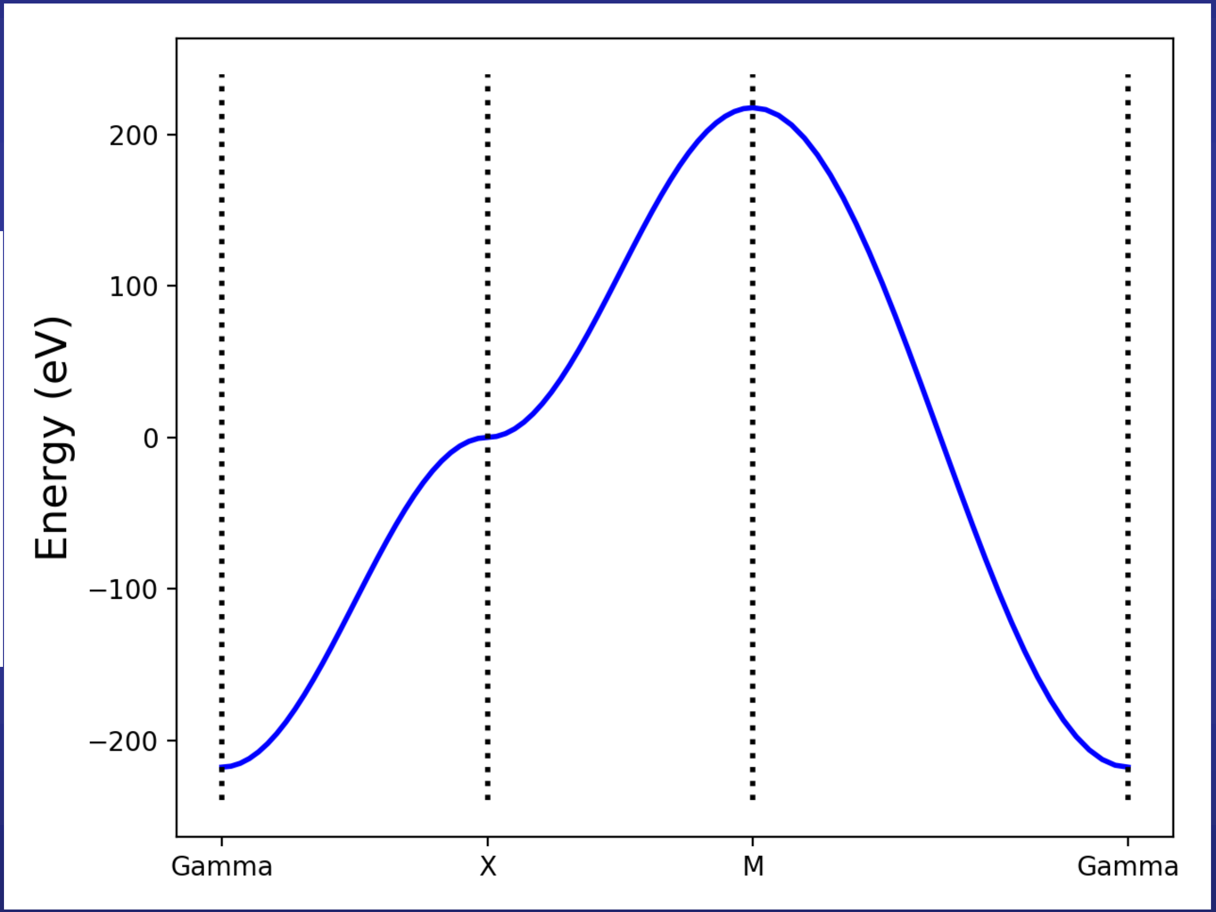
$$\left[\alpha + 2\gamma\left[\cos(k_x a_x) + \cos(k_y a_y)\right] - E(\vec{k})\right] c_\mu(\vec{k}) = 0$$

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

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

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



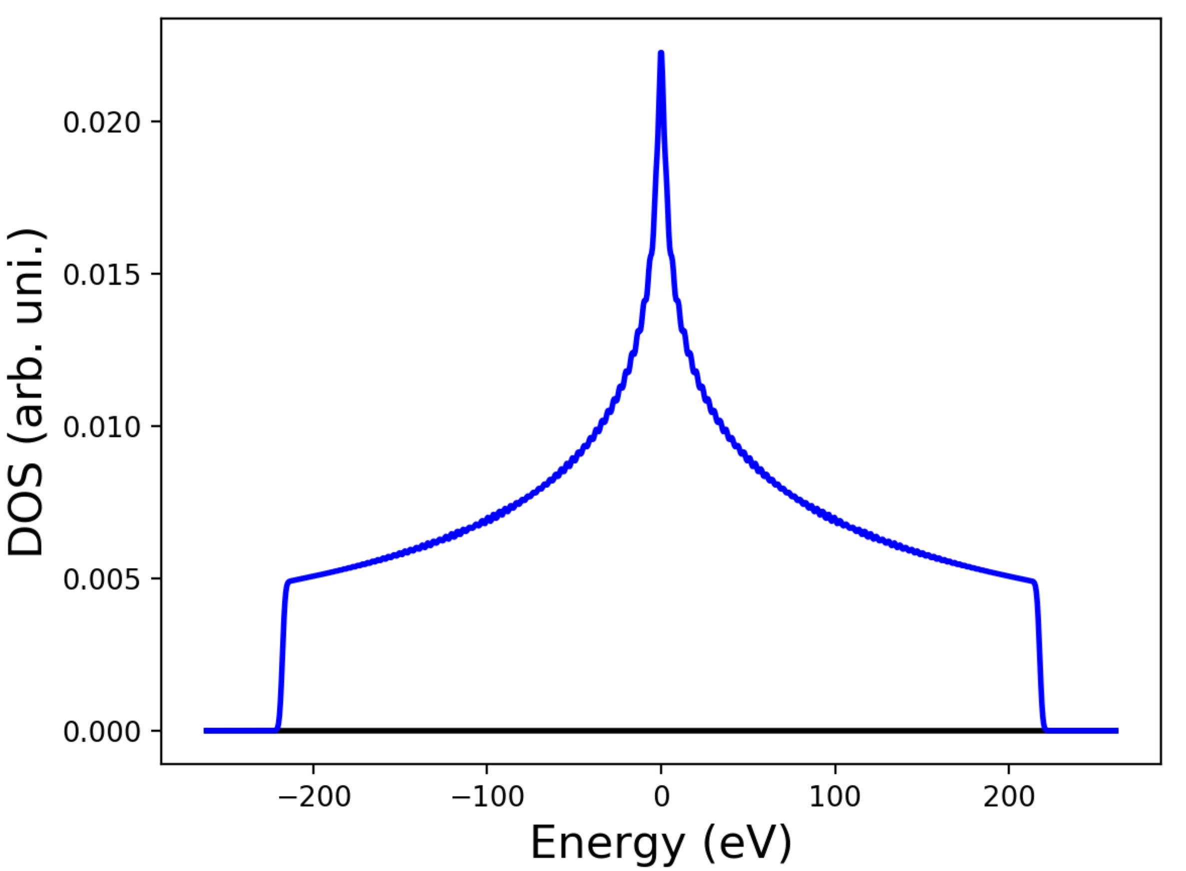


$+4\gamma$

Change in bandwidth

-4γ

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



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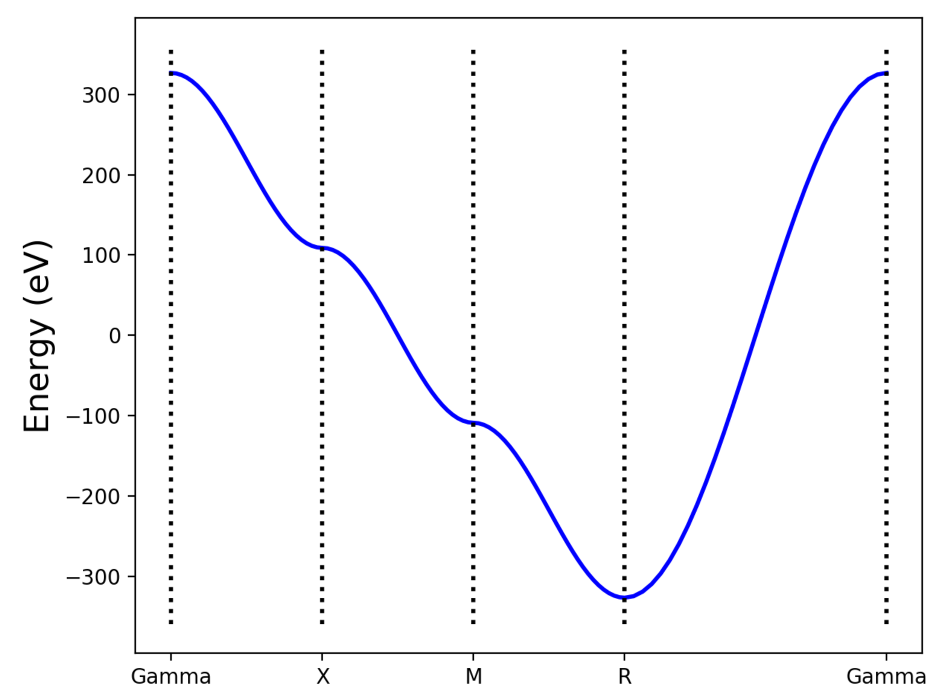
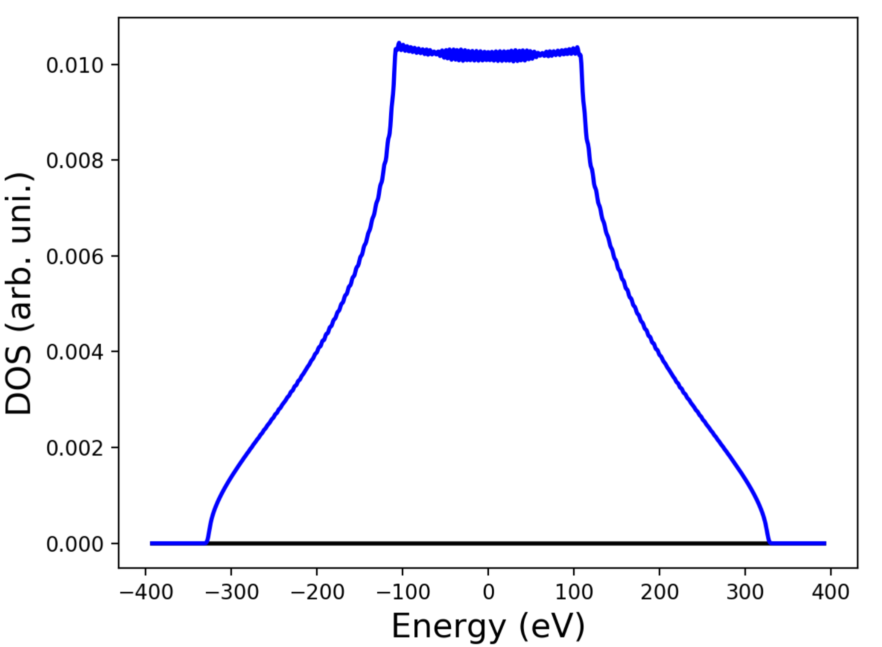
3-D Monoatomic cube with only *s*-orbitals

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

Band structure



Density Of States



Change in bandwidth to $2 \times \text{dimension} \times (2\gamma)$