Imperial College London

Computational lab 3

Understanding trends in catalytic activity for hydrogen evolution

Technical introduction

Dr. Clotilde Cucinotta, Department of Chemistry, ICL

email: c.cucinotta@imperial.ac.uk

Born Oppenheimer approximation

Within Born-Oppenheimer approximation we decouple the motion of electros from the motion of the nuclei:

$$H_{\boldsymbol{R}}\Psi(\boldsymbol{R}_\mu) = E\Psi(\boldsymbol{R}_\mu)$$

$H_{\boldsymbol{R}}=T_{\text{I}}+V_{\text{I-e}}+E_{\text{e}}$

Nuclear problem under the effective potential generated by the electrons

$$H_e\psi_{\{\boldsymbol{R}\}}(\boldsymbol{r}_i) = E_e\psi_{\{\boldsymbol{R}\}}(\boldsymbol{r}_i)$$

$H_{\boldsymbol{e}}=T_{\text{e}}+V_{\text{e-e-}}+V_{\text{e-I}}$

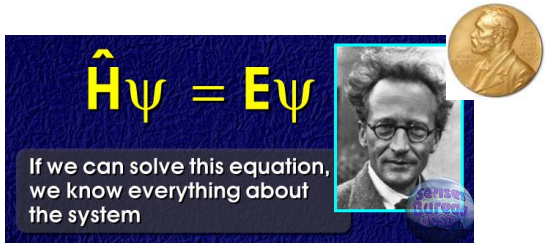
Equation for the electrons, parametric function of atomic positions **R**

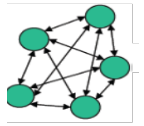
K. Burke, Wagner L., Int. J. Quant. Chem., 2013, 113, 96-101.

P. Hohenberg, W. Kohn, Phys. Rev, 1964, 136, B864; M. Levy, PNAS, 1979, 76, 6062

The equation for the electrons

Finding ground state energy of electrons for defined position of nuclei, within Born-Oppenheimer approximation, assuming the nuclei are immobile:

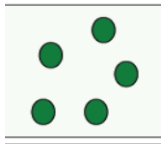




Many Body Problem

Interacting electrons real potential

DFT



Density dependent functional → Single particle problem

Non interacting fictitious particle -Effective approximate potential (small error)

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\rho)\right]|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$

K. Burke, Wagner L., Int. J. Quant. Chem., 2013, 113, 96-101.

P. Hohenberg, W. Kohn, Phys. Rev, 1964, 136, B864; M. Levy, PNAS, 1979, 76, 6062

The Kohn and Sham equations

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}) \Rightarrow \rho(\mathbf{r},\mathbf{R})$$

$$\hat{H}\Psi = \left[\hat{T}+\hat{V}+\hat{U}\right]\Psi = \left[\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_i}\nabla_i^2\right)+\sum_{i=1}^{N}V(\mathbf{r}_i)+\sum_{i<j}^{N}U(\mathbf{r}_i,\mathbf{r}_j)\right]\Psi = E\Psi,$$

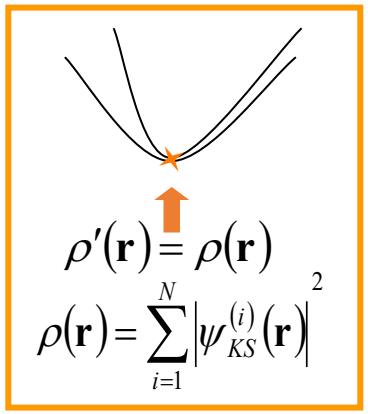
$$E_{GS}[\rho_{GS}] = \min_{\rho} E[\rho]$$

$$\int \rho(\mathbf{r})d\mathbf{r} = N$$

Hoemberg & Kohn Theorem

Electron density is univocally determined by an *external potential* acting on electrons

Ground state energy of N electrons in a external potential represents the minimum of a *unic* funtional of charge density ρ



$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\rho)\right]|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$

Kohn & Sham equations

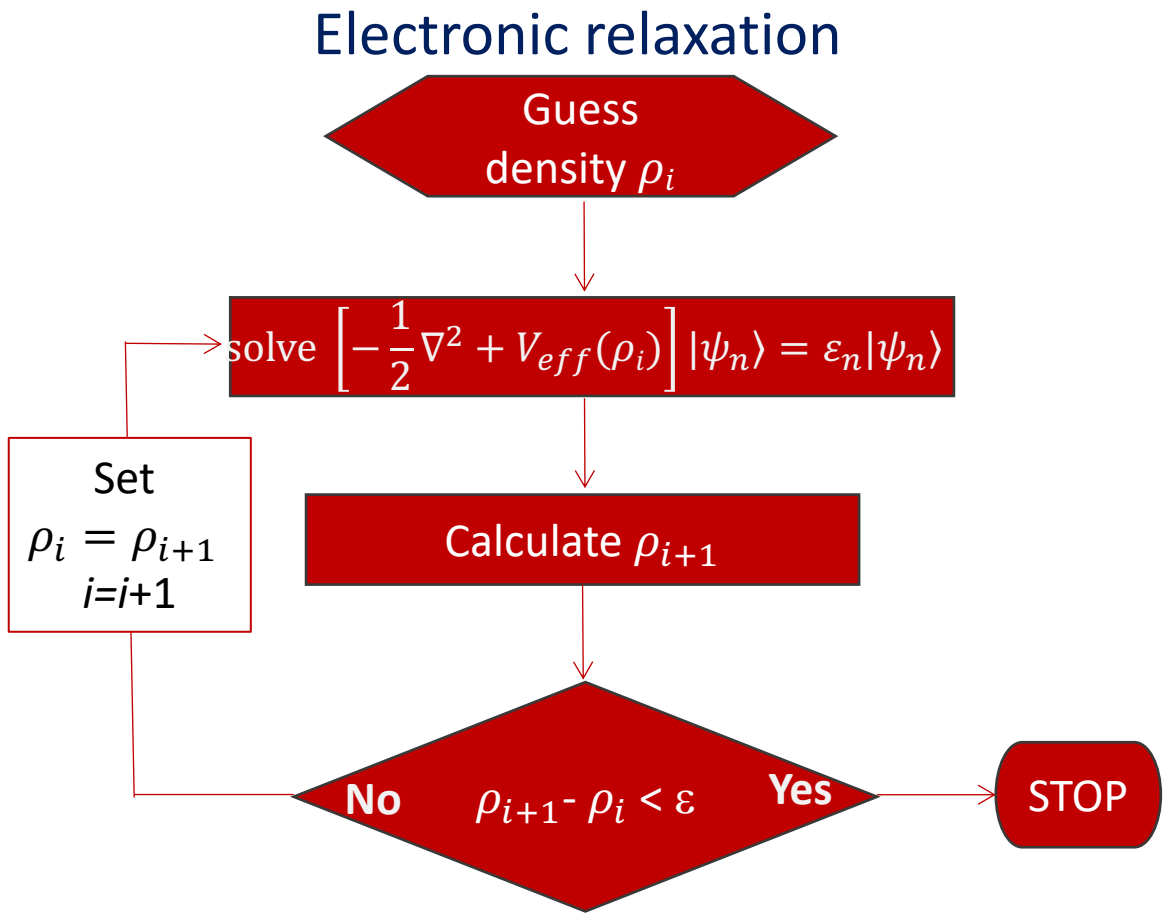
$$\rho(\mathbf{r}) = \sum_{n}^{N}|\psi_n|^2$$

Solving the KS equations for the electrons

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\rho)\right]|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$

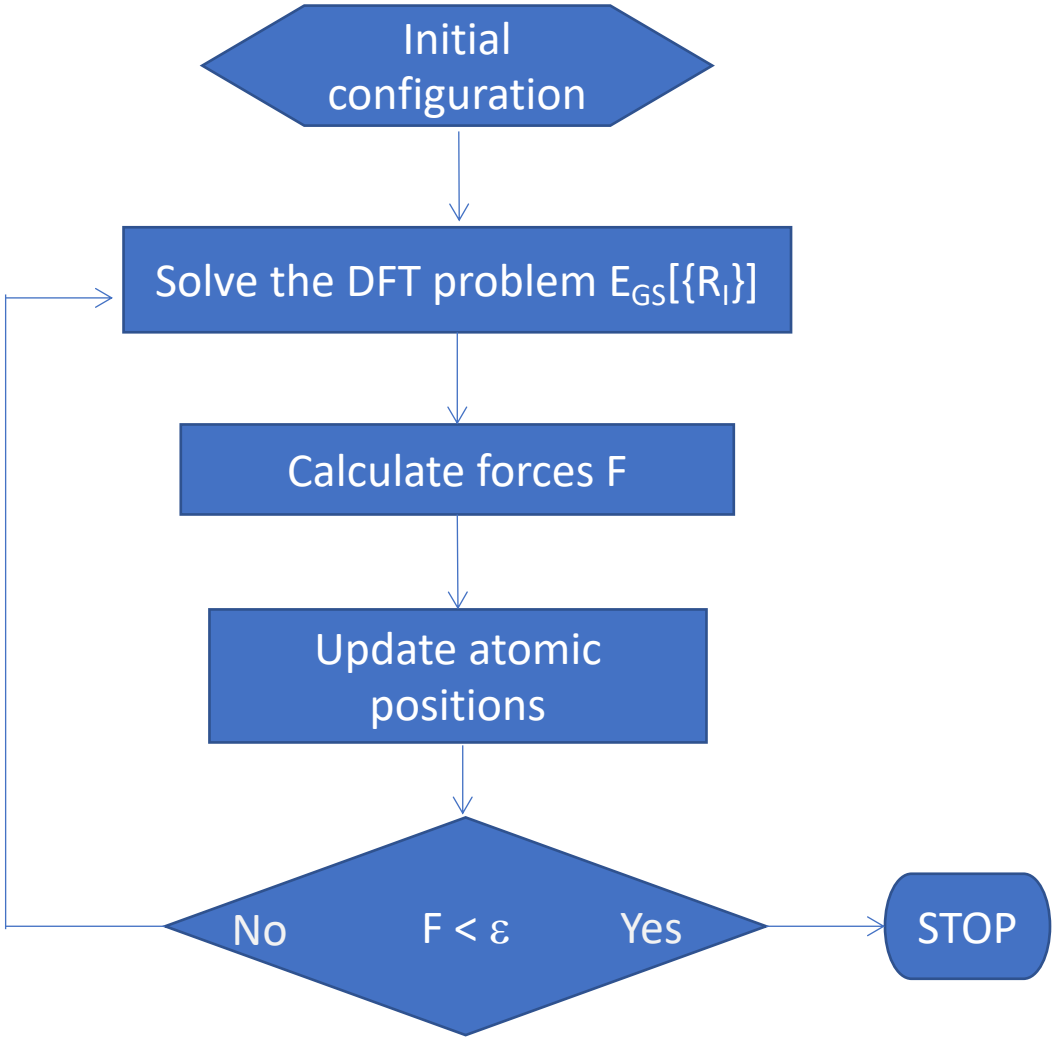
$$\rho(\mathbf{r}) = \sum_n^N |\psi_n|^2$$

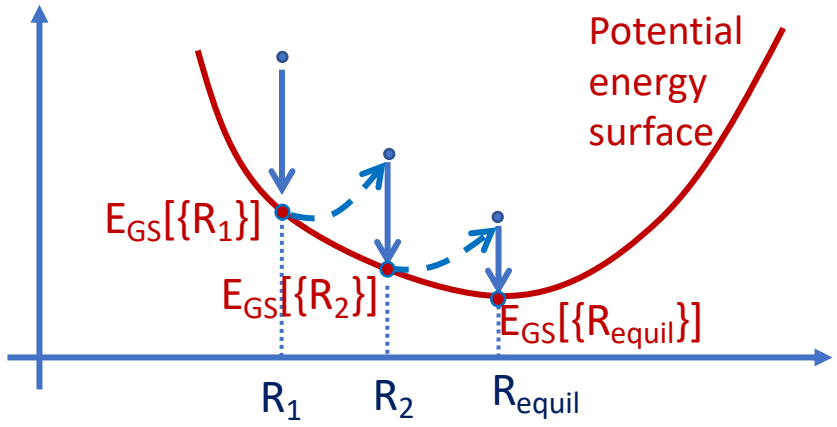
The solution to the DFT- Kohn-Sham equation results in the total energy



Self consistent solution of the electronic problem

Geometry optimization

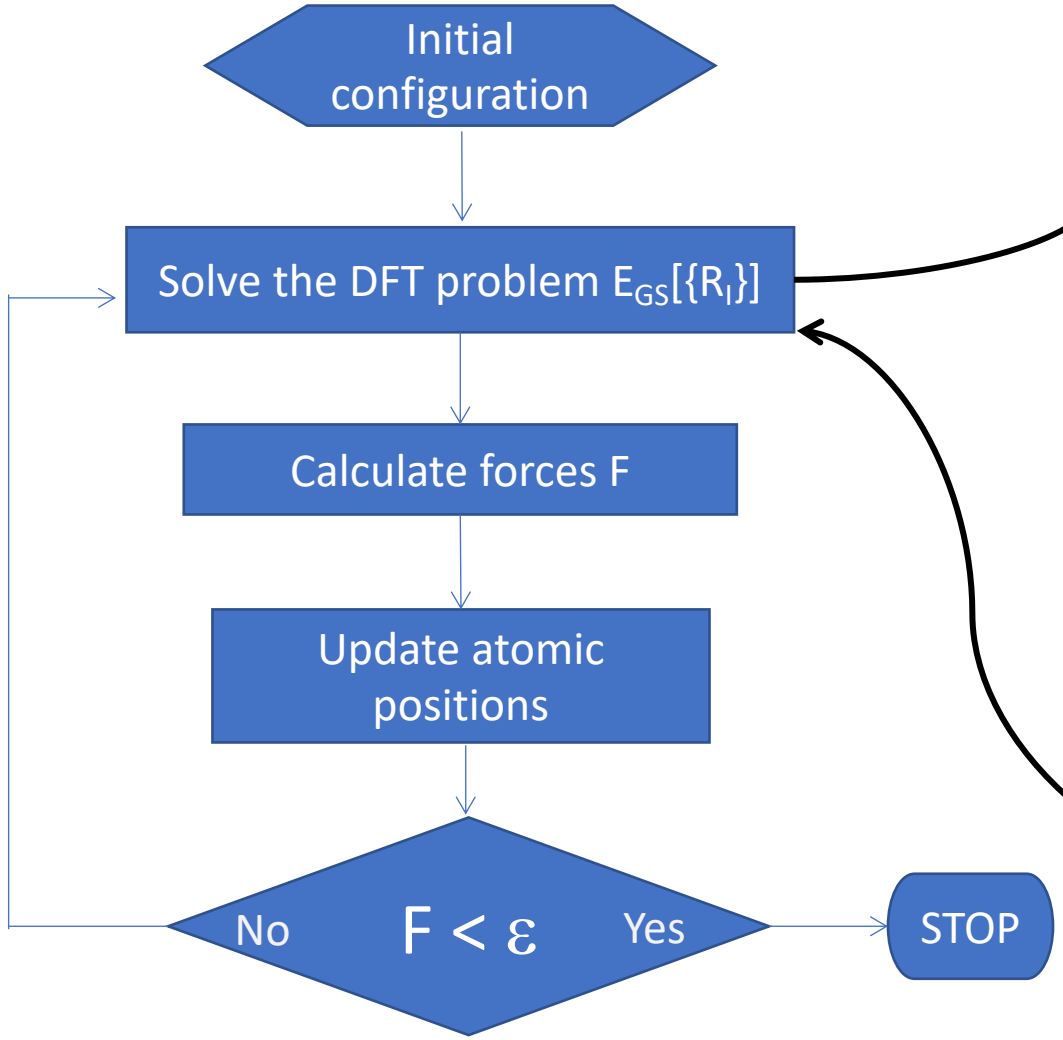




Within BO approximation electrons adjust instantly to position of ions

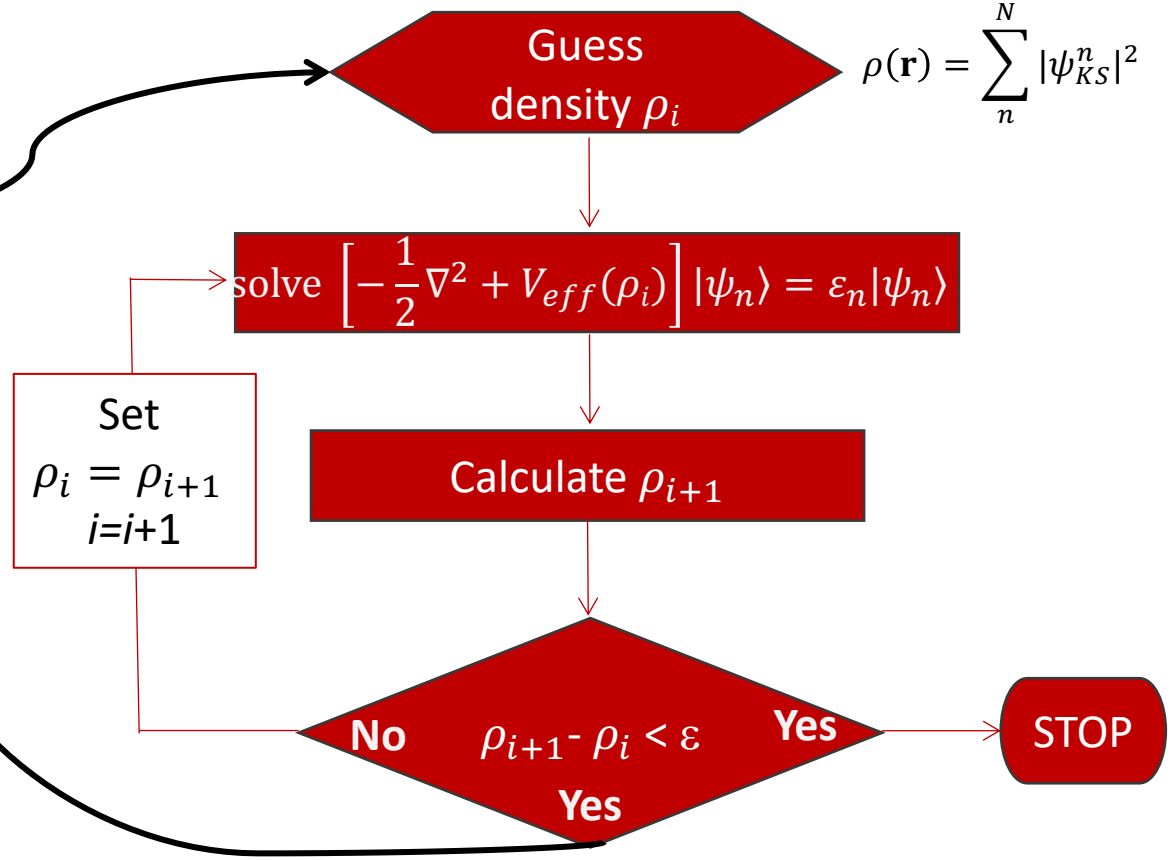
We have a multi-dimensional potential energy surface and want to find global minimum

Geometry optimization



Electronic relaxation

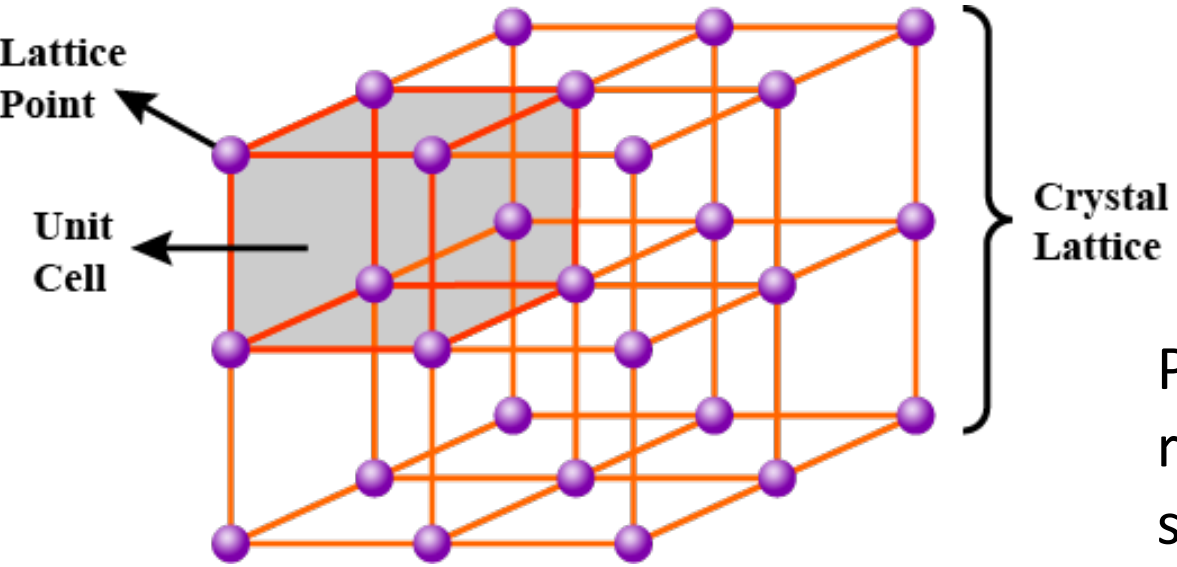
$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\right]|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$



Self consistent solution of the electronic problem

Imperial College London

How we model crystals



https://www.toppr.com/content/story/amp/types-of-unit-cells-732/

The structure of a crystal is given by a three-dimensional array of identical cells, arranged in the so called Bravais lattice

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

Periodicity of the crystal leads to the existence of the reciprocal space, which mathematically reflects the symmetry of the lattice

$$\mathbf{a}\cdot\mathbf{b} = 2\pi l, \qquad l \in \mathrm{N} \qquad \mathbf{b} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$$

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

$$\boldsymbol{b}_1 = 2\pi\frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{|\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)|} \qquad \boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}\,,$$

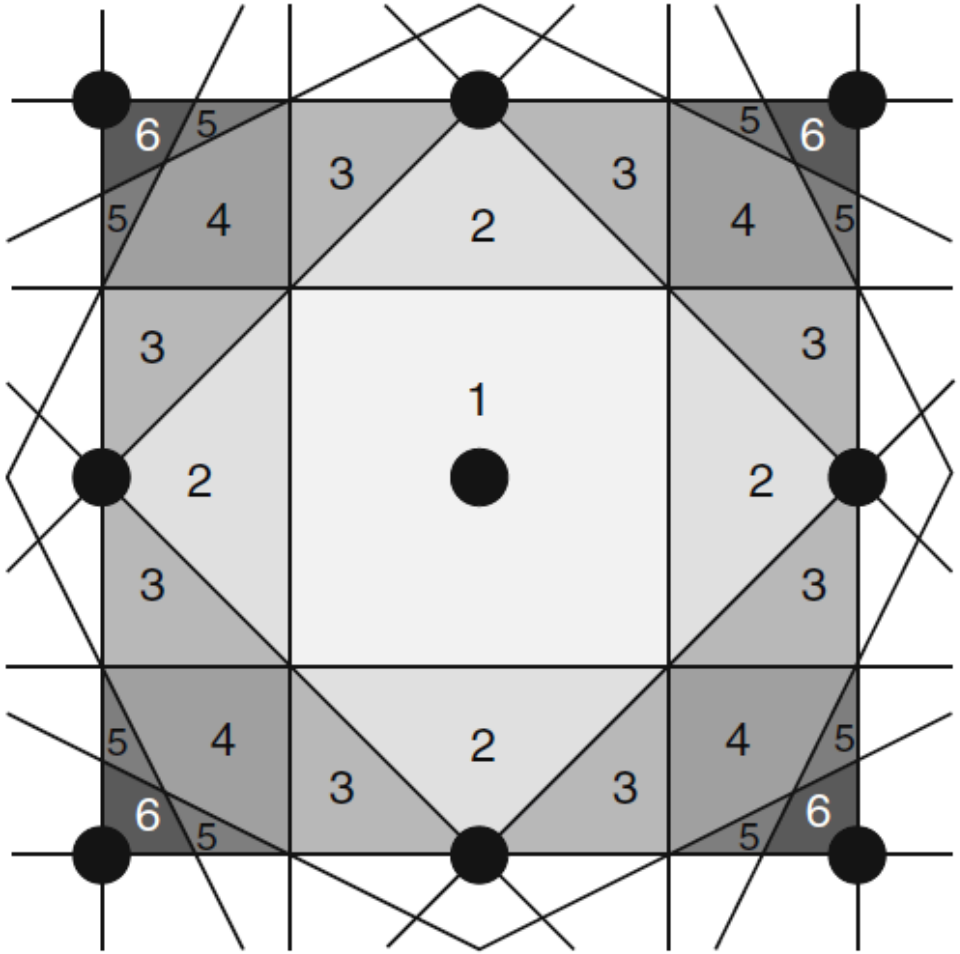
http://cmt.dur.ac.uk/sjc/thesis_prt/node26.html

https://en.wikipedia.org/wiki/Bloch%27s_theorem#Preliminaries:_Crystal_symmetries,_lattice,_and_reciprocal_lattice

Ashcroft/Mermin,, Solid State Physics, Holt,,Rinehart, Winston. A. Gross, Theoretical surface science A microscopic perspective, second edition, Springer

Imperial College London

Brillouin zone



A. Gross, Theoretical surface science A microscopic perspective, second edition, Springer

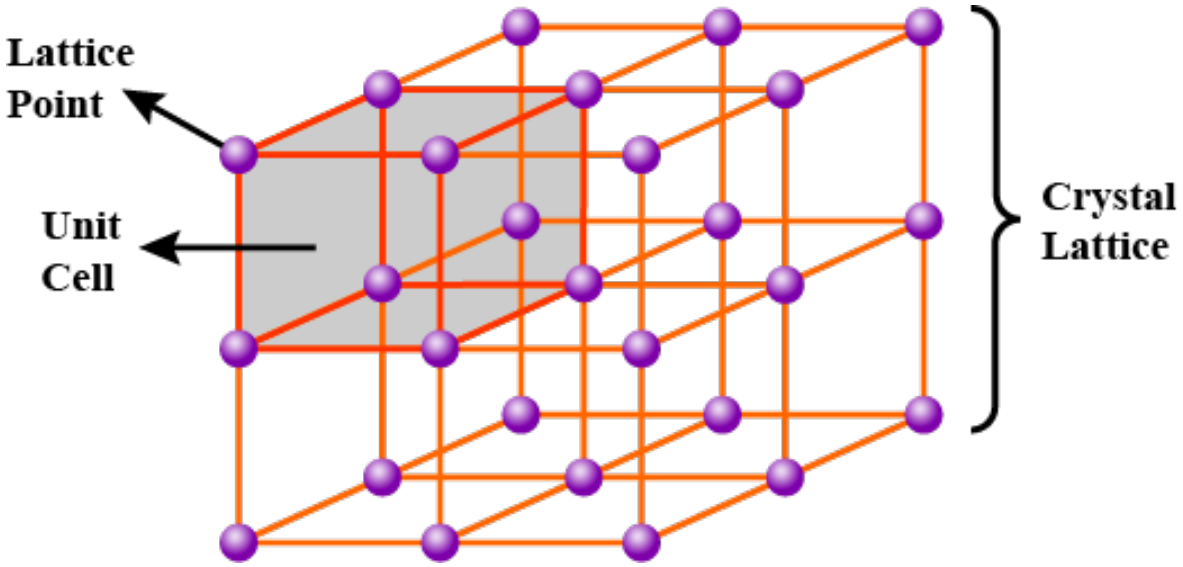
http://cmt.dur.ac.uk/sjc/thesis_prt/node26.html

Ashcroft/Mermin,, Solid State Physics, Holt,,Rinehart, Winston.

https://en.wikipedia.org/wiki/Bloch%27s_theorem#Preliminaries:_Crystal_symmetries,_lattice,_and_reciprocal_lattice

Imperial College London

How we model crystals



https://www.toppr.com/content/story/amp/types-of-unit-cells-732/

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\right]|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$

Bloch theorem

$$\psi_n = e^{i\boldsymbol{k}\boldsymbol{r}}u_n(\boldsymbol{r})$$

$$u_n(\boldsymbol{r}) = u_n(\boldsymbol{r}+\boldsymbol{R})$$

} solution of the KS equations

In periodic crystals the solution ψ_n of the KS equations is characterised by a crystal momentum *k* that act as a quantum number

https://en.wikipedia.org/wiki/Bloch%27s_theorem#Preliminaries:_Crystal_symmetries,_lattice,_and_reciprocal_lattice

How we model crystals

$$\psi_n = e^{i\boldsymbol{k}\boldsymbol{r}} u_n(\boldsymbol{r})$$

$$u_n(\boldsymbol{r}) = u_n(\boldsymbol{r} + \boldsymbol{R})$$

$\boldsymbol{k}$ is a reciprocal lattice vector that spans the first Brillouin zone

$\boldsymbol{R}$ is a bravais lattice vector

k-vectors outside of the first Brillouin zone can be mapped back in by the operation **k'** = **k**+**G**

where **G** is a reciprocal lattice vector. Due to this mapping we introduce a second suffix for the eigenstate which corresponds to the **k**-vector.

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

https://en.wikipedia.org/wiki/Bloch%27s_theorem#Preliminaries:_Crystal_symmetries,_lattice,_and_reciprocal_lattice

K point sampling

$$\psi_{nk} = e^{ikr} u_{nk}(\boldsymbol{r}) \qquad u_{nk}(\boldsymbol{r}) = u_{nk}(\boldsymbol{r} + \boldsymbol{R})$$

Bloch's theorem for a periodic system changes the problem of considering a infinite number of electrons into considering the number of electrons in the cell at an infinite number of k-points

In practice it is not necessary to consider all these k-points, but only a finite set which appropriately samples the Brillouin zone.

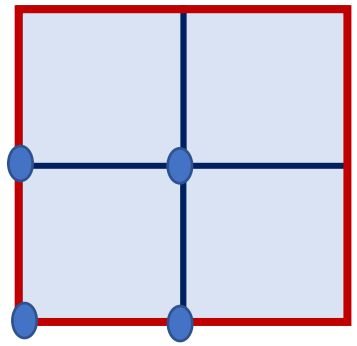
The error incurred by sampling the Brillouin zone with a finite number of k points can be made arbitrarily small by choosing a sufficiently dense set of k-points.

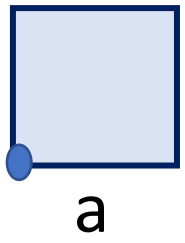
The two most common sets of k points those of Chadi and Cohen and Monkhorst and Pack

H. A. Gasteiger, S. S. Kocha, B. Sompalli, and F. T. Wagner, Appl. Catal. B56(2005) 9
Hendrik J. Monkhorst and James D. Pack Phys. Rev. B 13, 5188 – Published 15 June 1976

How we model crystals

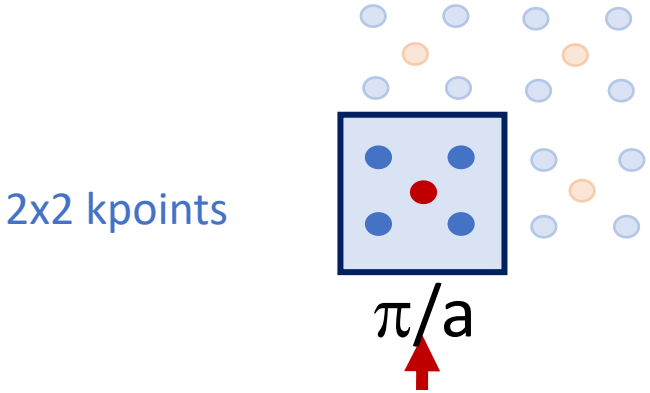
cell in real space
direct lattice



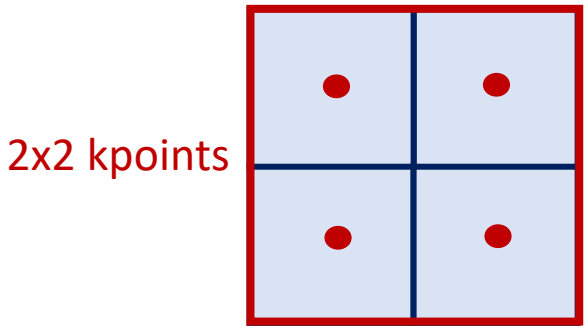


1st Brillouin zone
reciprocal lattice

• k point



Same k points density → similar accuracy



http://cmt.dur.ac.uk/sjc/thesis_prt/node26.html
https://en.wikipedia.org/wiki/Bloch%27s_theorem#Preliminaries:_Crystal_symmetries,_lattice,_and_reciprocal_lattice
Ashcroft/Mermin,, Solid State Physics, Holt,,Rinehart, Winston. A. Gross, Theoretical surface science A microscopic perspective, second edition, Springer

Basis sets

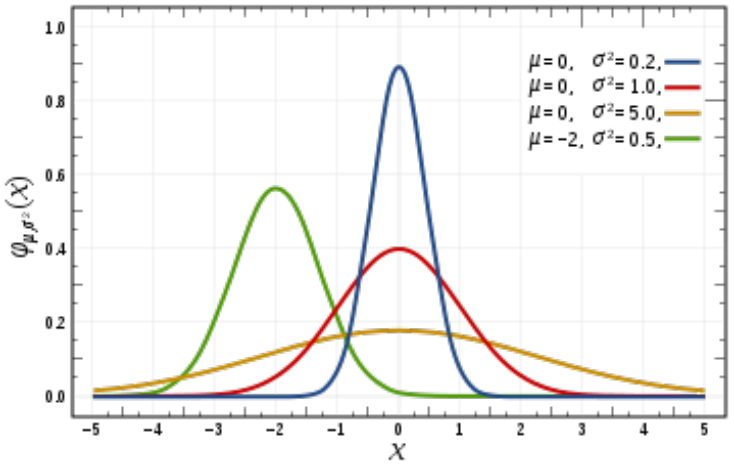
To represent the KS wavefunction it is necessary to expand it in terms of a set of known functions

$$\psi_n = \sum_i^{\infty} |c_n| \varphi_i$$

In CP2K we use gaussians basis set:

$$\varphi_i(\vec{r}) = R_i(r) \cdot Y_{l_i,m_i}(\theta,\phi)$$

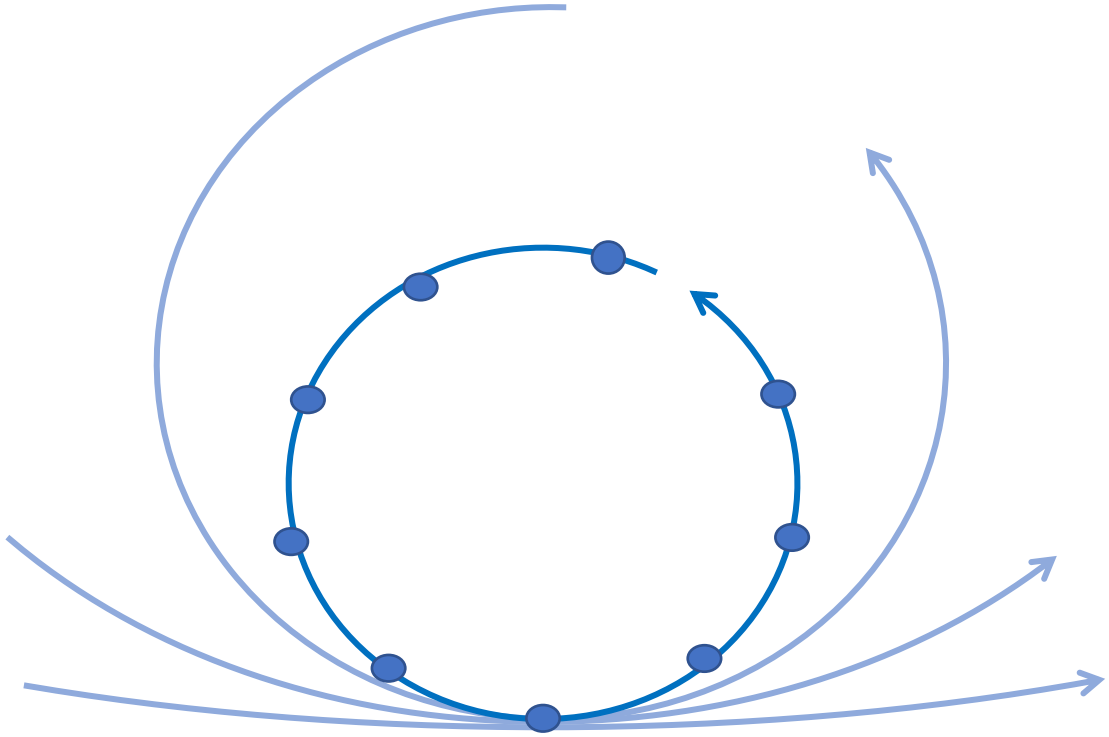
$$R_i(r) = r^{l_i} \sum_{j=1}^{N} c_{ij} \cdot \exp(-\alpha_j \cdot r^2)$$

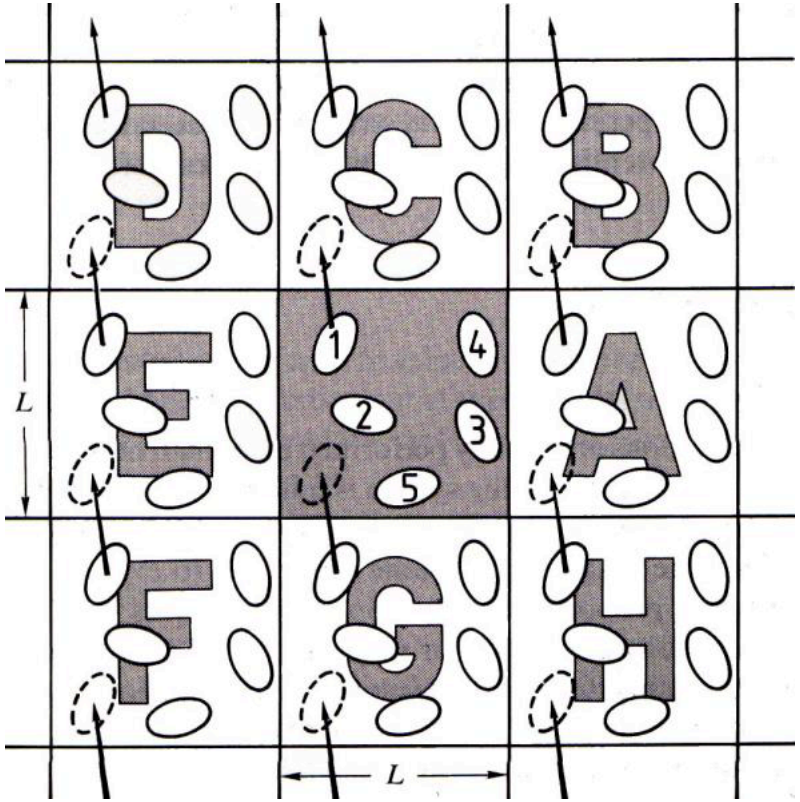


The minimal basis or single-z, corresponds to a basis with a single orbital per angular momentum channel

https://www.cp2k.org/basis_sets

Periodic boundary conditions

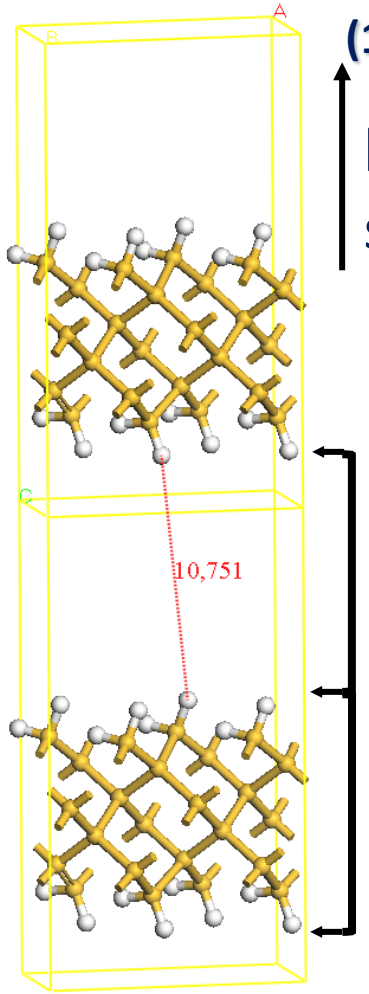




Extracted from M. P. Allen & D. J. Tildeslay,Computer Simulation of Liquids, Oxford Science publications

Imperial College London

How we model surfaces with periodic boundary conditions

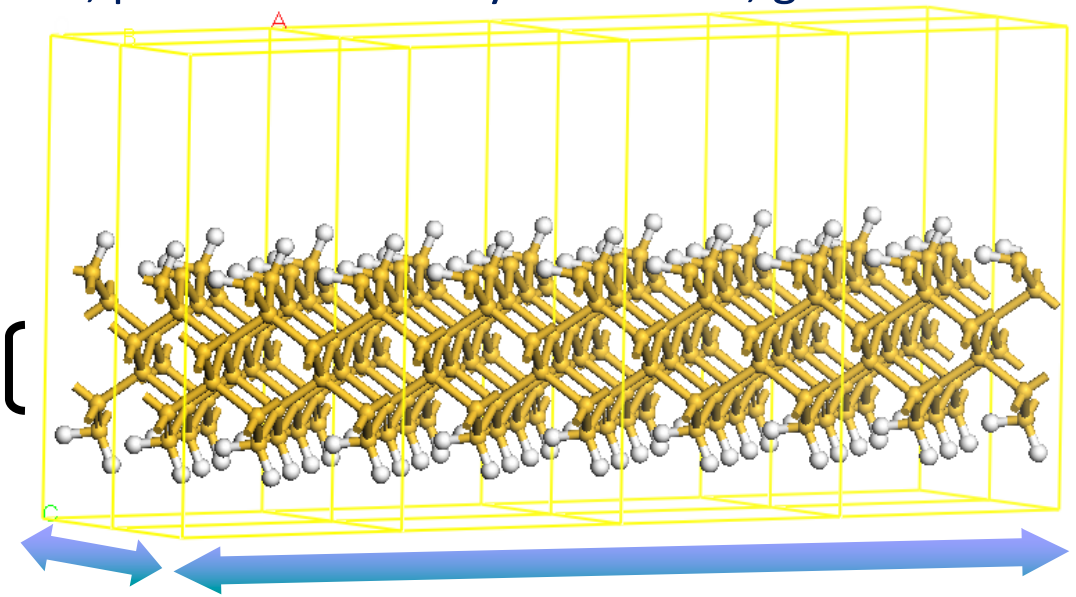


(100)

broken simmetry

non interacting surfaces

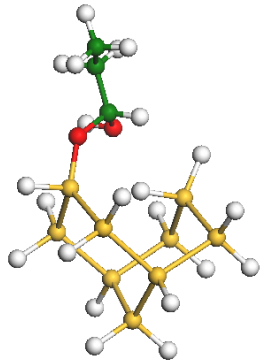
Supercell approach, periodic boundary conditions, gaussian basis set



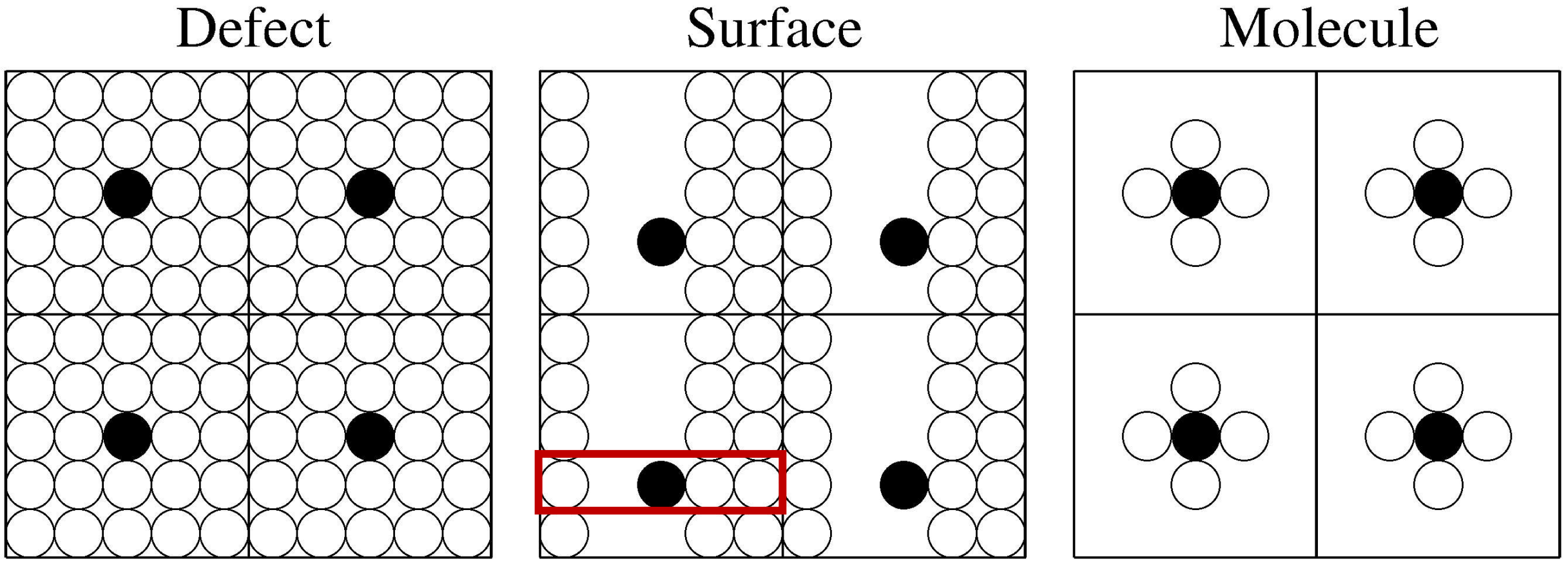
bulk conditions

replicas

Improved description wrt cluster approaches

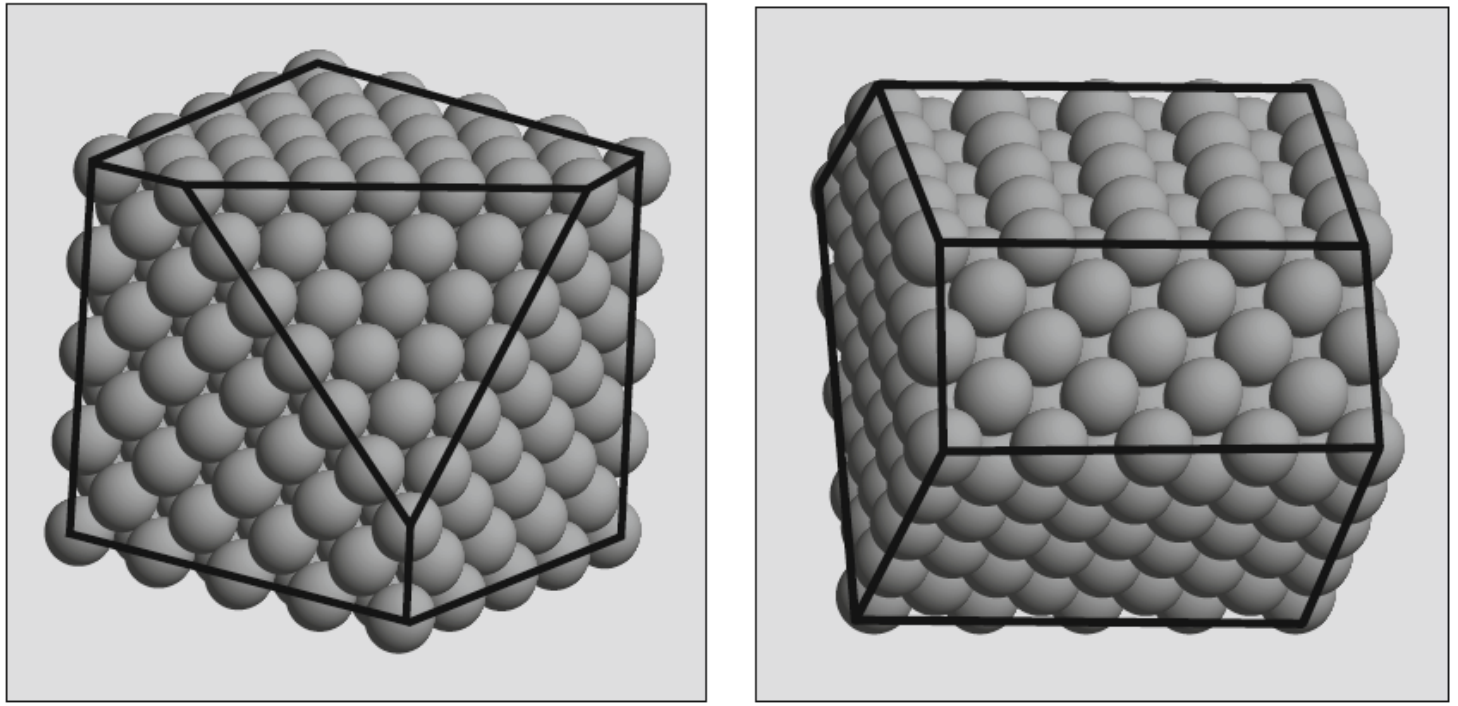


How we model surfaces: the supercell approach



Extracted from Tom Archer Thesis, Cambridge

How do we model surfaces: different facets



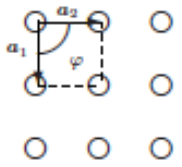
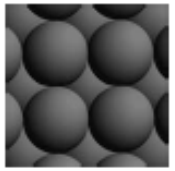
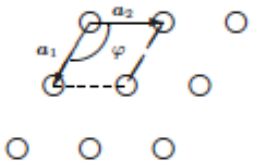
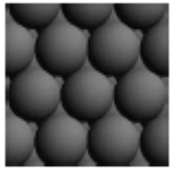
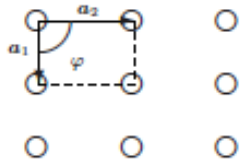
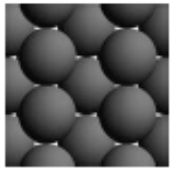
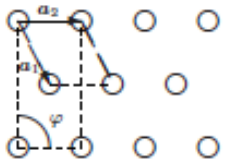
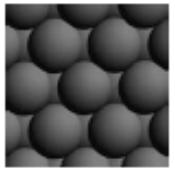
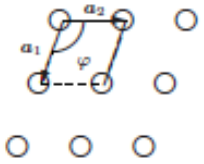
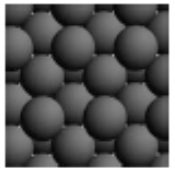
Extracted from A. Gross, Theoretical surface science A microscopic perspective, second edition, Springer

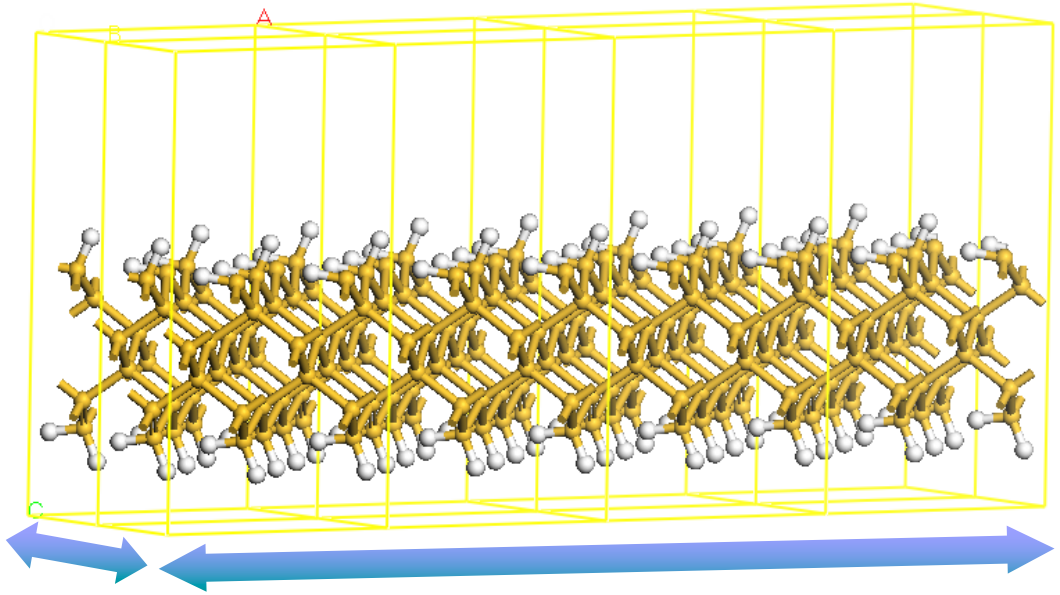
Fig. 2.3. Left panel: fcc crystal with 100 faces and one 111 face, right panel: fcc crystal with 100 faces and one 110 face

Imperial College London

How we model surfaces: two dimensional bravais lattices

Table 2.1. The five two-dimensional Bravais lattices. In addition, examples of low-index planes of fcc and bcc crystal with the corresponding symmetry are plotted

2D lattice	Schematic sketch	Examples
Square $\|a_1\| = \|a_2\|$ $\varphi = 90°$		fcc(100) 
Hexagonal $\|a_1\| = \|a_2\|$ $\varphi = 120°$		fcc(111) 
Rectangular $\|a_1\| \neq \|a_2\|$ $\varphi = 90°$		fcc(110) 
Centered rectangular $\|a_1\| \neq \|a_2\|$ $\varphi = 90°$		bcc(110) 
Oblique $\|a_1\| \neq \|a_2\|$ $\varphi \neq 90°$		fcc(210) 



replicas

Extracted from A. Gross, Theoretical surface science A microscopic perspective, second edition, Springer