

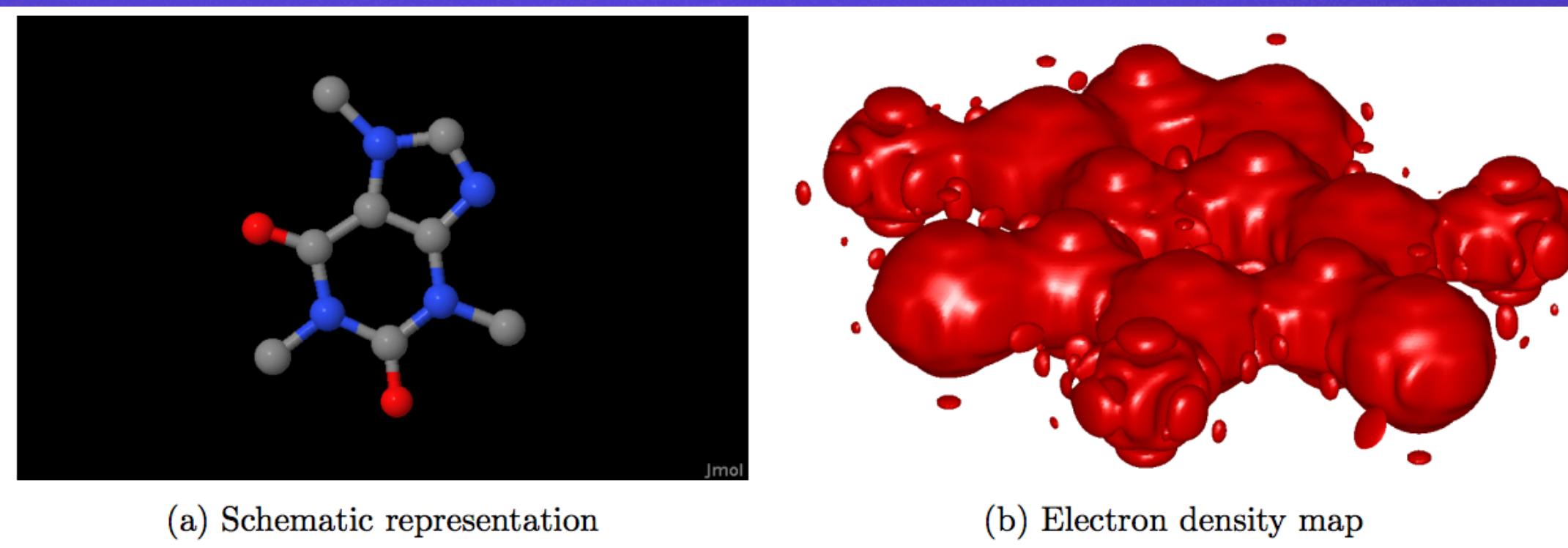
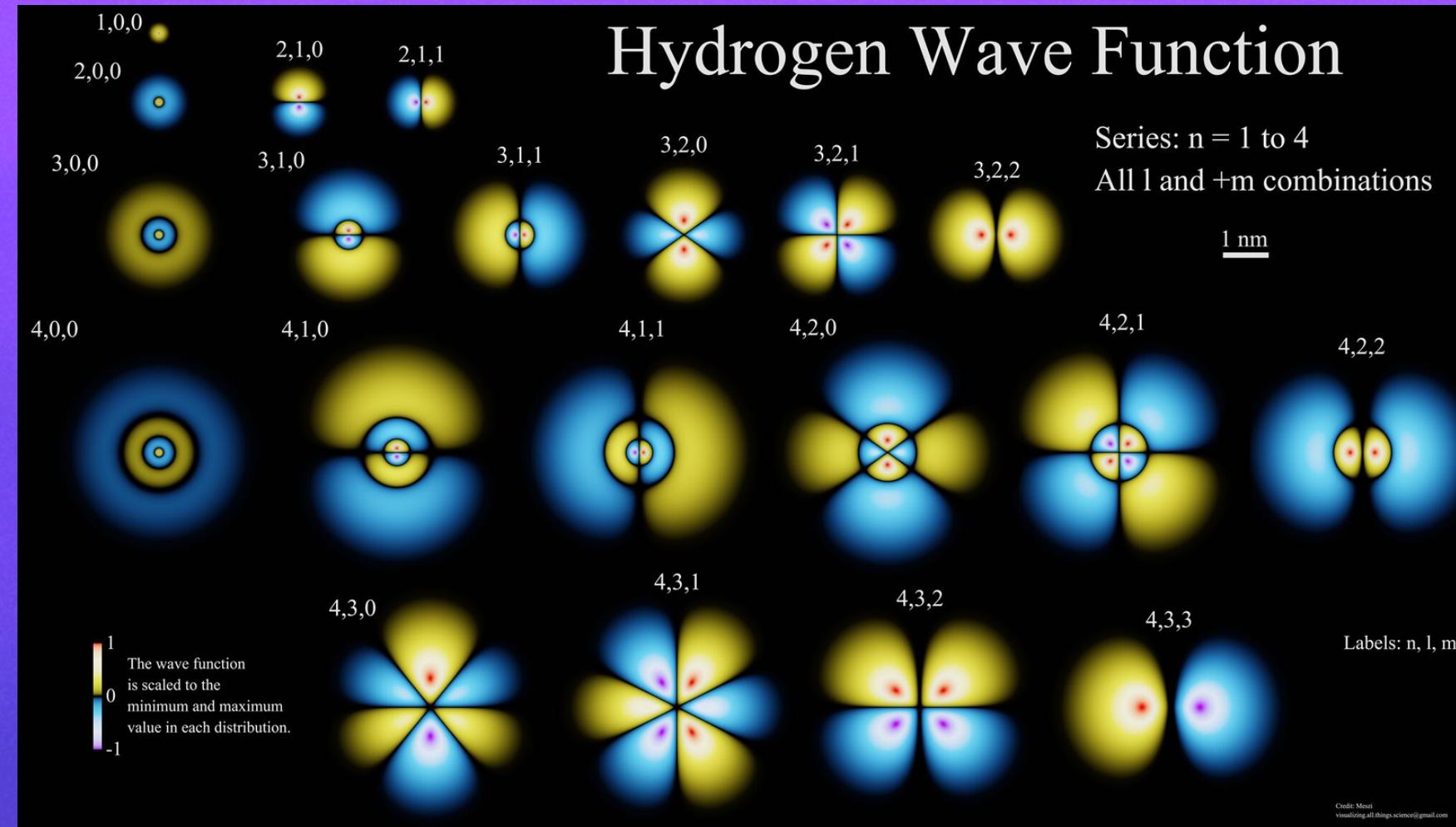
DFT with periodic bordering conditions

Module 1: Bands Structure and Convergences.

Theoretical Fundaments

Density Functional Theory

The Perfect Balance: Cost vs. Accuracy



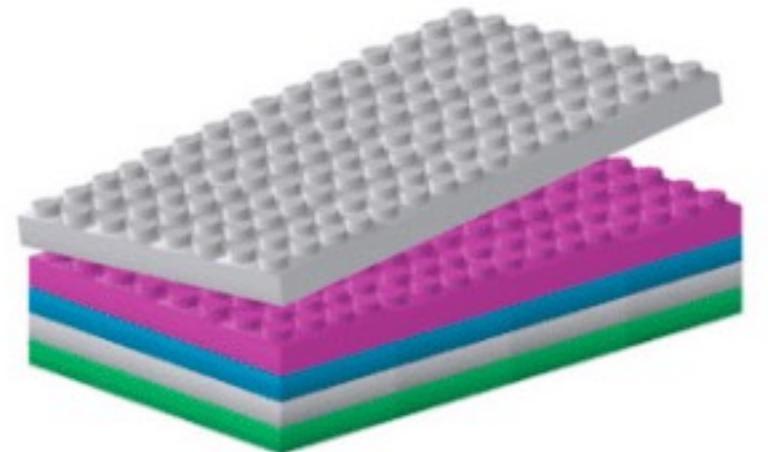
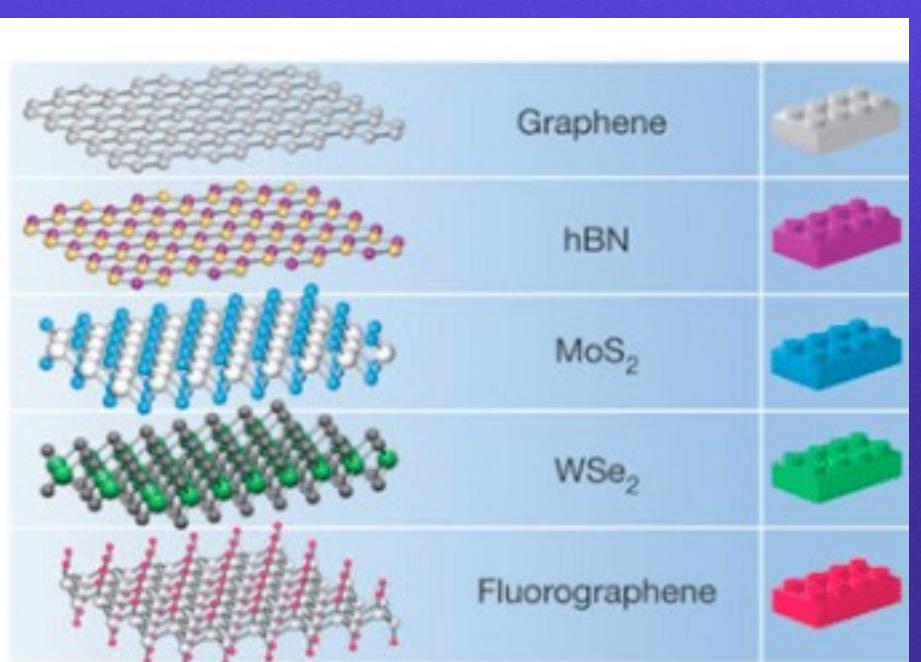
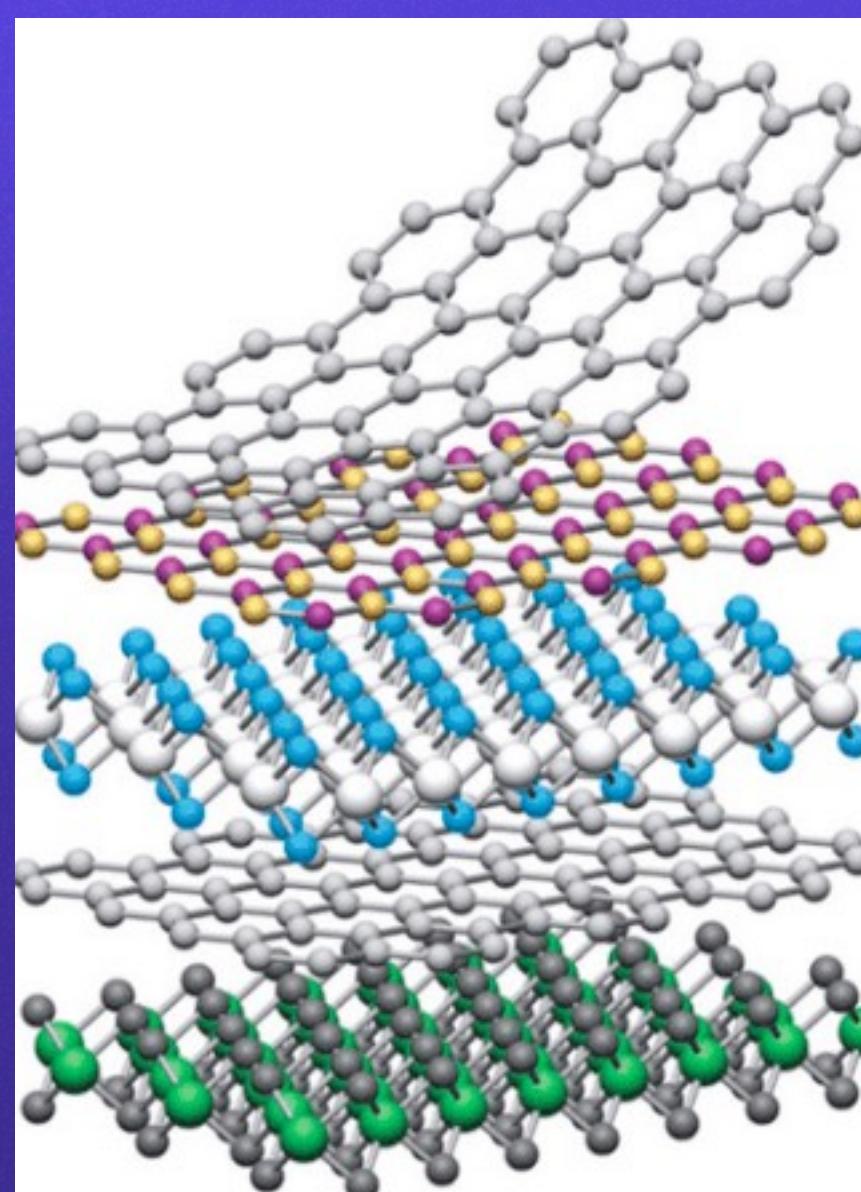
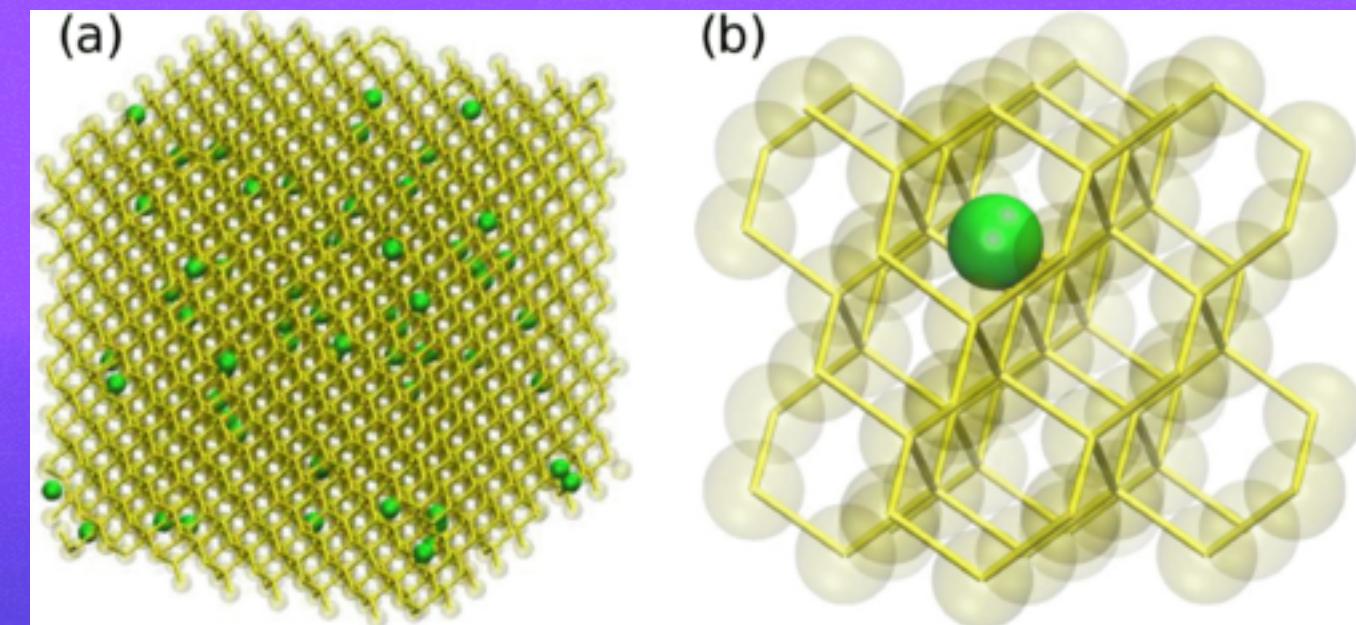
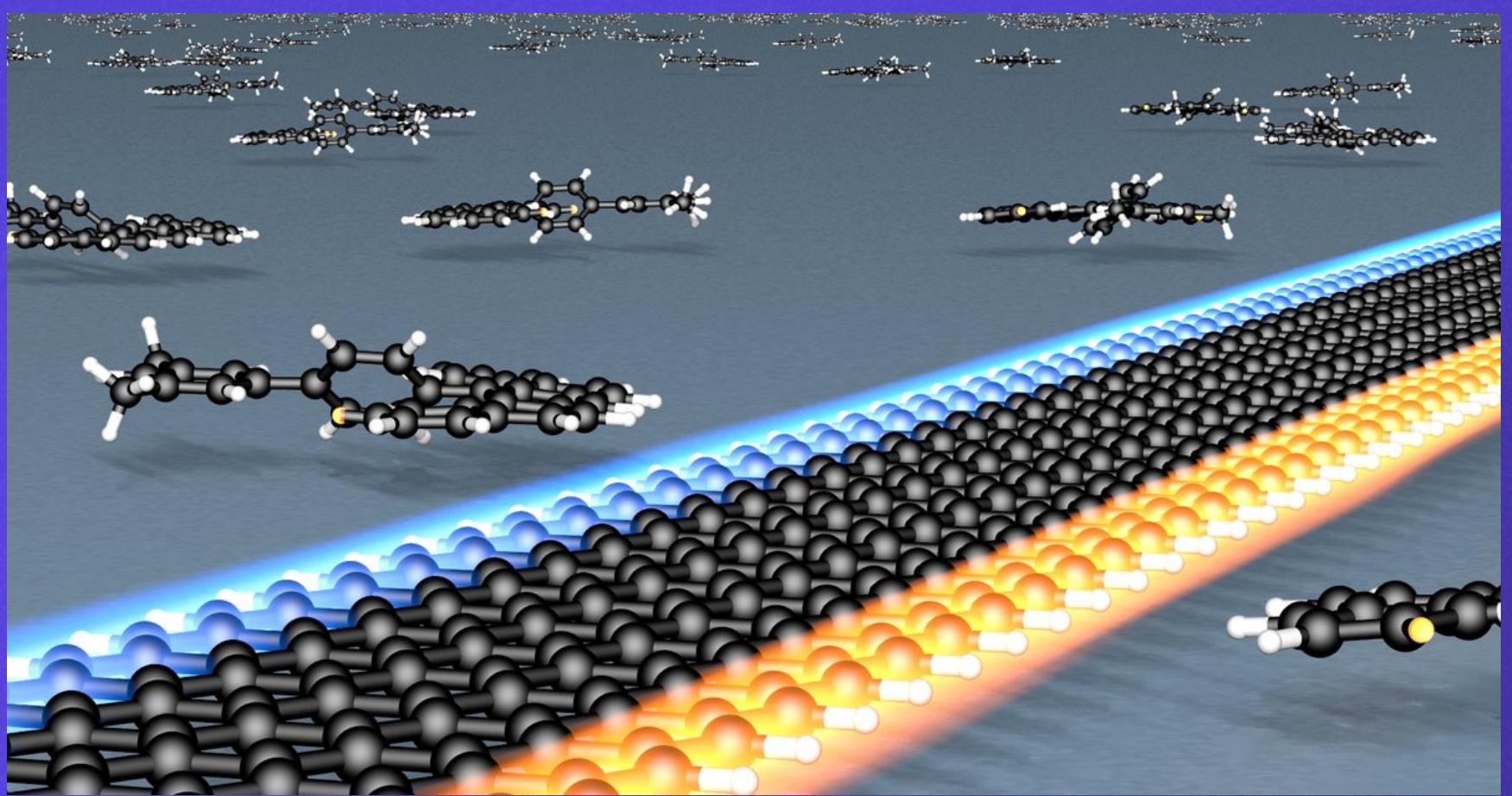
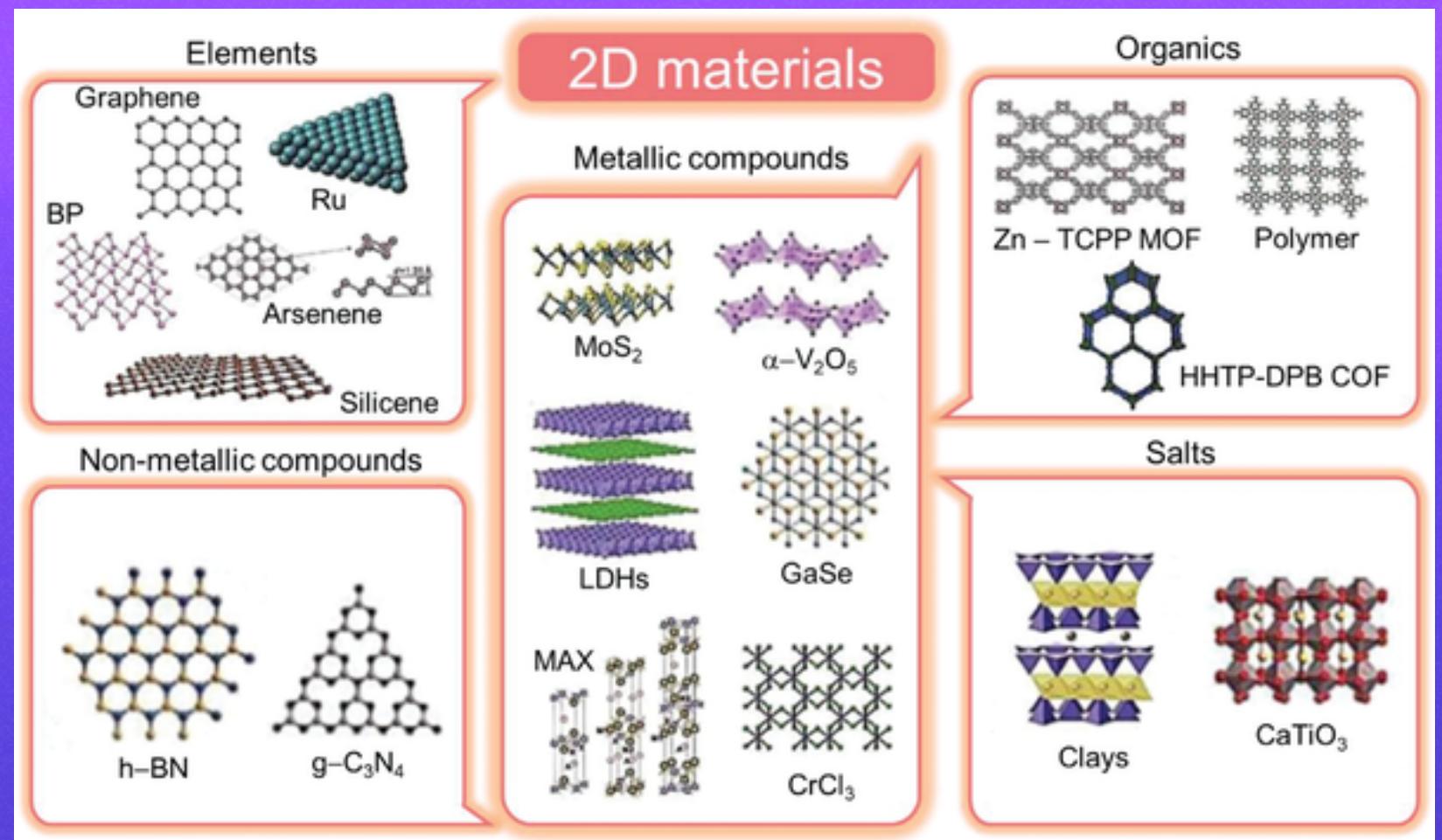
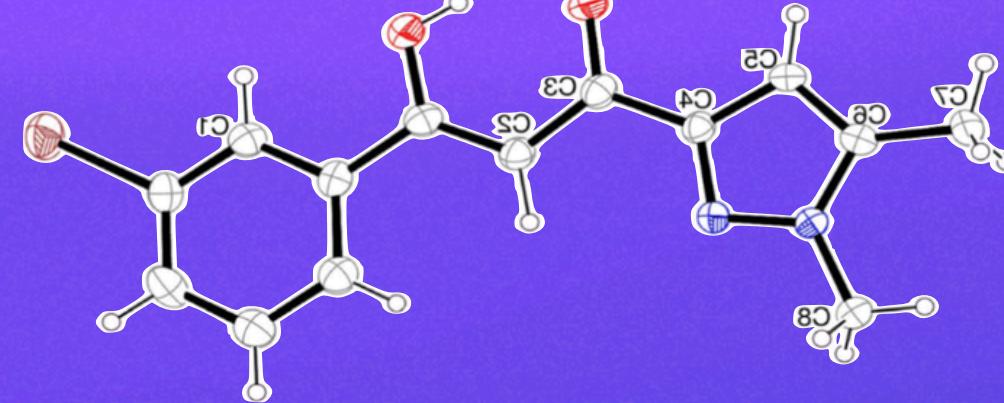
The Goal is Density: Instead of searching for the N -electron wave function, DFT proves that the electron density contains all the system's information.

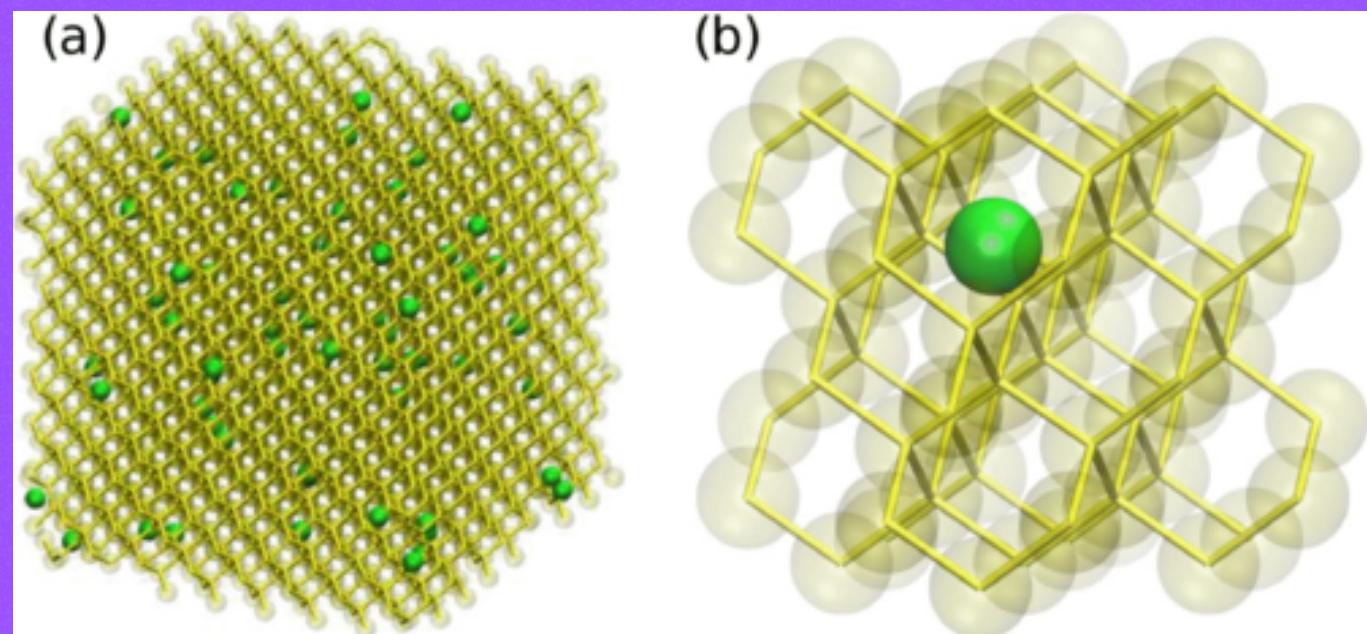
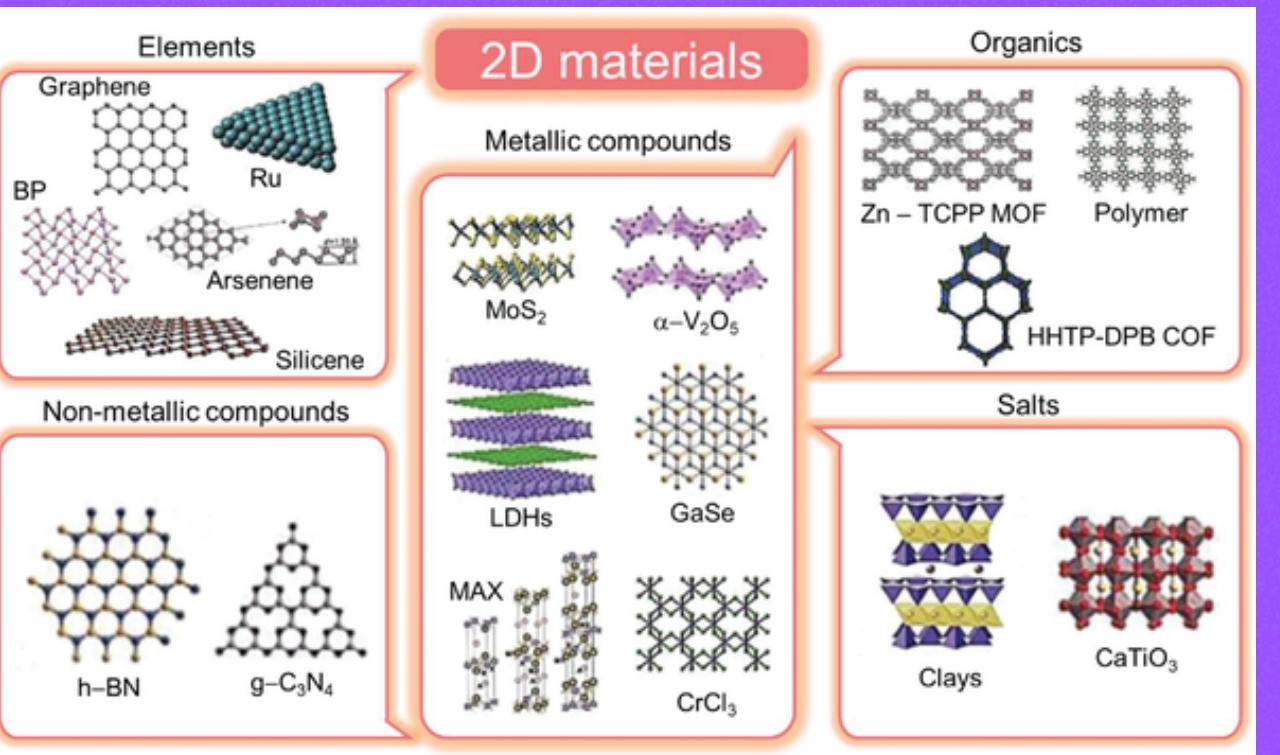
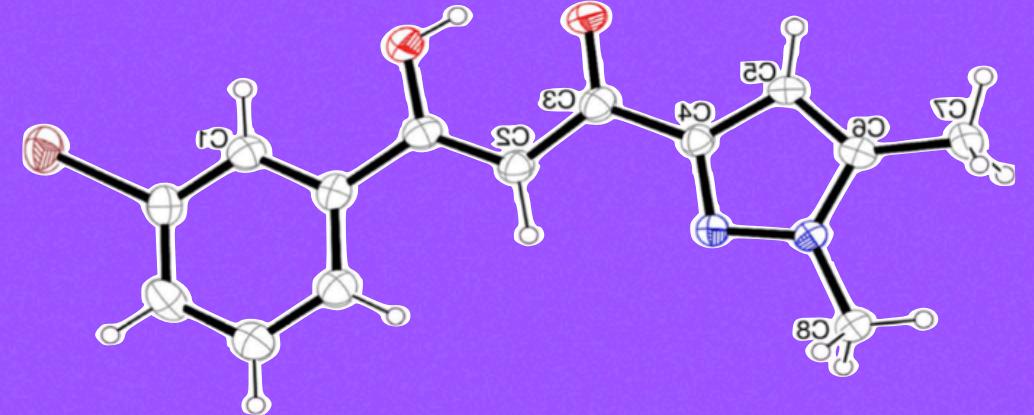
The Kohn-Sham "Shortcut": A fictitious system of non-interacting electrons is solved, which by design has the same density as the real system.

All the complex quantum physics (exchange and correlation) that Post-HF methods calculate explicitly and expensively, DFT groups into a single term: **the exchange-correlation functional.**

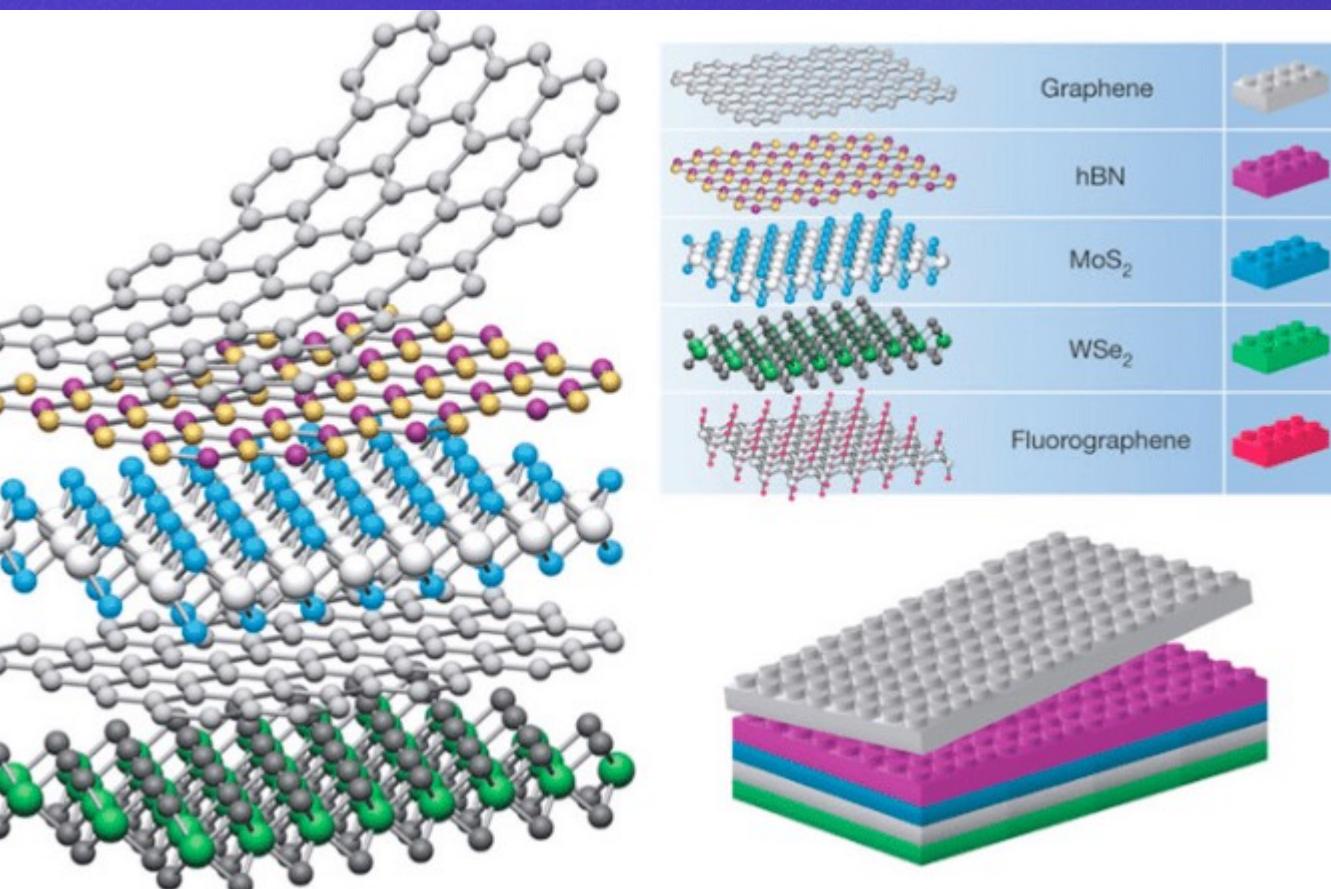
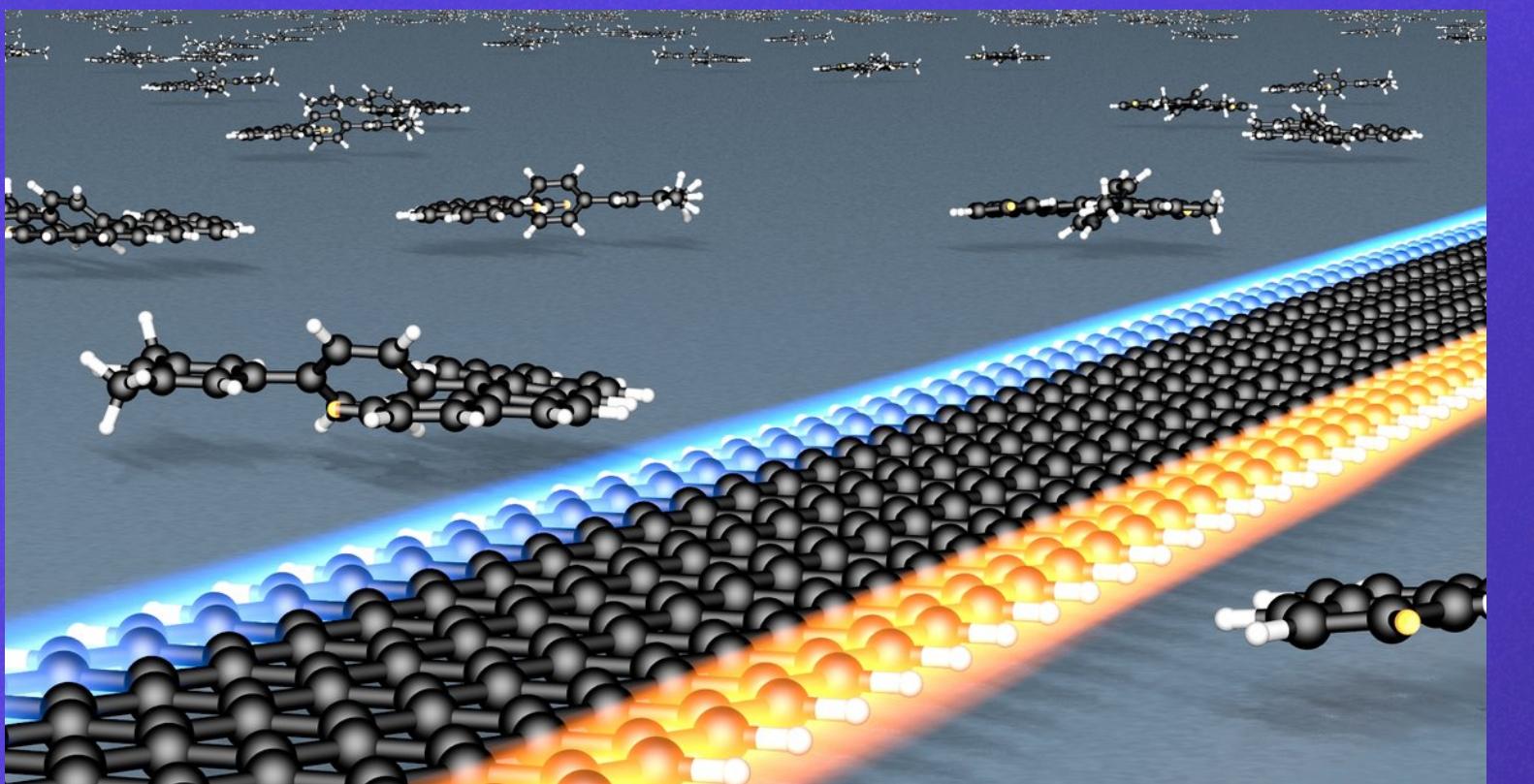
DFT & Periodic Materials

From molecules to crystal lattices





What is different in a solid state?



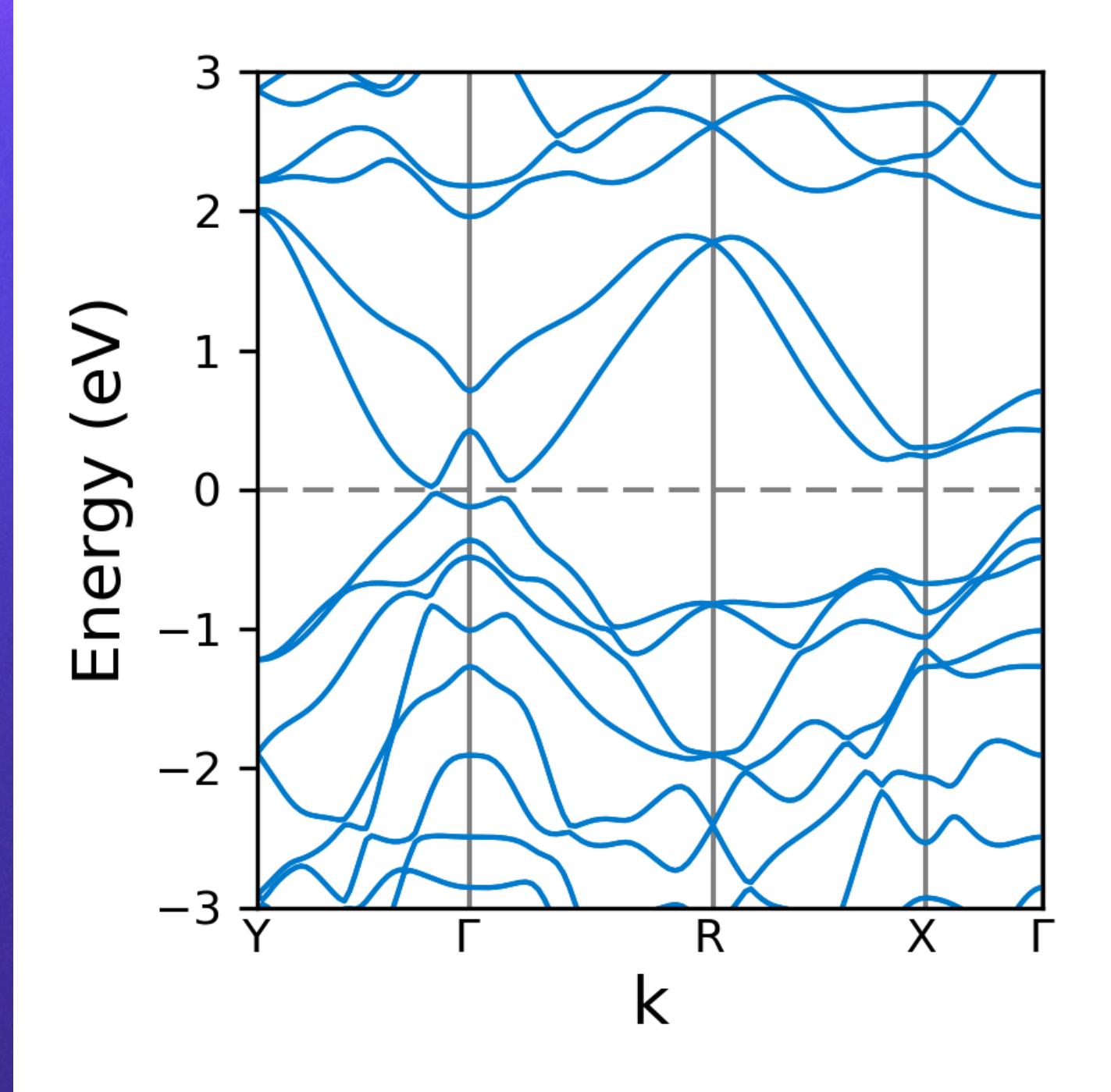
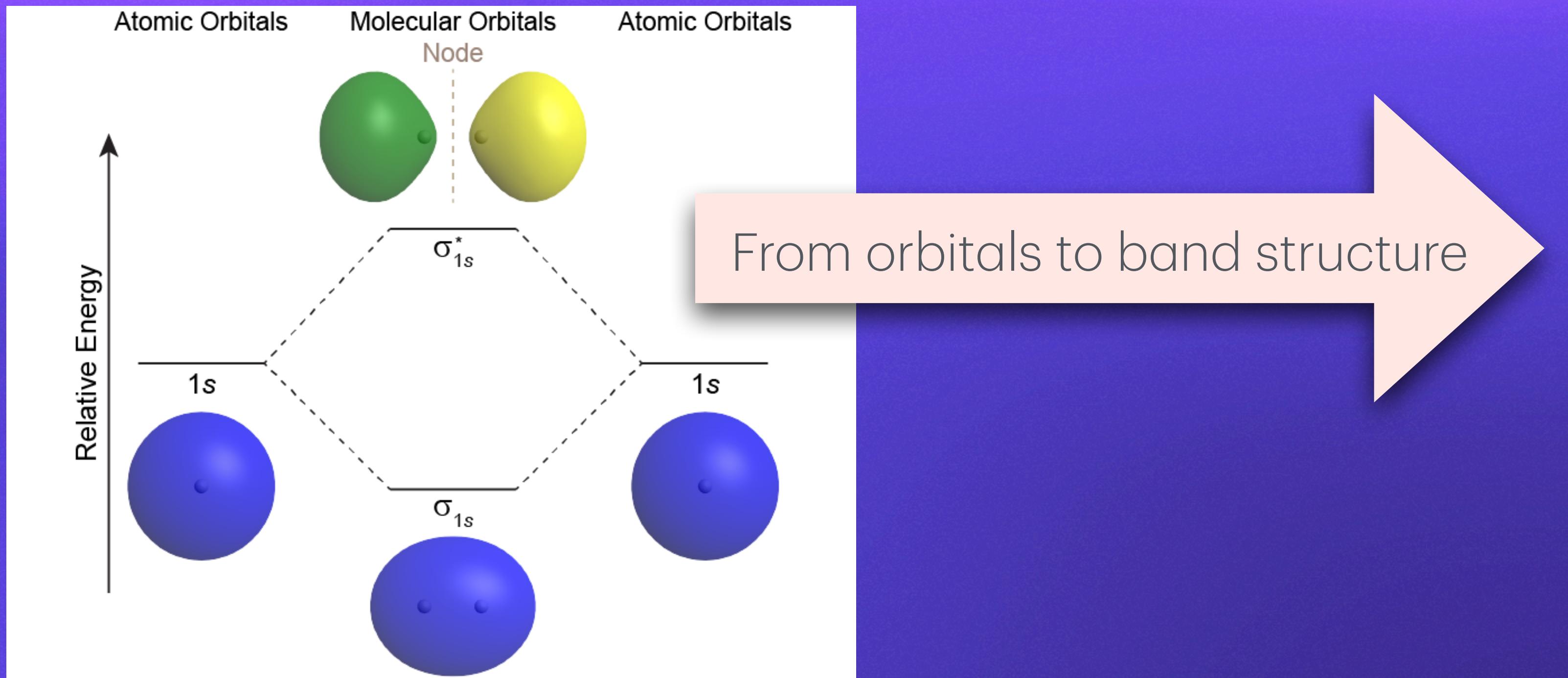
DFT & Periodic Materials

From molecules to crystal lattices

Pseudopotentials

Reciprocal Space

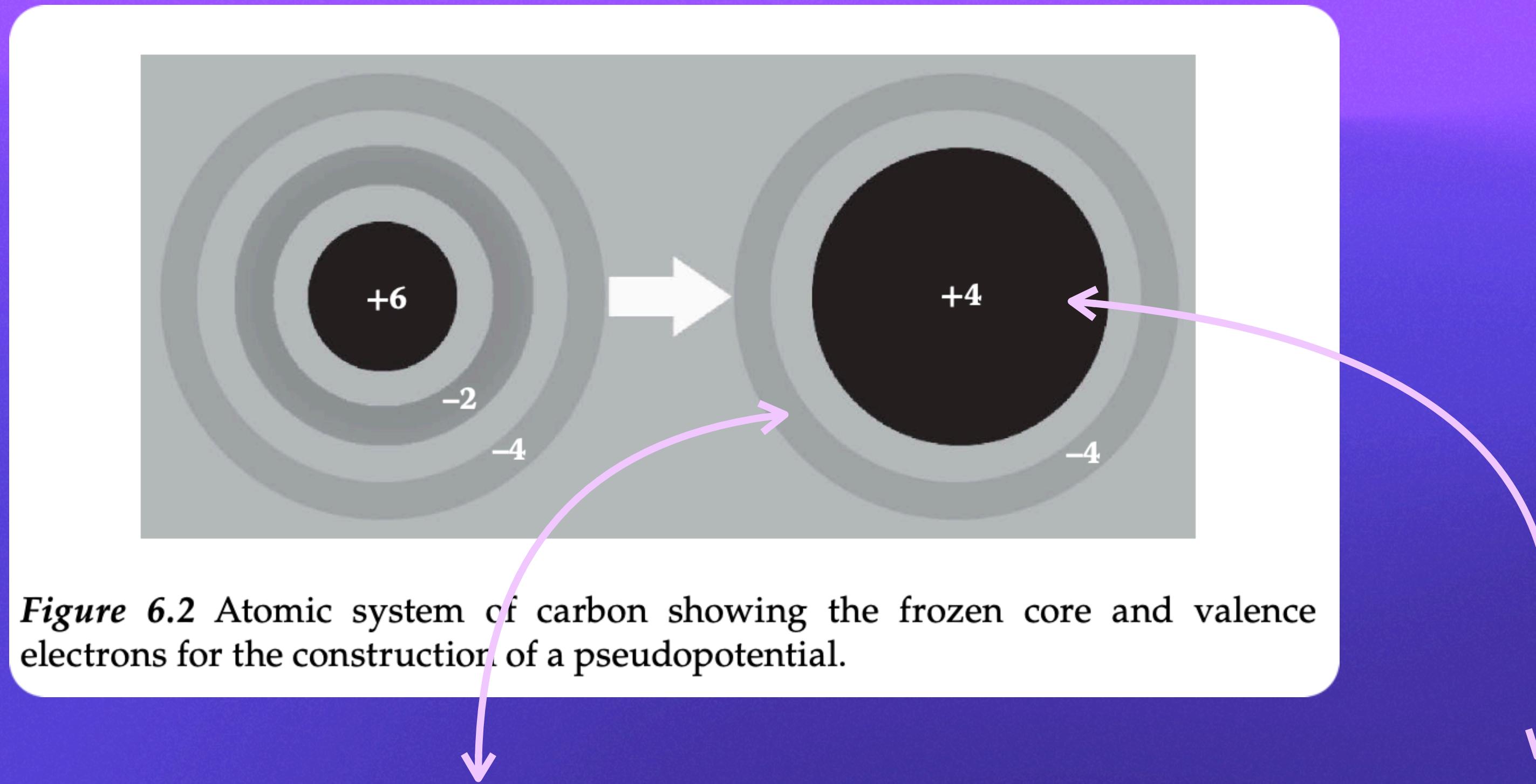
Bloch Theorem



Pseudopotentials

DFT & Periodic Materials

Pseudopotentials (PPs)



Forming bonds, being ionized,
conducting electricity in metals, and
performing other atomic activities

Freezing the nucleus and
the core electrons
together

Intro DFT & Materiales periódicos

Pseudopotentials (PPs)

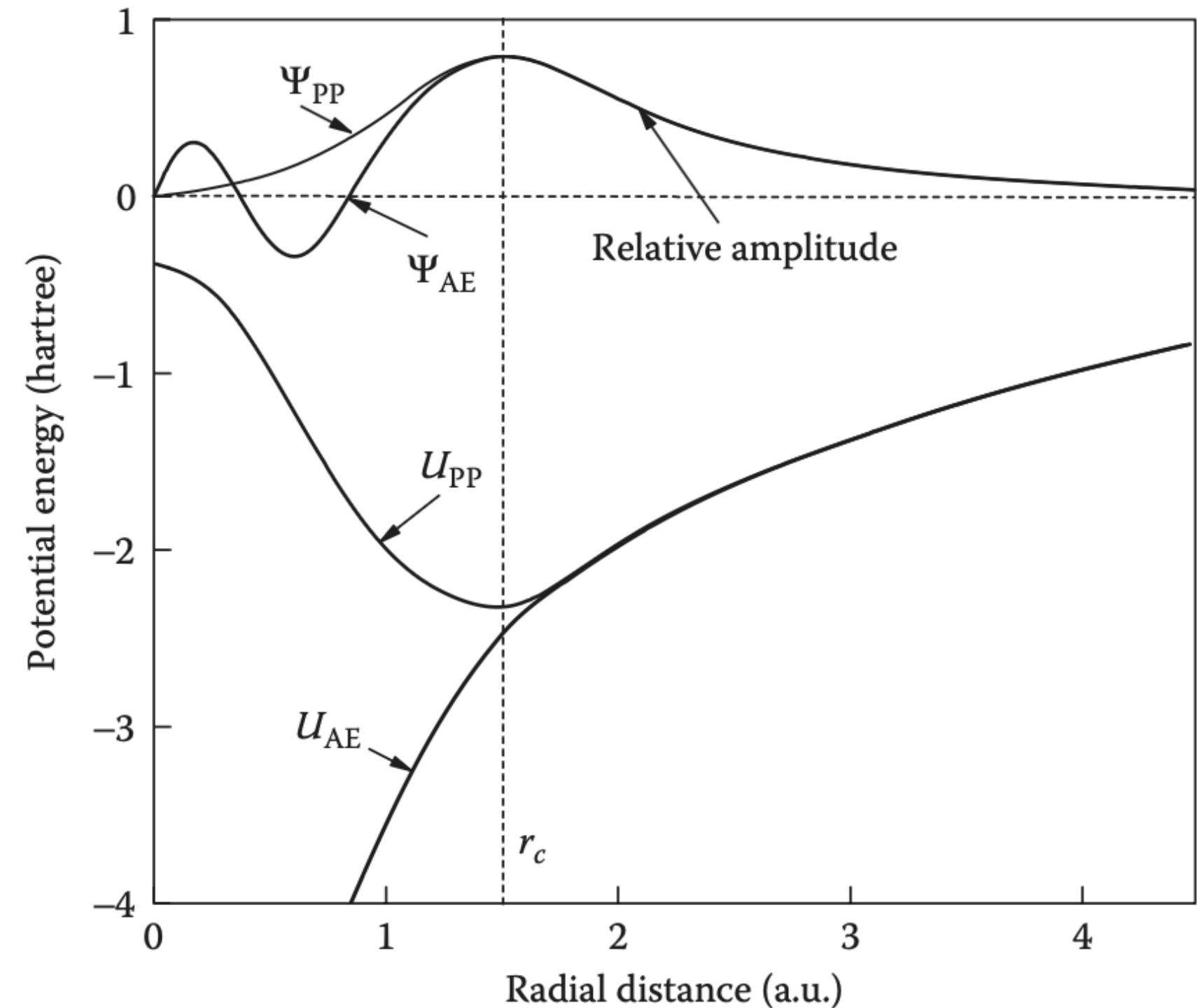


Figure 6.3 Schematic illustration of a pseudo wave function pseudized from a 3s wave function (showing the relative amplitude in arbitrary unit) and the corresponding pseudo- and all-electron (AE) potentials.

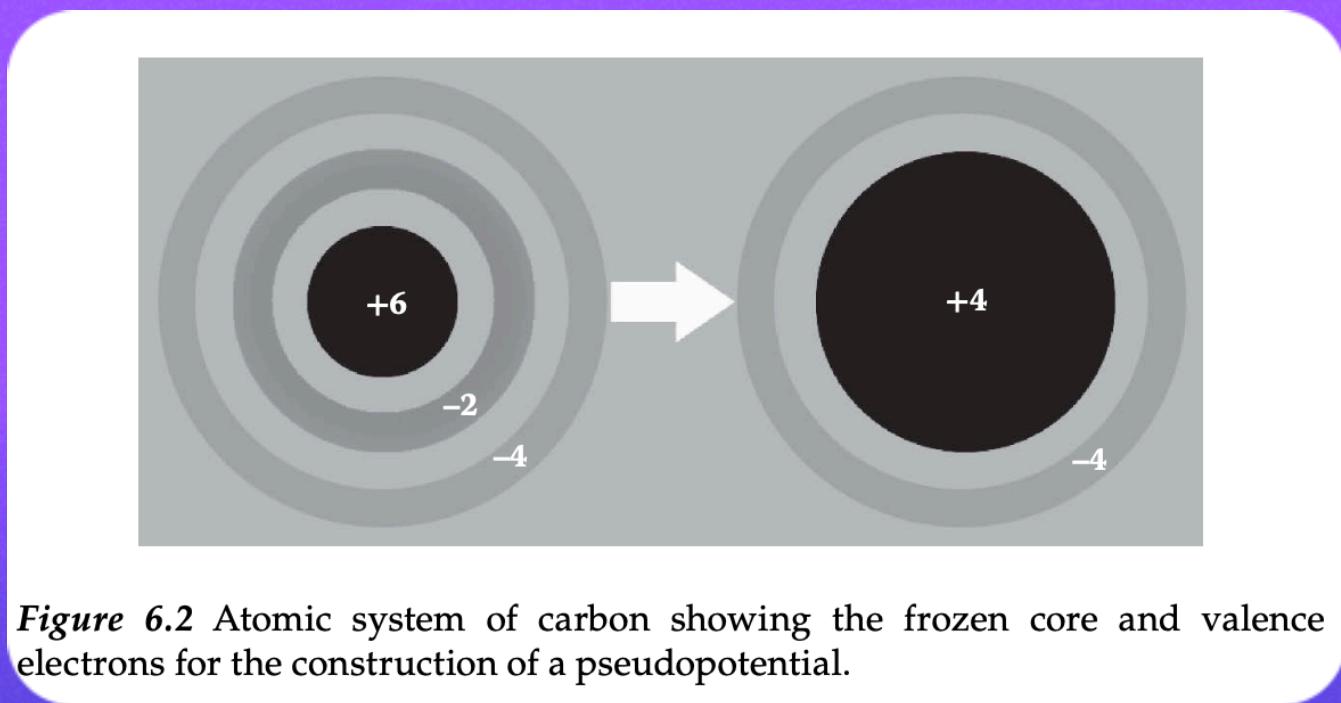


Figure 6.2 Atomic system of carbon showing the frozen core and valence electrons for the construction of a pseudopotential.

- Markedly reduces the number of PWs needed for the expansion of the pseudo-wavefunction.
- Allows for more noticeable energy changes.
- Eliminates the relativistic effect of core electrons.

Intro DFT & Materiales periódicos

Pseudopotentials (PPs)

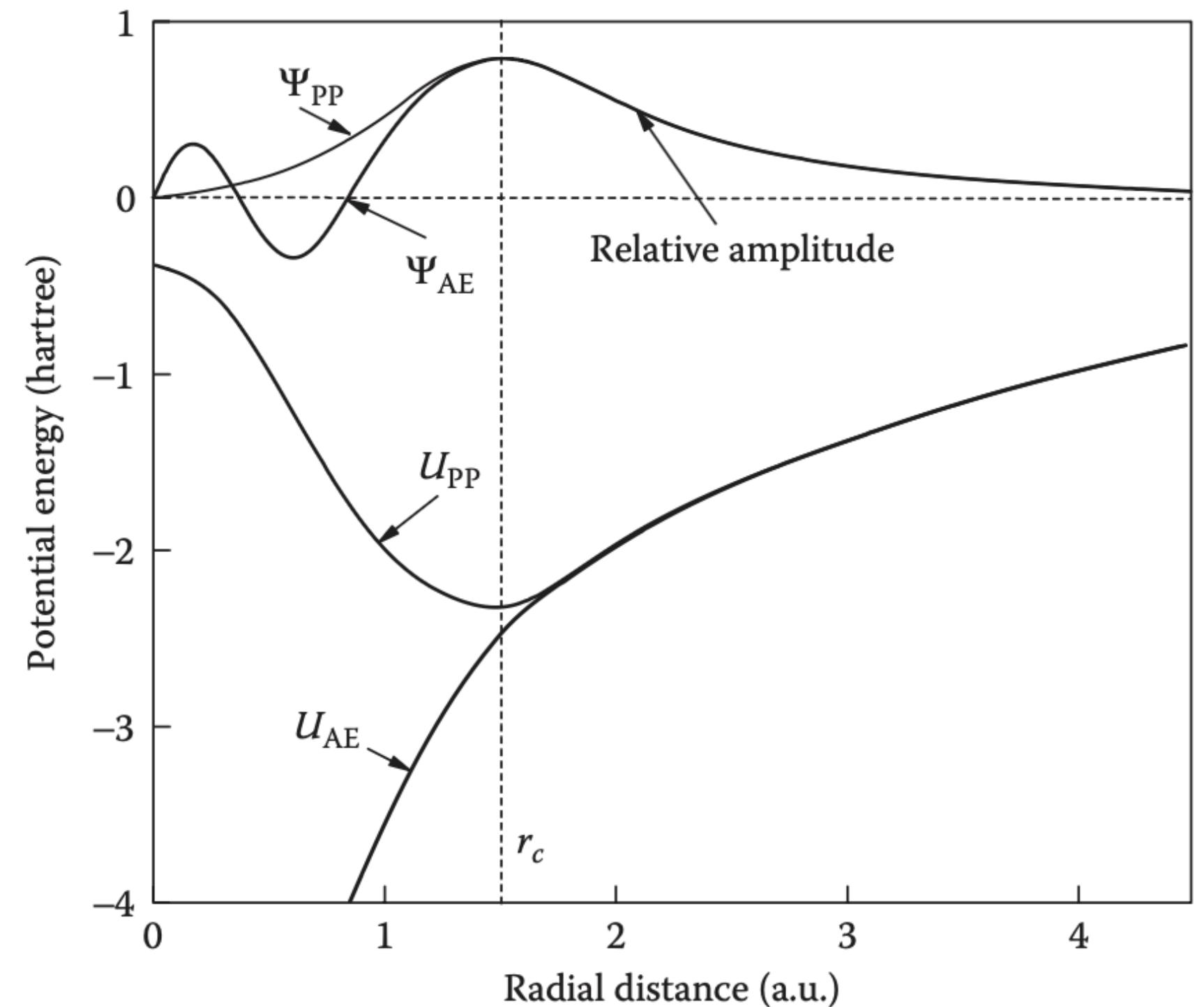


Figure 6.3 Schematic illustration of a pseudo wave function pseudized from a 3s wave function (showing the relative amplitude in arbitrary unit) and the corresponding pseudo- and all-electron (AE) potentials.

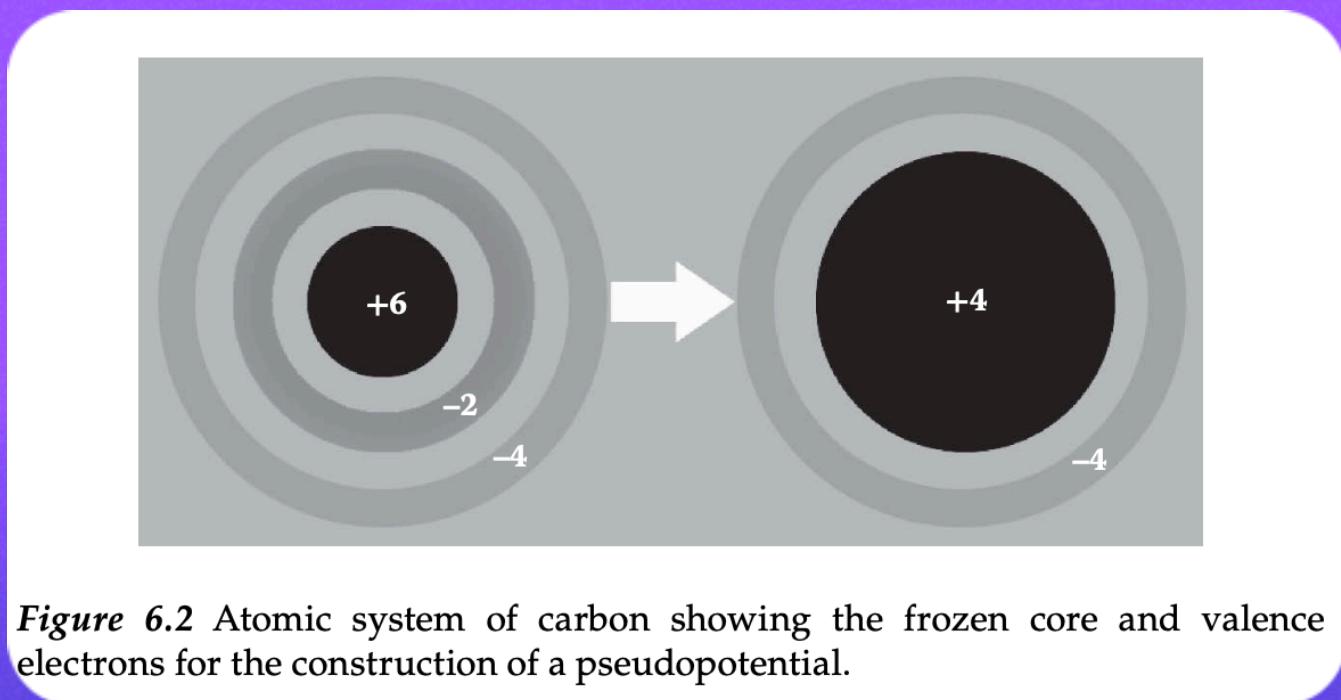


Figure 6.2 Atomic system of carbon showing the frozen core and valence electrons for the construction of a pseudopotential.

$$\left[-\frac{1}{2} \nabla^2 + U_{\text{PP}}[\rho(\mathbf{r})] \right] \psi_i^{\text{PP}}(\mathbf{r}) = \varepsilon_i \psi_i^{\text{PP}}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i |\psi_i^{\text{PP}}(\mathbf{r})|^2$$

Intro DFT & Materiales periódicos

Pseudopotentials (PPs)

Norm-Conserving (NCPPs):

Ultrasoft (USPPs):

Projector Augmented-Wave (PAW):

Intro DFT & Materiales periódicos

Pseudopotentials (PPs)

Norm-Conserving (NCPPs):

- It ensures that the total integrated charge within a defined radius (the "core radius") is identical to that of the all-electron (AE) atom.
- It guarantees that, outside of this radius, the valence electrons feel the exact same potential.

Ultrasoft (USPPs):

Projector Augmented-Wave (PAW):

Intro DFT & Materiales periódicos

Pseudopotentials (PPs)

Norm-Conserving (NCPPs):

- Relaxes the norm-conservation rule to create much "softer" (smoother) wavefunctions.

Ultrasoft (USPPs):

- Drastically reduces the required number of plane waves.

Projector Augmented-Wave (PAW):

Intro DFT & Materiales periódicos

Pseudopotentials (PPs)

Norm-Conserving (NCPPs):

Ultrasoft (USPPs):

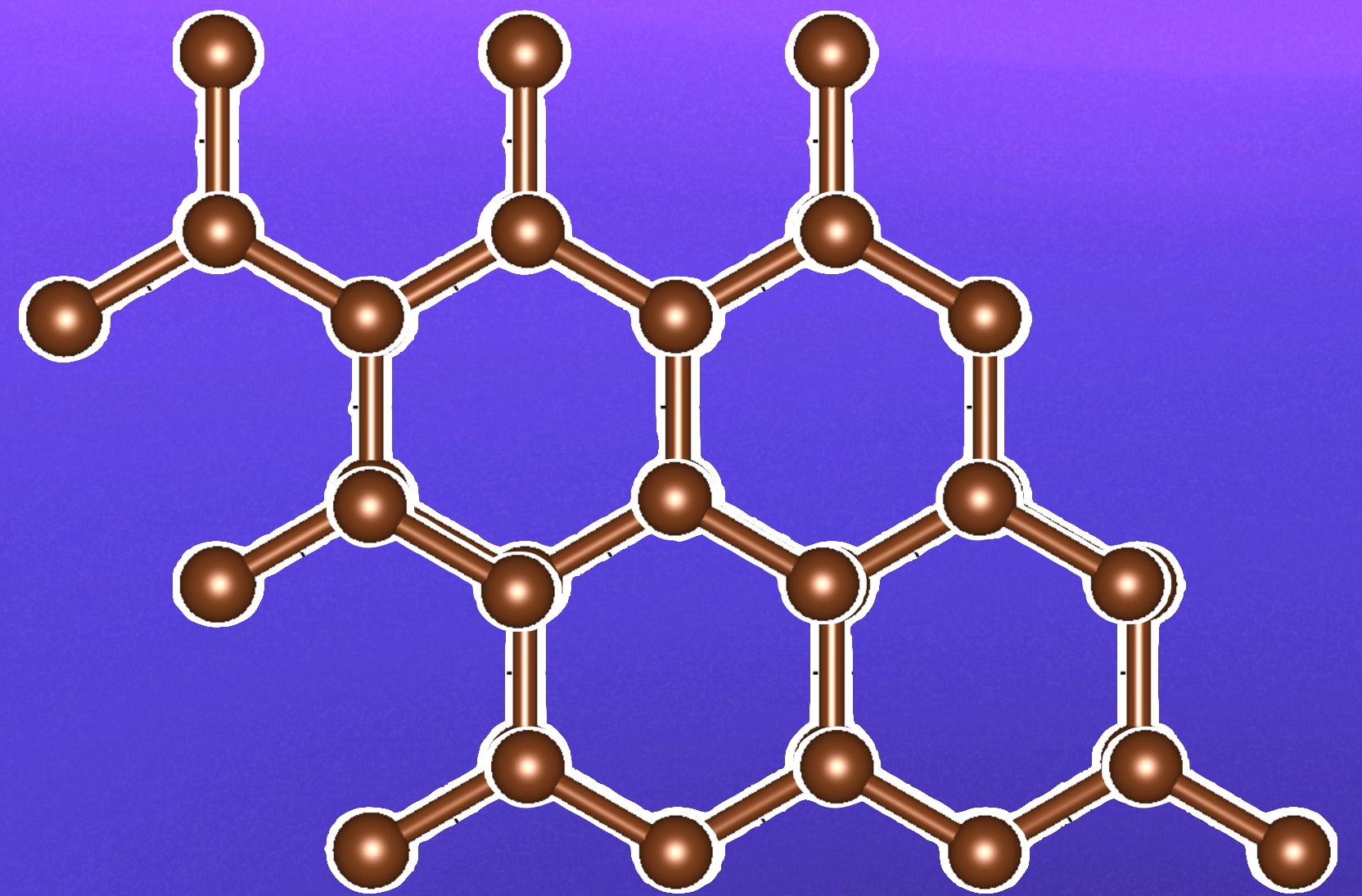
Projector Augmented-Wave (PAW):

- Combines the efficiency of ultrasoft potentials with the accuracy of an all-electron calculation.
- Uses a transformation to reconstruct the exact wavefunctions near the core.

Symmetry and Periodicity

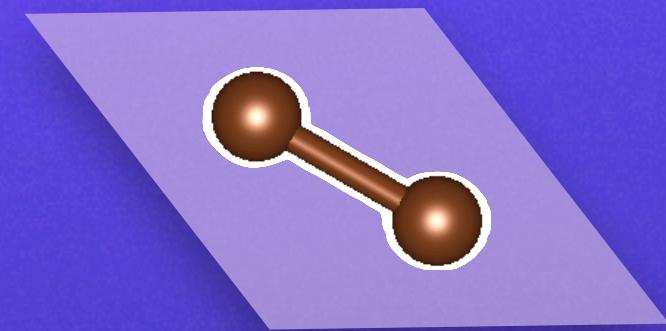
Symmetry and Periodicity

Unit Cell - Supercell



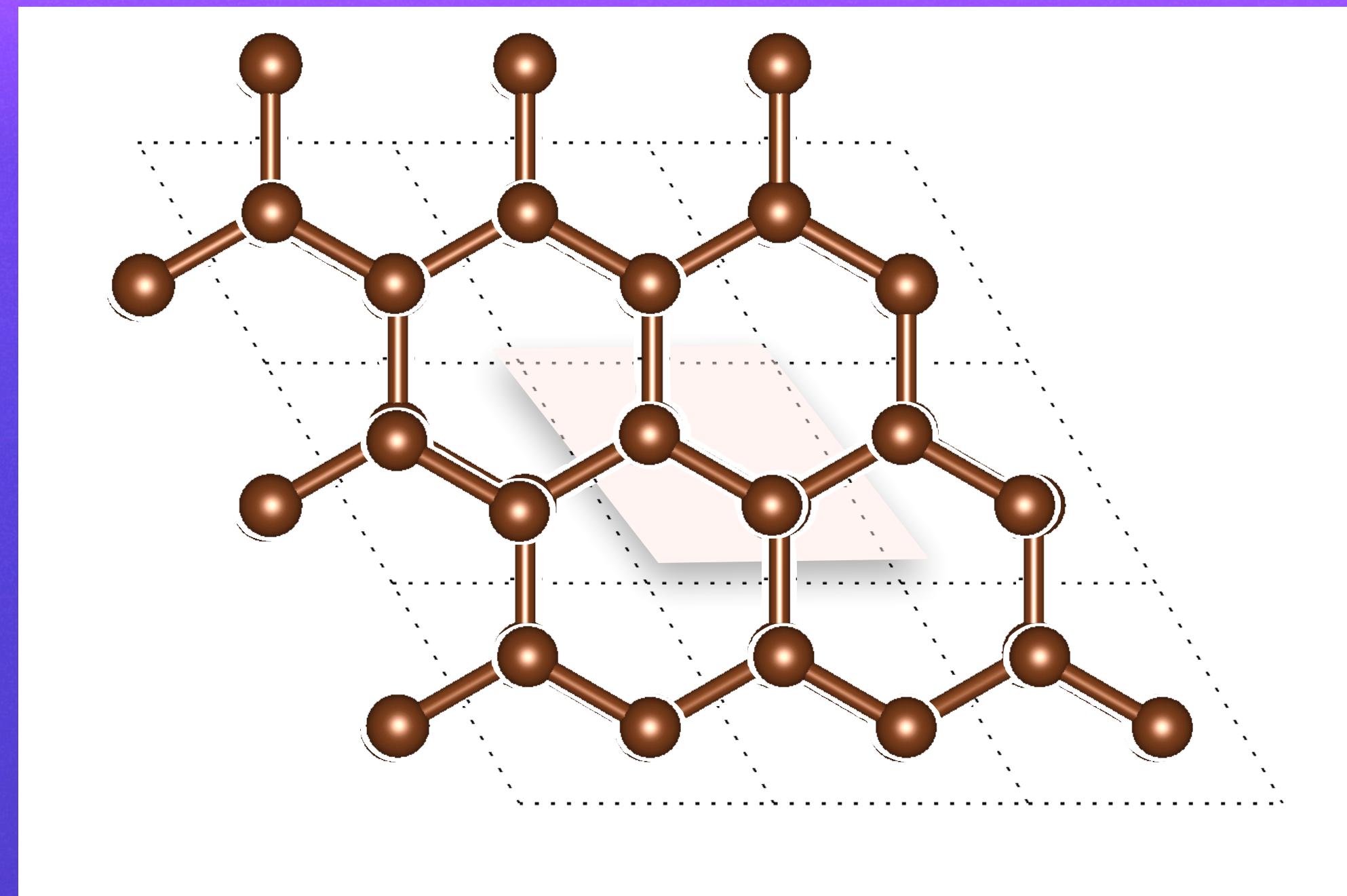
Symmetry and Periodicity

Unit Cell - Supercell



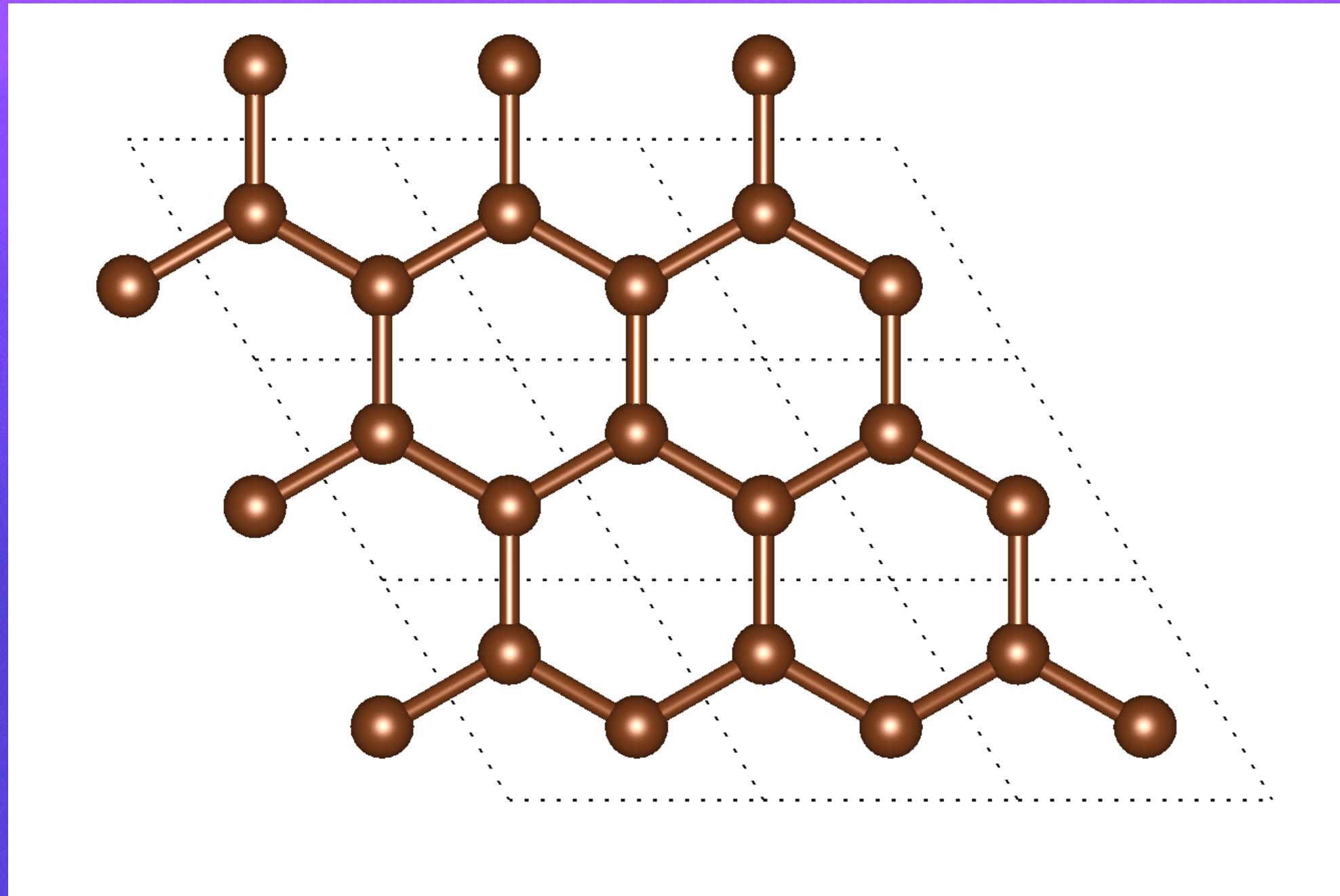
Symmetry and Periodicity

Unit Cell - Supercell

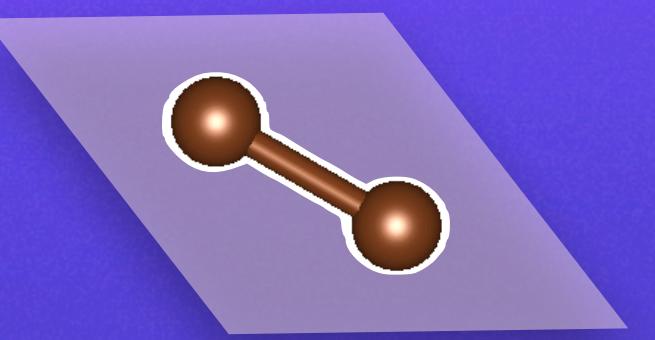


Symmetry and Periodicity

Unit Cell - Supercell



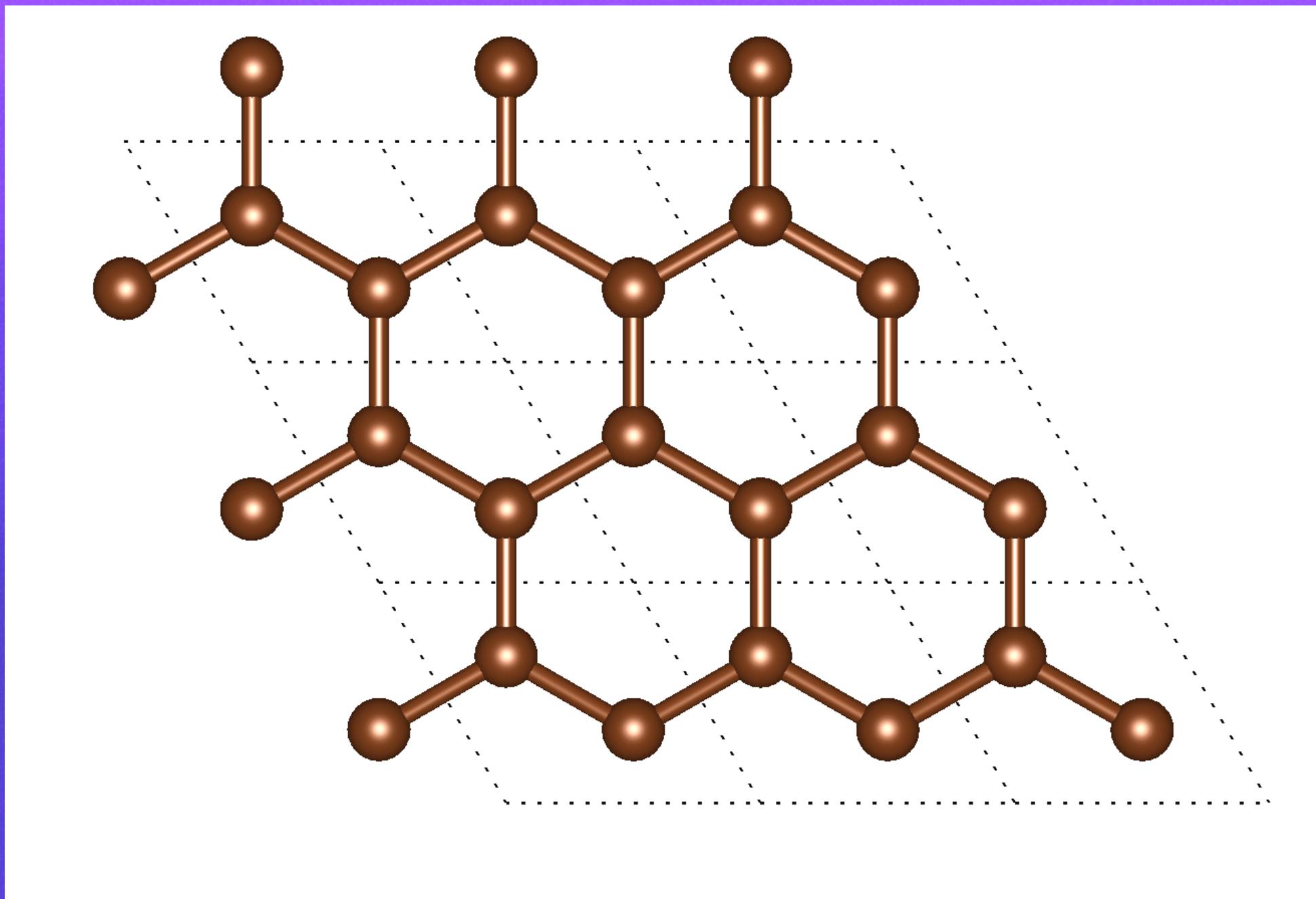
Supercell 3x3



Unit Cell: The minimal representation of the system.

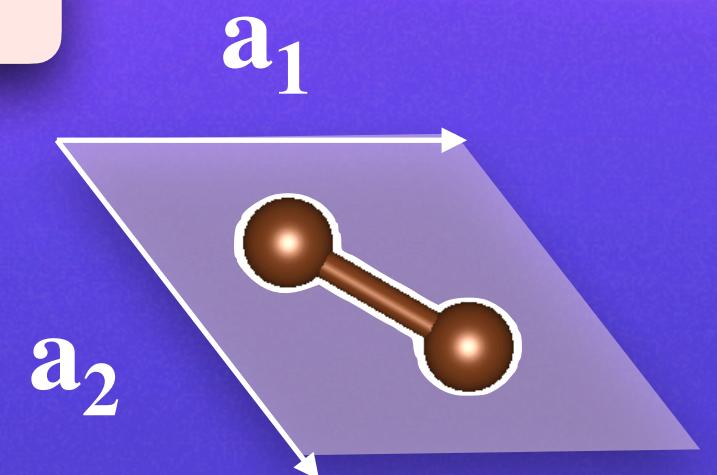
Symmetry and Periodicity

Unit Cell - Supercell



Supercell 3x3

Primitive basis



Unit Cell: The minimal representation of the system.

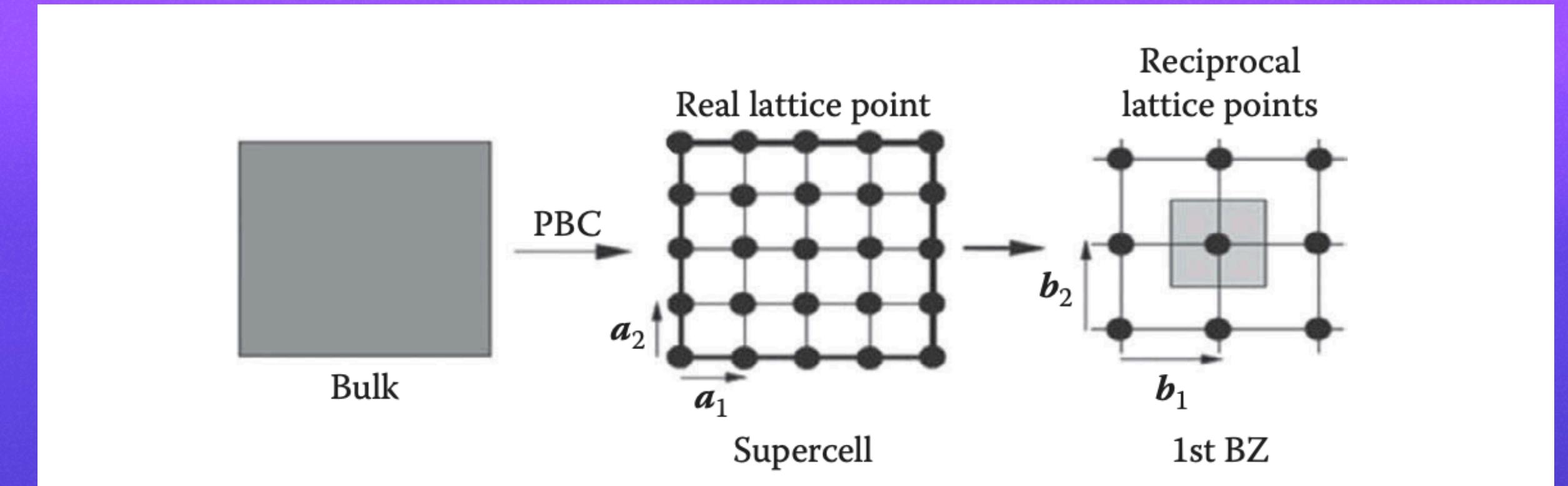
Bravais lattice

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

Symmetry and Periodicity

Reciprocal Space

Mathematical transformation of the crystal lattice into a new "space" which describes **periodicity and wave vectors \mathbf{K}** .



$$e^{i\mathbf{K} \cdot \mathbf{r}} = e^{i\mathbf{K} \cdot (\mathbf{r} + \mathbf{R})}$$

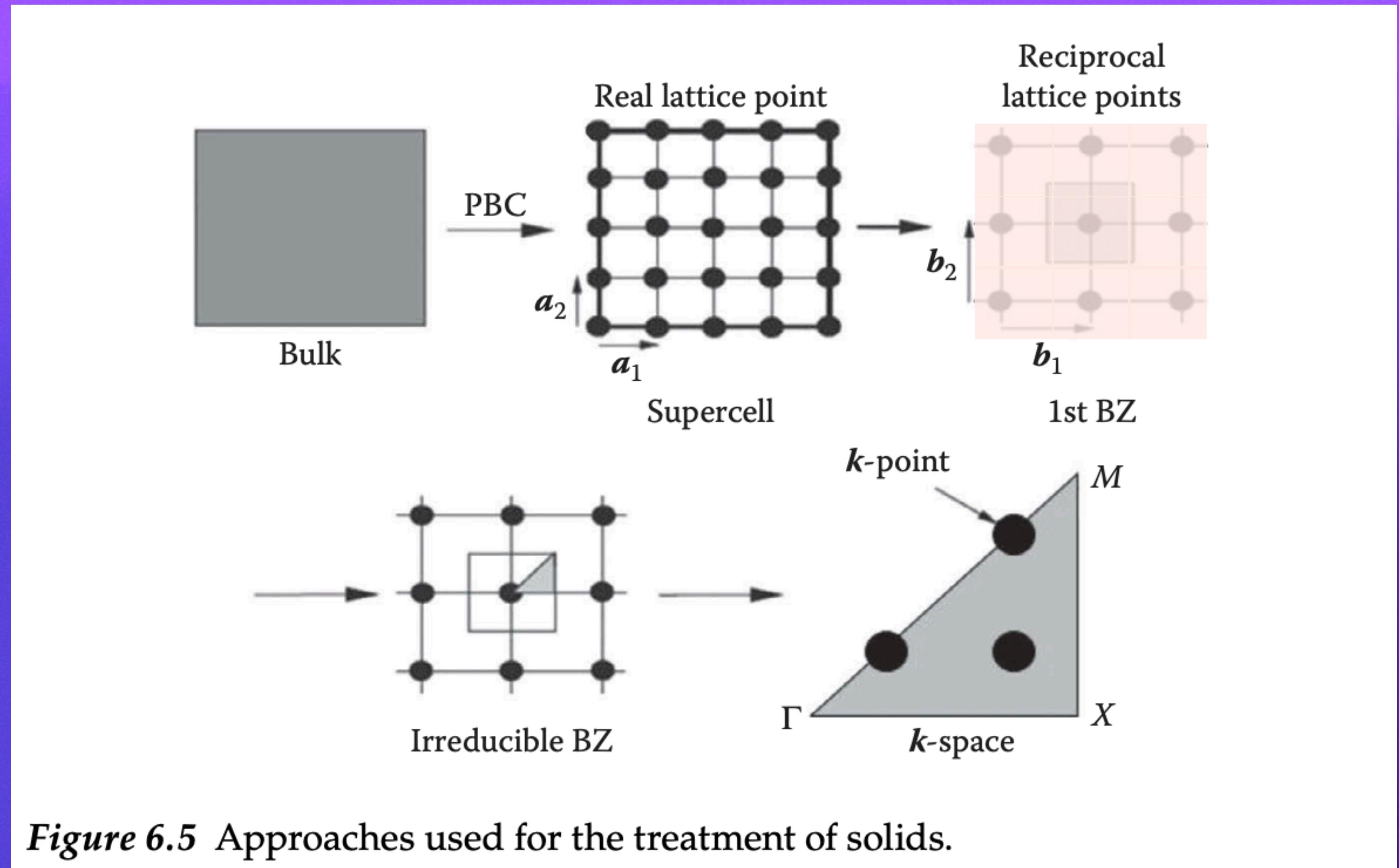
$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)} \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$$

Reciprocal space vectors

$$\mathbf{K} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3$$

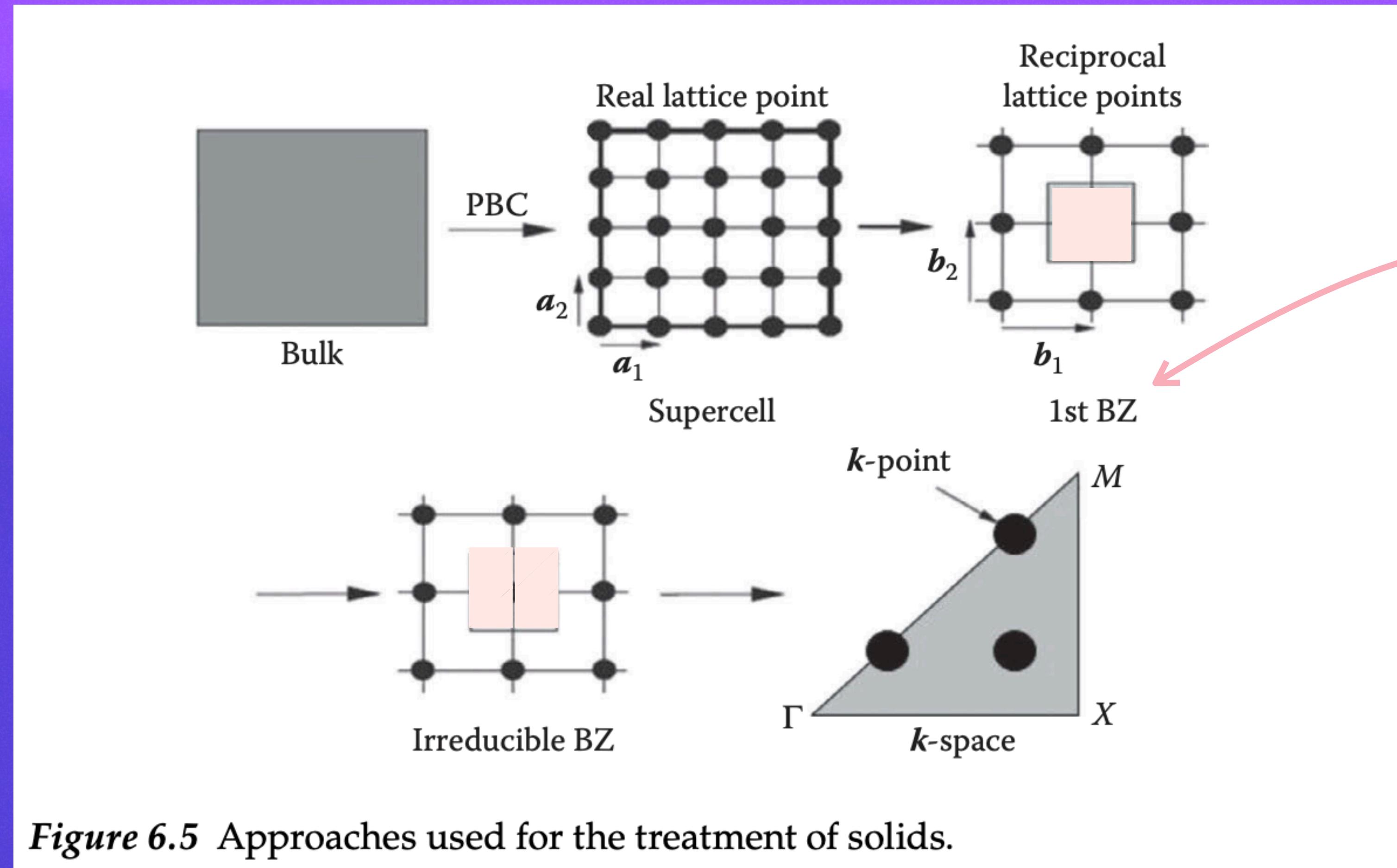
Symmetry and Periodicity

Reciprocal Space- Brillouin Zone



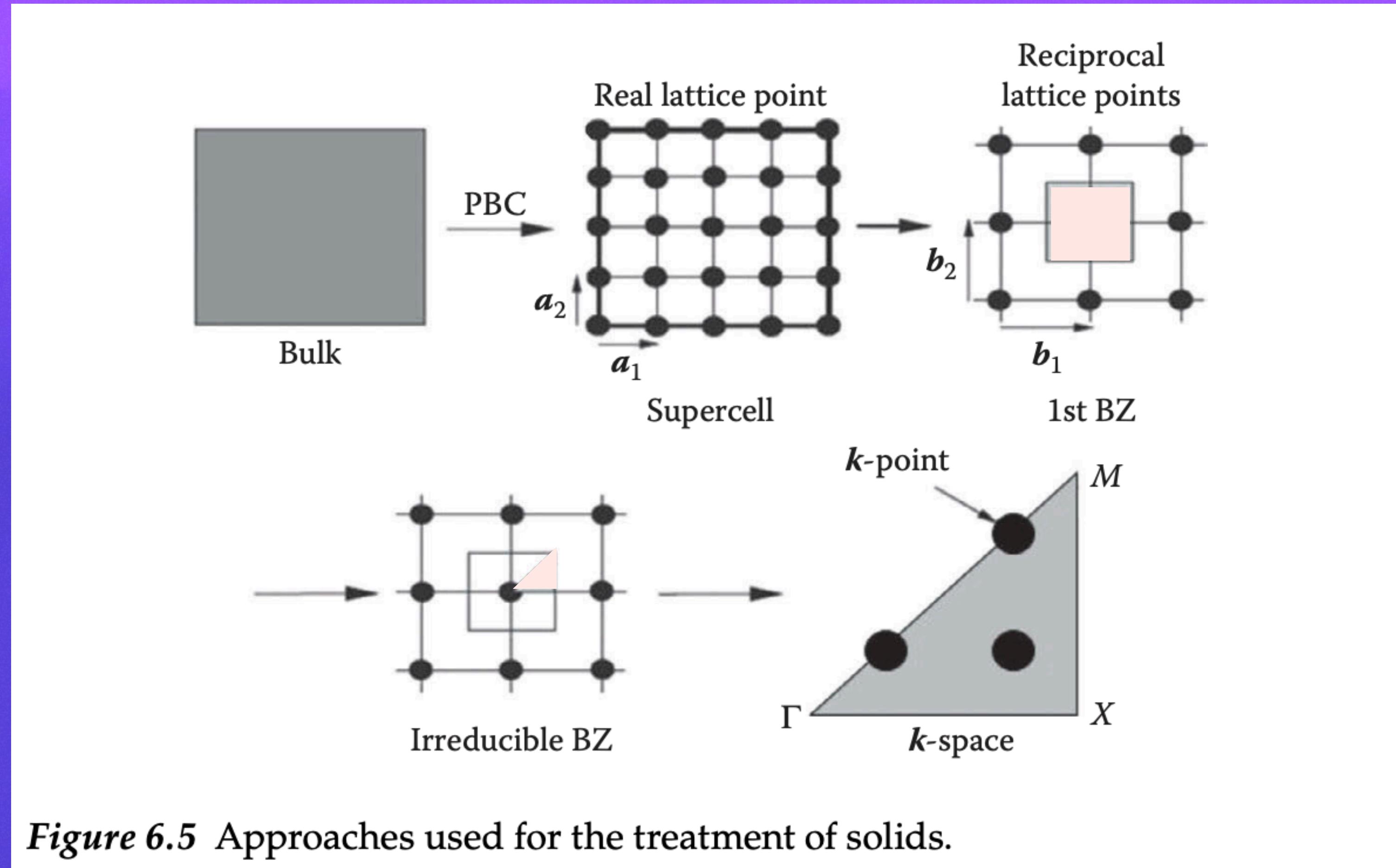
Symmetry and Periodicity

Reciprocal Space- Brillouin Zone



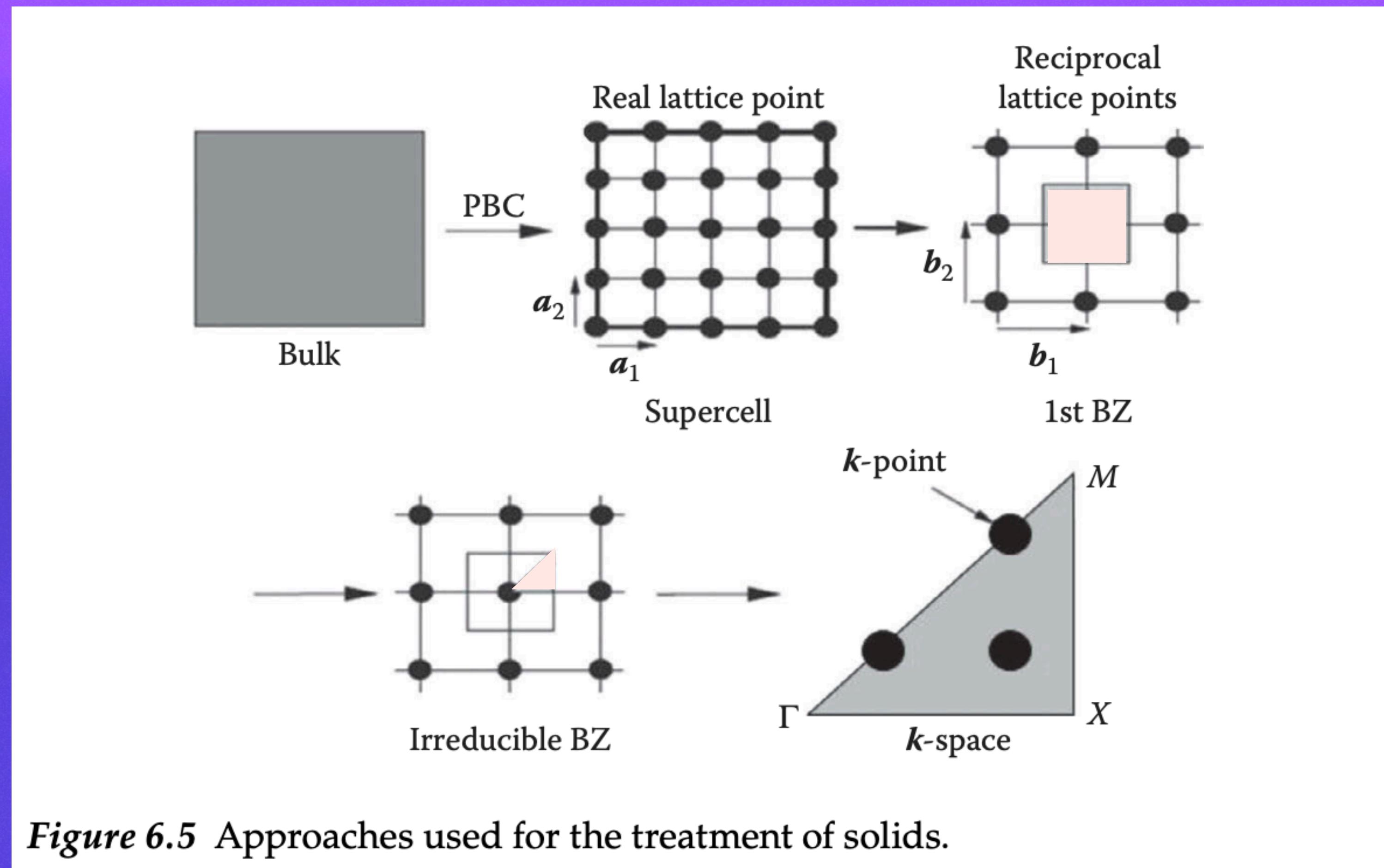
Symmetry and Periodicity

Reciprocal Space- Irreducible Brillouin Zone



Symmetry and Periodicity

Reciprocal Space- Brillouin Zone



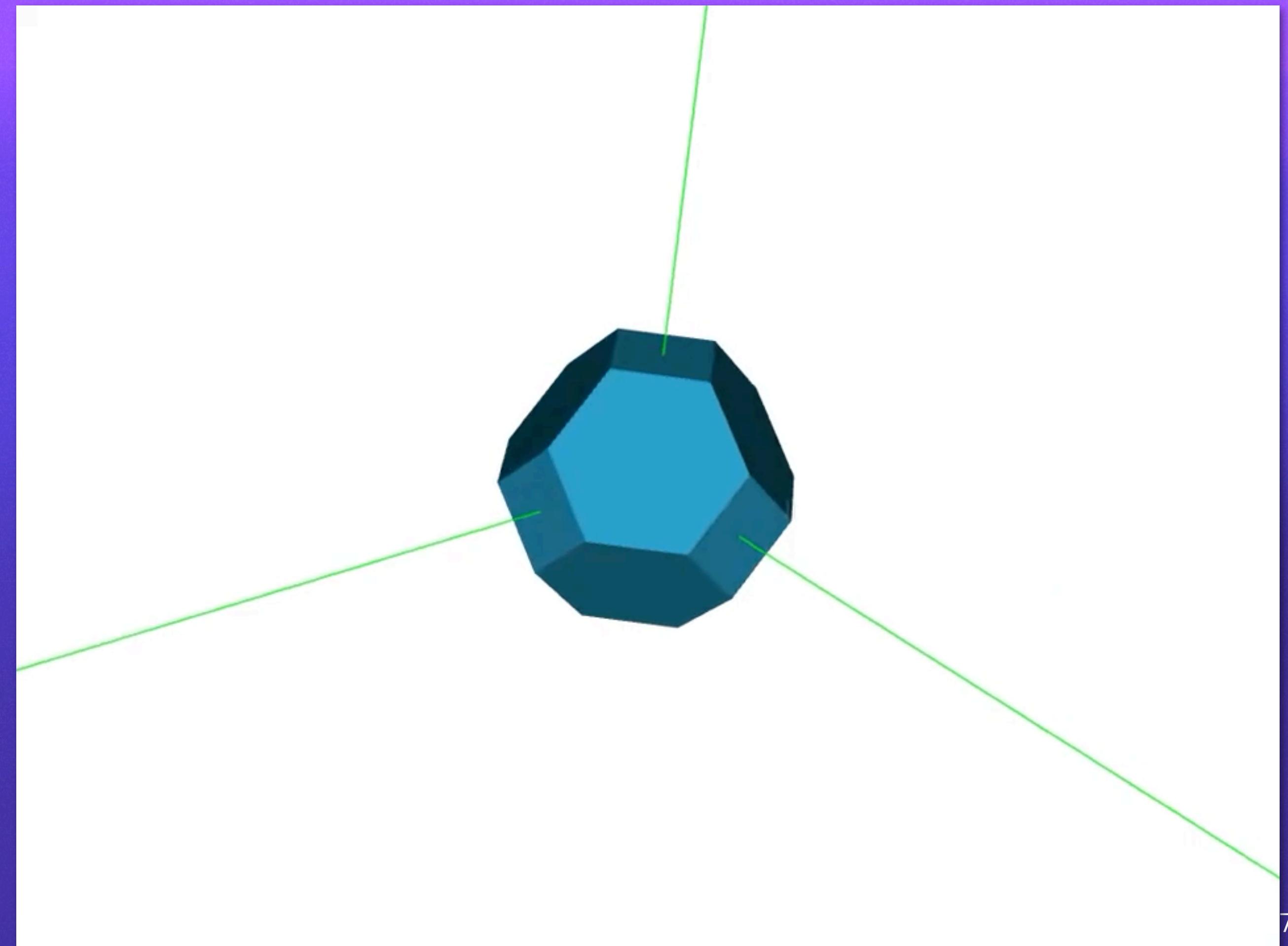
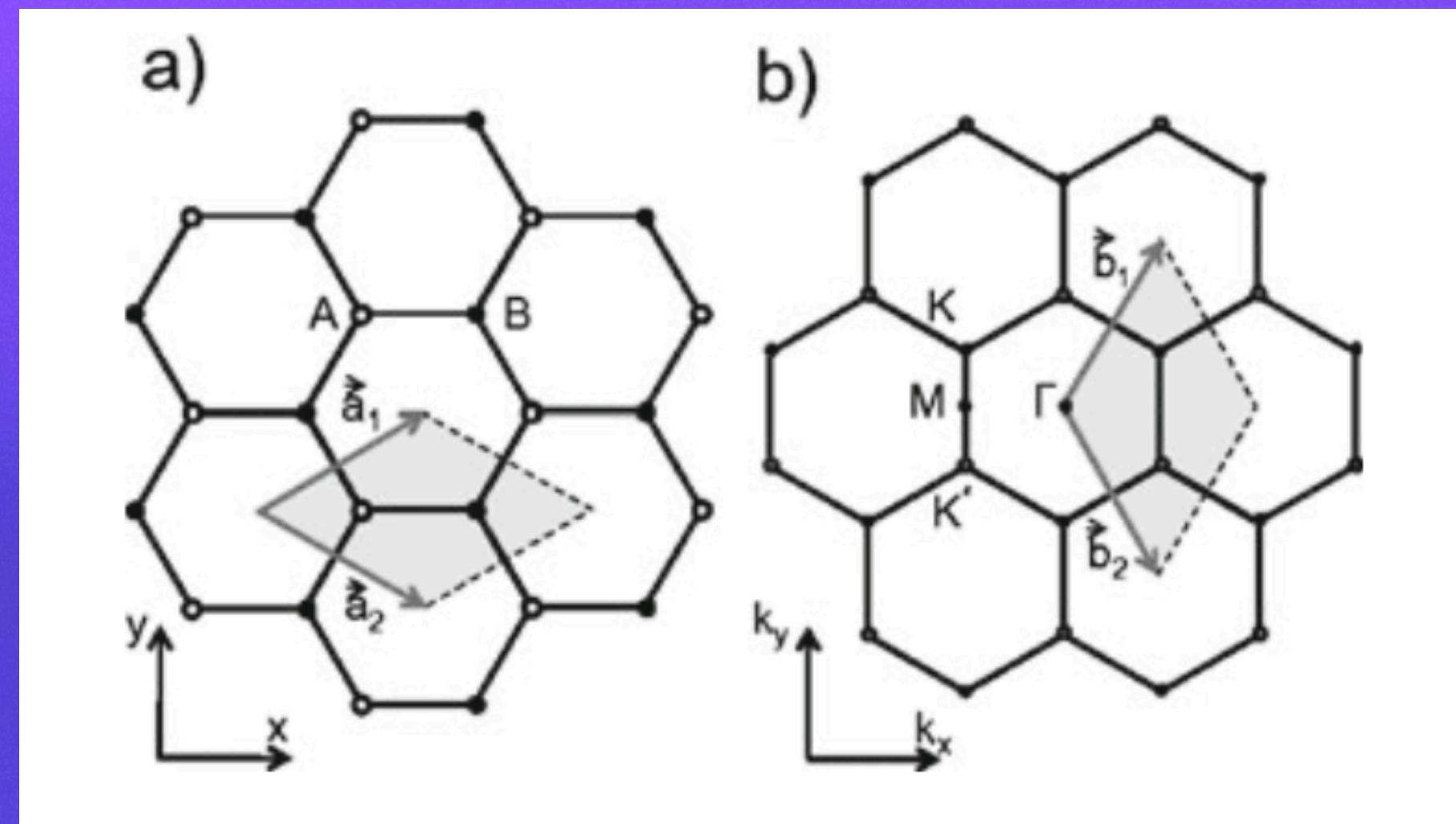
The 1st BZ is reduced to IBZ by symmetry operations without losing any information.

- The IBZ is mapped with discrete k-points, and all necessary quantities are obtained by integration/summation/extrapolation on these points.



Symmetry and Periodicity

Reciprocal Space for different symmetries



Bloch Theorem

Bloch Theorem

A consequence of the periodicity

- Periodicity in the real lattice



Valence Electrons like 'free electrons'

- Periodicity in the potential



$$\Psi(\mathbf{r}) = C \exp(i\mathbf{k} \cdot \mathbf{r})$$

- Periodicity of the density



Solution 'modulated' by a periodicity

- Periodicity of the wave function?



$$u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R}), \text{ then}$$

$$\Psi_k(\mathbf{r}) = u_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$$

$$\Psi_k(\mathbf{r} + \mathbf{R}) = \Psi_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{R})$$



I Can do it!

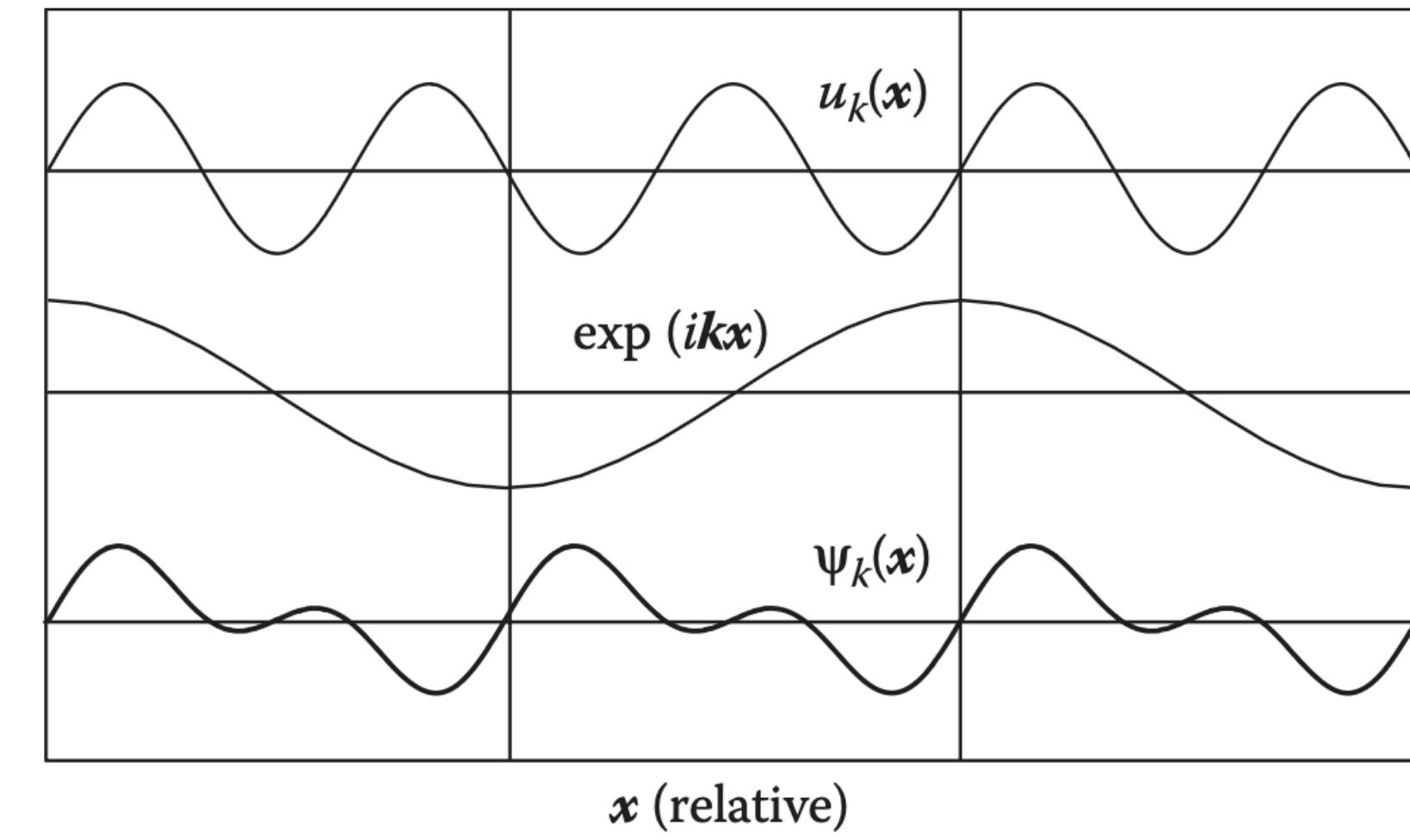
Bloch Theorem

A consequence of the periodicity

- Periodicity in the real lattice 
- Periodicity in the potential 
- Periodicity of the density 
- Periodicity of the wave function? 



I Can do it!



$$\Psi_k(\mathbf{r}) = u_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$$

$$\Psi_k(\mathbf{r} + \mathbf{R}) = \Psi_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{R})$$

Bloch Theorem

Expansion Fourier

$u_k(\mathbf{r})$ is a periodic function...

$$u_k(\mathbf{r}) = \sum_G c_k(G) \exp(i\mathbf{G} \cdot \mathbf{r})$$

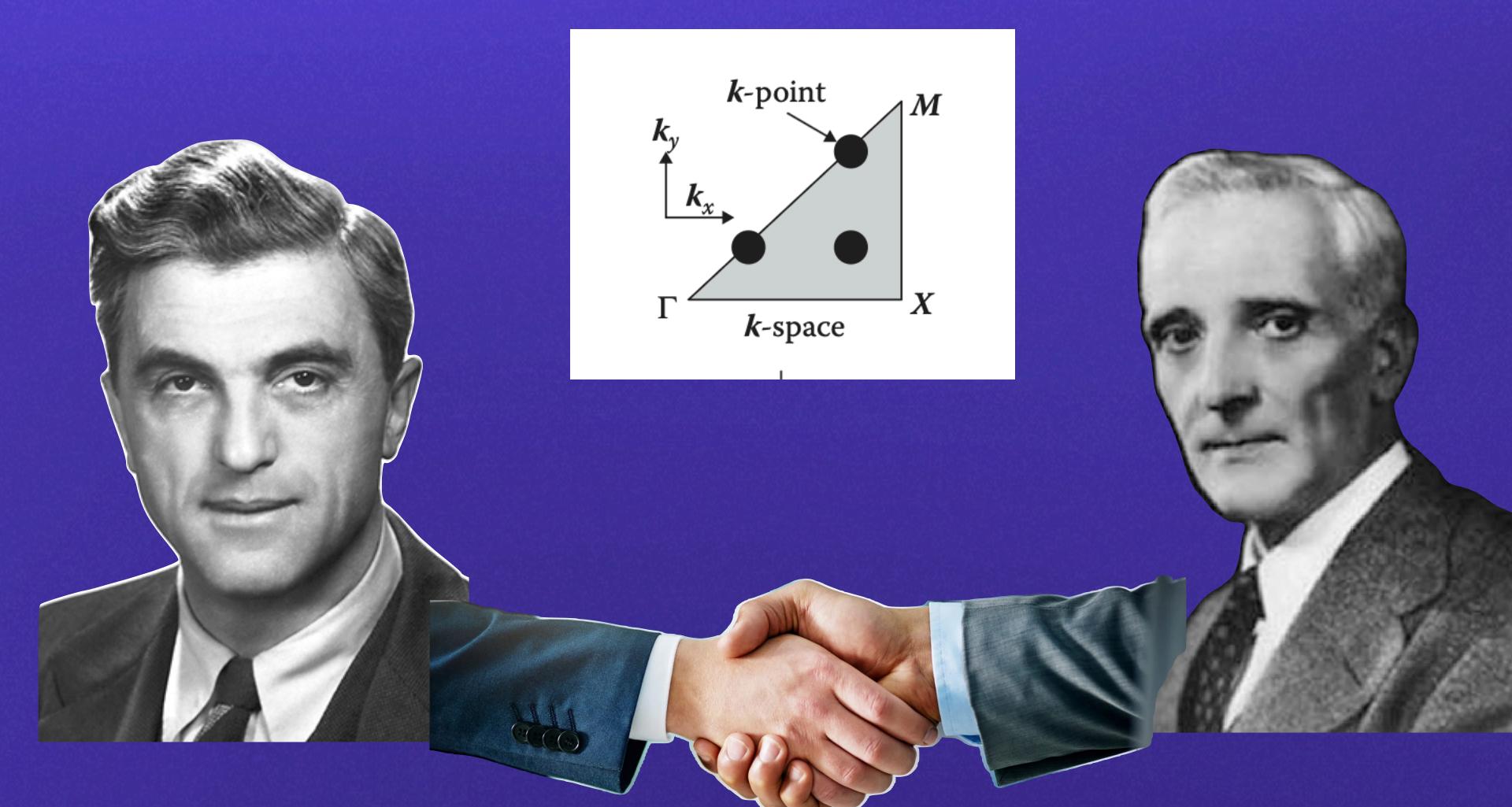
Then...

$$\Psi_k(\mathbf{r}) = u_k(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r})$$

$$\Psi_k(\mathbf{r}) = \sum_G c_k(G) \exp[i(\mathbf{G} + \mathbf{K}) \cdot \mathbf{r}]$$

This ensures the expansion perfectly matches the crystal's periodicity, because \mathbf{G} are the reciprocal lattice vectors.

The final result is that any electron state in a crystal can be expressed as a simple sum of plane waves. This makes the problem computationally feasible and is the foundation for most electronic structure calculations, like DFT.



Bloch Theorem

KS orbitals

Same Bloch idea, a periodic contribution

$$\phi_{jk}(\mathbf{r}) = \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{r}) \phi_j(\mathbf{r} - \mathbf{R})$$

Now we can transform the Schrödinger equation to reciprocal space:

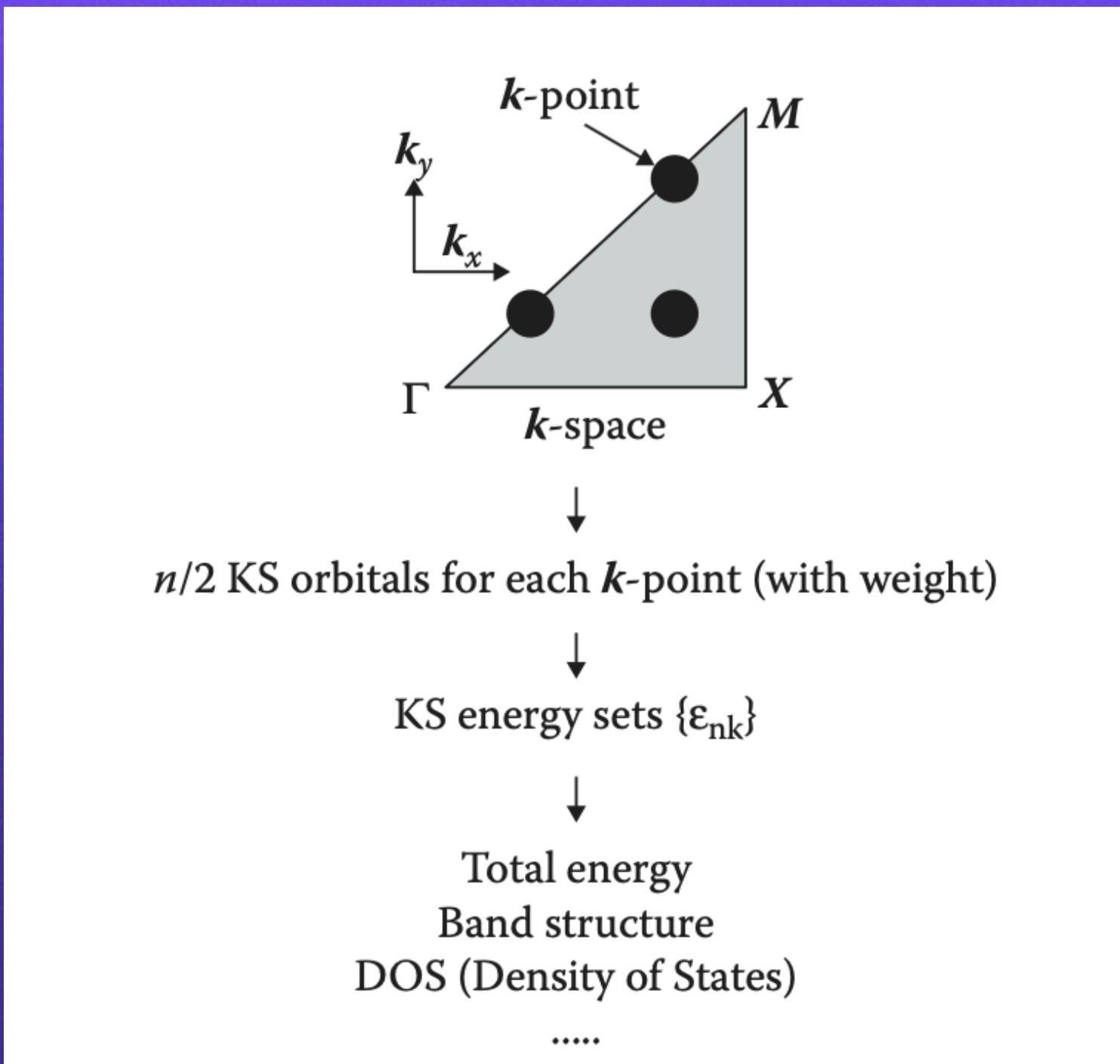
$$\hat{H}\Psi_{\alpha}(r) = E_{\alpha}\Psi_{\alpha}(r)$$

$$\sum_j c_{j\alpha} \hat{H} \phi_{jk}(r) = E_{\alpha} \sum_j c_{j\alpha} \phi_{jk}(r)$$

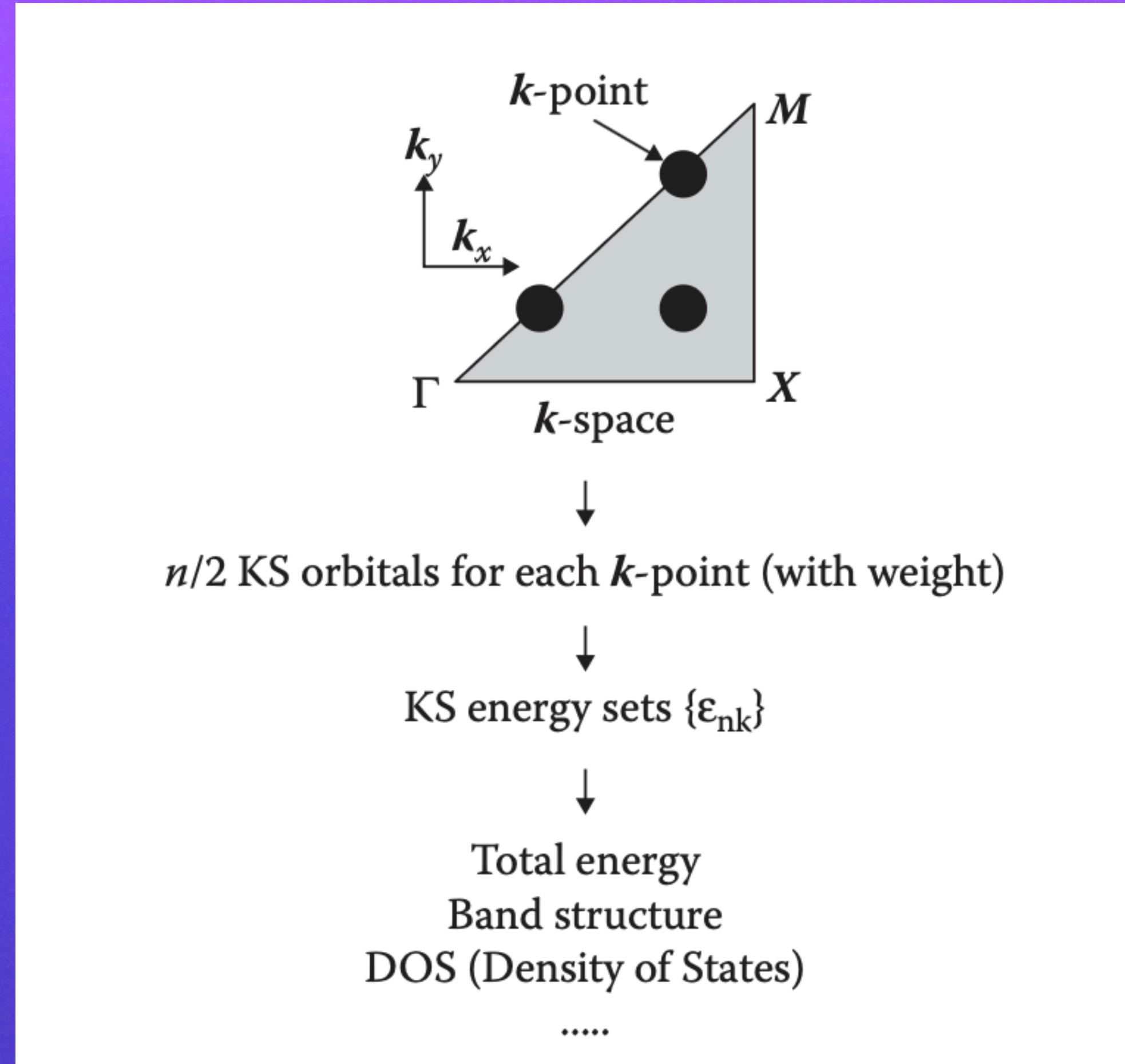
$$\sum_j c_{j\alpha} H_{lj}(\mathbf{k}) = E_{\alpha} \sum_j c_{j\alpha} S_{lj}(\mathbf{k})$$

The problem is decoupled. We solve a small, independent equation for each \mathbf{k} -point of interest in the Brillouin Zone.

$$|H(k_i) - E_{\alpha}S(k_i)| = 0$$

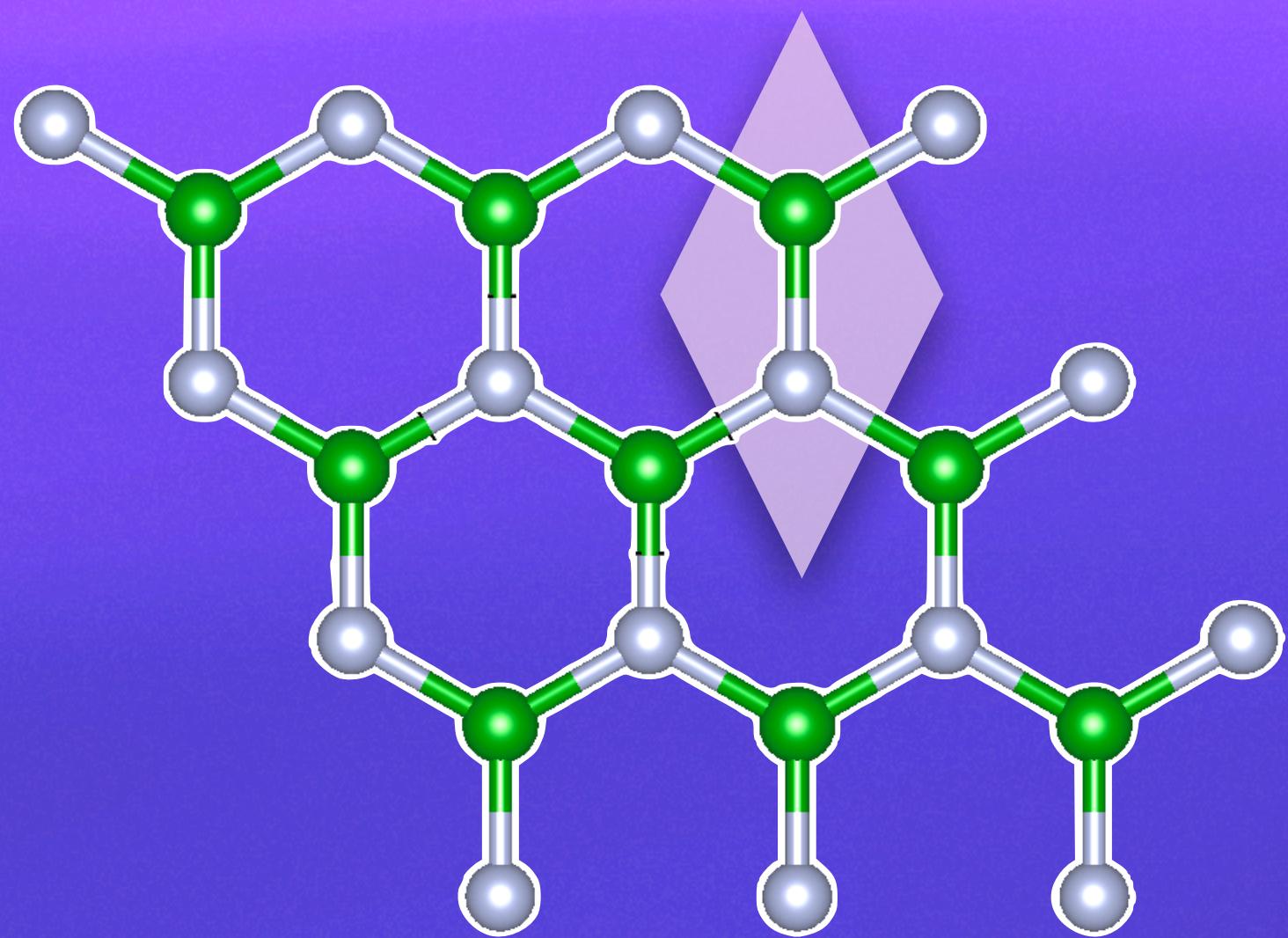


Band Structure



Band Structure

hBN Case



Boron (B): 3 valence electrons

Nitrogen (N): 5 valence electrons

Unit Cell: Contains 1 Boron atom and 1 Nitrogen atom.

$3 + 5 = 8$ valence electrons per unit cell.

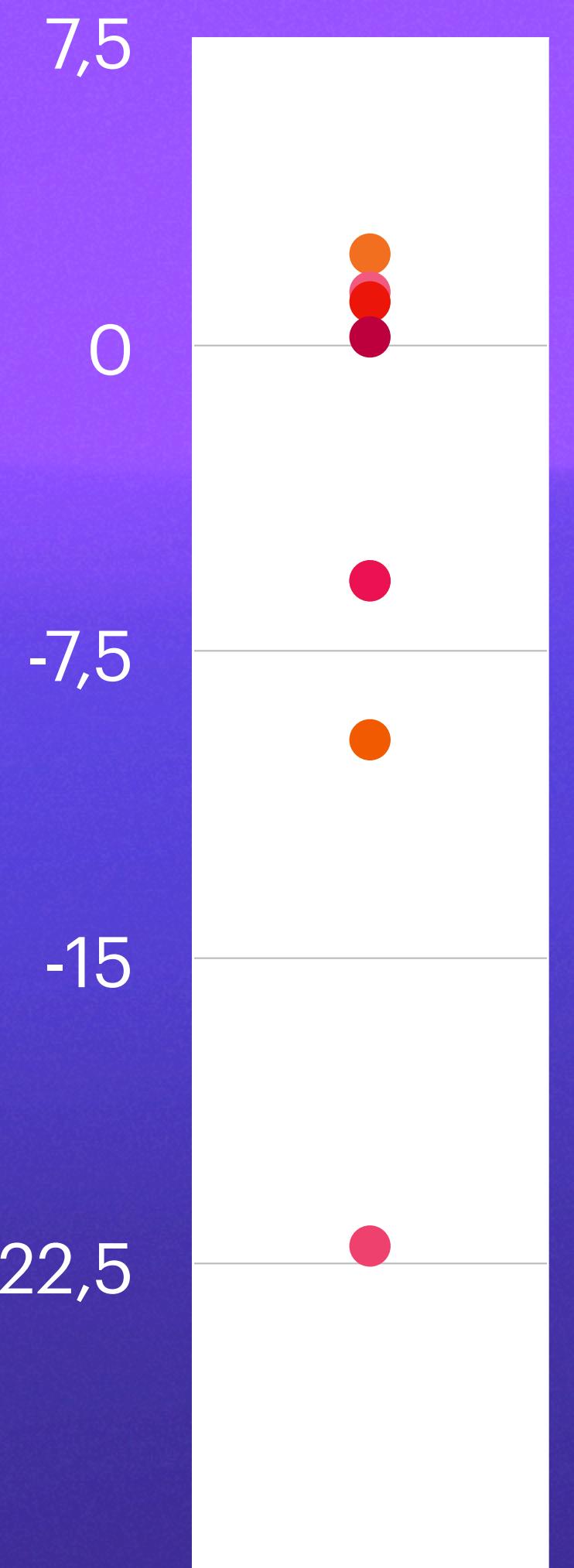
8 bands!

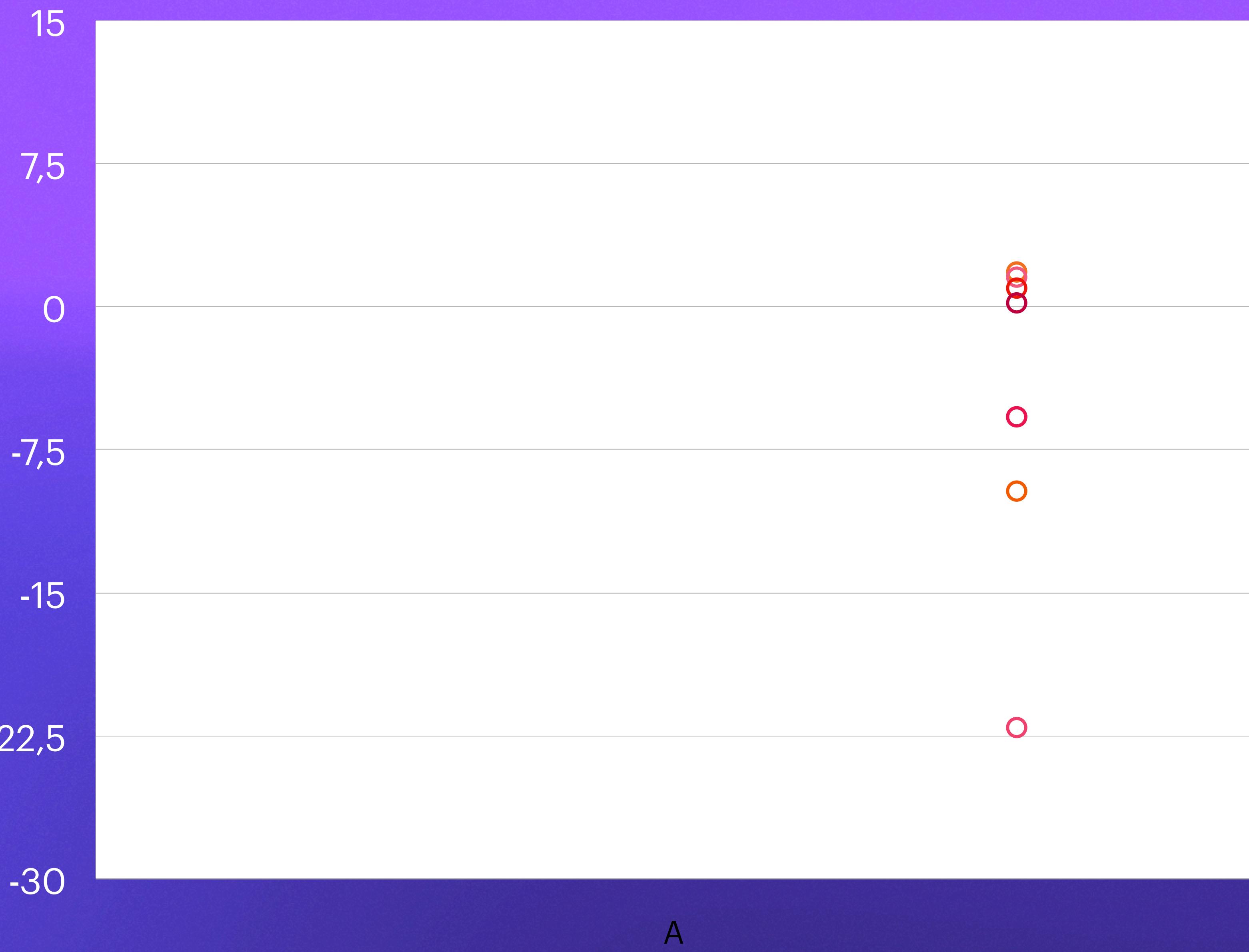
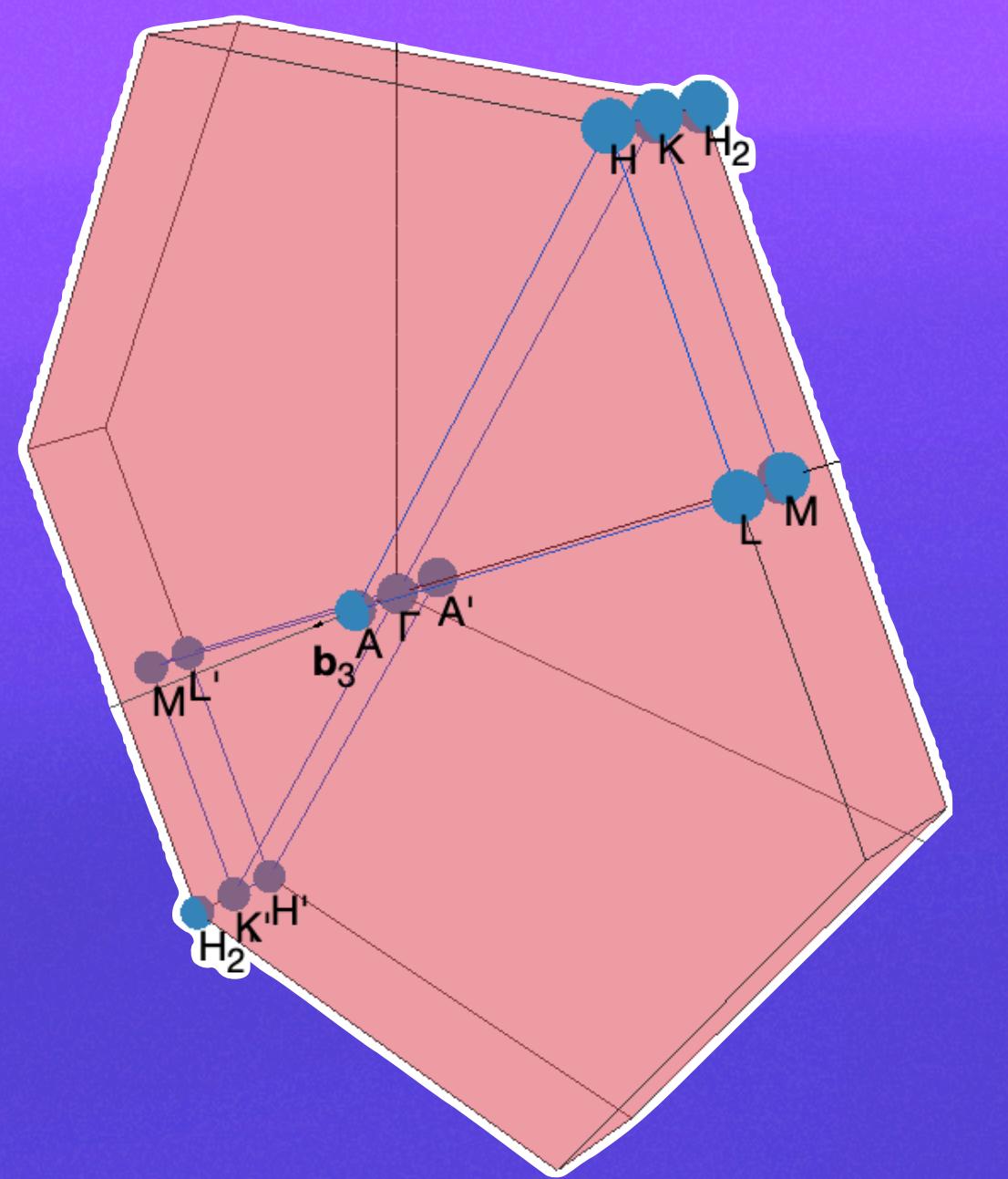
Band Structure

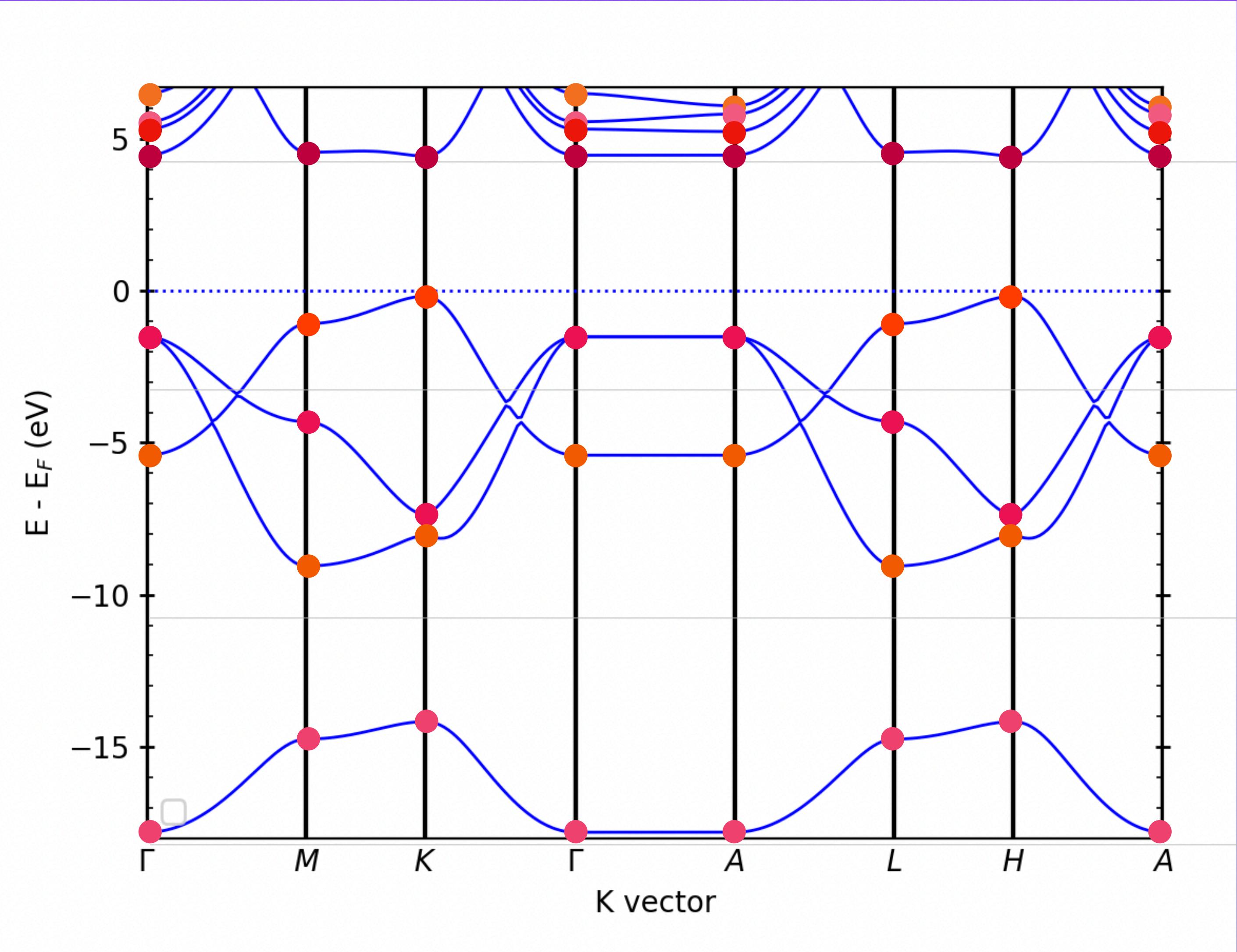
Energy calculation for Γ point

The problem is decoupled. We solve a small, independent equation for each **k**-point of interest in the Brillouin Zone.

$$|H(k_i) - E_\alpha S(k_i)| = 0$$

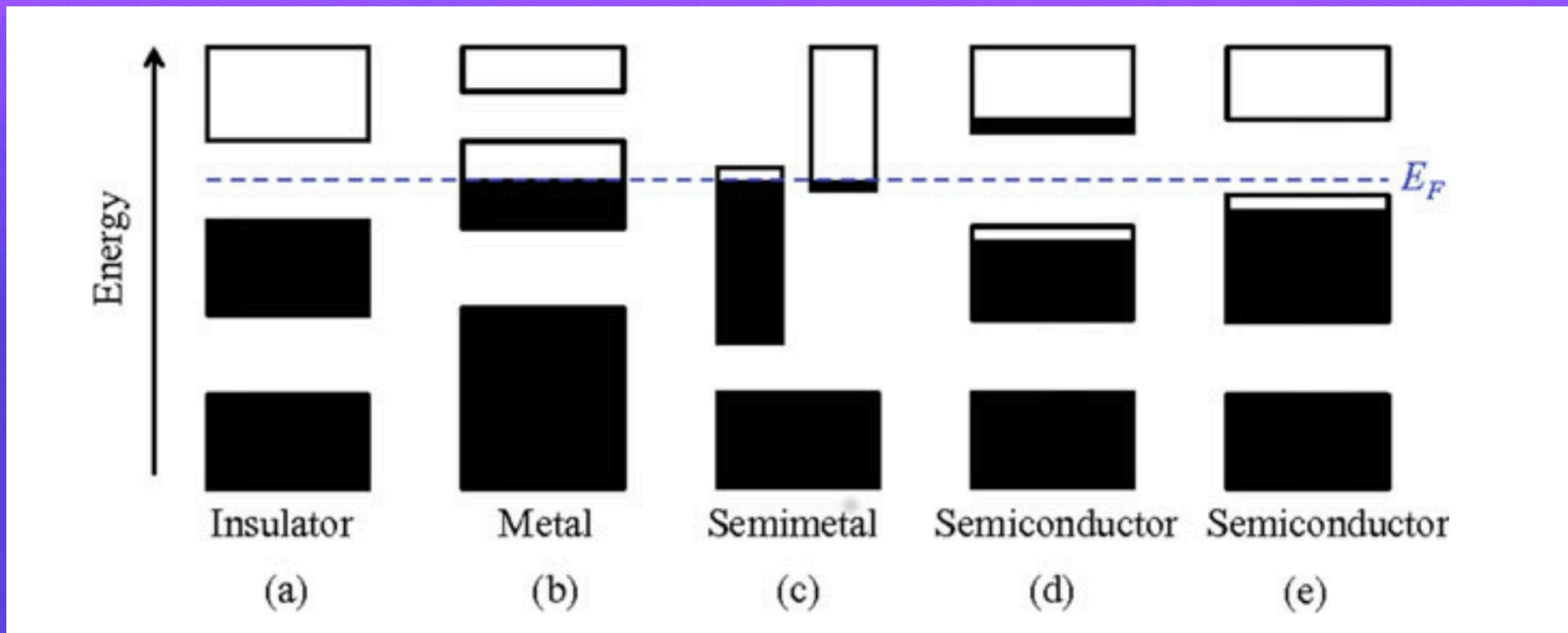






Band Structure

Interpretación





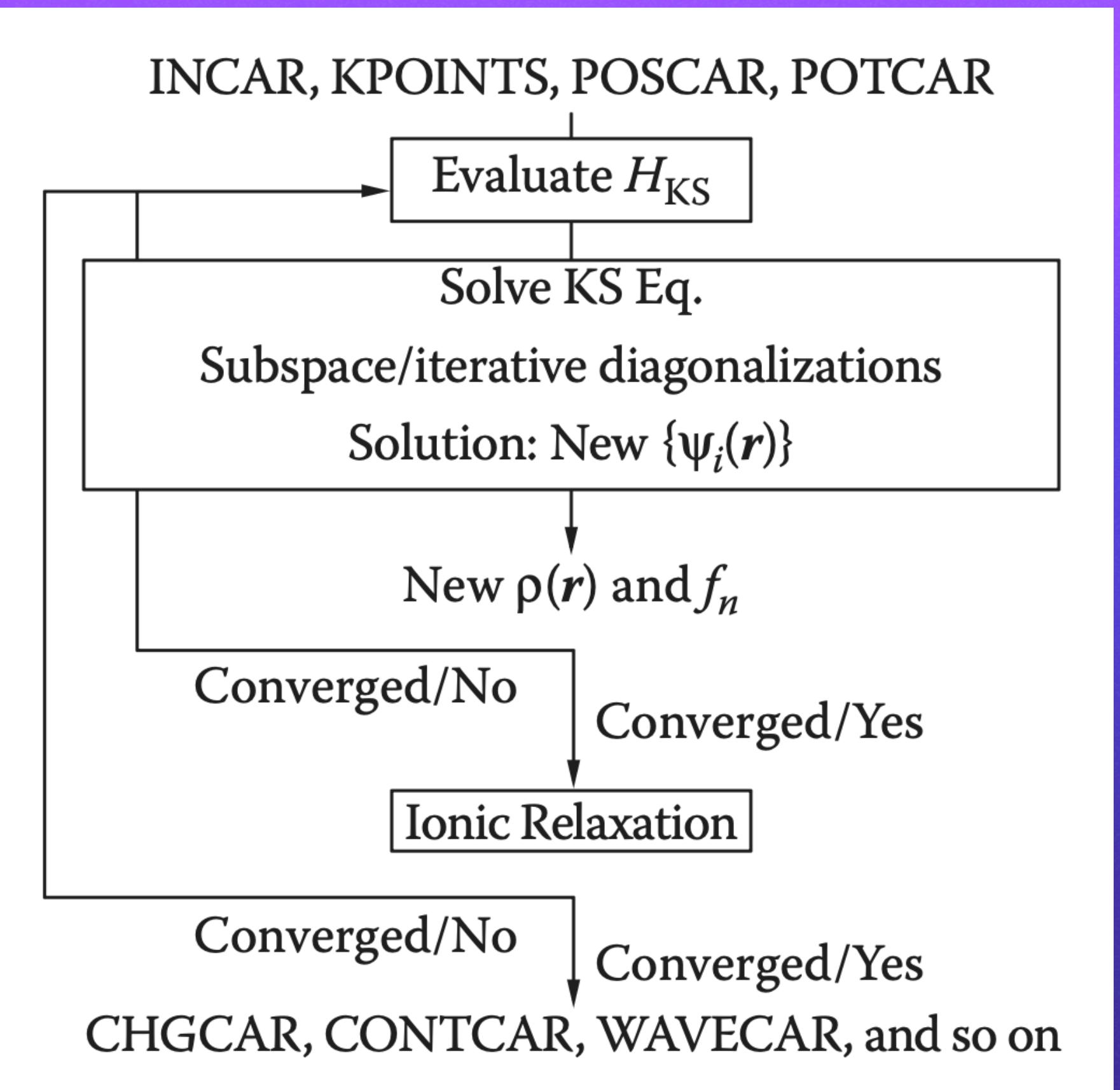
Coffee Break

Hands-on: VASP

Hand-on: VASP

Inputs files

- POSCAR
- INCAR
- KPOINTS
- POTCAR



Step 0: Perform convergence tests to correctly prepare the inputs.

Step 1: Ionic Relaxation

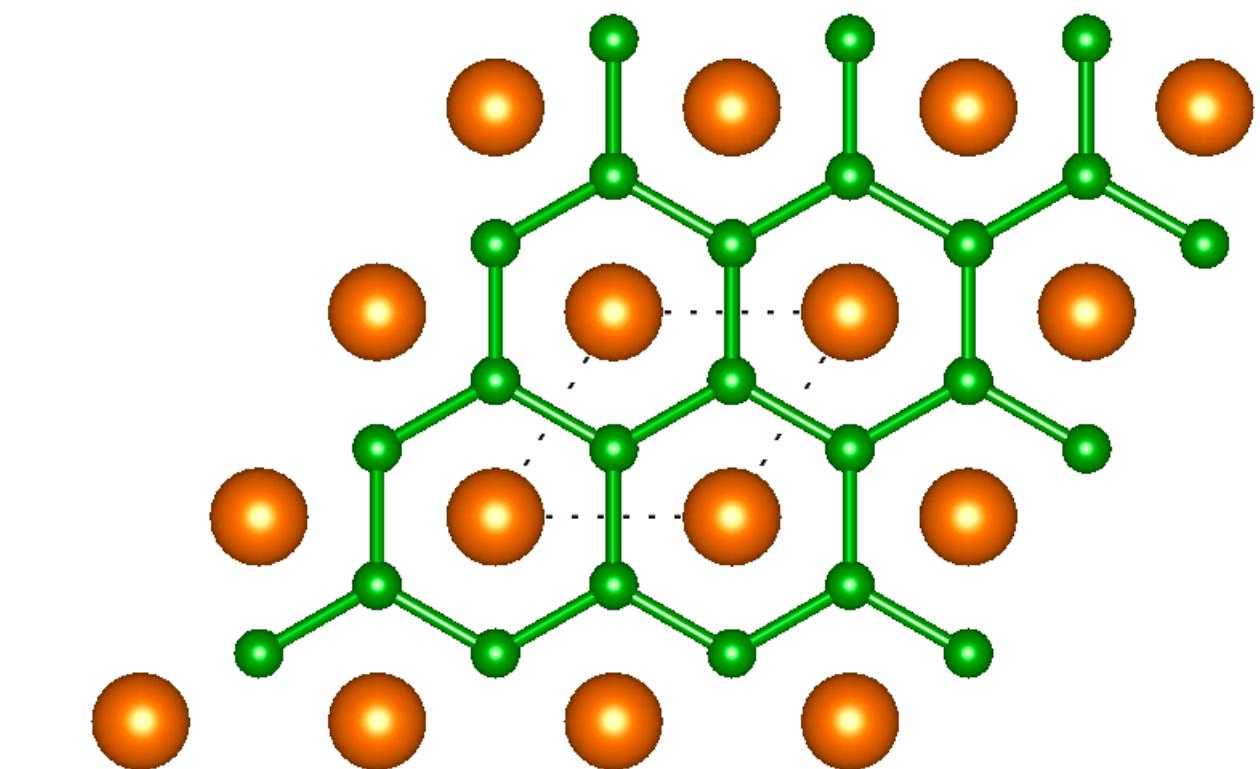
Step 2: SCF for the CHGCAR

Step 3: NSCF for bands

Hand-on: VASP

MgB₂

- Hexagonal Lattice
- Spacial group P6/mmm No. 191
- 3 atoms for unit cell
- Superconductor (Useful for tomorrow)



The Materials Project

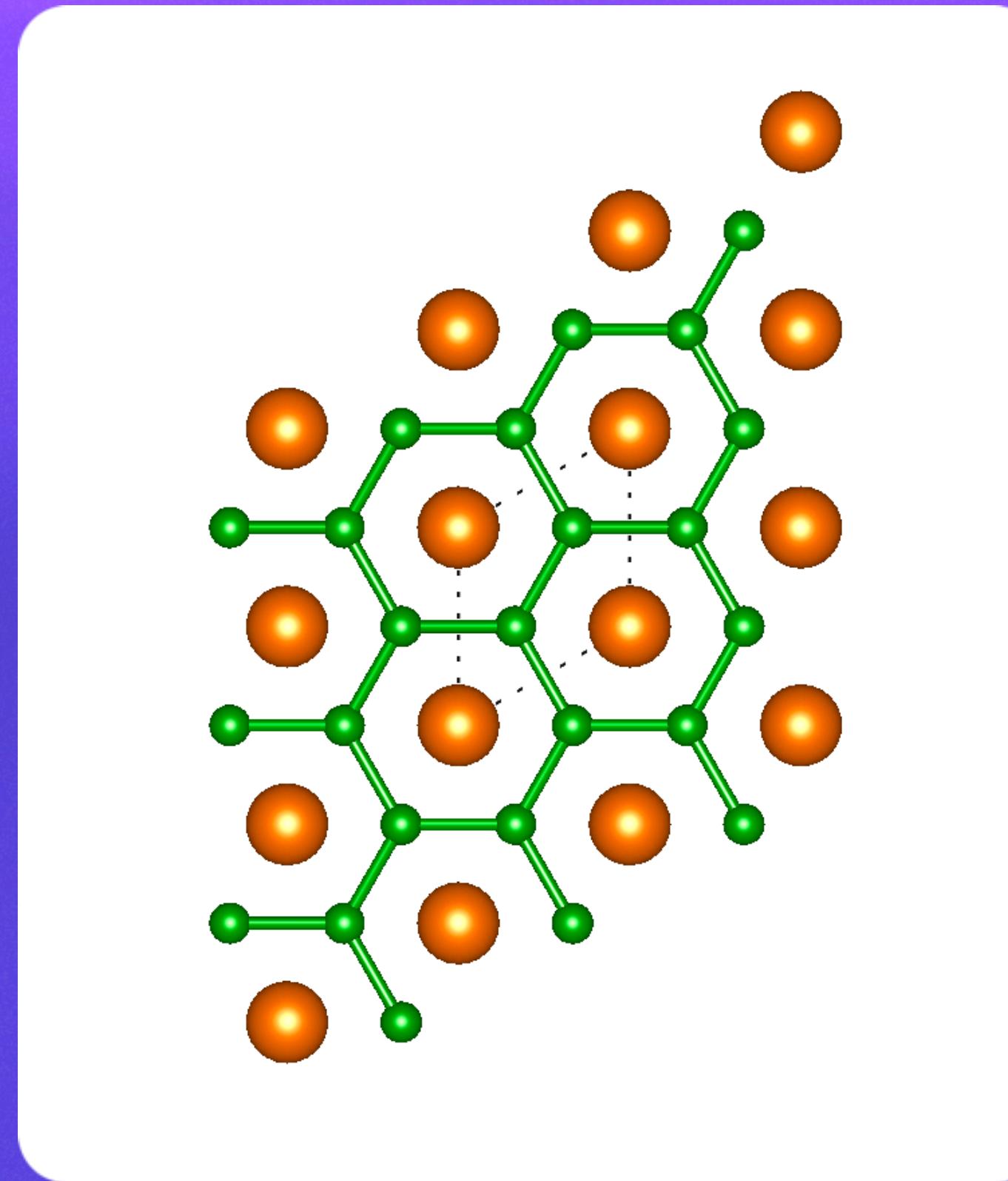
NOMAD

 **OQMD**
The Open Quantum
Materials Database

NEMAD
North East Materials Database

Hand-on: VASP

POSCAR



```
[student25@leftraru2 scf]$ less POSCAR
```

Mg1B2

| | | |
|--------------------|---------------------|--------------------|
| 1.000000000000000 | | |
| 1.5357094241588196 | -2.6599267483054190 | 0.000000000000000 |
| 1.5357094241588196 | 2.6599267483054190 | 0.000000000000000 |
| 0.000000000000000 | 0.000000000000000 | 3.5308220899090061 |

Mg B

1 2

Direct

| | | |
|--------------------|--------------------|-------------------|
| -0.000000000000000 | -0.000000000000000 | 0.000000000000000 |
| 0.6666666666666643 | 0.3333333333333357 | 0.500000000000000 |
| 0.3333333333333357 | 0.6666666666666643 | 0.500000000000000 |

Hand-on: VASP

POTCAR

Standard (Recommended)

- Includes the most important valence electrons.
- Suitable for most general-purpose calculations.
- Offers a good balance between accuracy and computational cost.

"Hard" & Specialized (_sv, _pv, _h, _GW)

- Provide higher accuracy by including more electrons (semicore) in the valence shell.
- They are significantly more computationally expensive.

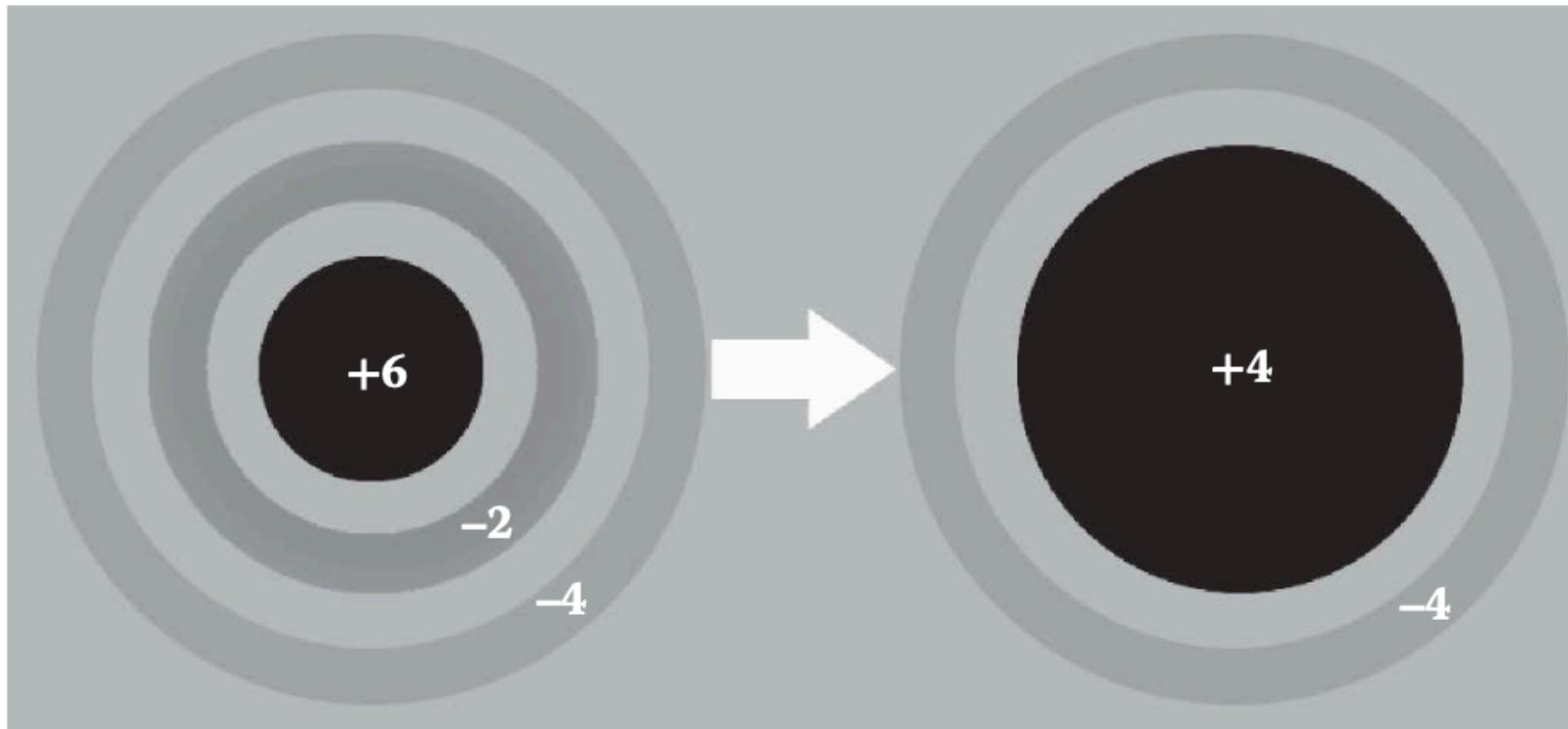


Figure 6.2 Atomic system of carbon showing the frozen core and valence electrons for the construction of a pseudopotential.

```
PAW_PBE Mg 13Apr2007
2.00000000000000
parameters from PSCTR are:
SHA256 = a90315392b5cf46bd986ff2010bfd53a40dec98e36f8d1f6277412e9d0e81a9f Mg/POTCAR
COPYR = (c) Copyright 13Apr2007 Georg Kresse
COPYR = This file is part of the software VASP. Any use, copying, and all other rights are regulated by
the VASP license agreement.
COPYR = If you do not have a valid VASP license, you may not use, copy or distribute this file.
VRHFIN =Mg: s2p0
LEXCH = PE
EATOM = 23.0369 eV, 1.6932 Ry
...
POMASS = 24.305; ZVAL = 2.000 mass and valenz
RCORE = 2.000 outmost cutoff radius
RWIGS = 2.880; RWIGS = 1.524 wigner-seitz radius (au A)
ENMAX = 200.000; ENMIN = 100.000 eV
```

Convergence Tests

Hand-on: VASP

ENCUT problem - Where do I stop summing?

$$\psi_k(r) = \sum_{|k+G| < cut} c_{k+G} \exp[i(k + G) \cdot r]$$

We only include in our sum those plane waves whose kinetic energy is less than E_{CUT} .

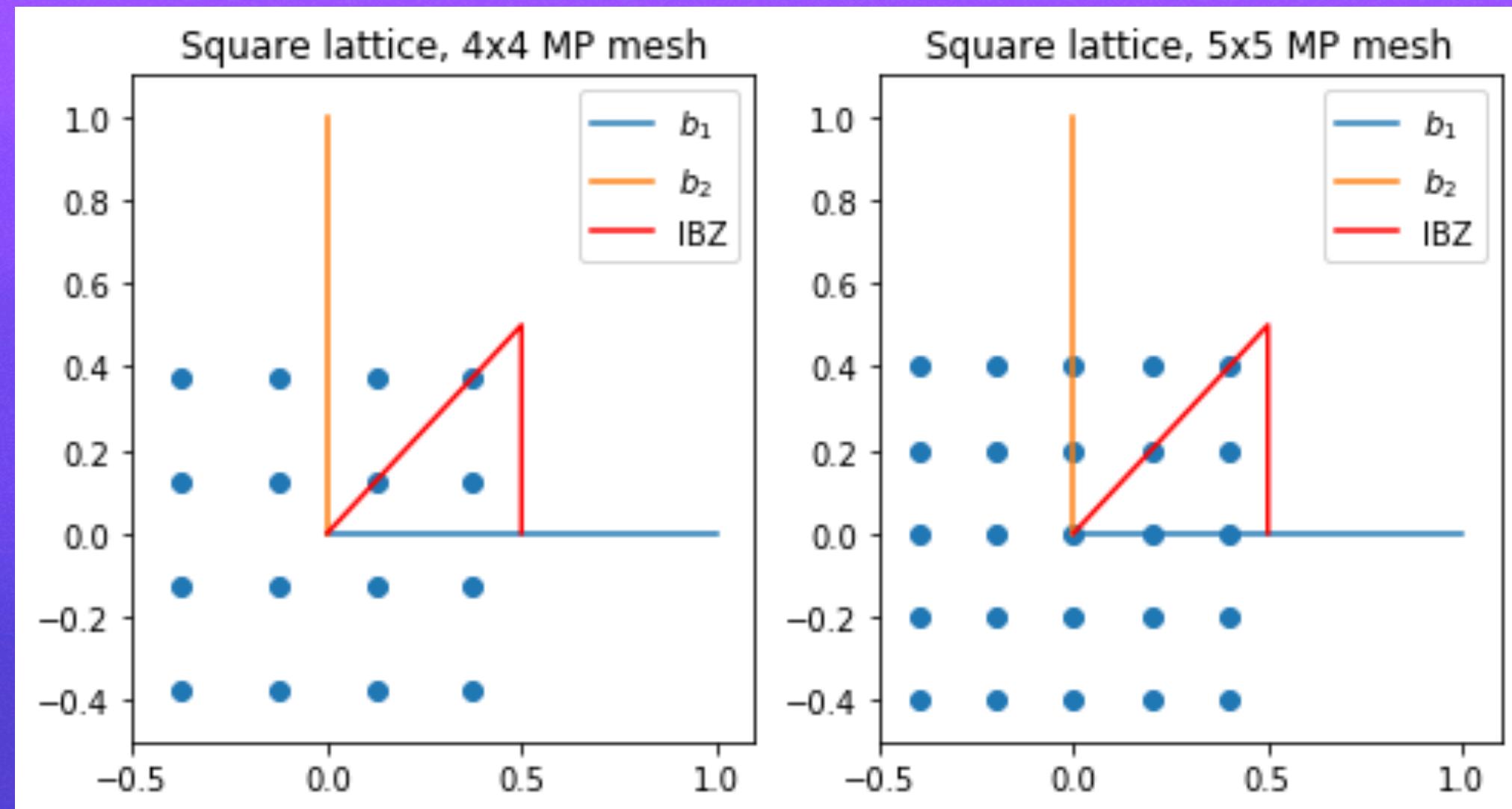
$$E_{kin} = \frac{1}{2} |k + G|^2 < E_{CUT}$$

```
ISTART = 0      ! doesn't read the WAVECAR file
ENCUT = 500     ! energy cutoff for the plane-wave basis in eV
ISMEAR = 0       ! method for the partial occupancies on each
                  orbital (=0 Gaussian smearing)
SIGMA = 0.01    ! width of the smearing in eV
EDIFF = 1e-8     ! global break condition for the electronic SC-
                  loop in eV

LORBIT = 11
LREAL = False
LWAVE = False
NPAR = 2
```

Hand-on: VASP

KPOINTS - How to star?



```
Regular 4 x 4 x 3 mesh centered #linea de comentario  
0  
Gamma  
4 4 3
```

Given reciprocal vector lengths with a ratio of
0.4 : 0.4 : 0.2:

- The normalized ratio is calculated by dividing by the smallest value (0.2), which gives **2 : 2 : 1**.
- **Rule:** We need more k-points for longer reciprocal vectors to maintain a uniform sampling density.
- **Conclusion:** The k-point mesh should follow this 2 : 2 : 1 ratio (e.g., 8x8x4, 10x10x5, etc.).

Hand-on: VASP

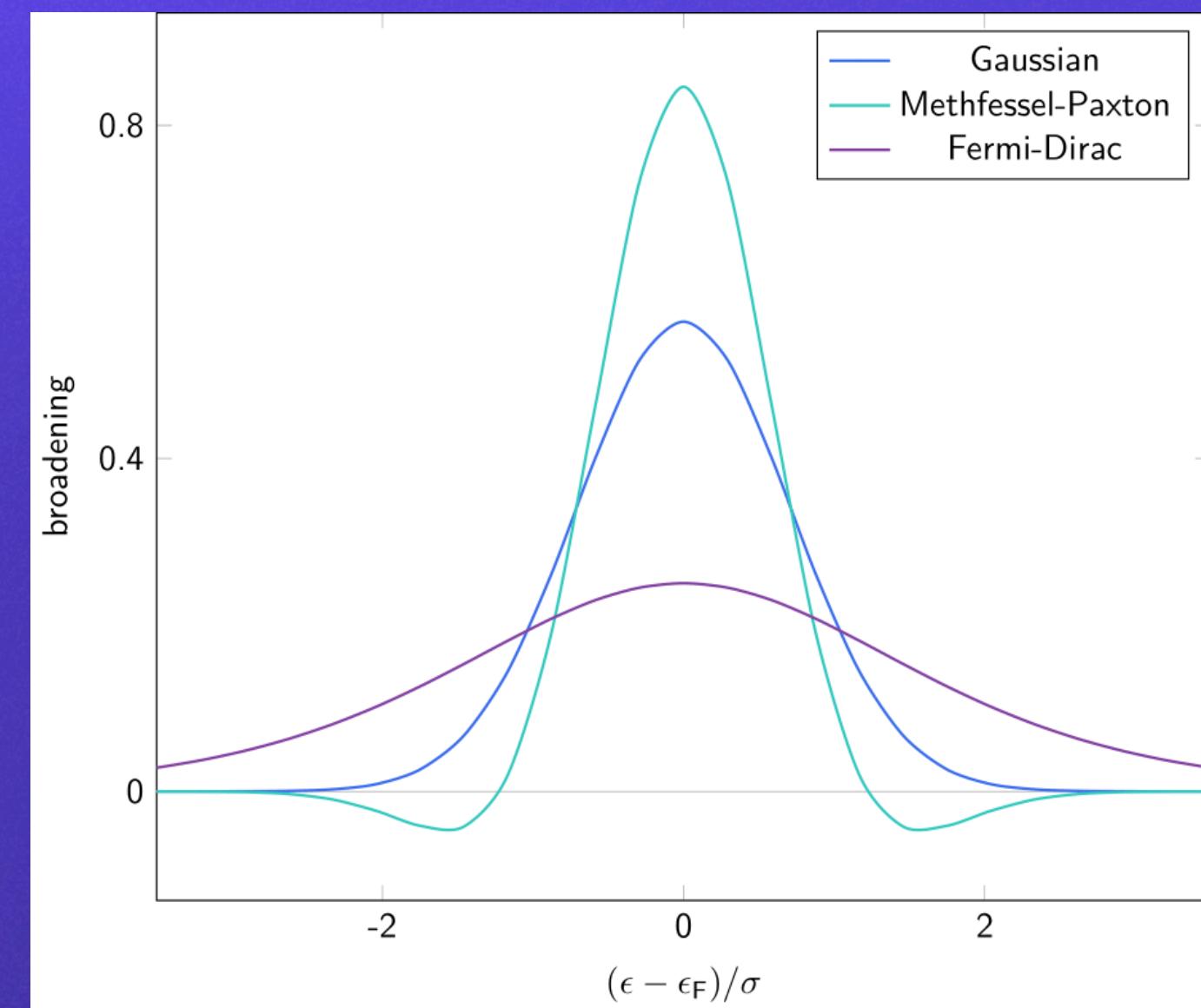
Other important tag: Smearing

Problem in Metals: Electron occupation drops abruptly ($1 \rightarrow 0$) at the Fermi level, requiring dense and computationally expensive k-point meshes to converge.

Solution (Smearing): It smears the occupation of electrons near the Fermi level to improve the stability and speed of the calculation.

```
ISTART = 0      ! doesn't read the WAVECAR file
ENCUT = 500      ! energy cutoff for the plane-wave basis in eV
ISMEAR = 0       ! Util si no sabes que es, 1 y 2 for metals:
                  method of Methfessel-Paxton
SIGMA = 0.01     ! width of the smearing in eV
EDIFF = 1e-8      ! global break condition for the electronic SC-
                  loop in eV

LORBIT = 11
LREAL = False
LWAVE = False
NPAR = 2
```



Smearing technique

Page [Discussion](#)

How to set ISMEAR

Hand-on: VASP

Structural Relaxation

Prerequisites: Ensure **ENCUT** and **KPOINTS** are converged from previous static calculations.

INCAR Setup: Add new tags required for relaxation (e.g., **IBRION**, **NSW**, **ISIF**).

Post-Relaxation Checklist: Review **OUTCAR** for convergence, **CONTCAR** for the new atomic positions, and **CHGCAR** for the final charge density.

```
SYSTEM = RELAX (ENCUT = 300, 12x12x9)
ISTART = 0           ! don't read WAVECAR
ENCUT = 300 ! energy cutoff
ISMEAR = 0           ! Gaussian smearing
SIGMA = 0.2          ! width of the smearing
EDIFF = 1e-6          ! electronic convergence

LORBIT = 11
LREAL = False
LWAVE = False

# Relax
NSW = 10            ! max number of ionic steps
IBRION = 2           ! ionic relaxation (conjugate gradient algorithm)
ISIF = 3             ! relajar todo
EDIFFG = -1E-2        ! break condition for the ionic relaxation loop
NELM = 100           ! max number of electronic SC steps
```

Hand-on: VASP

Bands Calculation

Prerequisites: Start with a converged self-consistent calculation (SCF or relaxation). You must have the converged **CHGCAR** file.

INCAR Setup: Modify the **INCAR** for a non-self-consistent run. Key tags include **ICHARG = 11** (to read the fixed charge density) and an appropriate **ISMEAR** for band structures (e.g., **ISMEAR = 0**).

```
SYSTEM = RELAX (ENCUT = 300, 12x12x9)
ISTART = 0           ! don't read WAVECAR
ENCUT = 300 ! energy cutoff
ISMEAR = 0           ! Gaussian smearing
SIGMA = 0.1          ! width of the smearing
EDIFF = 1e-6          ! electronic convergence

LORBIT = 11
LREAL = False
LWAVE = False

# Relax
#NSW = 10           ! max number of ionic steps
#IBRION = 2          ! ionic relaxation (conjugate gradient algorithm)
#ISIF = 3           ! relajar todo
#EDIFFG = -1E-2       ! break condition for the ionic relaxation loop
#NELM = 100          ! max number of electronic SC steps

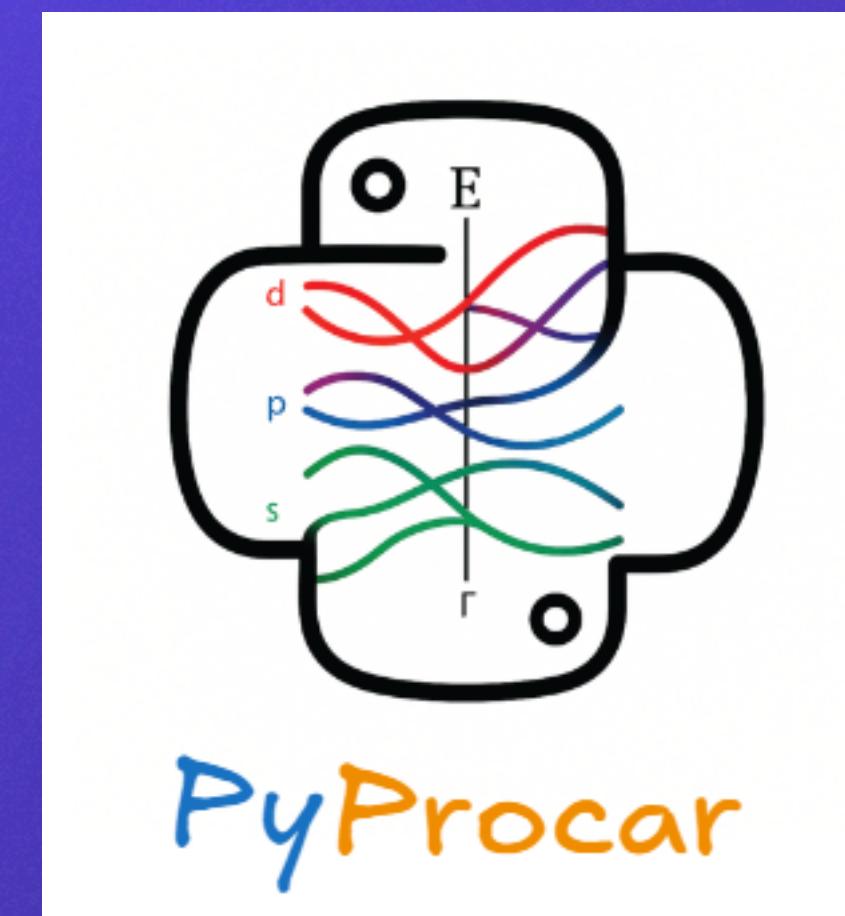
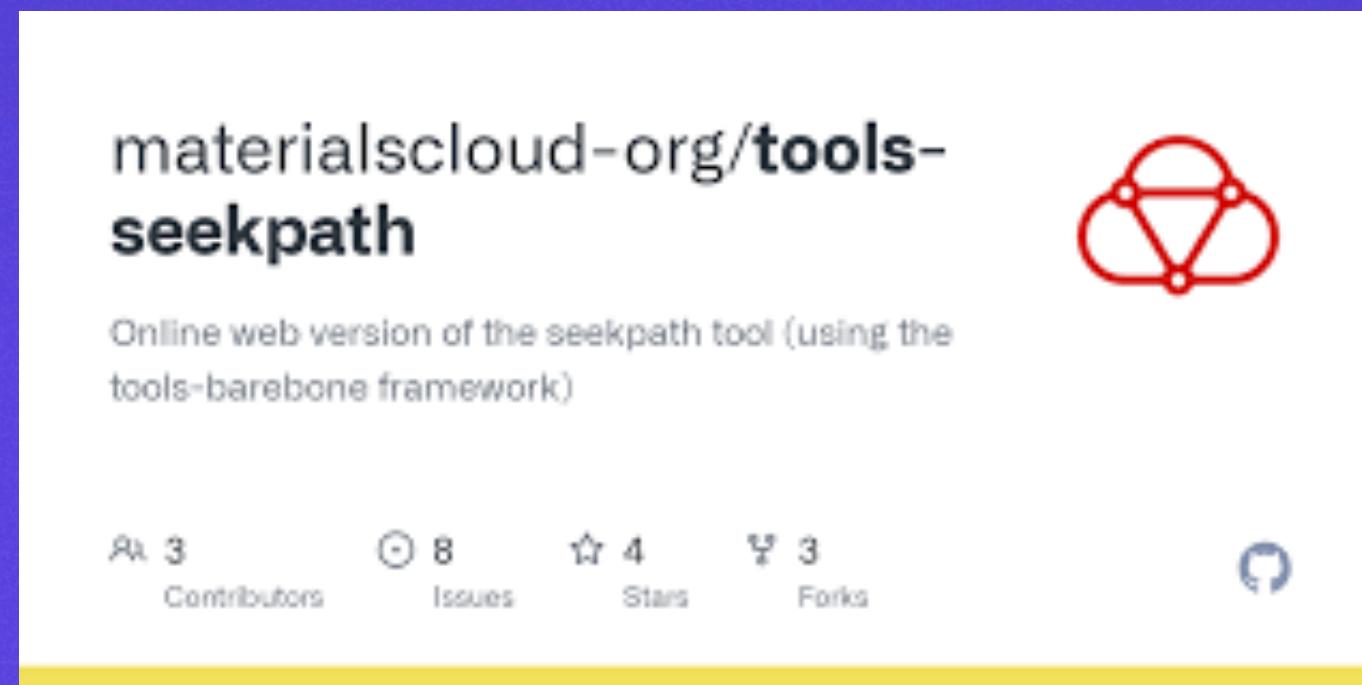
ICHARG=11
```

Hand-on: VASP

Bands Calculation

KPOINTS File: Replace the standard k-point mesh with a new file defining the path along high-symmetry lines in the Brillouin Zone.

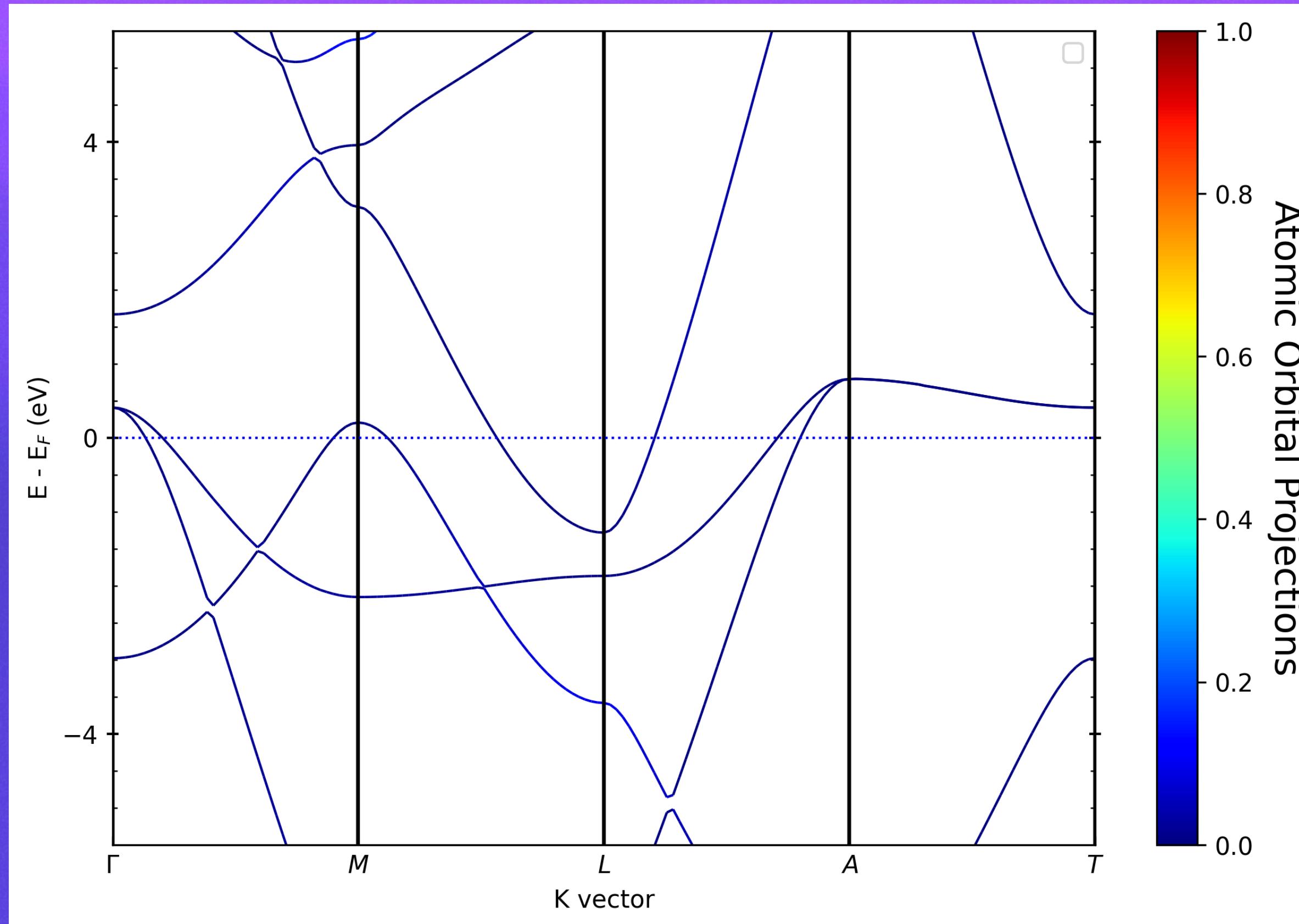
Post-Calculation Checklist: Use Pyprocar



```
K-Path Gamma-M-L-A-T  
40  
Line-mode  
reciprocal  
0.000000000 0.000000000 0.000000000 Gamma  
0.500000000 0.000000000 0.000000000 M  
  
0.500 0 0 M  
0.5 0 0.5 L  
  
0.500000000 0.000000000 0.500000000 L  
0.000000000 0.000000000 0.500000000 A  
  
0 0 0.5 A  
0.000000000 0.000000000 0.000000000 T
```

Hand-on: VASP

Bands Calculation- Post processing



```
import pyprocarr
import numpy as np
import matplotlib.pyplot as plt

fermi_energy= 5.3669
pyprocarr.bandsplot(code='vasp',
                     dirname='./',
                     elimit=[-8.5,8.5],
                     mode='plain',
                     color='pink',
                     fermi= fermi_energy,
                     savefig='./bands1.png',
                     show=False,
                     print_plot_opts=True)

pyprocarr.bandsplot(code='vasp',
                     dirname='./',
                     elimit=[-5.5,5.5],
                     mode='parametric',
                     atoms=[0],
                     orbitals=[1,3],
                     fermi= fermi_energy,
                     savefig='./bands2.png',
                     show=False,
                     print_plot_opts=True)
```