

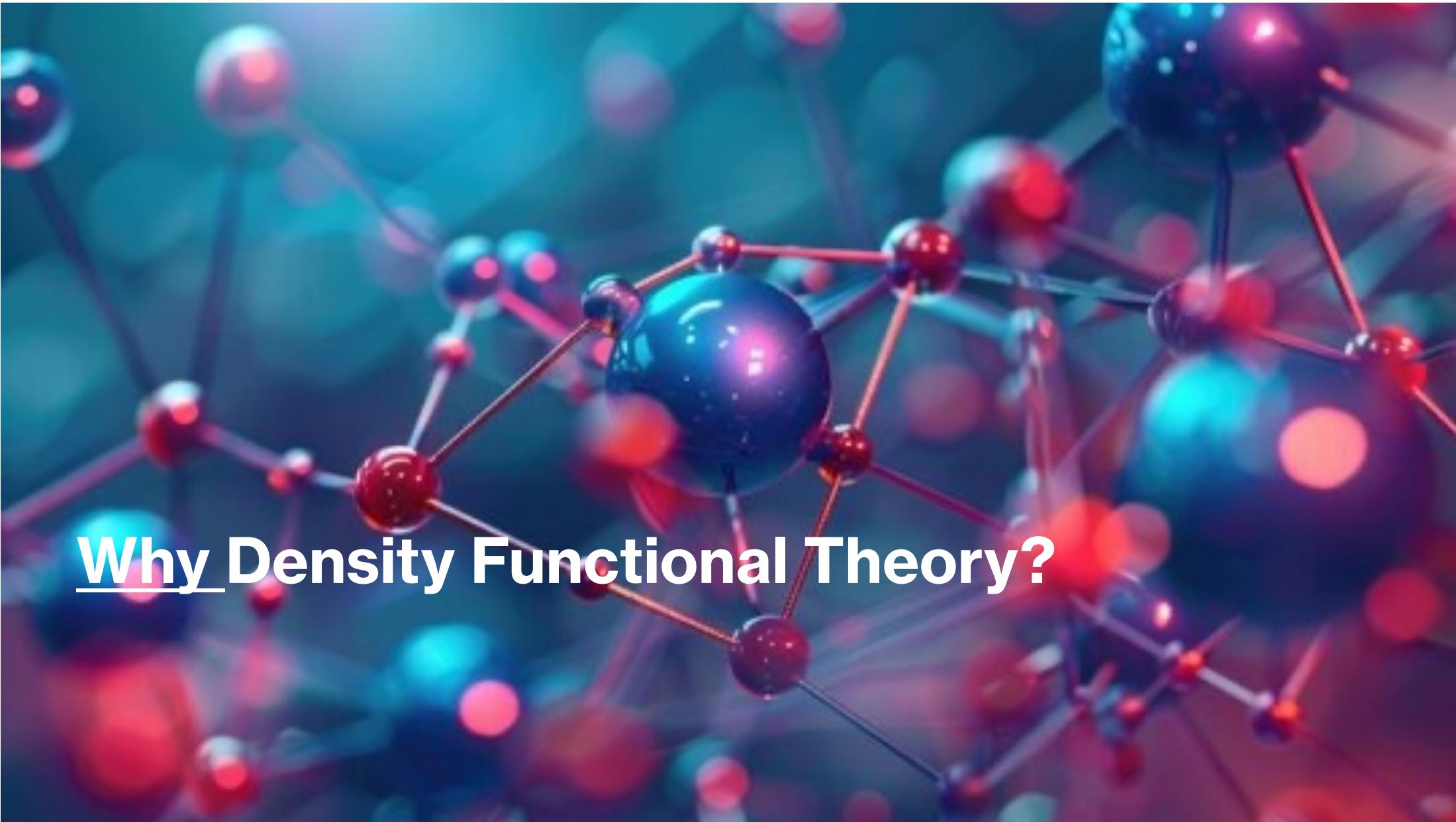
# Computational Solid State Physics, part II

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# Outline

- **Why Density Functional Theory?** Content and Structure of the Course
- **Practical Information:** References and Software Requirements
- **Theoretical Background:** Recap of useful Theoretical Concepts
- **Questions**

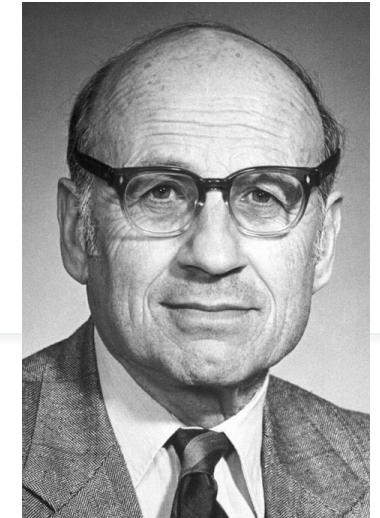
# Why Density Functional Theory?



# Density Functional Theory

## ➤ Key Concepts:

- **Density Functional Theory** is considered the workhorse method to compute the electronic and vibrational properties of solids, and their response to external perturbations - ***ab-initio* method**.
- DFT provides a formally exact mapping of an interacting electron system onto a **system of non-interacting effective quasi-particles** (Kohn-Sham quasi-particles) – **single particle approximation**.
- It provides a reliable approximation to the **ground-state energy** and **charge density** of a system of interacting ions and electrons – **ground-state theory**.

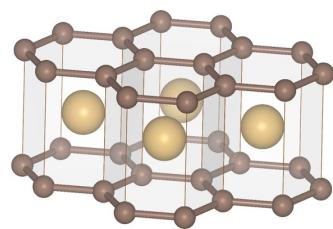
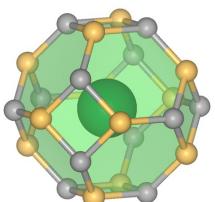


Walter Kohn, Nobel Prize in Chemistry (1998).

# Density Functional Theory

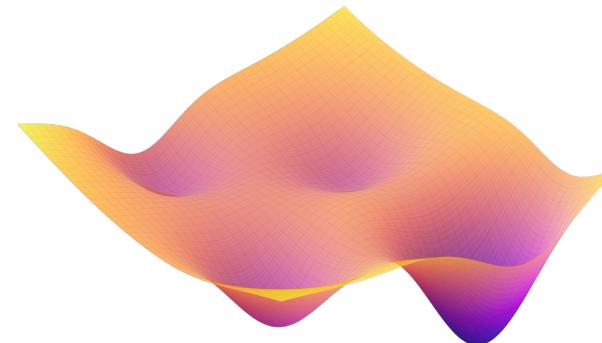
## ➤ Why is it so powerful?

### *Ab-initio* theory:



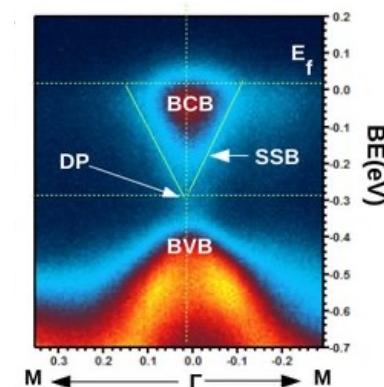
The only input parameters are the types and position of atoms in the system (molecule, solid, surface, wire...)

### Total Energies:



Knowing the total energy of the system of atoms in a given configuration permits to compute forces, response to perturbation, predict phase diagrams etc.

### Quasi-particle Energies:

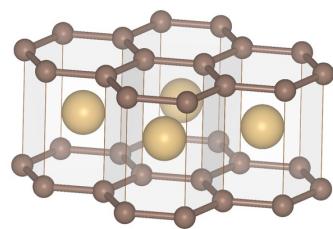
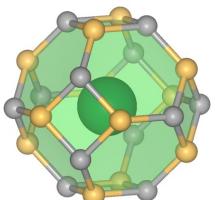


DFT quasi-particle spectra are often used to interpret experiments, or as starting point of more complex many-body techniques.

# Density Functional Theory

## ► Limits & Beyond:

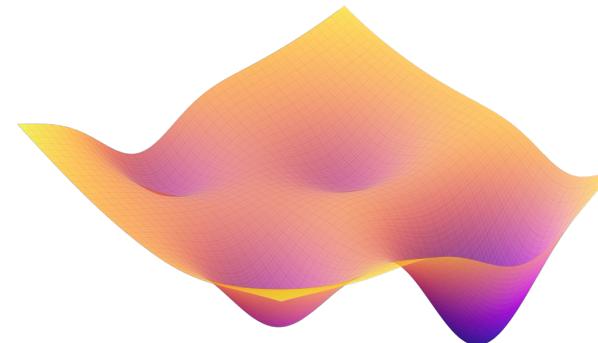
### *Ab-initio theory:*



DFT is mostly used for extended/periodic systems (solids, surfaces, wires).

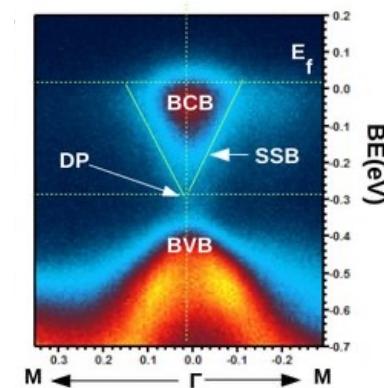
**For few-atoms systems, wavefunction-based methods are usually preferred.**

### Total Energies:

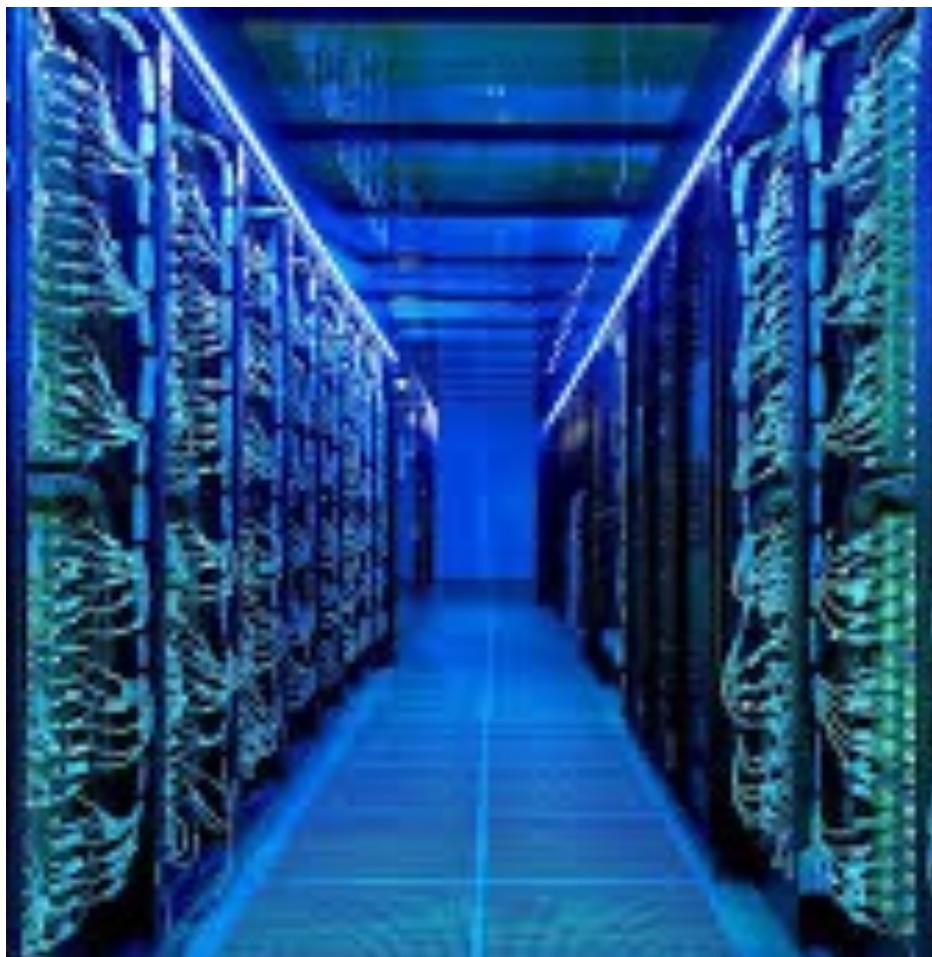


- Density Functional Perturbation Theory.
- Crystal Structure Prediction.
- High-Throughput/AI.

### Quasi-particle Energies:



- LDA + U/DMFT
- GW Approximation
- Bethe Salpeter (Excitons etc).



# Density Functional Theory:

## Typical Questions:

- Is this material a metal/insulator?
  - What are the typical energies of a vibrational/electronic excitations?
  - Can this material superconduct?
  - Is it magnetic?
  - Is it a topological insulator?
  - Can these two/three elements mix and form a solid?
  - What kind of solid will they form?
  - What is the preferred structure?
  - What is a supersolid?
  - When will He become superfluid?
  - What are the eigenstates of a given model Hamiltonian?
-

# Density Functional Theory

## ➤ What will you learn in this course?

- **Density Functional Theory (DFT)** is a very general method. **In principle**, it is a formally-exact ground-state theory for interacting electrons (Hohenberg-Kohn Theorems).
- In practice, DFT works because **Kohn-Sham quasi-particles equations** can be solved self-consistently **under controlled approximations** (GGA/LDA) which work for many CM systems.
- Implementing KS equations in practice is extremely complicated because of the large number of degrees of freedom involved. Methods (and codes) have been developed for over 50 years.
- **In this course** we will learn in detail a **specific implementation** of DFT, which works for periodic solids, and is based on **plane-waves** and **pseudopotentials**.

# Density Functional Theory

## ➤ Structure of the Course:

- **Theoretical Lectures:**

Introduce DFT basics and explain what is behind the practical implementation used in QE.

- **Hands-on Labs:**

Learn to use a state-of-the-art DFT code, interpret the results, simulate simple physical problems. Since our course focuses on solids, we will also learn some concepts and tools for advanced real- and reciprocal-space symmetry analysis (space groups, complex unit cells, BZ analysis, etc).

# Content:

- **TH1: Introduction to the Course &** background concepts.
- **LAB1: Crystal Structure and Symmetry.**
- **TH2: Theory of DFT, PART I:** Hohenberg-Kohn, Kohn-Sham, Basis Functions.
- **LAB2: Setting up a DFT Calculation** with Quantum Espresso, Input & Output Files.
- **TH3: Theory of DFT, Part II:** Pseudopotentials and k-space Integration.
- **LAB3: Reciprocal Space:** Band Structure Plots, K-space Integration, Density of States.
- **TH4: Theory of DFT, Part III:** Hellmann-Feynman Theorem, Structural Relaxation, Equation of State.
- **LAB4: Forces,** Structural Relaxations, Equations of State.
- **TH5: Theory of DFT, Part V:** Linear Response, Phonons, Other Perturbations.
- **TH6: Theory of DFT, Part VI:** Advanced Topics.

# Tentative Schedule (dates):

Oct	2	Intro	6	QMC LAB1	9	QMC TH1	13	QMC LAB2	16	QMC TH2	20	QMC LAB3	23	QMC TH3	27	QMC LAB4	30	QMC TH4
Nov	3	QMC TEST	6	DFT TH1	10	DFT LAB1	13	DFT TH2	17	SKIP	20	SKIP	24	DFT LAB2	27	DFT TH3		
Dec	1	DFT LAB3	4	DFT TH4	8	SKIP	11	DFT TH5	15	DFT LAB4	18	DFT TEST	22	✓ 22 ✓ = QFA				

# Theory LECTURES:

- **Background:** Born Oppenheimer Approximation and Self-consistent field approximation, Periodic solids
  - **Density Functional Theory:** Hohenberg-Kohn theorems, Kohn-Sham equations.
  - **Practical Implementation of Density Functional Theory:** Use of Basis Functions, Most common types of basis functions.
  - **Plane Waves, Pseudopotentials** and their role in electronic structure calculations.
  - **Practical aspects of DFT calculations:** FFTs, K-Space Integration, Convergence tests.
  - **Total energies and interatomic forces:** The Hellmann-Feynman theorem.
  - **Structural Relaxation and Equation of State.**
  - **Advanced topics:** Crystal structure prediction, Machine Learning Interatomic Potentials.
- 

# Lab1: Crystal Structure and Symmetry:

- **What is a Crystal Structure?** Lattice, Unit cells, Bravais lattices, etc.
- **Symmetry in Crystals:** Types of Symmetry operations, Point Groups, Space Groups.
- **Space Groups:** Definition, Notations – International Tables of Crystallography.
- **Wyckoff Positions:** Definition of Wyckoff Positions.
- Using the **Bilbao Crystallographic Server** - <https://www.cryst.ehu.es/> 
- **Setting up and visualizing simple and complex crystal structures.**



**For this lab you need to have downloaded and Installed VESTA:**  
<https://jp-minerals.org/vesta/en/>

SOLIDS / extended Systems

QMC ~ very accurate  $\lesssim 8$  atoms (HPC)

DFT less accurate  $\lesssim 10^{10}$  atoms

$\hookrightarrow$  AD-MTTS Molecular dynamics

AIMLP = Ab initio Machine Learning Potentials  
"Classical potentials"

$\hookrightarrow$  100'000 - 1'000'000 atoms

# Lab2: Setting up a DFT calculation with QE

- **Introduction to Quantum Espresso:** How to run the code, input/output files.
- **Setting up a “real” DFT calculation:** Fcc Neon.
- **Running the Calculation:** Understanding output files, Troubleshooting, Convergence Tests.
- **Setting up a more complex calculation (semiconductor):** Silicon in the cubic (diamond) structure.



**For this lab you need to have downloaded and Installed Quantum Espresso:**

<https://www.quantum-espresso.org/>



# Lab3: Reciprocal Space

- **Brillouin Zone:** Definition and meaning of reciprocal space, Brillouin Zone, special k points.
- **Band Structure and Density of States (DOS):** Definitions, how to interpret them.
- **Setting up a band structure and DOS calculation (semiconductor):** Silicon in the diamond structure.
- **Setting up a band structure calculation (metal):** FCC aluminum.



**For this lab you need to have downloaded and Installed Quantum Espresso:**

<https://www.quantum-espresso.org/>

# Lab4: Forces, Structural Relaxation, Equation of State

- **Forces in Solids:** Physical Origin and Definition of Forces in Solids.
- **Practical Calculation of Forces:** Finite Differences and Hellman-Feynmann Theorem.
- **Structural Relaxation:** Definition of Structural Relaxation and Equation of State.
- **Practical Calculation of a Structural Relaxation:** Automatic Relaxation of Simple and Complex Structures.
- **Equation of State Calculation.**

The background of the slide features a complex network graph. It consists of numerous glowing, translucent spheres of various sizes and colors, primarily in shades of red, orange, yellow, and blue. These spheres are interconnected by a web of thin, glowing lines of the same color palette, creating a sense of a dynamic, interconnected system. The overall effect is futuristic and suggests concepts like data flow, connectivity, or molecular structures.

## **Practical Information:**

References, Software Requirements, Evaluation

# Useful References:

## Books (suggested):

- Prerequisites: Any standard solid state theory book (Ashcroft, Kittel, Pastori-Parravicini etc)
- If you want to buy/read a book on DFT, I recommend: F. Giustino, *Materials Modelling using Density Functional Theory: Properties and Predictions*, Oxford University Press.

## Reviews:

- F. Nogueira, Tutorial in «*A primer in Density Functional Theory*» (can be downloaded for free from several sources);
- R. O. Jones and O. Gunnarsson, *The Density functional formalism, its applications and prospects*, Rev. Mod. Phys. **61**, 689 (1989).
- **Additional Material on Elearning:** <https://elearning.uniroma1.it/course/view.php?id=16985>

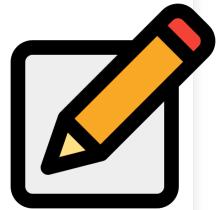


# DFT Code: Quantum Espresso

- For the practical part of our lecture we will use the code **Quantum Espresso (QE)**, which can be **downloaded** from: <https://www.quantum-espresso.org/>.
- QE is a publicly distributed **planewaves-pseudopotential** code. The QE package comprises several executables; for this part of the course we will only use the main program (**pw.x**) and the basic post-processing tools (**pp.x**). You don't need to install the GUI (Graphic User Interface).

- 
- If you are running a **linux/unix environment**, download the **latest stable version** and follow the installation instructions. The configure script usually works without problems if you have installed all necessary compilers (google is your friend!).
  - If you are running on a mac, I recommend installing the **macports version**.

# Editor for Quantum Espresso I/O files:



Quantum espresso input and output files are regular (ASCII) txt files. You will need a simple text editor (emacs, vim, textpad, etc) to create your input files.

```
&control
  calculation= 'scf'
  prefix= 'SI'
  pseudo_dir = './pseudo/'
 outdir= './tmp/'
  tprnfor = .true.,
  tstress = .true.,
/
&system
  ibrav= 2, celldm(1)=10.262913,
  nat= 2, ntyp= 1,
  ecutwfc= 40,
/
&electrons
  conv_thr = 1.0D-6
  mixing_beta = 0.7
/
ATOMIC_SPECIES
Si 28.085 Si.LDA.upf
ATOMIC_POSITIONS crystal
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25
K_POINTS automatic
4 4 4 0 0 0
```

# Quantum Espresso I/O files:

## Text Editor:

Quantum espresso input and output files are regular (ASCII) txt files. You will need a simple text editor (emacs, vim, textpad, etc) to create your input files.



## Plotting:

You will also need some simple plotting program to visualize total energies, bands, densities of states etc. I recommend installing gnuplot and/or the python3 matplotlib library (<https://matplotlib.org/>).



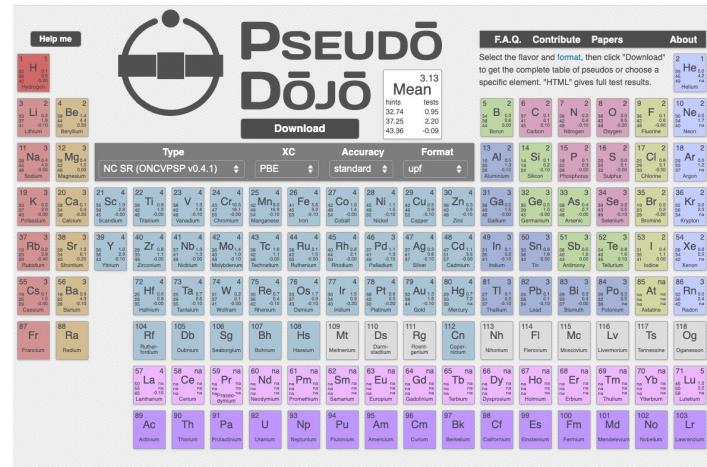
We will provide simple scripts for data visualization that you can modify for your needs.

BASH SCRIPTING

# Pseudopotentials: Pseudodojo

DFT is an ***ab-initio* method**: the only information required to compute the physical properties of a system are:  
1) the **types of atoms** and 2) their spatial arrangement (**crystal structure**).

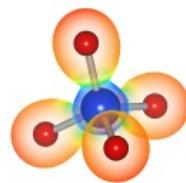
## ► 1) Types of atoms:



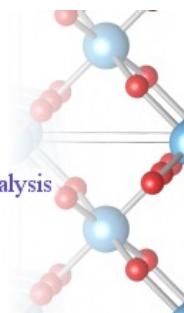
We will use ONCV (optimized norm-conserving Vanderbilt pseudopotentials) from the pseudodojo website:  
<http://www.pseudo-dojo.org/>. - D.R. Hamann, Phys. Rev. B **88**, 085117 (2013).

# Crystal Structure Visualization: VESTA

## ► 2) Crystal Structure



VESTA  
Visualization for Electronic and STructural Analysis



VESTA will be used **to visualize Crystal Structures and understand Symmetry operations, space groups, etc** (1° lab).

Download it from: <https://jp-minerals.org/vesta/en/> (Linux, Windows and Mac versions); Install following the installation instructions on the website.

# Exams:

- **Practical Computer Test + (Optional) Oral Exam**

The students will have the opportunity to take two tests in progress ("prove diesonero") at the end of each part of the course, or a final test after the end of the course. The mark **can** be improved taking an **oral exam**.

To pass the exam you are required to successfully pass both tests *in itinere*.

If you failed one or both tests, you have the possibility to take part in a practical test in January.

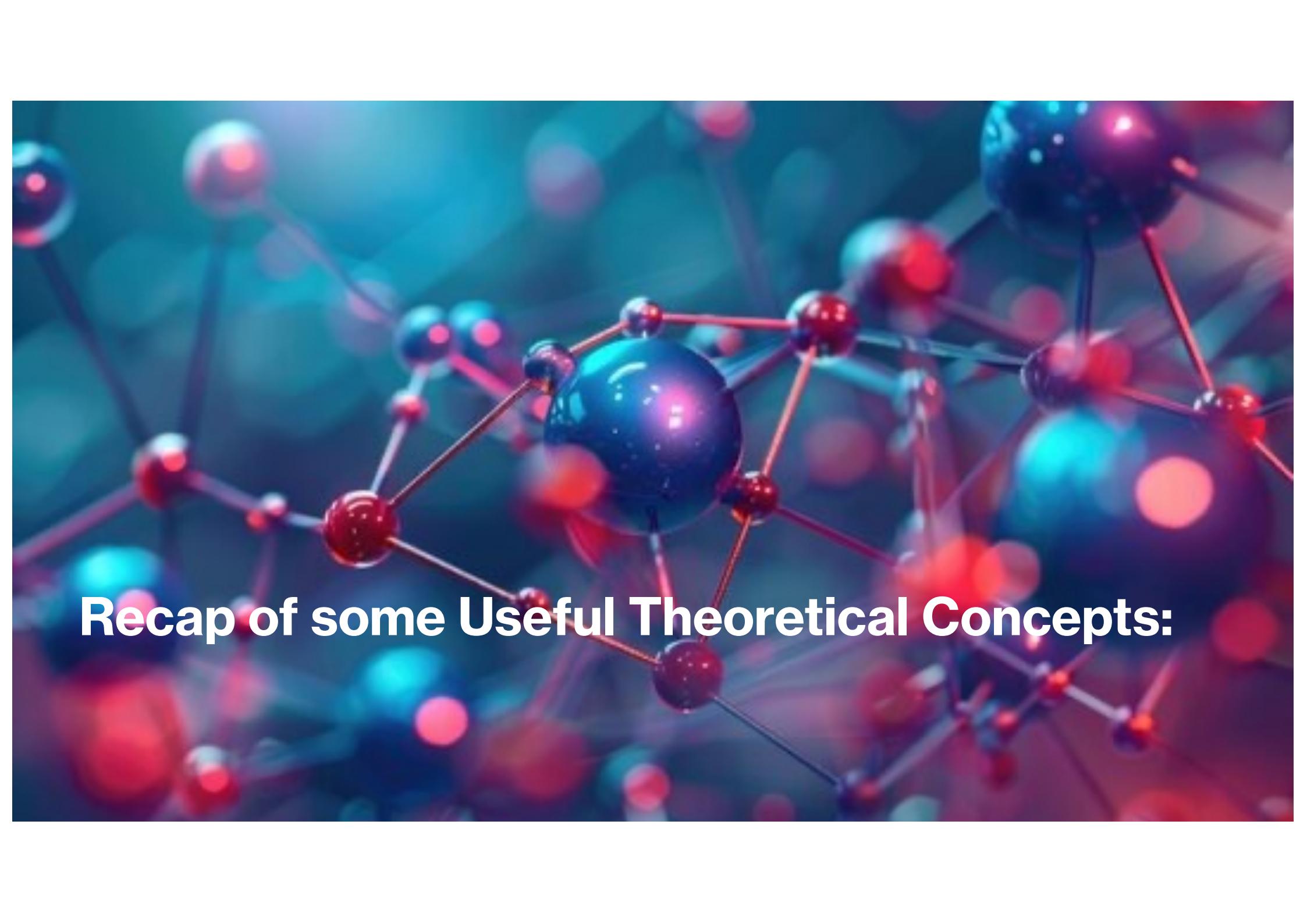
For students taking who will take the exam after the winter call, there is the opportunity to replace the written exam with a small (group) project.

**Exams and tests are considered passed only if the mark is  $\geq 18/30$ .**

# Group Projects (2024)

- **Examples of group projects:**

- Liquid-Solid transition in of 2D Helium at T=0 (QMC).
- Formation of new superhydride phases at high pressures (DFT).
- Electride Behaviour in Noble Gas Solids at High Pressures (DFT).
- Suppression of Magnetism in Ni<sub>3</sub>Al in the Stoner Model (DFT)
- Doping Graphene with Metal Contacts (DFT).
- Magnetic Properties of 2D Van der Waals Materials (DFT)
- Strain Effects on the Bandgap of Monolayer MoS<sub>2</sub> (DFT)
- Defects in Graphene: Vacancy vs. Substitutional Doping (DFT)
- Superconductivity in Alkali-doped graphene via interlayer band doping (DFT).



**Recap of some Useful Theoretical Concepts:**

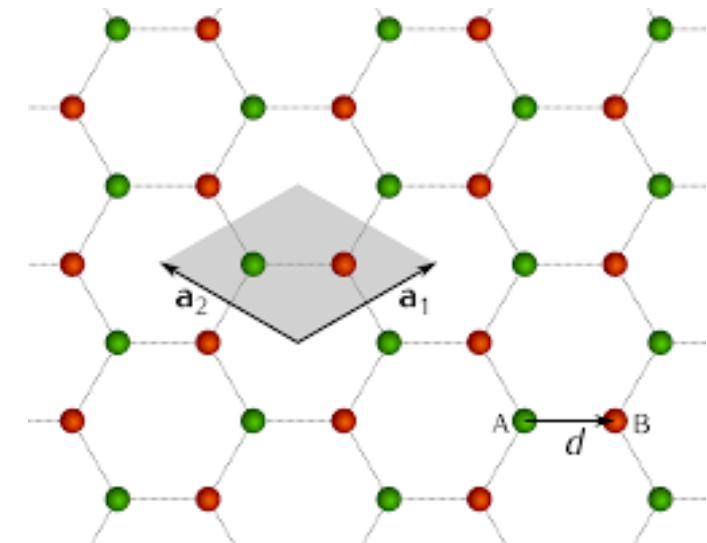
# Crystal Lattices:

A crystal lattice is generated by periodically repeating the same **unit cell**, defined by 3 **lattice vectors** and **m basis** vectors:

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

$$\mathbf{R}_i = \mathbf{R} + \underline{\tau_i}, \quad i = 1, \dots, m$$

Brewans  
letta



The **Wigner Seitz** cell is the region of space closer to a given lattice point than to any other lattice point – i.e., the **Voronoi cell** of a lattice point in a crystal.

# Bloch's Theorem

Bloch's theorem states that any excitation in a solid can be written as:

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

Please Note

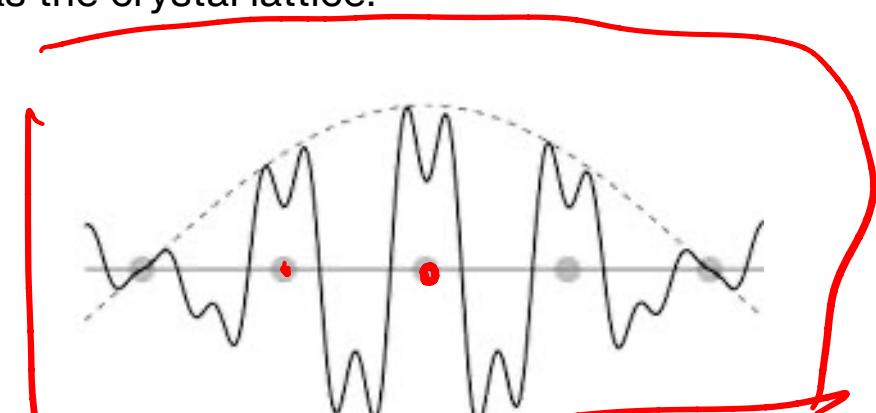
Where  $u_{\mathbf{k}}(\mathbf{r})$  is a periodic function with the same periodicity as the crystal lattice:

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$$

This also implies:

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

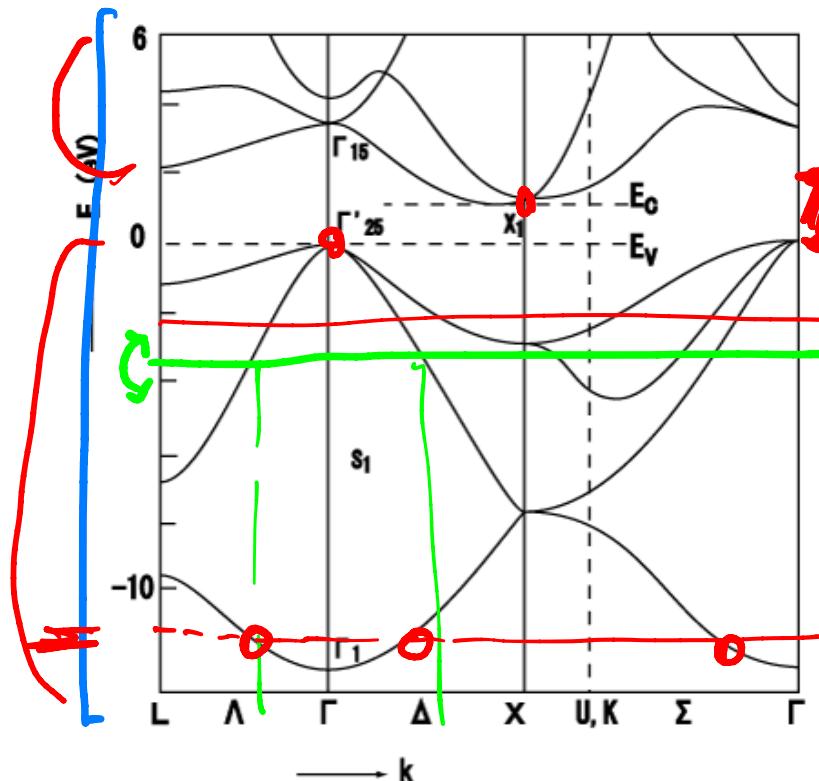
$$\psi_{\mathbf{k}}(x + na) = \psi_{\mathbf{k}}(x) \cdot e^{ik(na)}$$





$$\varphi(a) = \varphi(0) = \varphi(2a) = \dots$$

# Energy Bands:



CHARGE

- A fundamental consequence of Bloch's theorem is that electronic energy levels in solids form **energy bands**; allowed energy levels can be separated by **gaps** of forbidden energies.
- The **Fermi energy** separates **Full** and **Empty** states.
- The **Fermi surface** is a 2D surface in 3D reciprocal space separating full and empty states.

$$N_{\text{e}}^{\text{val}} = \int_{-\infty}^{E_F} N(\varepsilon) d\varepsilon = \beta$$

$$N(\varepsilon) = \sum_{k,n} \delta(\varepsilon - \varepsilon_n(k))$$

# The Quantum-Many Body Problem:

All properties of a solid can be in principle computed solving the **Quantum Many-Body Problem**, i.e. finding the eigenvalues and eigenstates of the Hamiltonian of interacting Nuclei and Electrons:

$$\hat{H}_{tot} = \hat{T}_N + \hat{T}_e + \hat{V}_{eN} + \hat{V}_{NN} + \hat{V}_{ee}$$

-      +      +

*Coulomb*

$$\hat{H}_{tot}\Phi(\mathbf{R}, \mathbf{r}) = E\Phi(\mathbf{R}, \mathbf{r}), \quad \mathbf{R} = \{\mathbf{R}_\alpha\}, \quad \mathbf{r} = \{\mathbf{r}_i\}$$

DFT permits to find an approximation to the **ground-state** solution (energy, eigenfunction).

# Main Concepts Behind DFT:

1. **Born-Oppenheimer Approximation:** Decouple ions & Electrons.
2. **Self-Consistent Field (Hartree 1926):** effective single particles.
3. **Fermionic Statistics (Exchange):** the Hartree-Fock Method.



4. **Density Functional Theory:** (Ground-state) **Density** is the main variable.
  - Hohenberg-Kohn Theorems.
  - Kohn & Sham Equations.
5. Approximate **Exchange-Correlation Functionals** (LDA, GGA).

$$\text{Density} = \sum_{\text{occ}} |\psi_i(\mathbf{r})|^2$$

Wavefunction-based  
↓  
CONFIGURATION  
INTERACTION,  
"better" WF:  
OrbC