Introduction to Density Functional Theory

Basic Idea & Practical Calculations

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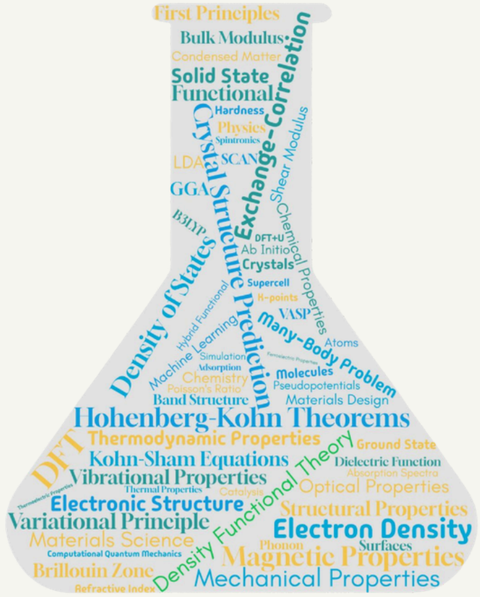
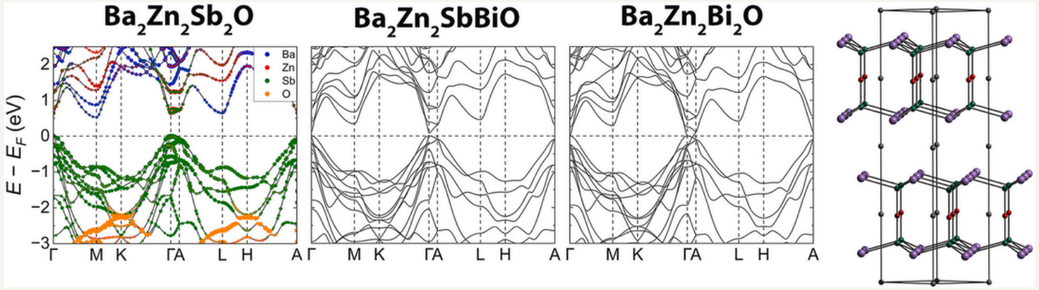
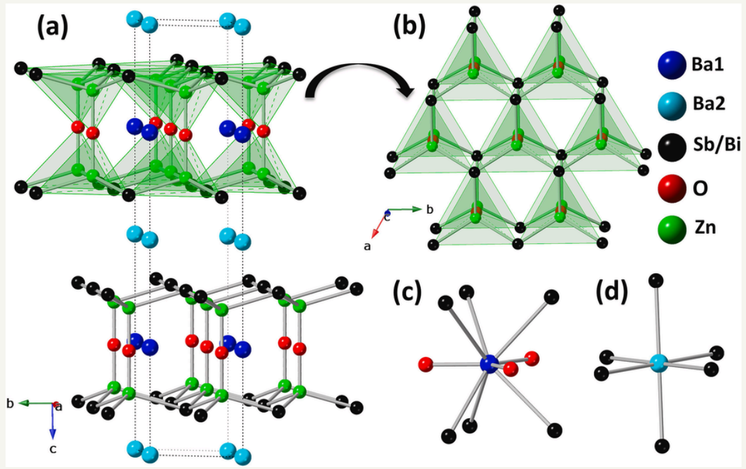


Computational material science

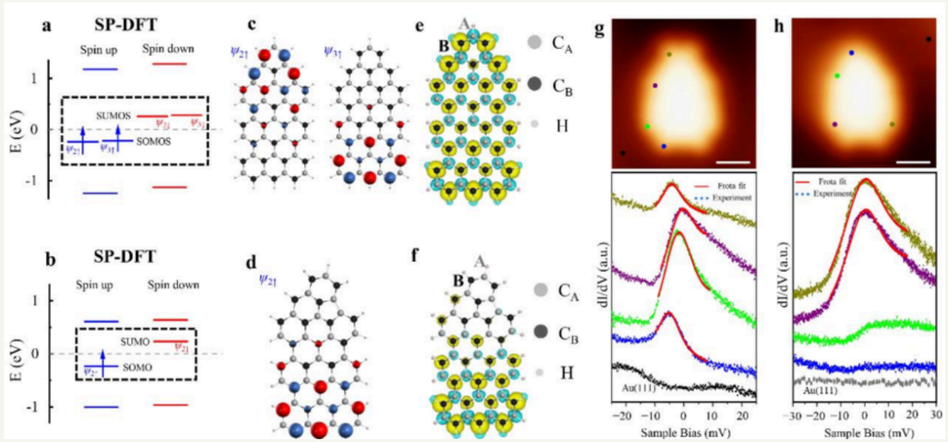
WHAT WE WANT TO ACHIEVE



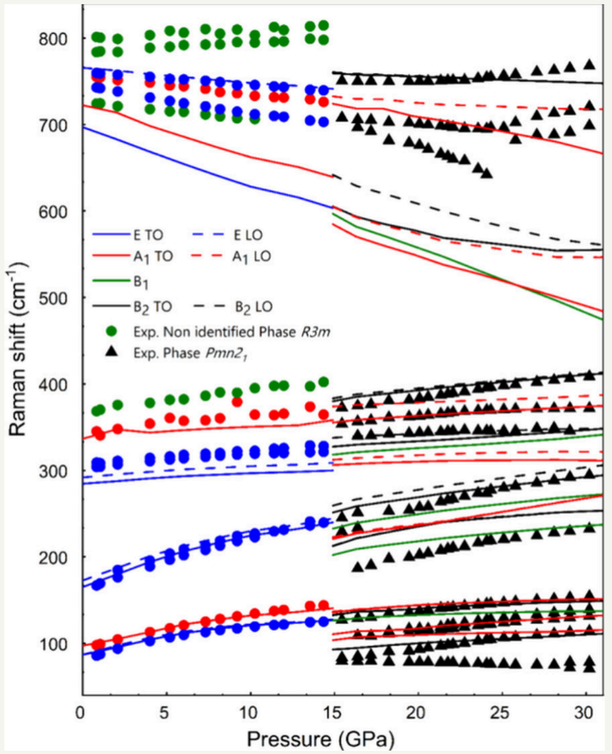
Electronic properties



Structure



Magnetic properties



Vibrational properties

Basic Definitions

- Wavefunction Ψ

Describes the quantum state of a system of particles and contains all measurable information.

- Electron density ρ

Probability density of finding electrons in space; central quantity in DFT.

- Operator

A mathematical object that acts on a function to produce another function.

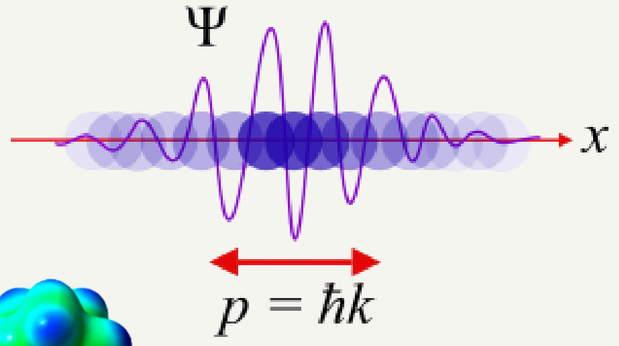
e.g. a derivative $\partial/\partial x$

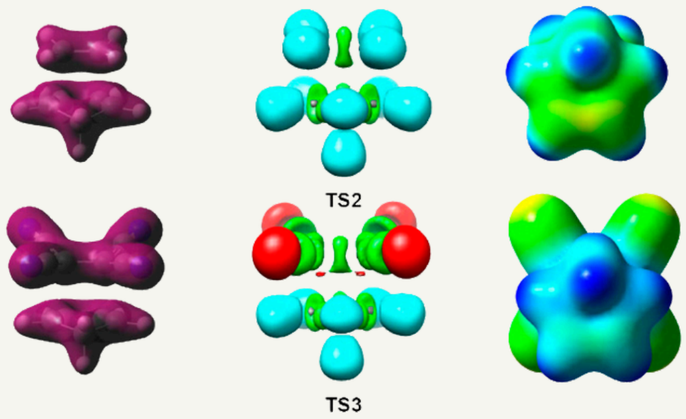
- Quantum mechanical operator:

Physical observables (e.g. energy, momentum) are represented by operators.

- Ground state:

The lowest-energy state of a system (most stable configuration).





$f(x)$	Any function of position, such as x, or potential V(x)	$f(x)$
p_x	x component of momentum (y and z same form)	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m} + V(x)$
E	Hamiltonian (time dependent)	$i\hbar\frac{\partial}{\partial t}$
KE	Kinetic energy	$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i\hbar\frac{\partial}{\partial \phi}$

Outline

Part I
The Framework of DFT

1. **Density Functional Theory (DFT)**
   - The many-body Schrödinger equation
   - Hohenberg–Kohn theorems
   - Kohn–Sham formalism
2. **Elements of Solid-State Physics for DFT**
   - Crystal structures and periodicity
   - Reciprocal space
   - Plane-wave basis sets
3. **Common Software in CC**
   - Electronic structure calculations
   - Analysis and specialised tools

Outline

Part II
Using DFT in Practice

1. Practical Aspects of DFT Calculations

- Input files
- Output files

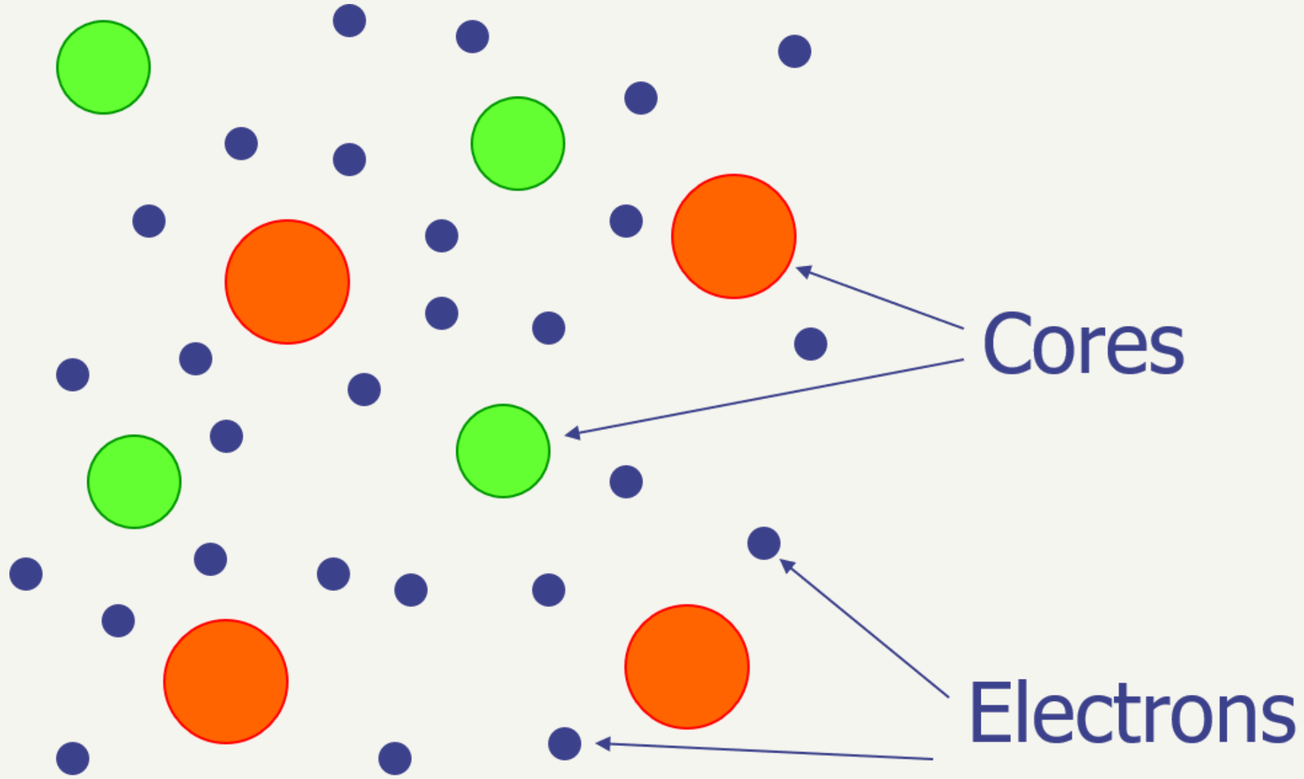
2. Key Parameters and Choices

- *k*-point sampling
- Pseudopotentials
- Exchange–correlation functional (LDA/GGA)
- Control parameters and convergence settings

3. Typical Applications

- Isolated systems (molecules, clusters)
- Bulk materials

The many-body problem



"If we have *N* electrons, the wavefunction depends on 3N spatial variables. This quickly becomes impossible to solve exactly."

Schrödinger's Equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi(R_i, r_i) = \varepsilon.\Psi(R_i, r_i)$$

Kinetic E

Potential E

(Coloumbic interactions + External Fields)

Energy levels

Wave function

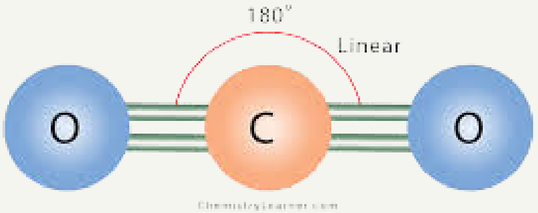
Hamiltonian operator

Many-Body Problem in solids

Example 1: CO_2 molecule > 22 electrons

– Each electron → 3 spatial coordinates

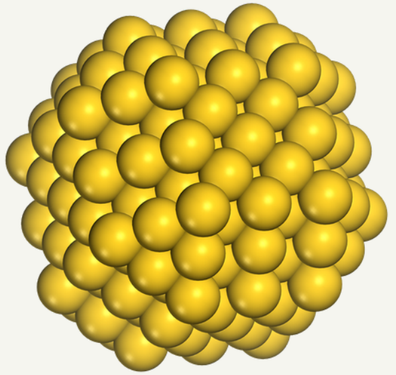
66-dimensional Schrödinger equation



Example 2: Pb nanocluster > 100 atoms

– 82 electrons/atom → 8200 electrons

24,600-dimensional problem



The dimensionality grows linearly with the number of electrons → the problem becomes intractable very quickly

Direct solution of the many-electron Schrödinger equation is impossible for realistic materials.

First Approximations

> Born–Oppenheimer (adiabatic) approximation

- Electrons are much lighter → move much faster than nuclei
- Separation of electronic and nuclear motion:

$$\Psi(Ri,ri) \approx \chi(Ri)\psi(ri;Ri)$$

- Electrons are solved for fixed nuclear positions

> Treatment of nuclei

- Nuclei are treated as "*classical point particles*" (to first approximation)
- They enter the Hamiltonian as an external potential for the electrons

Density Functional Theory

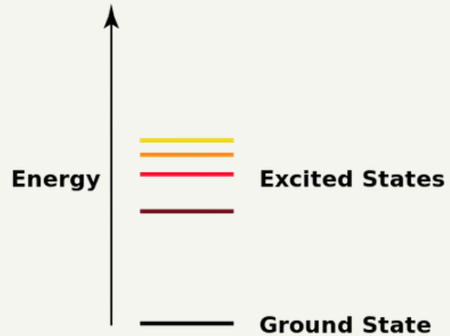
From wavefunctions to electron density

Hohenberg–Kohn Theorems

Theorem 1

> The ground-state energy is a unique functional of the electron density:

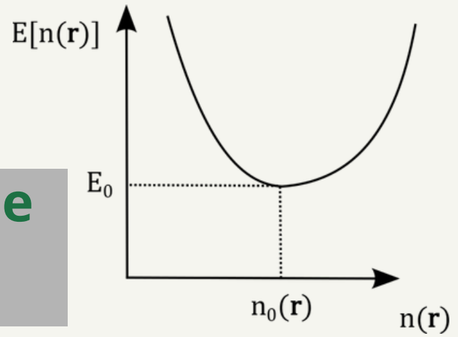
$$E = E[n(r)]$$



Theorem 2

> The ground-state electron density minimises the energy functional:

$$E[n(\mathbf{r})] \geq E_0[n_0(\mathbf{r})]$$



The electron density *n(r)* fully determines the ground-state properties of the system

Density Functional Theory

From wavefunctions to electron density

The Kohn Sham scheme

> Replace the interacting many-electron problem with an auxiliary system of non-interacting electrons

$$[-\hbar^2/2m\nabla^2 + V_{ext}(r) + V_H(r) + V_{XC}(r)]\psi_i(r) = \varepsilon_i\psi_i(r)$$

V_{ext} : electron–nucleus potential
V_H : Hartree (electron–electron) term
V_{XC} : exchange–correlation potential

Self consistent loop

STEP 1

Trial *n(r)*

STEP 2

Solve KS equation with n(r) to obtain single electron wave function $\Psi i(r)$

STEP 3

Calculate the electron density based on the single electron wave functions $n^{(k+1)}(r) = 2\sum_i \mid \psi i(r) \mid^2$

STEP 4

Compare:

1. If different, then process begins from STEP 2 with new *n(r)*
2. If identical, true ground state density is obtained.

Summary: Key Ideas of DFT

HOHENBERG–KOHN (HK) → **KOHN–SHAM (KS)** → **PRACTICAL SOLUTION**

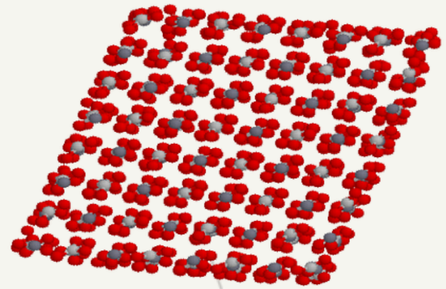
The ground-state energy is uniquely determined by the electron density

The interacting many-electron problem can be mapped onto a set of single-particle equations

Simple approximations are often sufficient:
LDA · GGA

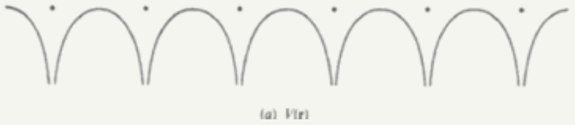
All many-body effects are contained in the exchange–correlation functional $E_{XC}[n]$

Crystalline Solids and Plane-Wave DFT



Crystal: Periodic arrangement of atoms

→ Leads to a periodic potential



(a) Periodic potential, $U(\mathbf{r})$

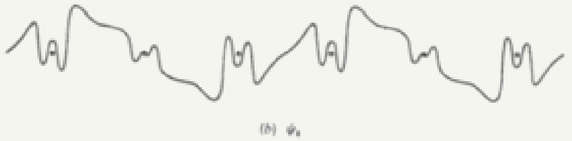
Free electrons: described by plane waves $\psi(r) = e^{ik.r}$

(d) Plane wave, $e^{i\mathbf{k}\cdot\mathbf{r}}$

Electrons in a crystal: Move in a periodic potential

→ Solutions are Bloch functions $\psi_{nk}(r) = e^{ik.r} u_{nk}(r)$

(c) Lattice-periodic part, $u_{n\mathbf{k}}$



(b) Bloch wave, $\psi_{n\mathbf{k}}$

$u_{n\mathbf{k}}(r)$: periodic with the lattice

Plane-Wave Basis: Cutoff Energy

Fourier representation

Any periodic function can be written as a sum of plane waves (Fourier series)

$$\psi_{nk}(r) = e^{ik.r} \sum_G c_{k+G} e^{iG.r}$$

"Wavefunction expanded in plane waves"

Kinetic energy of plane waves $E = \frac{\hbar^2}{2m} \mid k + G \mid^2$

Cutoff energy: only plane waves with $E \leq E_{cut}$ are included → Finite basis set for calculations

Practical requirement:

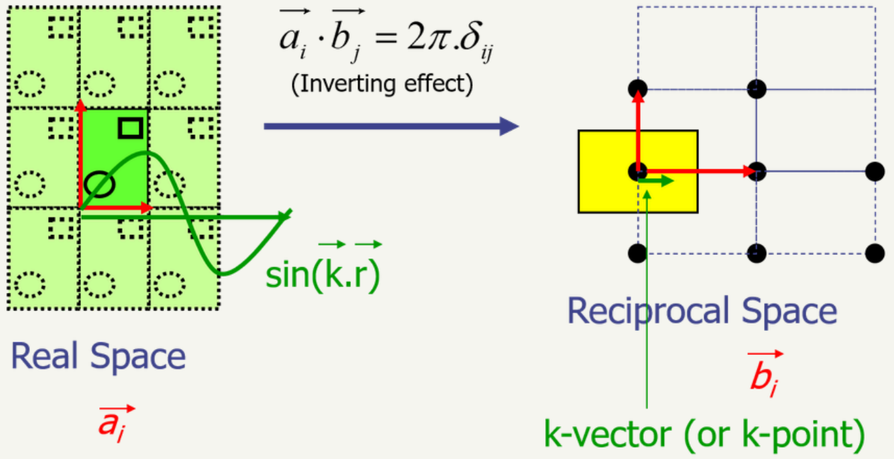
- **Converge results with respect to E_{cut}**
- **Larger cutoff → higher accuracy (and computational cost)**

MORE PLANE WAVES
=
BETTER DESCRIPTION OF THE WAVEFUNCTION

Plane-Wave Basis: *k*-Point Sampling in Crystals

<u>Reciprocal space:</u>

- Wavevectors ***k*** describe electronic states in periodic systems
- The primitive cell in reciprocal space is the 1st Brillouin Zone (BZ)

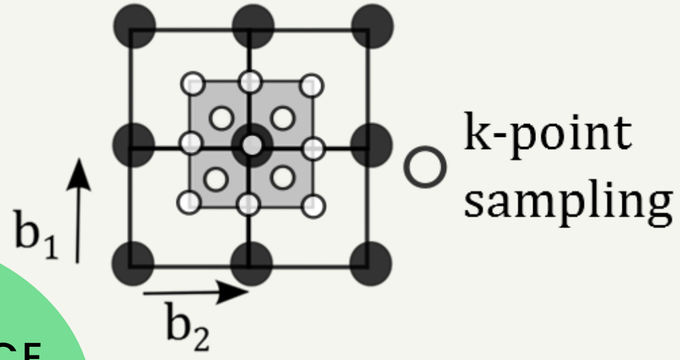


<u>Bloch periodicity:</u>

k and ***k+G*** are equivalent. G: reciprocal lattice vector
→ Only the 1st Brillouin Zone needs to be sampled

<u>Integration in the BZ:</u>

- Physical quantities involve integrals over ***k***
- In practice → replace integrals by a finite set of ***k***-points



<u>*k*-point sampling</u>

- Choose a mesh of *k*-points (e.g. Monkhorst–Pack grid)
- Accuracy depends on the number of *k*-points

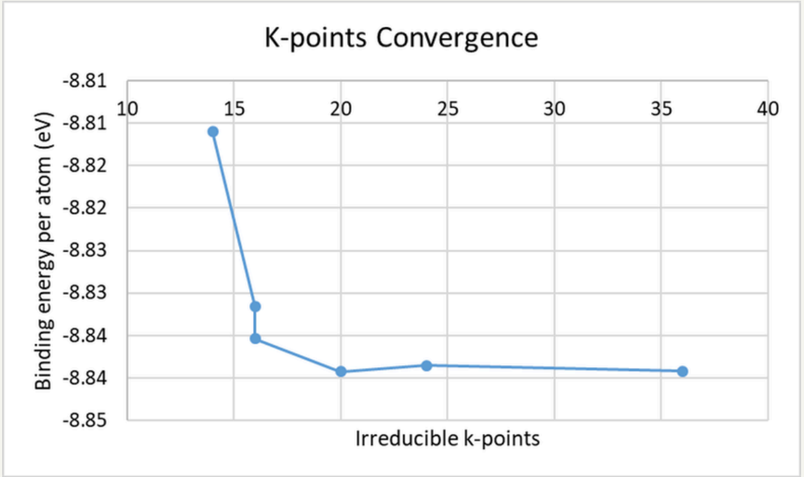
CONVERGENCE MUST BE TESTED

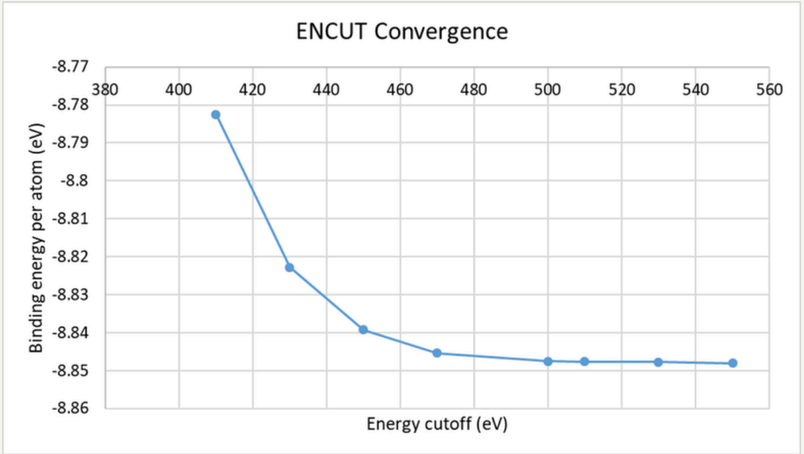
Obtaining Reliable Total Energies

Convergence with numerical parameters

- Total energy depends on:
  - *k*-point sampling
  - plane-wave cutoff energy
- These parameters must be converged

→ Results should not change significantly with further increase





Absolute total energies are not meaningful in DFT

- Only energy differences are physically relevant
- Typical accuracy: ~1 meV / atom

Plane-Wave Basis: Pseudopotentials

Physical idea

- Chemical properties are mainly determined by valence electrons
- Core electrons are tightly bound and relatively inert

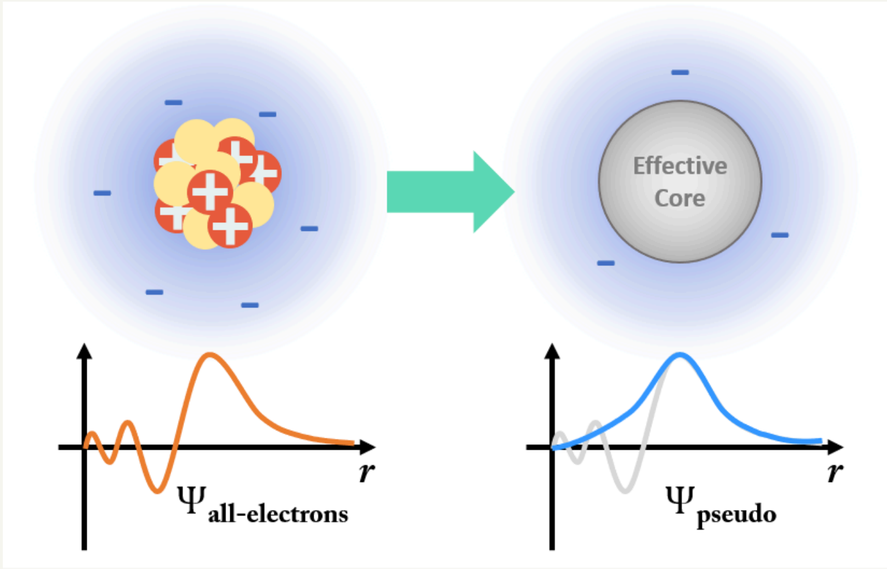
Pseudopotential approximation

- Core electrons are replaced by an effective potential
- Valence electrons interact with a smoothed potential:

Frozen core approximation

Why use pseudopotentials?

- Reduces the number of electrons treated explicitly
- Smoothes the wavefunctions → fewer plane waves needed
- Improves computational efficiency

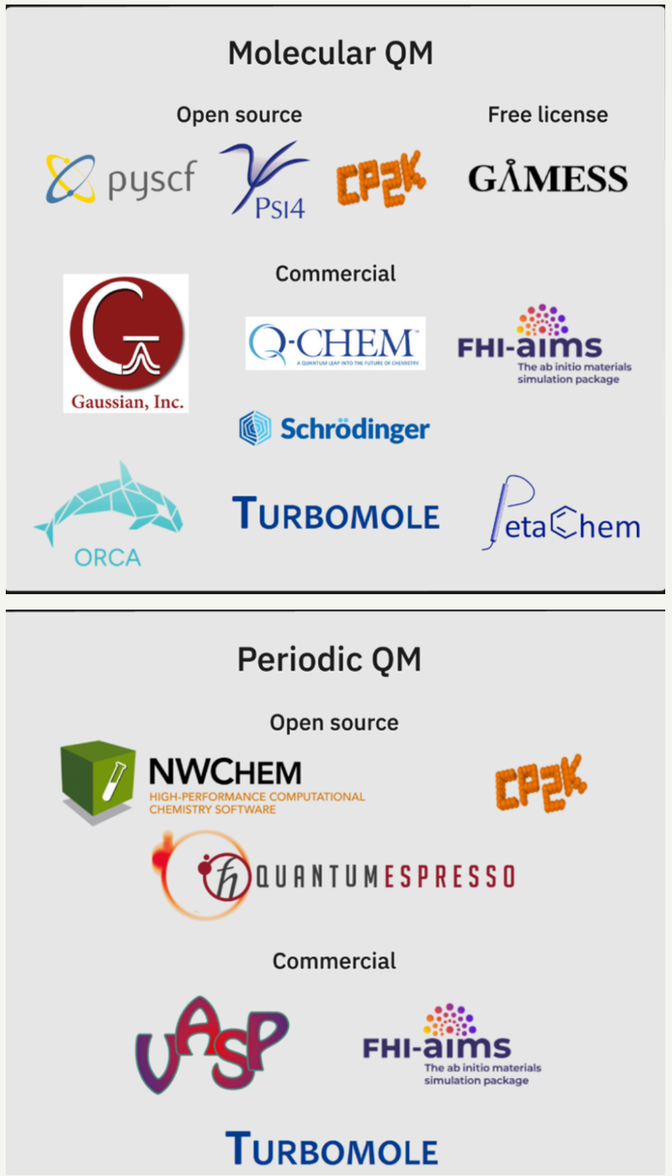


In practice

- DFT codes provide libraries of pseudopotentials
- Choose appropriate potential for each element

Smooth wavefunctions → fewer plane waves

Common Software in Computational Chemistry



Molecular modelling and visualisation

VESTA

3D visualisation software for crystal structures and volumetric data. Visualise:

→ crystal structures

→ electron density,

→ charge density

→ isosurfaces

Electronic structure (Quantum Chemistry / DFT)

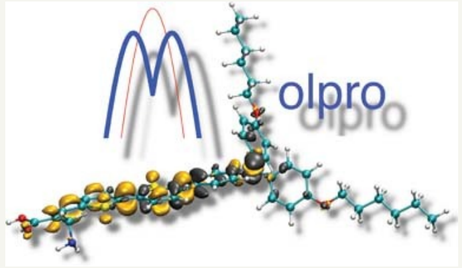
Gaussian: Quantum chemistry package → Electronic structure (HF, DFT, post-HF), energies, spectra.

GAMESS: Ab initio quantum chemistry code → Hartree–Fock, DFT, molecular properties

Molpro: High-accuracy quantum chemistry software → Advanced correlated methods (CI, CC, multireference)

Quantum ESPRESSO: Plane-wave DFT code for periodic systems → Solids, surfaces, materials properties

VASP: Plane-wave DFT code (commercial) → Electronic structure, geometry optimisation, molecular dynamics in solids

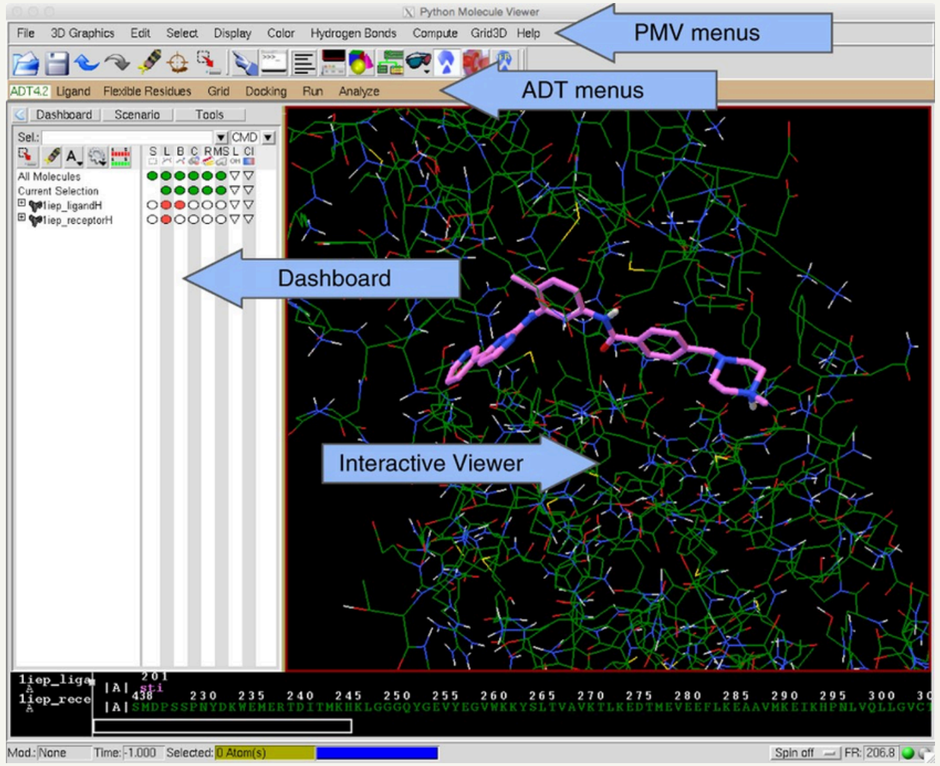


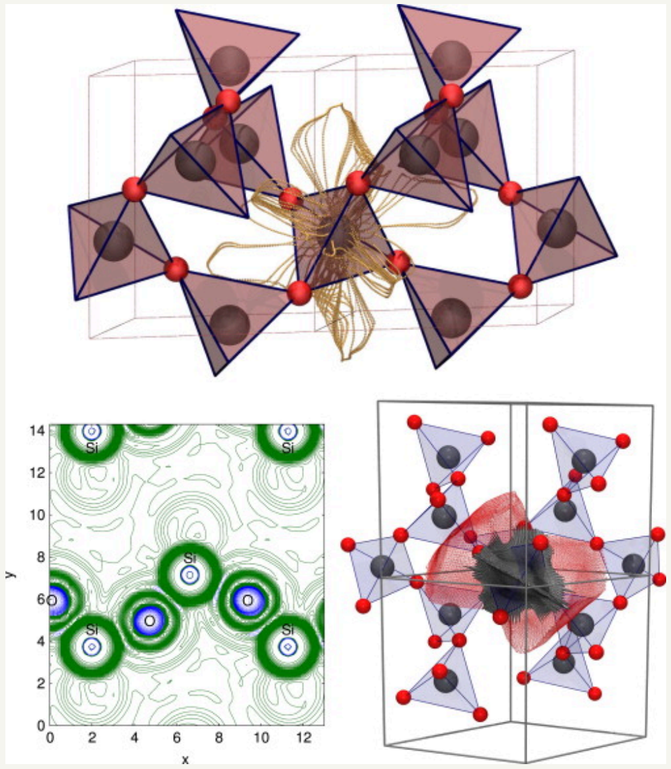
Analysis and specialised tools

CRITIC2: Topological analysis of electron density → Bonding analysis, critical points, charge density

AutoDock: Molecular docking software → Ligand–receptor binding, drug design

AutoDock 4

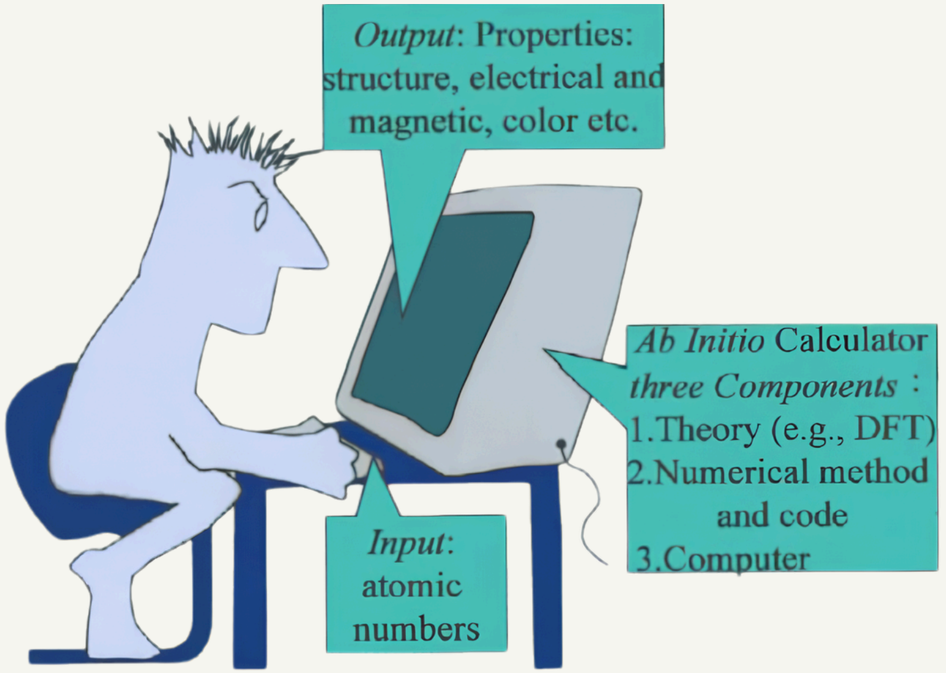




CRITIC2

Doing DFT calculations

— PRACTICAL ASPECTS



Vienna *Ab initio* Simulation Package (VASP)

WHAT IS VASP?

Widly used software for DFT calculations. It is designed for periodic systems (solids, surfaces, interfaces).

USES

It uses plane-waves basis set, pseudopotentials (PAW method), and periodic boundary conditions.

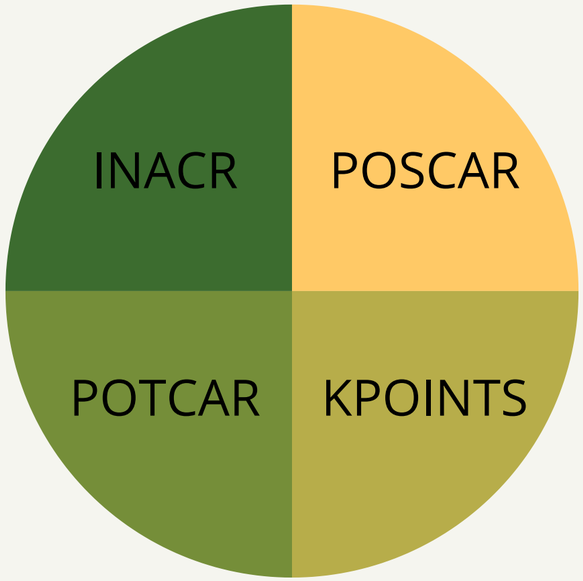
CAPABILITIES

Electronic structure - geometry optimisation - molecular dynamics in solids. (Typical system size ~ 100-2000 atoms

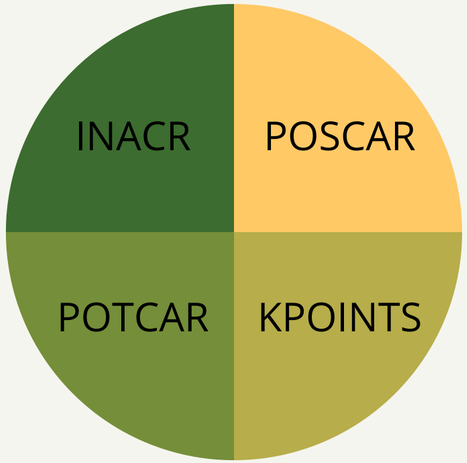
RELATED DFT PACKAGES (OPEN-SOURCE)

- Quantum ESPRESSO (https://www.quantum-espresso.org)
- ABINIT (https://www.abinit.org)
- SIESTA (http://icmab.cat/leem/siesta/)

VASP Input Files



VASP Input Files



INCAR – Calculation parameters

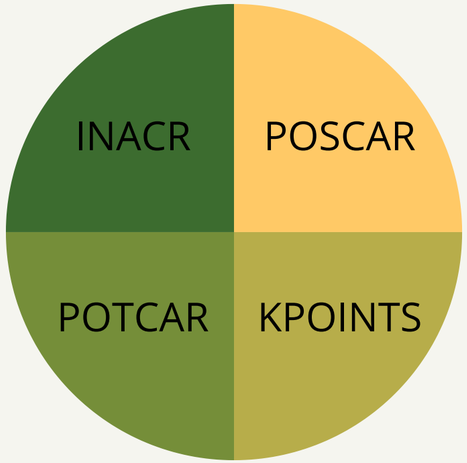
- Defines the simulation settings
  - Energy cutoff
  - Convergence criteria (electronic/ionic)
  - Relaxation settings (ions, cell)

Table 1: The INCAR file for a Copper surface calculation.

```
SYSTEM = Rhodium surface calculation

Start parameter for this Run:
  ISTART =      0    job   : 0-new  1-cont  2-samecut
  ICHARG =      2    charge: 1-file 2-atom 10-const
  INIWAV =      1    electr: 0-lowe 1-rand

Electronic Relaxation 1
  ENCUT  = 200.00 eV
  IALGO  =     18    algorithm   NELM   =     60;   NELMIN= 0; NELMDL=  3    # of ELM steps m
  EDIFF  =   1E-04   stopping-criterion for ELM
  BMIX = 2.0
  TIME = 0.05

Ionic Relaxation
  EDIFFG =  .1E-02   stopping-criterion for IOM
  NSW    =       9   number of steps for IOM
  IBRION = 2

  POTIM  =   10.0    time-step for ion-motion

  POMASS = 102.91
  ZVAL   =   11.0

DOS related values:
  SIGMA  =    0.4;  ISMEAR =  1  broad. in eV, -4-tet -1-fermi 0-gaus
```

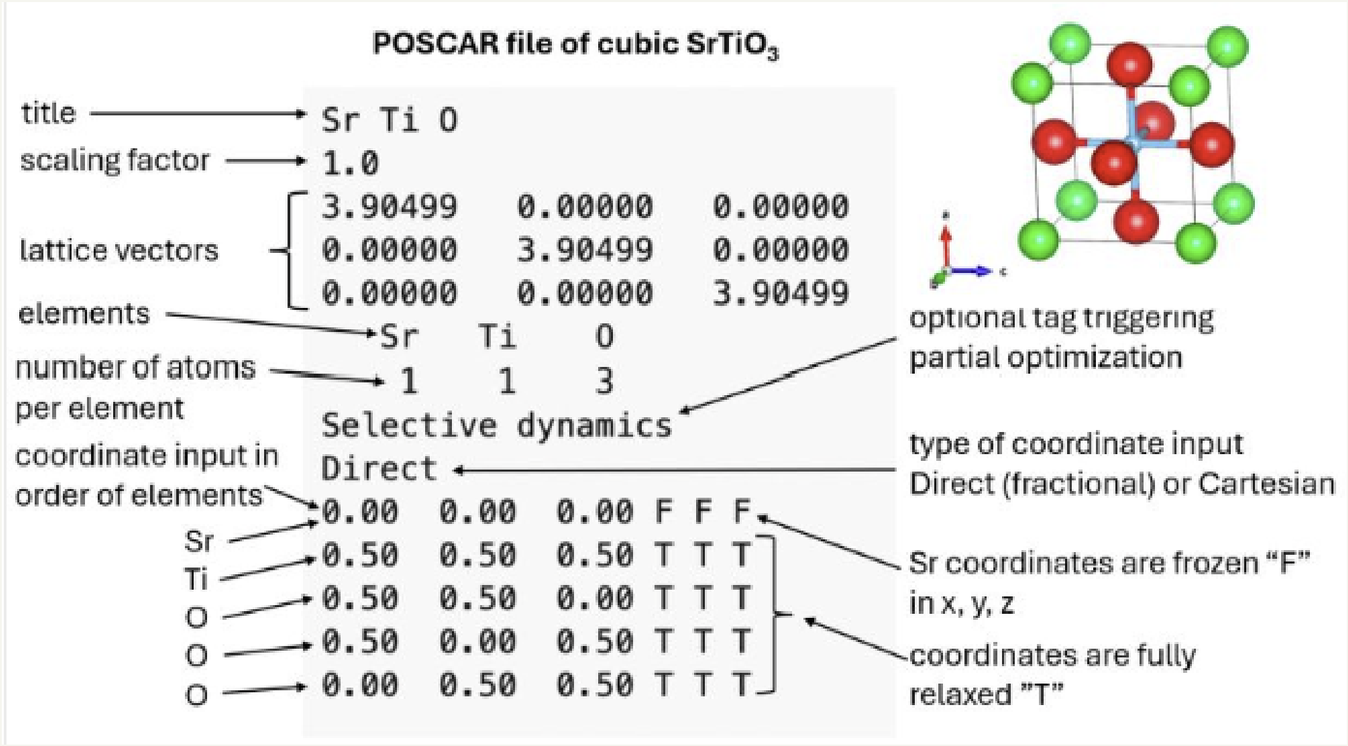
Many more tags can be set

VASP Input Files

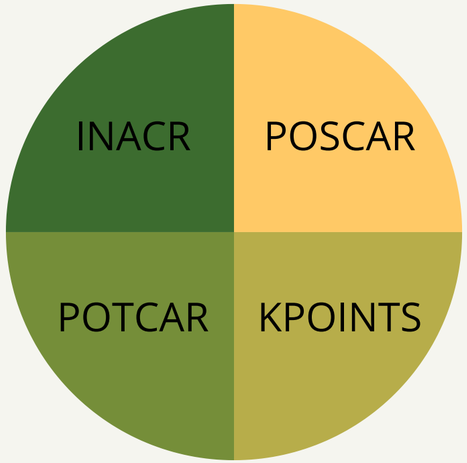


POSCAR – Structure definition

- Defines the simulation cell. Contains:
  - Lattice vectors
  - Atomic positions



VASP Input Files



POTCAR – Pseudopotentials

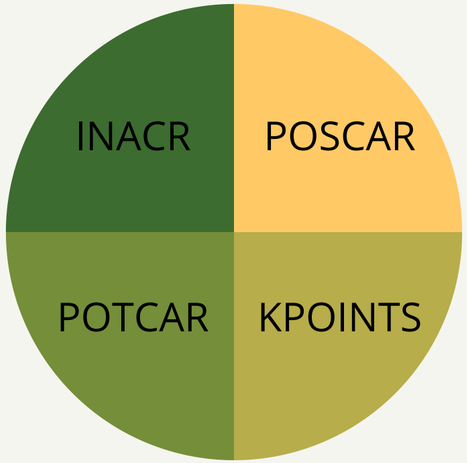
- Contains pseudopotential data for each element
  - Core–valence interaction
  - Exchange–correlation functional

Library of pseudopotentials

Eu_2/	H.25/	Lu_3/	Np/
Eu_3/	H.33/	Mg/	Np_s/
Eu_GW/	H.42/	Mg_GW/	N_s/
F/	H.5/	Mg_new/	N_s_GW/
F_d_GW/	H.58/	Mg_pv/	N_vs/
Fe/	H.66/	Mg_pv_GW/	O/
Fe_GW/	H.75/	Mg_pv.old/	O_GW/
Fe_pv/	H_AE/	Mg_sv/	O_GW_new/
Fe_pv_new/	He/	Mg_sv_GW/	O_h/
Fe_sv/	He_GW/	Mn/	Os/
Fe_sv_GW/	Hf/	Mn_GW/	O_s/
Fe_sv_h/	Hf_pv/	Mn_pv/	O_s_GW/
F_GW/	Hf_sv/	Mn_pv_new/	Os_pv/
F_GW_new/	Hf_sv_GW/	Mn_sv/	Os_sv_GW/
F_h/	Hg/	Mn_sv_GW/	O_sv/
Fr_sv/	H_GW/	Mo/	P/
F_s/	H_h/	Mo_pv/	Pa/
Ga/	H_h_GW/	Mo_pv_new/	Pa_s/
Ga_d/	Ho/	Mo_sv/	Pb/
Ga_d_GW/	Ho_3/	Mo_sv_GW/	Pb_d/
Ga_GW/	H_s/	N/	Pb_d_GW/
Ga_h/	I/	Na/	Pb_d_rel/
Ga_pv_GW/	I_GW/	Na_pv/	Pb_d_rel2/
Ga_s/	In/	Na_sv/	Pd/
Ga_sv_GW/	In_d/	Na_sv_GW/	Pd_GW/

```
PAW_PBE Ba_sv 06Sep2000
10.00000000000000000
parameters from PSCTR are:
  VRHFIN =Ba: 5s5p6s
  LEXCH  = PE
  EATOM  =   700.2255 eV,   51.4651 Ry

  TITEL  = PAW_PBE Ba_sv 06Sep2000
  LULTRA =        F    use ultrasoft PP ?
  IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
  RPACOR =    2.400    partial core radius
  POMASS =  137.327; ZVAL   =   10.000    mass and valenz
  RCORE  =    2.800    outmost cutoff radius
  RWIGS  =    3.740; RWIGS  =    1.979    wigner-seitz radius (au A)
  ENMAX  =  187.210; ENMIN  =  140.408 eV
  RCLOC  =    2.516    cutoff for local pot
  LCOR   =        T    correct aug charges
  LPAW   =        T    paw PP
  EAUG   =  351.165
  DEXC   =     .000
  RMAX   =    3.370    core radius for proj-oper
  RAUG   =    1.300    factor for augmentation sphere
  RDEP   =    2.976    radius for radial grids
  QCUT   =   -3.709; QGAM   =    7.419    optimization parameters

  Description
    l     E      TYP  RCUT    TYP  RCUT
    0   .000      23  2.800
    0   .000      23  2.800
    1   .000      23  2.700
    1  2.000      23  2.700
    2   .000      23  2.700
    2   .000      23  2.700
  Error from kinetic energy argument (eV)
  NDATA  =      100
  STEP   =   20.000   1.050
 142.      135.      131.      124.      120.      113.      105.      102.
 94.7      87.8      84.4      77.8      71.4      65.3      59.6      54.1
 49.0      44.2      39.7      33.6      29.9      26.5      22.0      19.3
 16.9      13.7      11.0      9.45      7.47      5.84      4.51      3.44
 2.59      1.93      1.41      1.02      .646      .450      .273      .185
 .111      .690E-01  .469E-01  .361E-01  .310E-01  .284E-01  .264E-01  .235E-01
 .207E-01  .169E-01  .130E-01  .102E-01  .738E-02  .531E-02  .378E-02  .311E-02
 .279E-02  .261E-02  .245E-02  .221E-02  .187E-02  .150E-02  .114E-02  .828E-03
```

VASP Input Files



KPOINTS – Brillouin zone sampling

- Defines the *k*-point mesh
- Controls integration in reciprocal space

```
Automatic mesh
0                ! number of k-points = 0 ->automatic generation scheme
Gamma            ! generate a Gamma centered grid
4  4  4          ! subdivisions N_1, N_2 and N_3 along recipr. l. vectors
0. 0. 0.         ! optional shift of the mesh (s_1, s_2, s_3)
```

Subject for convergence testing

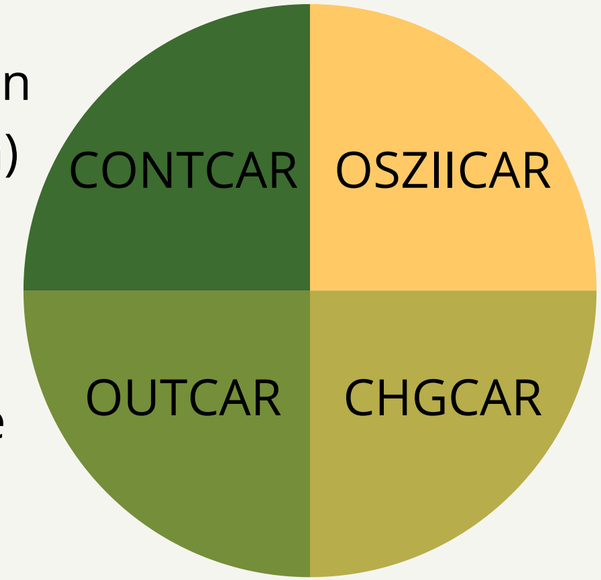
VASP Output Files

Final structure

- Atomic positions after the calculation
- Updated geometry (after relaxation)

Detailed output

- Complete information about the calculation includes:
  - Total energy
  - Forces on atoms
  - Charge distribution
  - Symmetry information



Convergence data

- Information on:
  Electronic steps & Ionic steps
- Useful for monitoring convergence

Charge density

- Final electron density of the system
- Used for:
  - Visualisation
  - Further analysis

Looking through the DFT

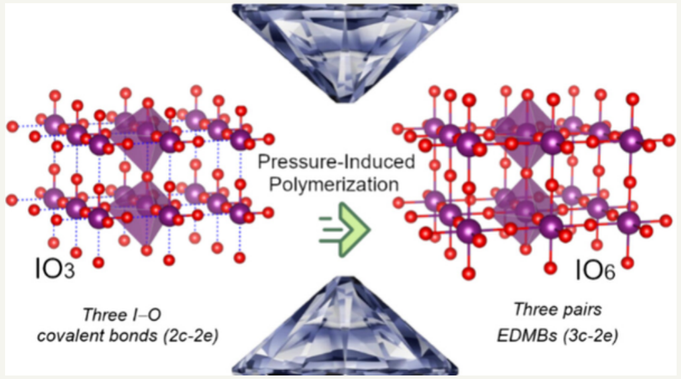
WHAT CAN WE OBSERVE?

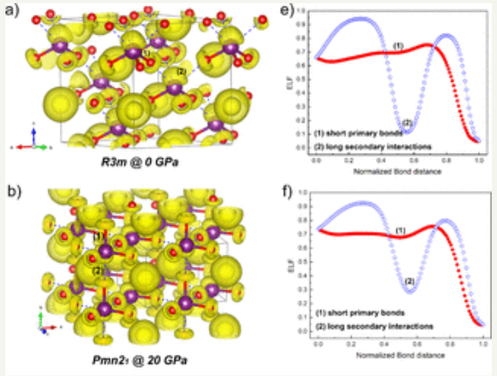
STRUCTURAL RESPONSE → **PARTIAL CHARGE DENSITY** → **DENSITY OF STATES**

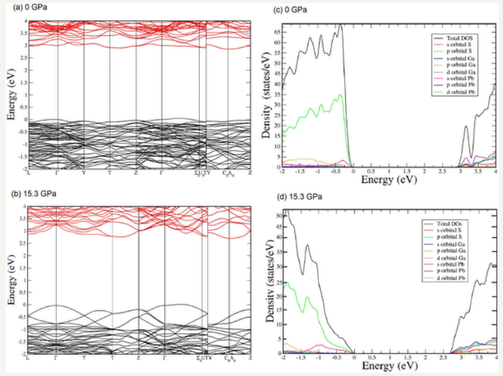
Changes in structure and properties

Contribution of specific states or regions.

Distribution of electronic states in energy







Conclusion

01 Theory

- Hohenberg–Kohn: Ground-state properties are determined by the electron density.
- Kohn–Sham: Many-electron problem → effective single-particle equations Theory

02 Method

- Plane-wave basis + pseudopotentials
- Periodic systems → Bloch functions and reciprocal space
- Self-consistent solution of the Kohn–Sham equations

03 Numerical aspects

- Accuracy controlled by:
  - k-point sampling
  - cutoff energy
- Results must be carefully converged

04 Applications

- Molecules, solids, surfaces, defects
- Electronic structure, forces, dynamics

Books

- David Sholl & Janice Steckel

Density Functional Theory: A Practical Introduction

- Richard M. Martin

Electronic Structure: Basic Theory and Practical Methods

- Jorge Kohanoff

Electronic Structure Calculations for Solids and Molecules

Online resources

- VASP Manual: https://www.vasp.at

- Quantum ESPRESSO: https://www.quantum-espresso.org

- ABINIT: https://www.abinit.org

- SIESTA: https://siesta-project.org/siesta/

- Critic2: https://aoterodelaroza.github.io/critic2/

- VESTA: https://jp-minerals.org/vesta/en/download.html

References & Further Reading

4ª Jornada del C3 – 26 de junio de 2026

> Abierta la inscripción para la 4ª Jornada del C3, que se celebrará el 26 de junio de 2026 en la Escuela Politécnica de Mieres.

C3 JORNADA EVENTOS NOTICIA

El próximo **26 de junio de 2026** tendrá lugar la **4ª Jornada del C3** en la **Sala de Grados de la Escuela Politécnica de Mieres**.

La jornada servirá como punto de encuentro para presentar las actividades desarrolladas en el C3, los nuevos servicios disponibles para la comunidad universitaria y los planes de crecimiento de la infraestructura.

La asistencia es gratuita, pero requiere inscripción previa.

MUCHAS GRACIAS POR VUESTRA ATENCIÓN

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MALTA MATERIA A ALTAS PRESIONES

EPM ESCUELA POLITECNICA DE MIERES

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