

Introduction to density functional theory

Mini course on DFT for PhD

LECTURE 5 - 18 March 2026

list of past exercises

- optimization of CO₂ molecular structure “by hands” (linear, C=O distance: 1.16 Å)
- optimization of CsCl bulk structure (energy vs. lattice parameter) 4.12 Å
- convergence tests w.r.t. k -point mesh and E_{cut} for bulk Si
- Band structure of Si ($E_{\text{gap}}=1.12$ eV, indirect)
- Cohesive energy of Si (exp: 4.63 eV/atom)
- Oxidation state of O in H₂O₂ (-2; peroxide: -1)

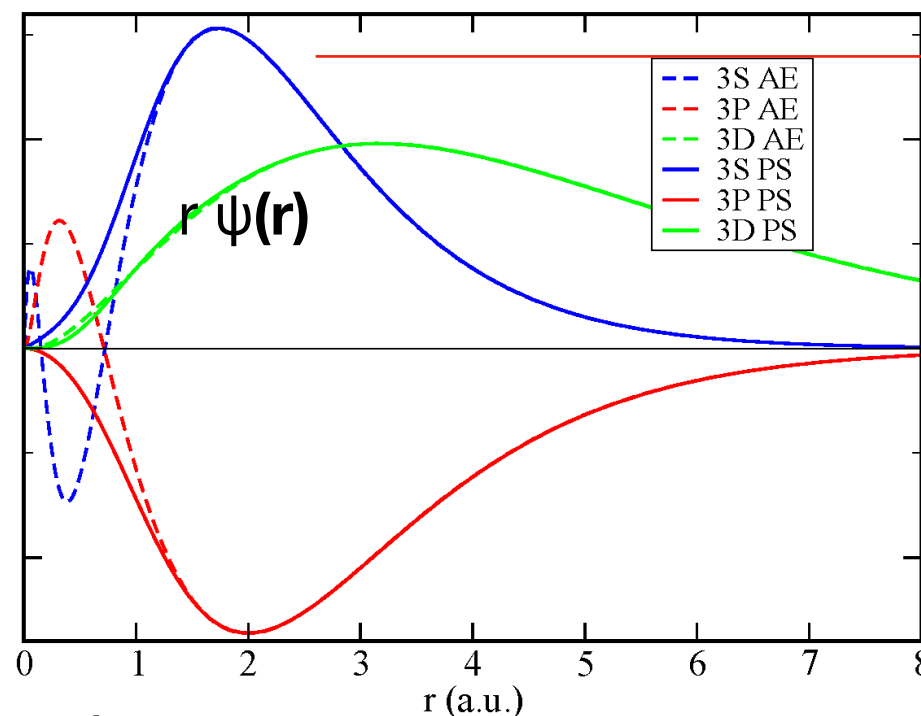
some additional general issues

1. pseudopotentials
2. extension to magnetic systems
3. dispersion forces or van der Waals
4. Hubbard correction
5. some postprocessing tools: charge density, STM, potential profiles (work function)
6. non periodic systems; compensating dipole field

1- Pseudopotentials - a

Norm-Conserving Pseudopotentials

Electron-ionic core interactions are typically represented by a nonlocal *Norm-Conserving Pseudopotential* (NCP): a soft potential, no core states, no orthonormality wiggles.



AE=“all electron”
(i.e. calculations including
also core electrons)

PS=“pseudopotential”

NCP's can be recast into the form:

$$V_l^{ps} = V_{loc}(r) + V_l(r)P_l = V(r) + \sum_m Y_{lm}(\mathbf{r})V(r)\delta(r-r')Y_{lm}^*(\mathbf{r}') \quad \text{with } V_{loc}(r) = -Z_v e^2 / r$$

In many systems, NCP's allow accurate calculations with moderate-size ($E_c \sim 10 - 20 Ry$) plane-wave basis sets

One pseudo potential for each angular momentum :

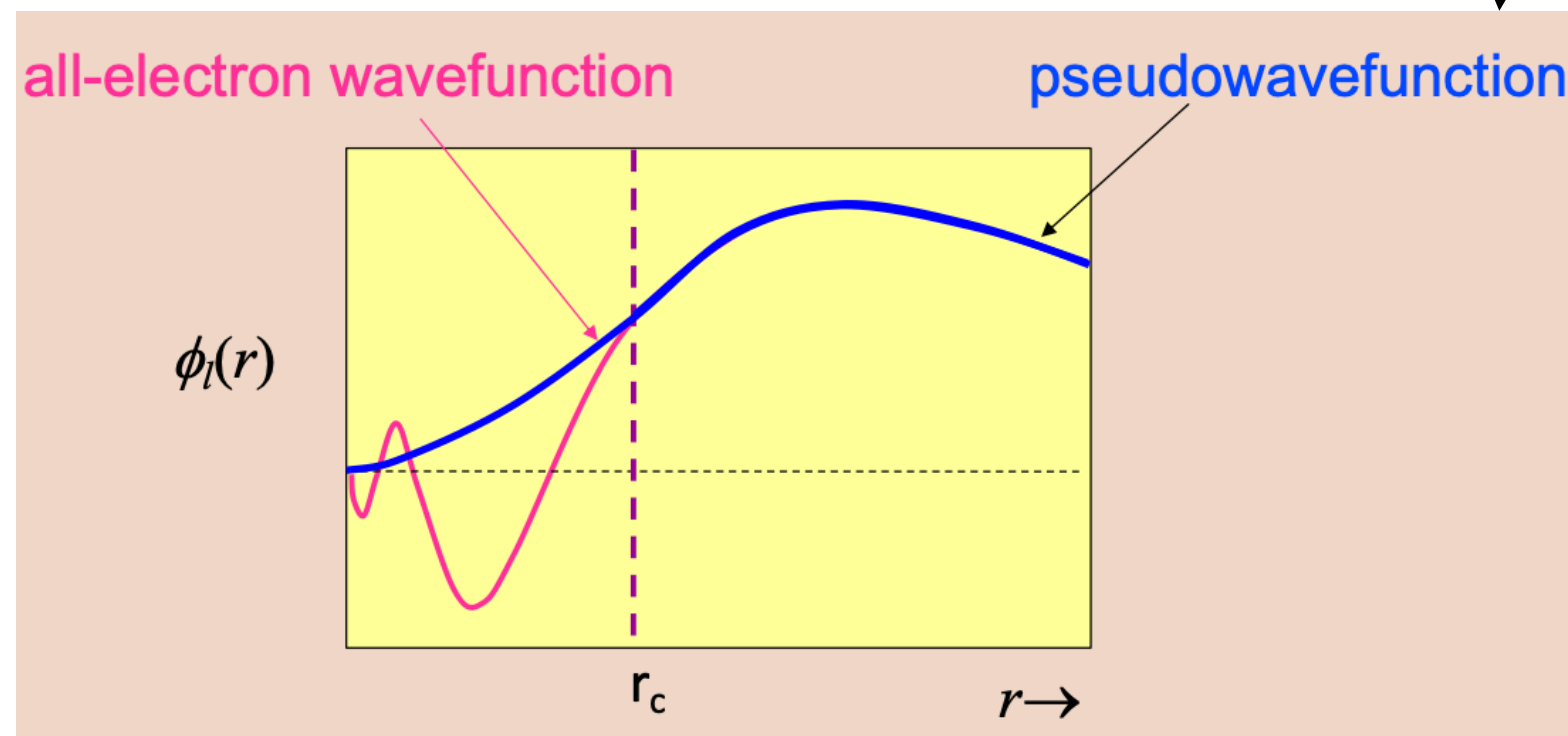
1 - Pseudopotentials - b

Norm-Conserving Pseudopotentials (continued)

NCPP's based on atomic DFT calculations, were introduced by Hamann, Schlüter, Chiang in 1979. For a given reference atomic configuration, they must meet the following conditions:

- $\epsilon_l^{ps} = \epsilon_l^{ae}$ **<= atomic energy levels must be reproduced**
- $\phi_l^{ps}(r)$ is nodeless
- $\phi_l^{ps}(r) = \phi_l^{ae}(r)$ for $r > r_c$ **<= coincidence between the “true” and “pseudo” wfc in the external region**
- $\int_{r < r_c} |\phi_l^{ps}(r)|^2 r^2 dr = \int_{r < r_c} |\phi_l^{ae}(r)|^2 r^2 dr$ **<= norm-conserving**

where $\phi_l^{ae}(r)$ is the radial part of the atomic valence wavefunction with l angular momentum, ϵ_l^{ae} its orbital energy. The *core radius* r_c is approximately at the outermost maximum of the wavefunction.

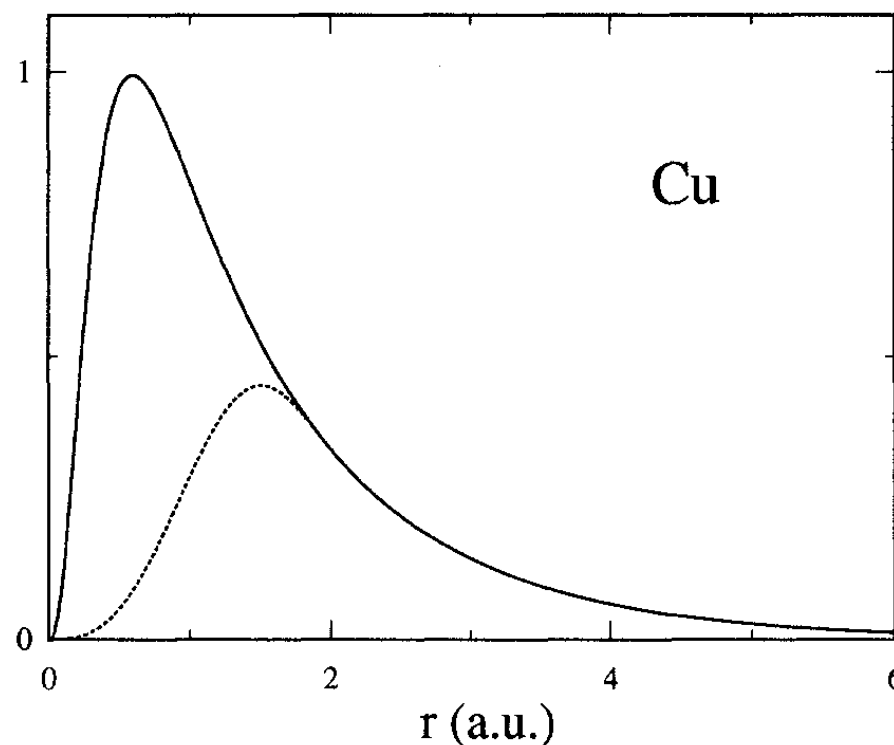


1- Pseudopotentials - c

“soft” or “**ultrasoft**” (US) pseudopotentials: **release the condition of norm-conservation**

=> smoother potentials => smoother wfc => less plane waves to describe them

The price to be paid: a more complicated expression for the electronic charge density:



$$n(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) + n^{aug}(\mathbf{r})$$

Augmentation charges, localized close to the nucleus account for “missing norm” expressed using projection functions

NB: Ultrasoft (US) and PAW pseudopotentials⁶ are (from the user’s perspective) very similar

Using US or PAW pseudopotentials, specify Ecutrho! It should be $> 4 \cdot E_{cutwfc}$

2. Extension to magnetic systems: spin density functional theory

Two independent variables: Density $n(\mathbf{r})$ and magnetization

$$m(\mathbf{r}) = -\mu_0(n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})).$$

$m(\mathbf{r})$ couples to the magnetic field ($\alpha = \uparrow, \downarrow$):

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_H(n; \mathbf{r}) + V_{ext}(n; \mathbf{r}) - \alpha \mu_0 B(\mathbf{r}) + V_{xc}^{\alpha}(n_{\uparrow}, n_{\downarrow}; \mathbf{r}) \right] \Phi_i^{\alpha}(\mathbf{r}) = \varepsilon_i^{\alpha} \Phi_i^{\alpha}(\mathbf{r}).$$

Use nspin=2 in &SYSTEM =>
the work is done twice for each k point

3. dispersion forces, or van der Waals interactions

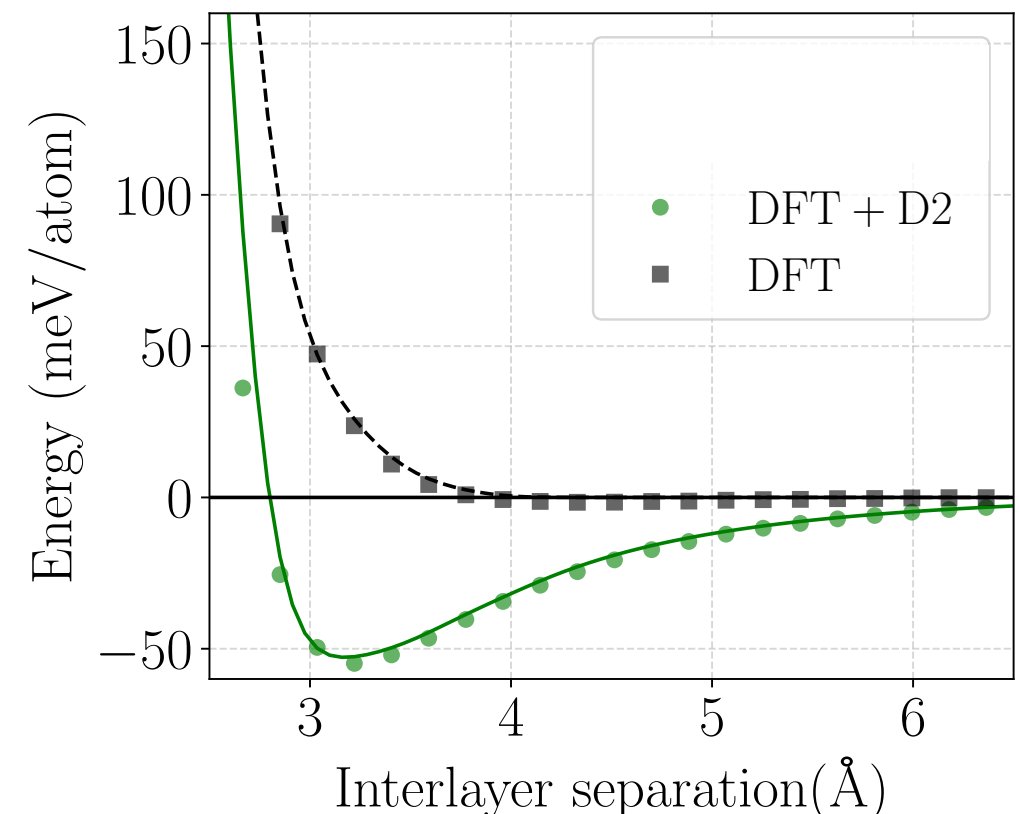
weak, long-range attractions resulting from instantaneous quantum fluctuations in electron clouds (non-local electron correlations)

Standard DFT functionals fail to capture these interactions,
=> interatomic distances are often overestimated (e.g., graphite)

Corrections required!

In &SYSTEM :

vdw_corr = 'grimme-d2' for example



4. Hubbard correction

Useful (sometimes necessary) in systems **with localised d or f electrons**. **Corrections to the standard hamiltonian required!**

Simple (and computationally low cost) **functional extension from DFT to DFT+U has low computational costs**

Introduction of an **on-site interaction of strength U (Hubbard parameter)** that represents the electron repulsion in the KS eq.:

In &SYSTEM :

$$\left[-\frac{1}{2}\nabla^2 + \hat{V}_{\text{KS}}^\sigma + \hat{V}_U^\sigma \right] \psi_{v\mathbf{k}}^\sigma(\mathbf{r}) = \varepsilon_{v\mathbf{k}}^\sigma \psi_{v\mathbf{k}}^\sigma(\mathbf{r})$$

```
&SYSTEM
```

```
...
```

```
lda_plus_u = .TRUE.
```

```
Hubbard_u(i) = 2.0 corresponding to each i of ntyp
```

Look at literature and try different parameters, checking some physical properties

5. post-processing tools

Purpose of **pp.x**: data analysis and plotting

in two steps:

(1) reads the output produced by **pw.x**, extracts and calculates the desired quantity/quantities (ρ , V , ...)

(2) writes the desired quantity to file in a suitable format for various types of plotting and various plotting programs

https://www.quantum-espresso.org/Doc/INPUT_PP.html

5. post-processing tools

plot_num = 0 : electron (pseudo-)charge density

plot_num = 11 : $V_{\text{bare}} + V_{\text{H}}$ potential

plot_num = 5 : STM

... and many others

6. What if a system is NOT 3D-periodic ?

Use a **supercell with** enough space between periodic replicas that the interaction is negligible

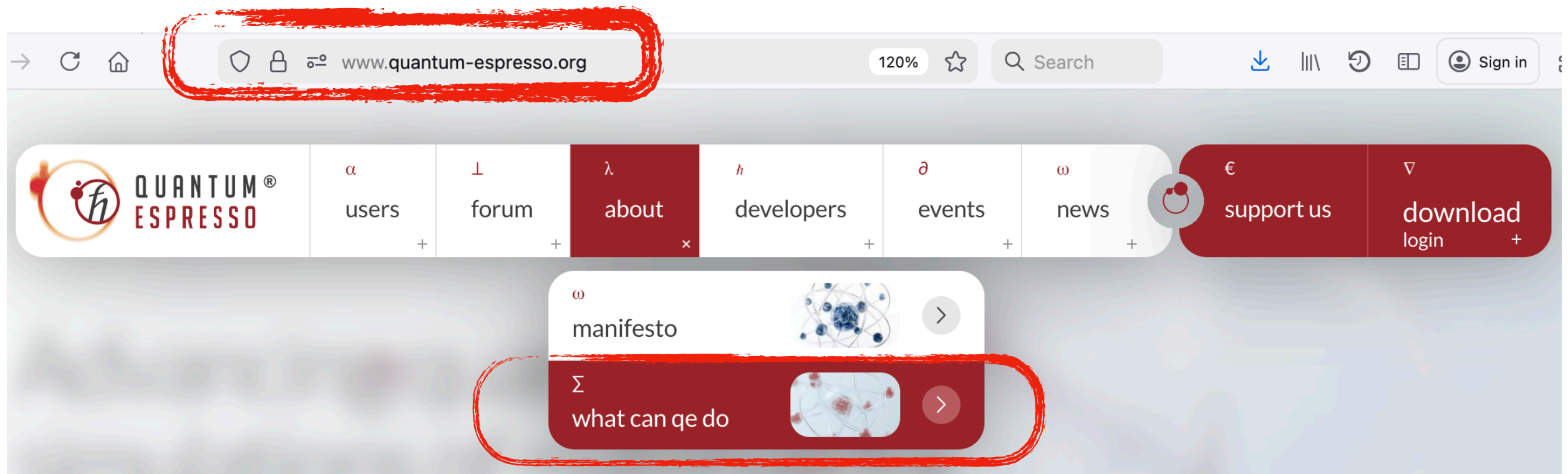


Can be problematic if the object is charged or has a dipole!

Solution:

- input variable **assume_isolated**: useful in 0-D (molecules, clusters, etc)
- introduce a **dipole layer** in the vacuum (**dipfield** in &CONTROL)

what we have done and what else we can do with QE



manifesto



what can qe do



Ground-state calculations



Structural Optimization, molecular dynamics, potential energy surfaces



Electrochemistry and special boundary conditions



Response properties (DFPT)



Spectroscopic properties



Quantum Transport



Constrained DFPT with Two Chemical Potentials to simulate photoexcited insulators

manifesto



+ what can qe do

Ground-state calculations

- Self-consistent total energies, forces, stresses, Kohn-Sham orbitals;
- Separable norm-conserving and ultrasoft (Vanderbilt) pseudo-potentials, PAW (Projector Augmented Waves);
- Many exchange-correlation functionals: from LDA to generalized-gradient corrections (PW91, PBE, B88-P86, BLYP) to meta-GGA, exact exchange (HF) and hybrid functionals (PBE0, B3LYP, HSE);
- VdW corrections: Grimme's D2 and D3, Tkatchenko-Scheffler, XDM (exchange-hole dipole moment), nonlocal VdW functionals (vdw-DF);
- Hubbard U (DFT+U, DFT+U+V);
- Berry's phase polarization;
- Noncollinear magnetism, spin-orbit coupling;

manifesto



what can qe do

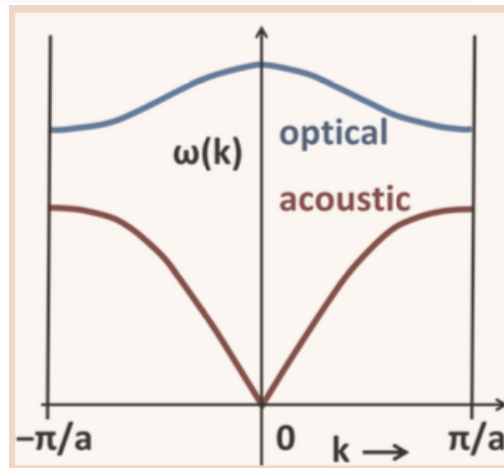
Structural Optimization, molecular dynamics, potential energy surfaces

- GDIIS with quasi-Newton BFGS preconditioning;
- Damped dynamics;
- Car-Parrinello Molecular Dynamics (CP package);
- Born-Oppenheimer Molecular Dynamics (PWscf package);
- Nudged Elastic Band (NEB) method;

Response properties (DFPT)

manifesto

what can qe do



- Phonon frequencies and eigenvectors at any wavevector;
- Full phonon dispersions; inter-atomic force constants in real space;
- Translational and rotational acoustic sum rules;
- Effective charges and dielectric tensors;
- Electron-phonon interactions and related properties with EPW;
- Third-order anharmonic phonon lifetimes, using the [D3Q](#) package;
- Infrared and (non-resonant) Raman cross-sections;
- EPR and NMR chemical shifts, using the [QE-GIPAW](#) package;
- Phonons for 2D heterostructures ([reference](#));
- Magnetic excitations (TurboMagnon package);

manifesto



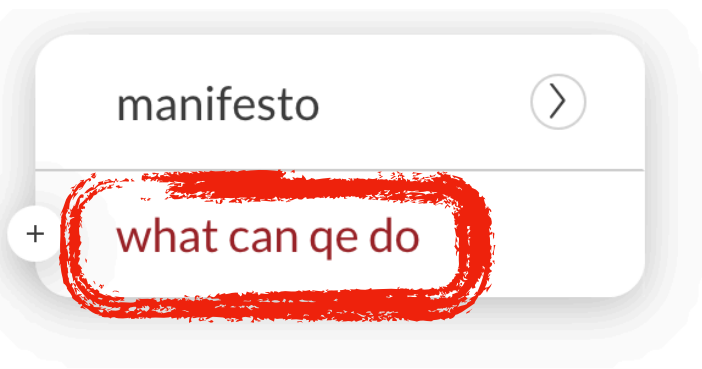
what can qe do



Spectroscopic properties

- K-edge, L1 and L2,3-edge X-ray Absorption Spectra (XSpectra package);
- Time-Dependent Density Functional Perturbation Theory (TurboTDDFT package);
- Electron energy-loss spectroscopy (TurboEELS package);
- Electronic excitations with Many-Body Perturbation Theory (GWL package);
- Electronic excitations with Many-Body Perturbation Theory, using the [YAMBO](#) package;
- Koopman's compliant functionals (KCW package);



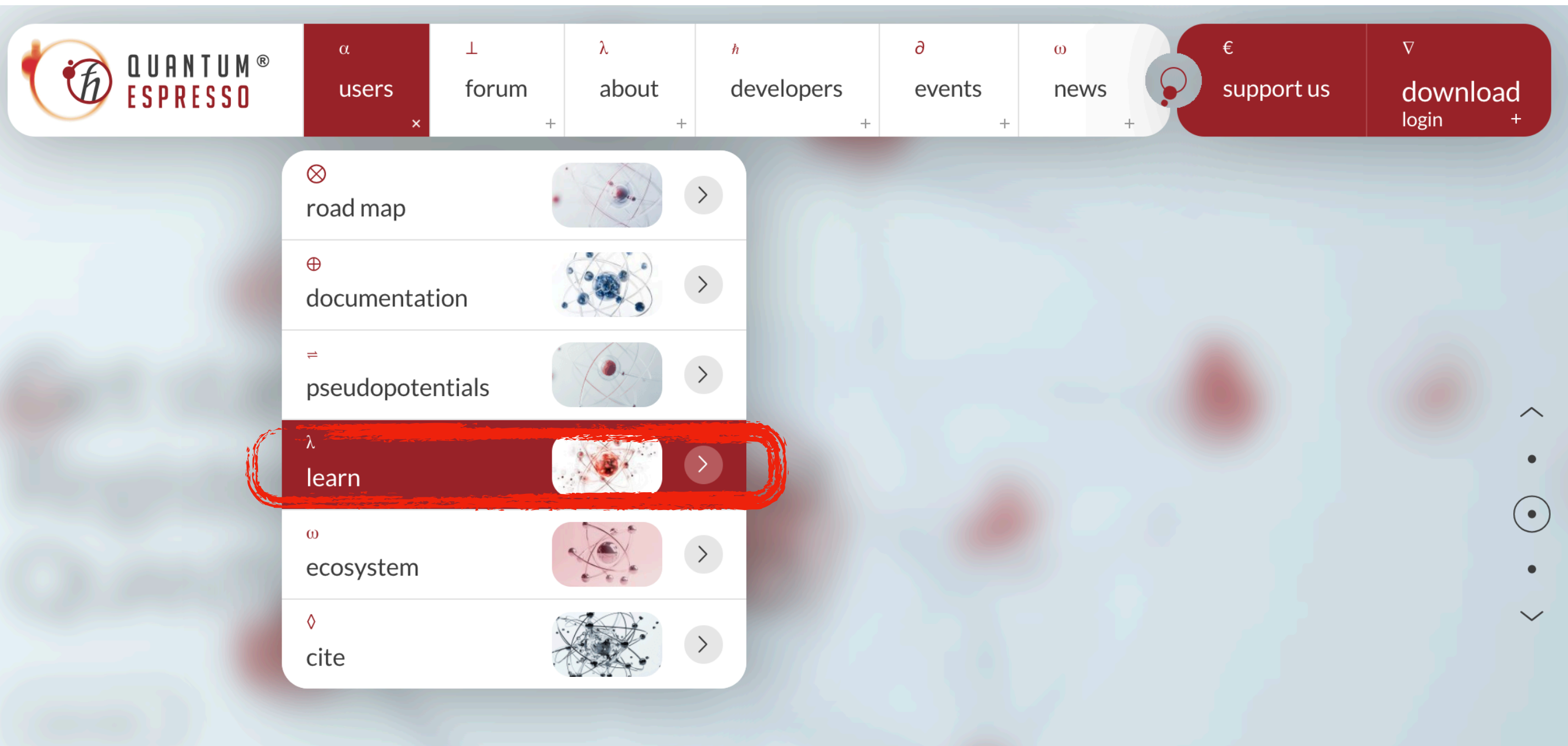


~~Quantum Transport~~

- Ballistic Transport (PWCOND package);
- Coherent Transport from Maximally Localized Wannier Functions, using the [WanT](#) code;
- ➔ • Maximally-localized Wannier functions and transport properties, using the [WANNIER90](#) code;
- Kubo-Greenwood electrical conductivity using the [KGEC](#) code;

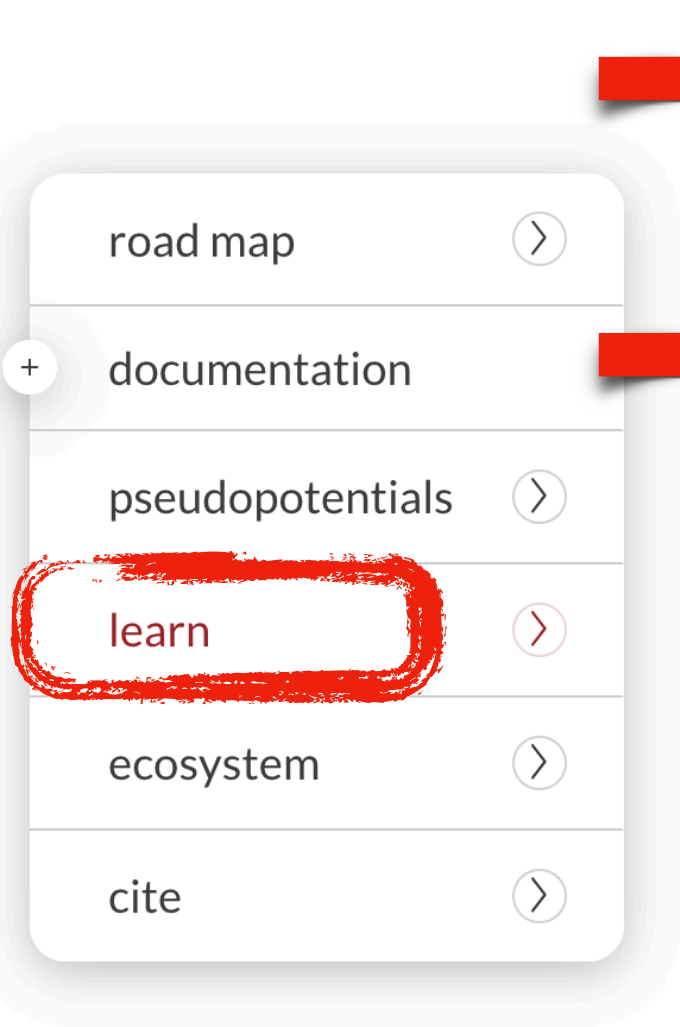


to learn more



to learn more

Tutorials and lectures from workshops



- [MaX e-School](#) on Advanced Materials and Molecular Modelling with QUANTUM ESPRESSO, May 17-28, 2021
- [Gitlab repository](#) of the material for the Summer school on [Advanced Materials and Molecular Modelling with QUANTUM ESPRESSO](#), Ljubljana, Slovenia, September 15-20, 2019
- Summer School on Materials Simulation Theory And Numerics, Pune, June 30 – July 12 2014
- ICTP-NSFC Joint School on Modern Electronic Structure Computations, Fudan University, Shanghai, July 10-12, 2013
- [IR and Raman spectra calculated with QUANTUM ESPRESSO](#): mini-tutorial by Julen Larrucea
- [NSF/Democritos Summer School on Materials Modeling from First-Principles: Theory and Practice](#), Santa Barbara, July 2009
- [Hands-on Tutorial of Quantum ESPRESSO](#), series of presentations providing both theoretical background information as well as practical help for calculations
- More QUANTUM ESPRESSO Tutorials during Schools and Workshops are listed in the [Past Events](#) page

to learn more

The screenshot shows the GitLab web interface for the 'q-e' project. The browser's address bar is highlighted with a red circle, showing the URL 'gitlab.com/QEF/q-e'. The left sidebar contains a 'Project' section with a list of items: 'q-e' (selected), 'Manage', 'Plan', 'Code', 'Build', 'Deploy', 'Operate', 'Monitor', and 'Analyze'. The main content area displays project information for 'q-e', including a commit count of 25,650, 5 branches, 53 tags, and 28 releases. It also shows a merge event: 'Merge branch 'develop' into 'develop'' by 'giannozz' 18 hours ago. Below this is a table of files and their last commit messages.

Name	Last commit
.ci	Update .ci/cineca.yml
.github	Misspell (just to test the buildbot)
COUPLE	More small Makefile tweakings
CPV	More small Makefile tweakings
Doc	Proper vdW-DF3-mc references and DOIs added
EPW	A reference to deleted LIRPHALIX was still present

and many other items...

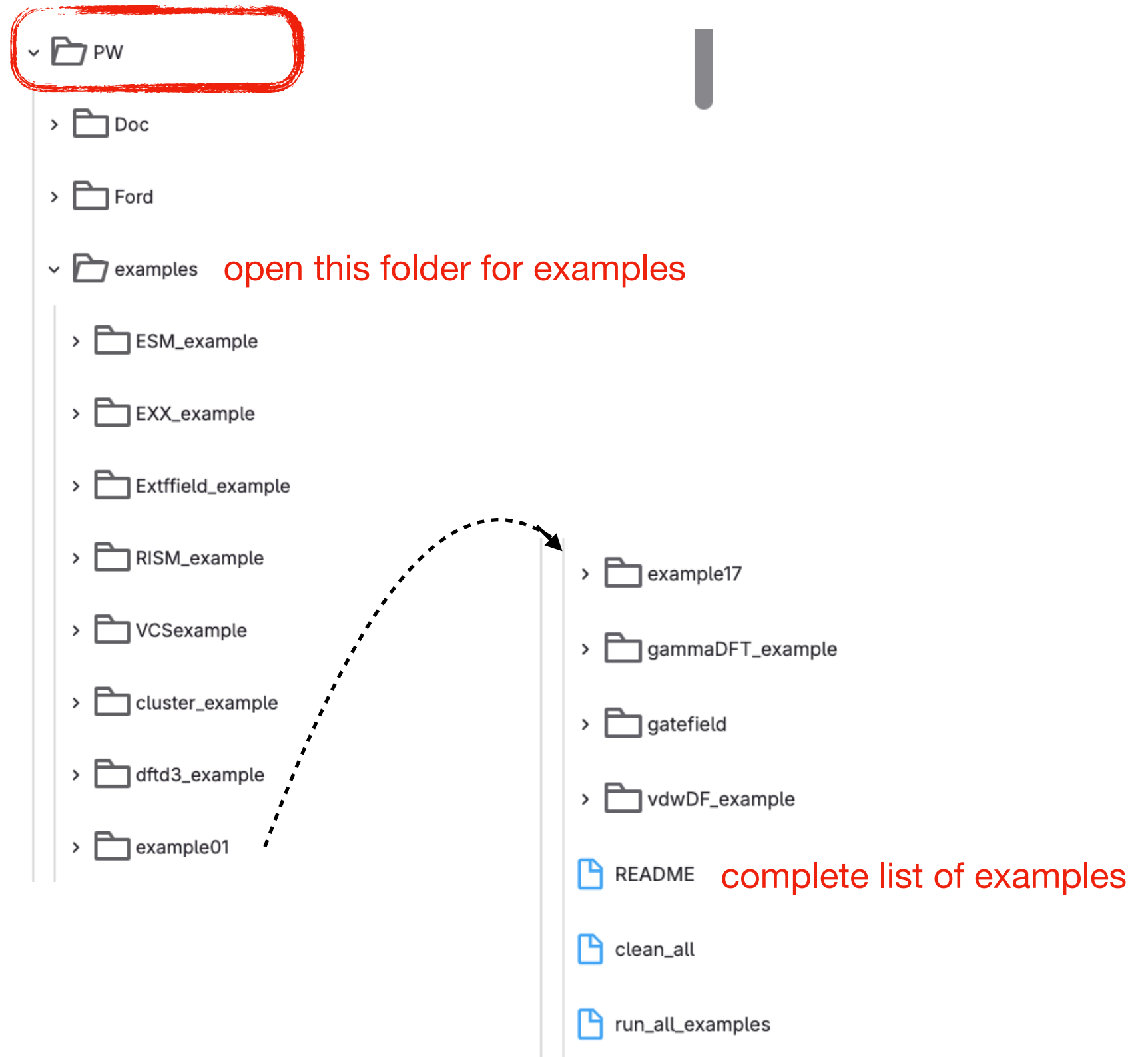
to learn more

select the one of interest...

NEB
PHonon
PIOUD
PP
PW
PWCOND
QEHeat
TDDFPT
UtilXlib
XClib
XSpectra
archive
atomic
cmake
dev-tools
dft-d3

to learn more

open folder...



to learn more

open folder...



> folder reference

here you can find the “correct” results

README

run_example



Joint ICTP MARVEL College: Materials Simulation in the Age of AI

DEADLINE FOR APPLICATION: 27 MARCH 2026

<https://indico.ictp.it/event/11146>



1 - 12 June 2026



Trieste, Italy
ICTP

TOPICS:

- Density-functional theory (DFT) and beyond
 - Linear response and lattice dynamics (DFPT, phonons)
 - Electronic, vibrational and core-level spectroscopies
 - Many-body perturbation theory (GW, BSE)
 - Topology and polarization (Berry phases, Wannier functions)
 - Advanced functionals (Hubbard, Koopmans)
-
- Introduction to statistical sampling by molecular dynamics
 - Sampling of different ensembles (thermostats, barostats, replica exchange)
 - Rare events and enhanced sampling (metadynamics, accelerated MD)
 - Machine learning for materials (descriptors, potentials, training and validation)
 - Advanced ML for sampling (fine tuning, direct force prediction, force-free integration)

1st week

2nd week

The end