# Environment Effects (Solvation, Electrochemistry, PBC) via the Environ plugin

Environ (www.quantum-environment.org) is a self-standing computational library, interfaced with the Quantum-ESPRESSO package, that allows to introduce several different external interactions in the Hamiltonian of a quantum-mechanical system. These new terms are used to represent the interaction of the system with an embedding environment. These terms will contribute to the total energy, Kohn-Sham potential and interatomic forces of the system, they may explicitly depend on the electronic density of the system (in particular for the shape of the embedding environment, i.e. of the cavity) and, thus, need to be computed and updated at each SCF step.

In this tutorial we will perform the following tasks:

1. Download and install Environ
2. Use Environ to compute the total solvation free energy of an isolated neutral solute
3. Use Environ to simulate isolated charged systems in vacuum or solution with different PBC correction schemes.
4. Use Environ to simulate a 2D system in vacuum or solution with a parabolic correction for PBC.
5. Use Environ to simulate a 2D charged system in the presence of a compensating charge distribution (Helmholtz layer).
6. Use Environ to compute the optical spectrum of a dye in vacuum and in solution using TDDFpT.

## Task #1: Downloading and Installation of the plugin

To run a simulation with Environ, first you will have to download it and install it on top of a working Quantum-ESPRESSO distribution. The code is not distributed together with the official QE package, but it is still hosted in the QE-Forge portal, under the project “Solvent models and electrochemistry”

http://qe-forge.org/gf/project/electroemb/frs/

Two official distributions of Environ have been released already, the last one compatible with QE-6.0 and previous versions up to QE-5.1.X.

The installation procedure at the moment is rather lengthy but reasonably straightforward, for the purposes of this school it has been already performed for you (you can find a specific set of executables). The procedure may be simplified or removed all together in the future (making Environ a permanent part of QE), nonetheless it is worth looking at the steps involved.

Installation instructions are summarized in the README file inside the main Environ/ directory and reported in the following:

Preliminary steps:

*-1. Configure QE following the standard procedure (running './configure' from QE-main-dir should be enough in most cases).*

0. *Compile QE without the Environ module (running 'make pw' from QE-main-dir).*

If there are problems with the preliminary steps, look up for solutions on the PW forum or Quantum-Espresso webpage.

For PW and NEB:

*1. In QE-main-dir/ run the script addsonpatch.sh*
*./install/addsonpatch.sh Environ Environ/src Modules -patch*
*2. In QE-main-dir/PW/src dir run*
*../../Environ/patches/environpatch.sh -patch*
*3. In QE-main-dir/install/ dir run*
*./makedeps.sh -addson Modules Modules*
*./makedeps.sh PW/src*
*4. In QE-main-dir re-compile pw.x and neb.x*
*make pw*
*make neb*
*5. Run pw.x (or neb.x) with -environ flag, e.g.*
*pw.x -environ < pwinput > pwoutput*

For TDDFPT:

*6. In the QE-main-dir/make.sys file generated by ./configure add -D__ENVIRON to the MANUAL_DFLAGS variable.*
*7. In QE-main-dir/install/ dir run*
*./makedeps.sh TDDFPT/src*
*8. In QE-main-dir compile tddfpt*
*make tddfpt*
*9. Run the executables with -environ flag.*

For CP (only starting from QE-5.3.0):

*10. In CPV/src dir run*
*../../Environ/patches/cp-patch.sh*
*11. In install dir run*
*./makedeps.sh CPV/src*
*12. In QE main dir re-compile cp*
*make cp*
*13. Run cp.x with argument cp.x -environ*

It is possible to revert the Quantum-ESPRESSO package to a pristine (Environ-free) state by following these steps:

*1. In QE main dir run the script addsonpatch.sh*
*./install/addsonpatch.sh Environ Environ/src Modules -revert*
*2. In PW/src dir run*
*../../Environ/patches/environpatch.sh -revert*
*3. In CPV/src dir run*
*../../Environ/patches/cp-revert.sh -revert*
*4. Be sure to remove objects, modules and executables*
*make clean*

## Task #2: Perform a full SCCS calculation of an isolated molecule

Environ requires a separate input file (environ.in) in order to specify how the cavity is built, which external interactions are turned on, what are their strengths (physical parameters) and which are the numerical parameters of the calculations involved with the different effects.
In a SCCS calculation all the external interactions implanted in Environ are involved and their strengths have been carefully parameterized for aqueous solutions of neutral and charged compounds. To specify an SCCS calculation the predefined, user-friendly, input keyword `environ_type` has been included in the environ.in file, allowing skipping most of the cumbersome set up.
The input of the first example will look like this

```
&ENVIRON
   !
   verbose = 0
   environ_thr = 1.d-1
   environ_type = 'water'
   tolrhopol = 1.d-11
   !
 /
```

The additional keyword that you find are debug and numerical parameters:

- the `verbose` keyword allows you to have a more detailed printout of the calculations performed inside Environ (if .EQ. 1 an extra environ.debug file is generated along the run) and, possibly, to dump large cube files containing some useful physical quantities (e.g. the polarization density as visualized in Figure 1).
- The `environ_thr` and `tolrhopol` keywords are IMPORTANT parameter to check in order to avoid poor/no convergence in the calculation (see FAQs http://www.quantum-environment.org/faq.html).

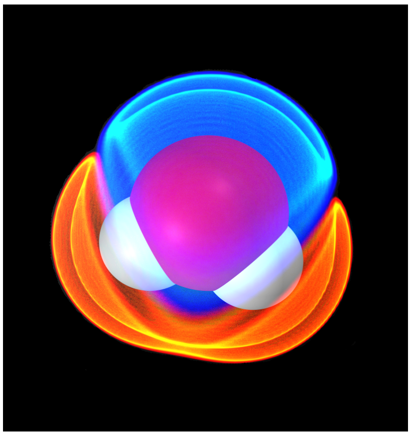


Figure 1: Polarization charge around a water molecule solvated in continuum water

By performing two different geometry optimization calculations, one in vacuum and one in solution, we can have access to the total solvation free energy of the system.

NOTE: there may be confusion with the definition of solvation free energy, solvation energy, total energy, etc. if you have any doubt, please ask or look at the FAQs.

## Task #3: Remove/decrease PBC errors in simulations of charged isolated systems

To avoid redundancy, since most PBC corrections schemes are integral part of QE programs, the keywords related to PBC corrections are not included in the environ.in file, but need to be specified using the `assume_isolated` keyword in the &SYSTEM namelist in the main PW input file. Together with the options implemented in standard QE, the parabolic correction potentials for 0D and 2D systems are available through Environ by specifying the ‘pcc’ and ‘slabz|slaby|slabz’ options and by running the simulation with the environ plugin (i.e. pw.x –environ).

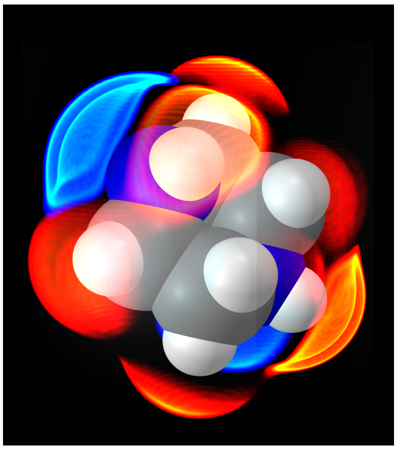


Figure 2 Polarization charge surrounding the simulated molecule

For the example in this task, different pbc correction schemes can be applied to a charged organic molecule simulated in vacuum or in solution: no correction, Makov-Payne, Martyna-Tuckerman, Point Counter-Charge. Which one is fastest? Which one is more correct?

## Task #4: Simulating a slab with continuum solvent and parabolic pbc corrections

In this example we will perform a simulation with and without the continuum dielectric embedding around a Pt slab (unphysically thin) with an absorbed atop CO molecule.

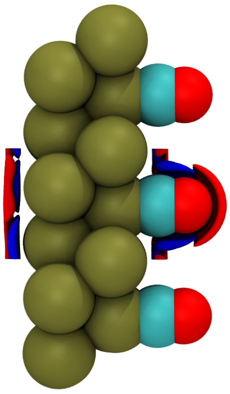


Figure 3 Polarization charge around the simulated Pt-CO slab

The input file for the calculation in the dielectric looks like this

```
&ENVIRON
   !
   verbose = 0
   environ_thr = 1.d0
   environ_type = 'input'
   eps_mode = 'full'
   tolrhopol = 5.D-13
   mixrhopol = 0.6
   env_static_permittivity = 80
   env_surface_tension = 0.D0
   env_pressure = 0.D0
   !
 /
```

Where you can clearly see how the additional external terms are turned on/off and tuned. Please note the additional `eps_mode = ‘full’` keyword, required by the presence of Pt among the atoms of the system. This is due to the fact that pseudopotentials for transition metals and halogens can present holes in the valence electronic density, that would give rise to spurious results or to unconverged results when continuum embedding are turned on (why?).

## Task #5: Simulating a charged slab with continuum solvent, parabolic pbc corrections and additional fixed layers of countercharge

In this example we will see how one can specify additional charge densities in the environ.in input file and use them to model Helmholtz layers of electrolyte countercharges (sorry for the misspelled helmotz in the input files!).

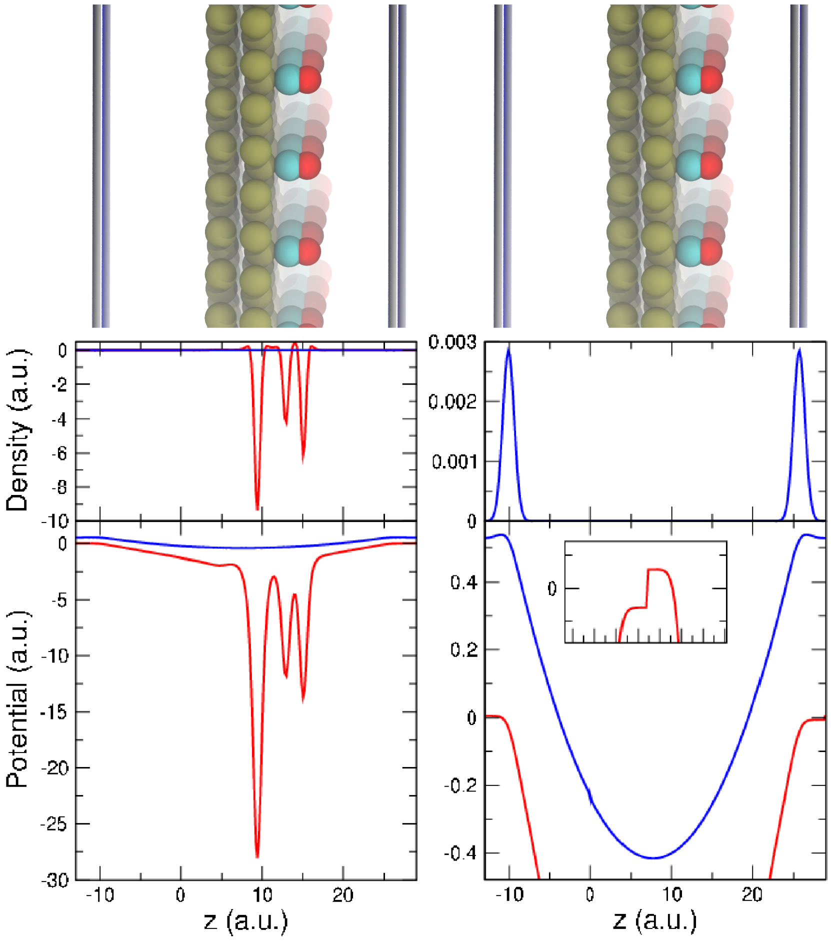
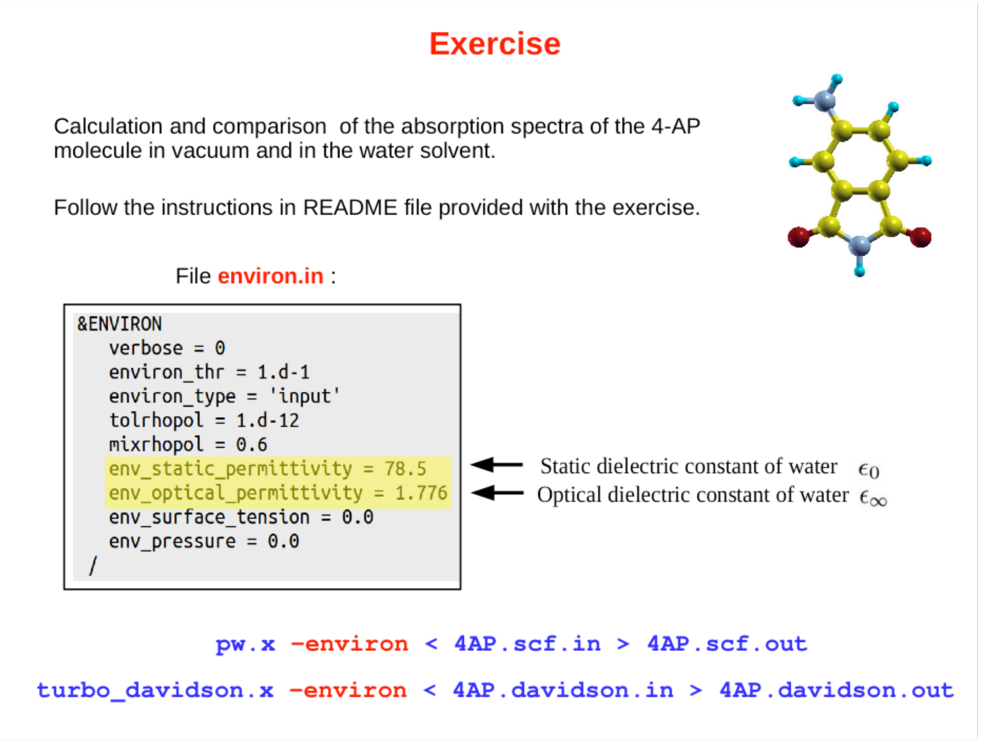


Figure 4: Same system as Figure 3, but in the presence of additional smeared charge layers. Bottom panels: charge densities (top) and electrostatic potentials of the system (in red) and of the external charge distribution (in blue).

```
&ENVIRON
   !
   verbose = 0
   environ_thr = 1.d0
   environ_type = 'input'
   eps_mode = 'full'
   tolrhopol = 5.D-13
   mixrhopol = 0.6
   env_static_permittivity = 1
   env_surface_tension = 0.D0
   env_pressure = 0.D0
   env_external_charges = 2
   !
 /
 EXTERNAL_CHARGES (bohr)
 0.5 0. 0. 25.697 1.0 2 3
 0.5 0. 0. -10.303 1.0 2 3
```

## Task #6: Perform TDDFpT calculations of a molecule in solution



**Exercise**

Calculation and comparison of the absorption spectra of the 4-AP molecule in vacuum and in the water solvent.

Follow the instructions in README file provided with the exercise.

File **environ.in** :

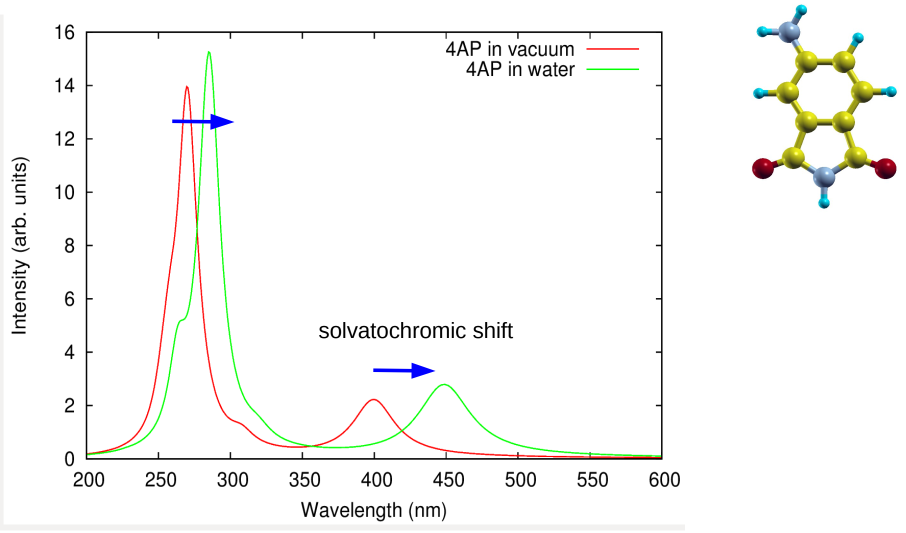
```
&ENVIRON
   verbose = 0
   environ_thr = 1.d-1
   environ_type = 'input'
   tolrhopol = 1.d-12
   mixrhopol = 0.6
   env_static_permittivity = 78.5
   env_optical_permittivity = 1.776
   env_surface_tension = 0.0
   env_pressure = 0.0
 /
```

← Static dielectric constant of water $\epsilon_0$

← Optical dielectric constant of water $\epsilon_\infty$

```
pw.x -environ < 4AP.scf.in > 4AP.scf.out
turbo_davidson.x -environ < 4AP.davidson.in > 4AP.davidson.out
```

**Exercise**



**Note 1:** The spectra are not converged (wrt the supercell size, number of Davidson eigenvalues, etc.).

**Note 2:** turboLanczos code can also be used with the Environ module.