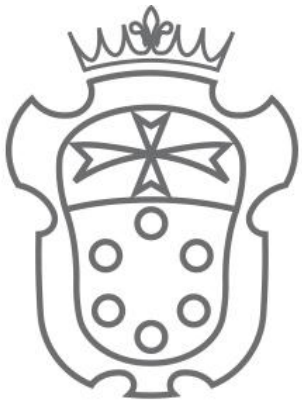
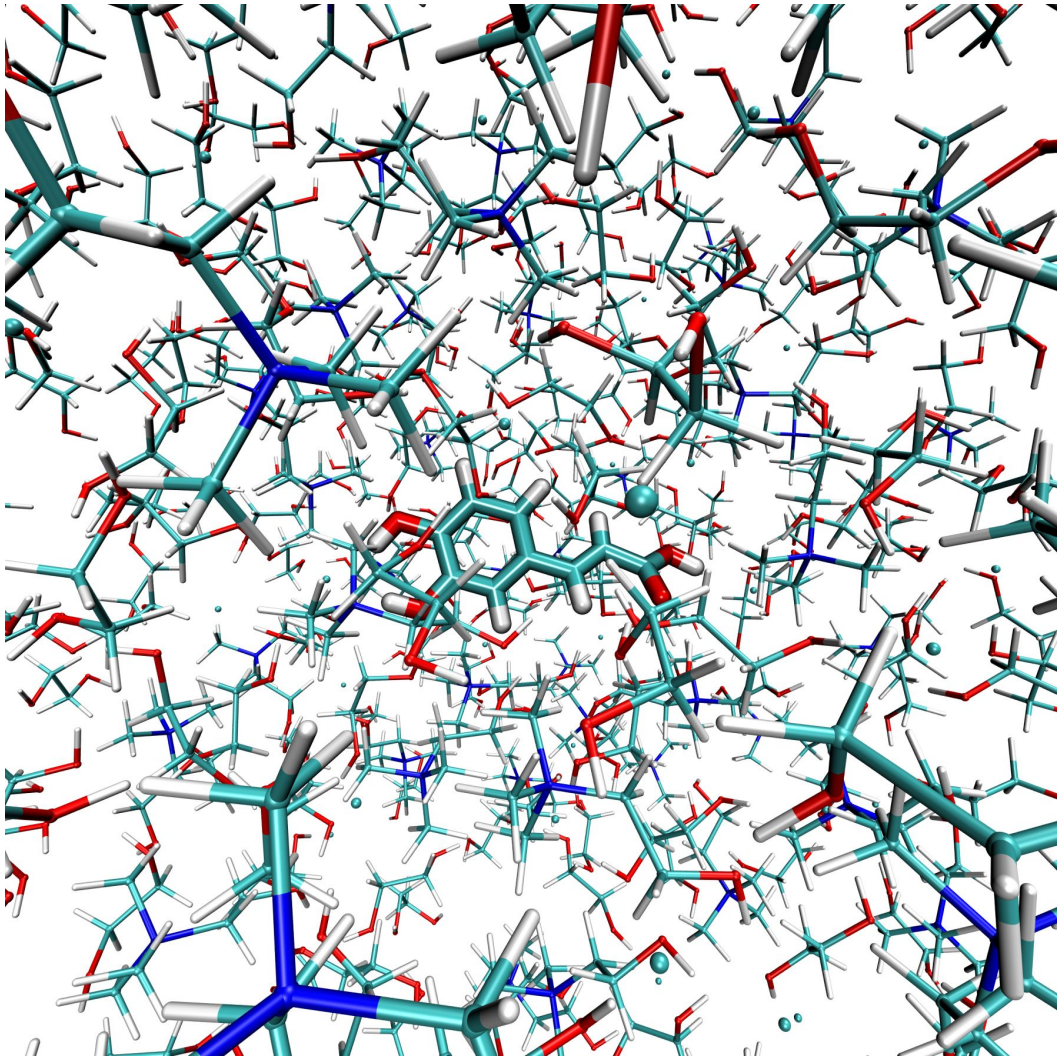


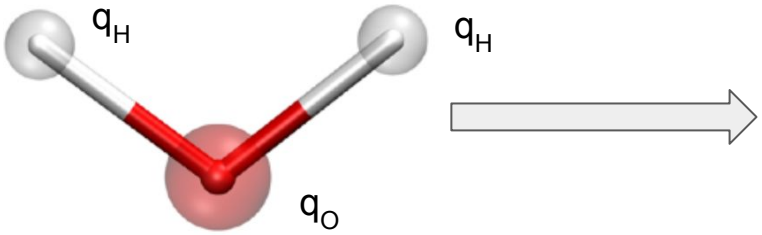
SCUOLA
NORMALE
SUPERIORE

Lab Session 2

Goal: Parameterizing a Fluctuating Charges forcefield for DES



Recap: QM/Fluctuating Charges Model



Depend on atomic electronegativity (χ) and chemical hardness (η)

$$E^{tot} = E_{QM} + E_{MM} + E^{int}_{QM/MM}$$

$$E^{tot} = E_{QM}[\rho] + \frac{1}{2}\mathbf{q}^{\dagger}\mathbb{J}\mathbf{q} + \mathbf{q}^{\dagger}\chi + \mathbf{q}^{\dagger}\lambda + \mathbf{q}^{\dagger}\Phi[\rho]$$

$$\frac{\delta E^{tot}}{\delta \rho(\mathbf{r})} = h^0_{KS}[\rho] + \hat{v}^{emb} = \tilde{F}$$

$$\frac{\delta E^{tot}}{\delta \mathbf{q}_\lambda} = \mathbb{D}\mathbf{q}_\lambda + \Phi[\rho] + \chi = 0$$

Fock Matrix

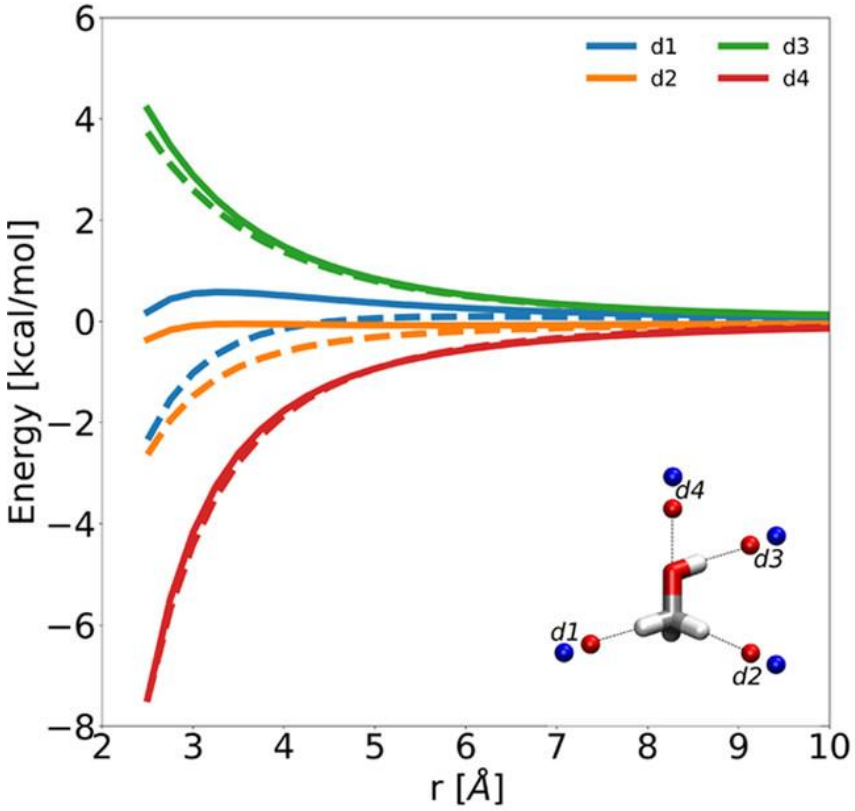
Polarization Equations

Solve with SCF procedure.

Recap: FQ Parameterization

Obtain χ and η by reproducing: 1) QM/EE interaction energies

QM/EE



(c) Methanol

Treat the molecule at the FQ level of theory and solve the system of equations with an external source of charge (FQ/EE).

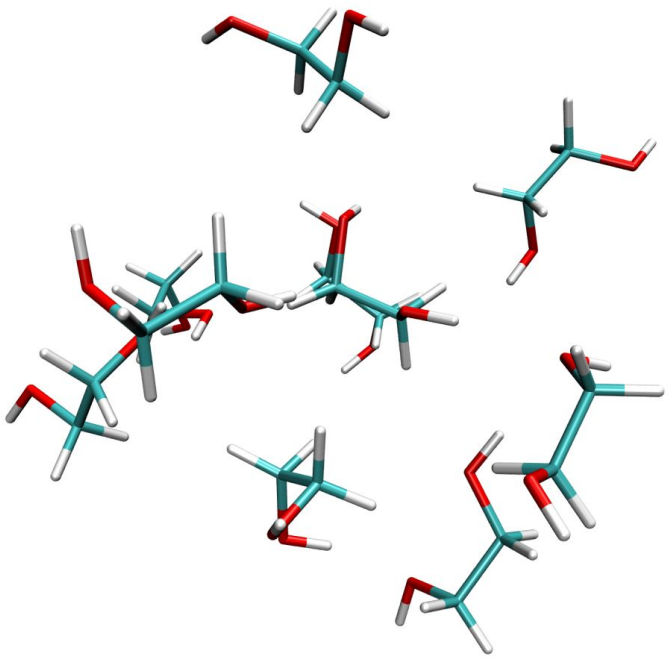
GOAL: Try to reproduce QM/EE results.

M. Ambrosetti et al, Journal of Chemical Theory and Computation **2021** *17* (11), 7146-7156

Recap: FQ Parameterization

Obtain χ and η by reproducing: 2) QM static polarizability

QM static polarizability tensor
of clusters of molecules



Treat the cluster of molecules at the FQ level of theory and obtain the polarizability tensor.

GOAL: Try to set the diagonal elements equal to QM results.

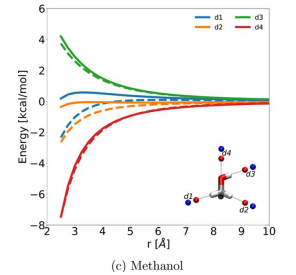
$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

Recap: FQ Parameterization

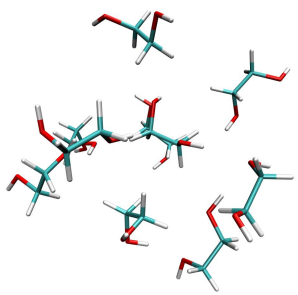
Obtain χ and η by reproducing:

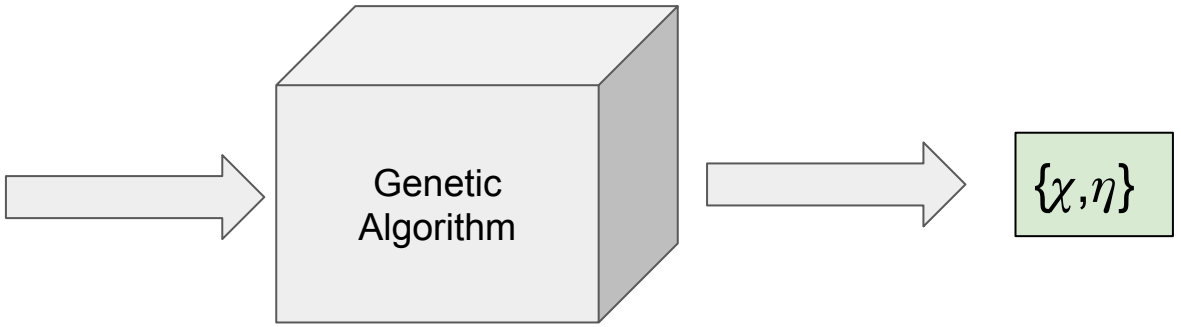
1) QM/EE interaction energies
2) QM static polarizability

The goal of this lab will be that of parameterizing the FQ parameters χ and η for a Deep Eutectic Solvent by using a Genetic Algorithm.
Our training set will be *QM/EE interaction energies* and *QM polarizabilities*

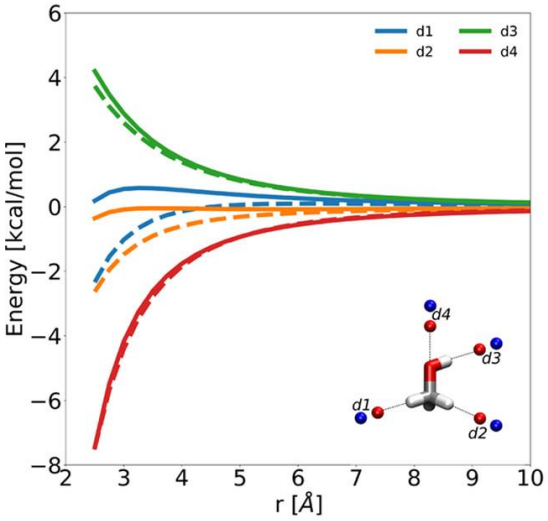


(c) Methanol

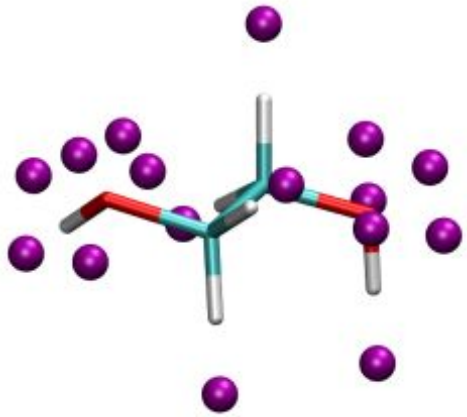




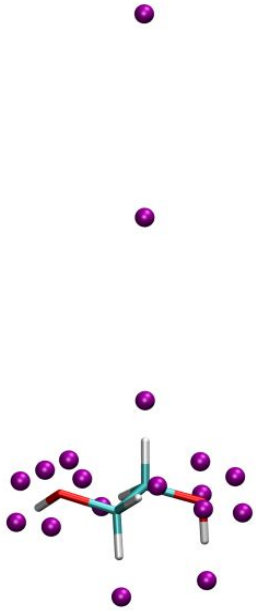
Recap: session 1



(c) Methanol



1) Positioned the CM of the fixed dipoles around the selected molecules (Cl/Choline and Ethylenglycol).

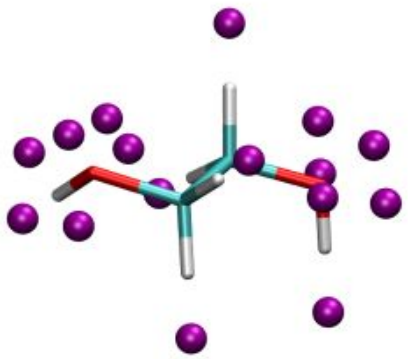


2) Translated the CM of each dipole along the correct direction.

This allowed us to set up the geometries for the QM/EE calculations.

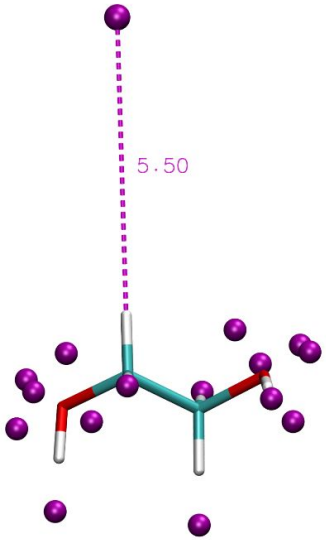
They will be used to generate the training set of the GA.

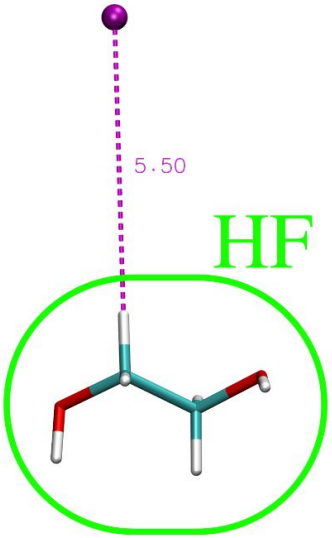
What we will do this time

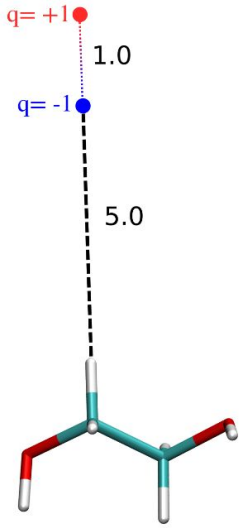


1) Start from our dipoles geometries,
2) Generate the QM/EE inputs
   Only with the translated dipole
3) Run the QM/EE calculations.

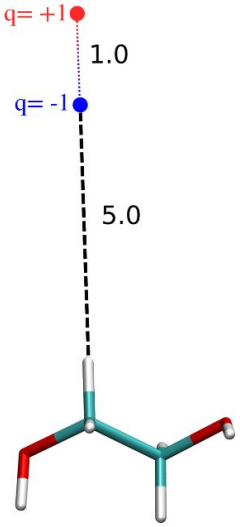
To do so we first need to recap the QM/EE model.







What we will do this time

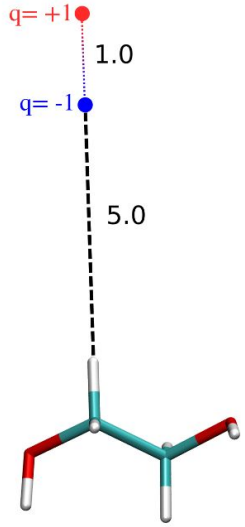


1) Start from our dipoles geometries,
2) Generate the QM/EE inputs
   Only with the translated dipole
3) Run the QM/EE calculations.

HF/EE

$$\mathscr{E}[\mathbf{D},\mathbf{q}] = \mathrm{tr}\mathbf{h}\mathbf{D} + \frac{1}{2}\mathrm{tr}\mathbf{D}\mathbf{G}(\mathbf{D}) + \mathbf{q}^{\dagger}\mathbf{V}(\mathbf{D})$$

What we will do this time



1) Start from our dipoles geometries,
2) Generate the QM/EE inputs
   Only with the translated dipole
3) Run the QM/EE calculations.

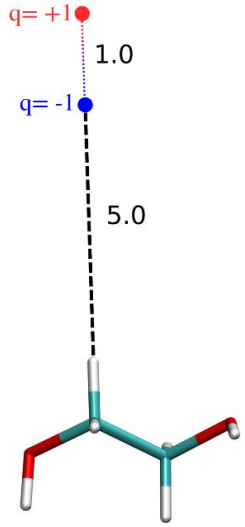
HF/EE

$$\mathscr{E}[\mathbf{D},\mathbf{q}] = \mathrm{tr}\mathbf{h}\mathbf{D} + \frac{1}{2}\mathrm{tr}\mathbf{D}\mathbf{G}(\mathbf{D}) + \mathbf{q}^{\dagger}\mathbf{V}(\mathbf{D})$$

$$F_{\mu\nu} = h_{\mu\nu} + G_{\mu\nu}(\mathbf{D}) + \sum_i q_i V_{i,\mu\nu}$$

Solve SCF

What we will do this time



1) Start from our dipoles geometries,
2) Generate the QM/EE inputs
   Only with the translated dipole
3) Run the QM/EE calculations.

HF/EE

QM/EE interaction energy

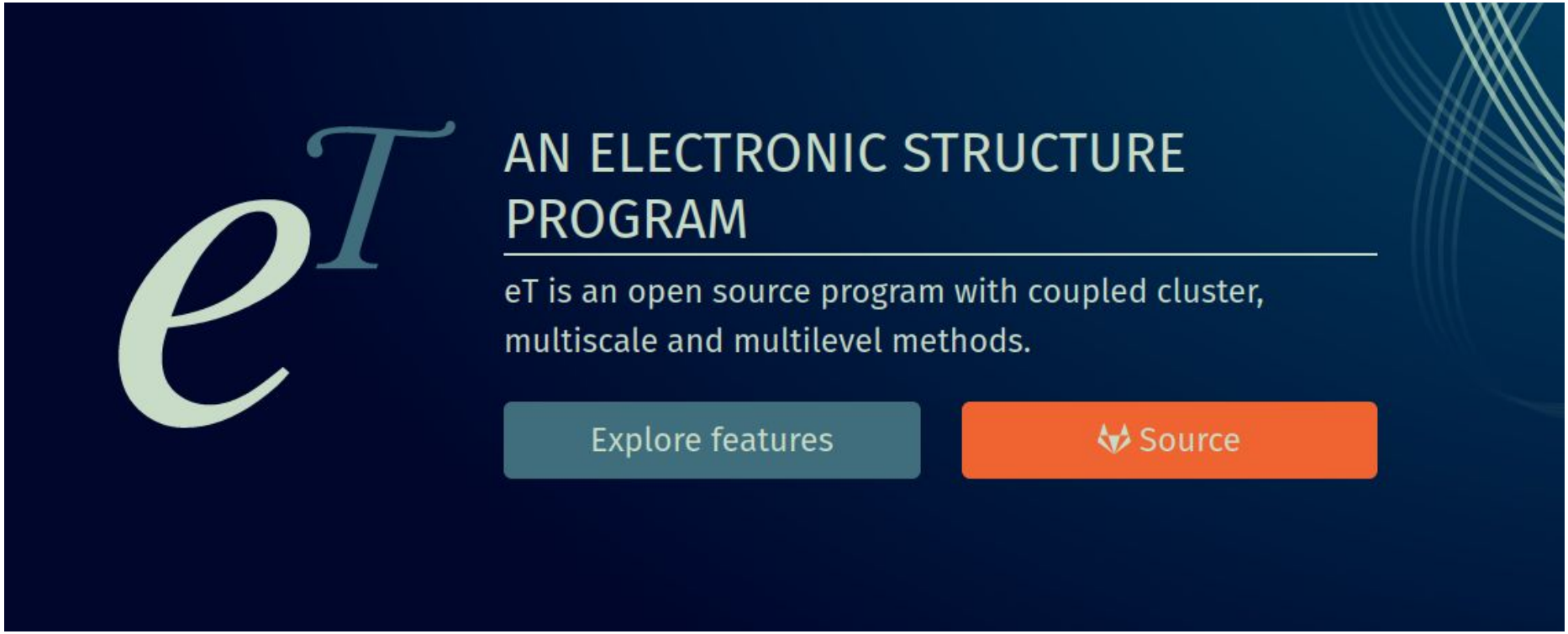
$$\mathscr{E}[\mathbf{D},\mathbf{q}] = \mathrm{tr}\mathbf{h}\mathbf{D} + \frac{1}{2}\mathrm{tr}\mathbf{D}\mathbf{G}(\mathbf{D}) + \mathbf{q}^{\dagger}\mathbf{V}(\mathbf{D})$$

$$F_{\mu\nu} = h_{\mu\nu} + G_{\mu\nu}(\mathbf{D}) + \sum_i q_i V_{i,\mu\nu}$$

Solve SCF

How to compute these energies?

To compute QM/EE energies we will use:

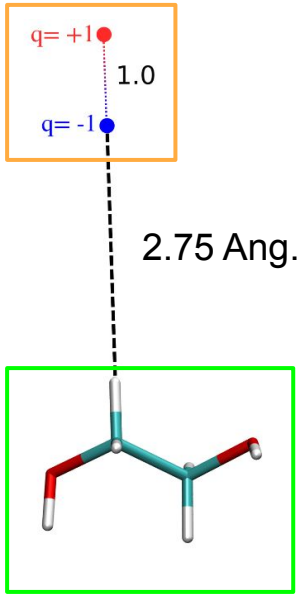


https://www.etprogram.org/

No need to know much about it, just how the input has to look like…

Input of an eT calculation

```
system
   name: ethylenglycol_ with embedding dipole number 0 at 2.75 Ang. and sign -+
   charge: 0
   multiplicity: 1
end system

do
  ground state
end do

memory
   available: 100
end memory

solver scf
   algorithm: scf-diis
end solver scf

molecular mechanics
   forcefield: non-polarizable
end molecular mechanics

method
   hf
end method

geometry
basis: aug-cc-pvdz
 C    -0.56892     0.51099    -0.03064
 H    -0.51105     1.12955    -0.93511
 H    -0.47590     1.18229     0.84327
 C     0.56889    -0.51100    -0.03086
 H     0.47606    -1.18258     0.84284
 H     0.51095    -1.12932    -0.93549
 O     1.85135     0.11502    -0.06109
 H     1.98849     0.59387     0.76543
 O    -1.85145    -0.11476    -0.06097
 H    -1.98757    -0.59578     0.76448
--
H  [IMol= 1]    -0.36601     2.67977    -3.20188  [q = -1.0]
H  [IMol= 1]    -0.31327     3.24349    -4.02616  [q = +1.0]
end geometry
```



Dipole: the one we translated

What you'll do this session:

Download session_2 folder from the shared drive.

Upload it on trantor (scp -r session_2 your-user-name@trantor01.sns.it/)

In session_2 you shall find:

1) des_param_code/: you worked on it last time (remember?).

2) et_input_creation/:

Once you downloaded them we will go through them together

Task 1: Creating and running a test QM/EE calculation

Open *make_test.py* in *example_qmee* folder.
make_test.py generates a .inp eT file, which we will run as test.
In order for it to work, you'll have to **complete *qm_interface.py*** in particular *create_et_EE_inp.py*

To do so, you can get a look on how a .inp file need to look like in *example_input/*

In particular you are asked to:
1) **Add the QM molecule geometry** with the right format and in the right position to the .inp file
2) **Add the dipole geometry** to the .inp file.
   Remember that the .dip files have information about the position of the CM of the dipoles.
   We want to add the dipole with the **correct sign** and with the charges in the **correct position.**

The output file need to look exactly like the one you find in *example_qmee/example_input*

Time: 1h. After this we will provide you with the solution and we will launch the calculation together.

NOTE WELL: *make_test.py* generates the file by using a *molecule_class* object, a *dipoles_class* object and a *seed.inp* file. You can find the files needed to initialize the molecule and dipoles object, and also the seed.inp file in *example_qmee/files/.*

The seed.inp file, accounts for all the information about the QM calculation, except for:
1) QM molecule geometry
2) Embedding dipole geometry

That's why we have task 1

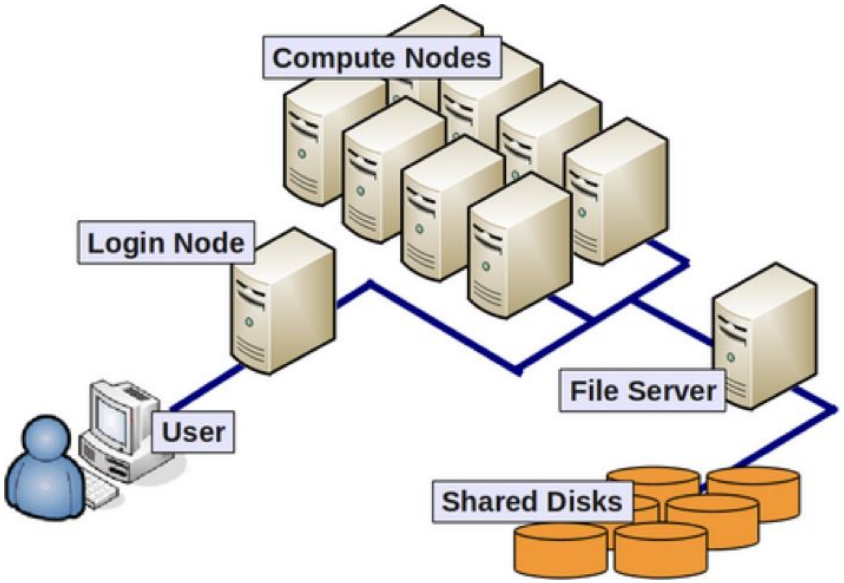
Task 2: Launching the test QM/EE calculation

Now we need to launch the calculation we just set up.

NOTE WELL: You need to be on the trantor cluster!

In the folder *example_qmee* you can find *run_qmee.sh*
This is a script which will launch our calculation on a node of the cluster.

In particular it will:
1) Reserve a machine with the specified computational resources requested,
2) Load the modules needed,
3) Do some stuff
4) Launch the calculation



You need to change *whereiam="PATH-TO-THIS-FOLDER"* with the path to your *example_qmee folder.*

Once you are done you just need to run on the terminal
'qsub run_qmee.sh'
This command will launch the calculation that will last some seconds.

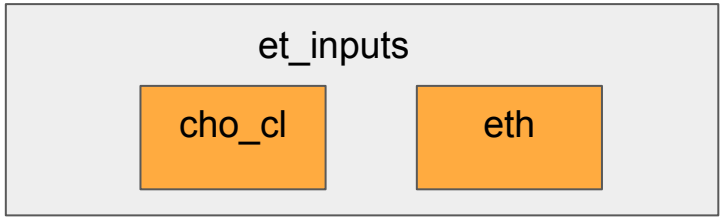
To see if your job is running, type in the terminal 'qstat -n -1 -u ${USER}'

Task 3: Prepare all the QM/EE calculations and run them

Now we need to prepare all the QM/EE calculations.

To do so you need to look in the folder *et_input_creation* and work on *make_et_inputs.py*
For each of the target molecules, *make_et_inputs.py* will cycle through all the translated dipoles you created last time and will create the right .inp file by using *qm_interface.py* you just fixed.

To do so you need to:
1) Define the QM molecule
2) Initialize the embedding dipole
3) Create the .inp file
4) Save the input files in a folder et_inputs/name_of_molecule



Time: 30 min. After this we will provide you with the solution and we will launch the calculations together.

Once you are done you need to run the calculations. To do so, go in the folder *run_scripts*.
Here you can find two run scripts used to launch the calculations for choline/cloride (cho_cl.sh) and ethylenglycol (eth.sh).

Inside, change whereiam="PATH-TO-THE-FOLDER-OF-ET-INPUTS" with the path of the folder '*et_inputs*'
Once you are done this, submit the jobs (qsub ….)