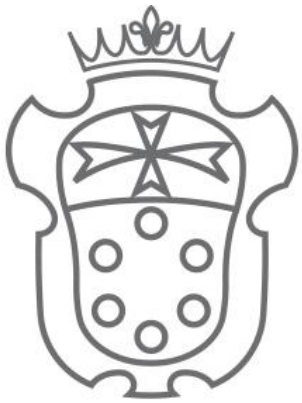


SCUOLA
NORMALE
SUPERIORE

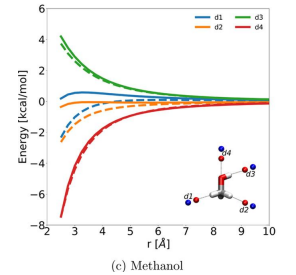
Lab Session 3

Recap: FQ Parameterization

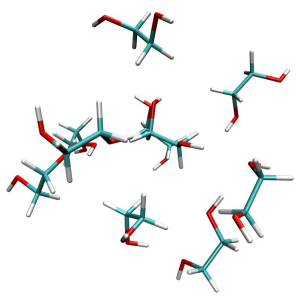
Obtain χ and η by reproducing:

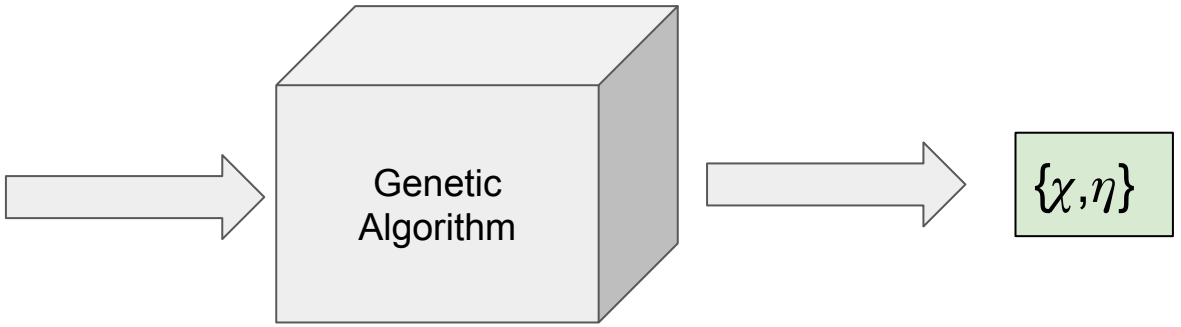
1) QM/EE interaction energies
2) QM static polarizability

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*

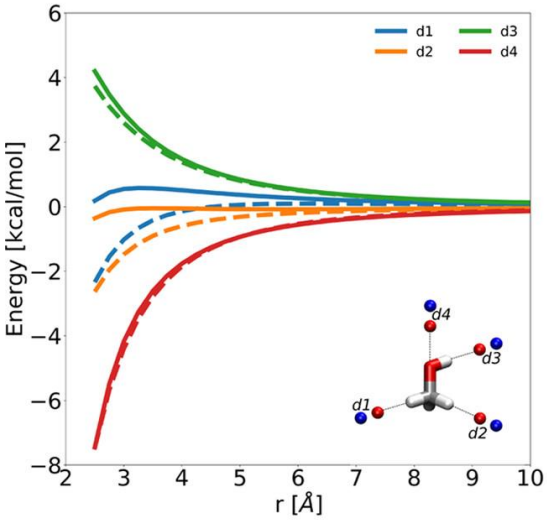


(c) Methanol

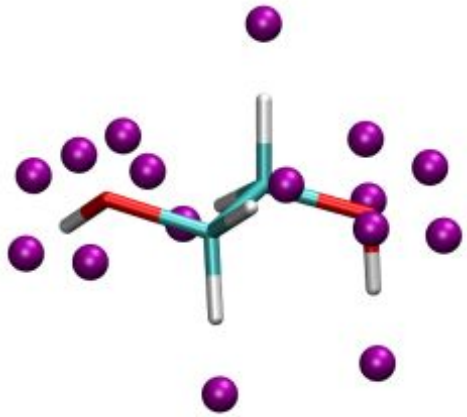




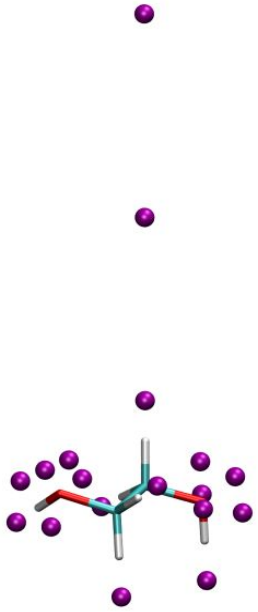
Recap: session 1



(c) Methanol



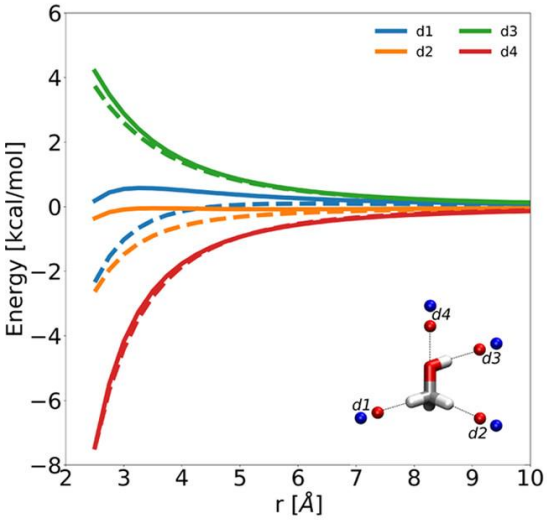
1) Positioned the CM of the fixed dipoles around the selected molecules (Cl/Choline and Ethylenglycol).



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

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

Recap: session 2



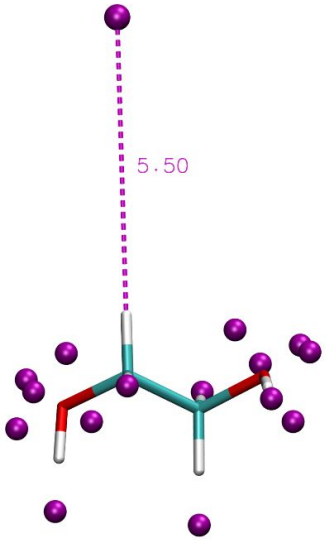
(c) Methanol

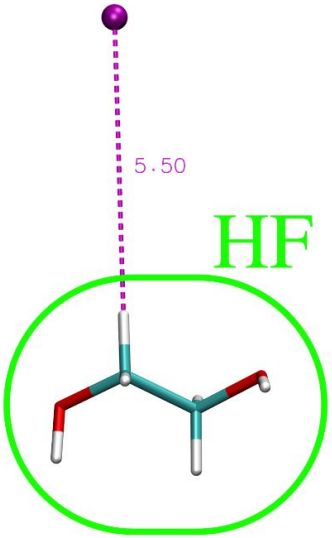
HF/EE QM/EE interaction energy

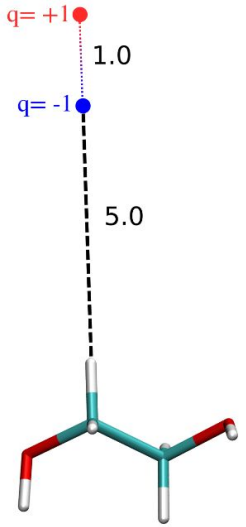
$$\mathscr{E}[\mathbf{D},\mathbf{q}] = \mathrm{tr}\mathbf{h}\mathbf{D} + \frac{1}{2}\mathrm{tr}\mathbf{D}\mathbf{G}(\mathbf{D}) + \mathbf{q}^{\dagger}\mathbf{V}(\mathbf{D})$$

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

Solve SCF

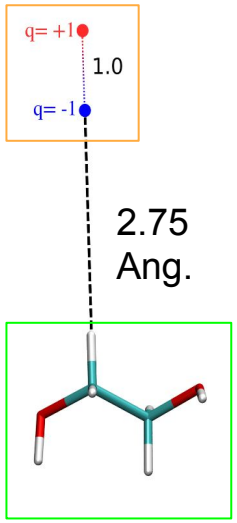






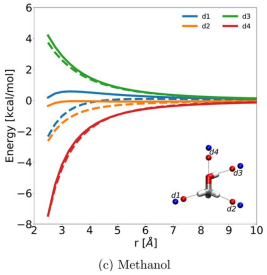
Recap: session 2

```
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
```

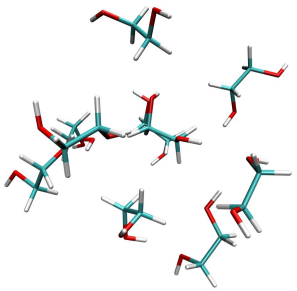


We ran QM/EE calculations for each molecule and for each dipole geometry

What we need to do?



(c) Methanol



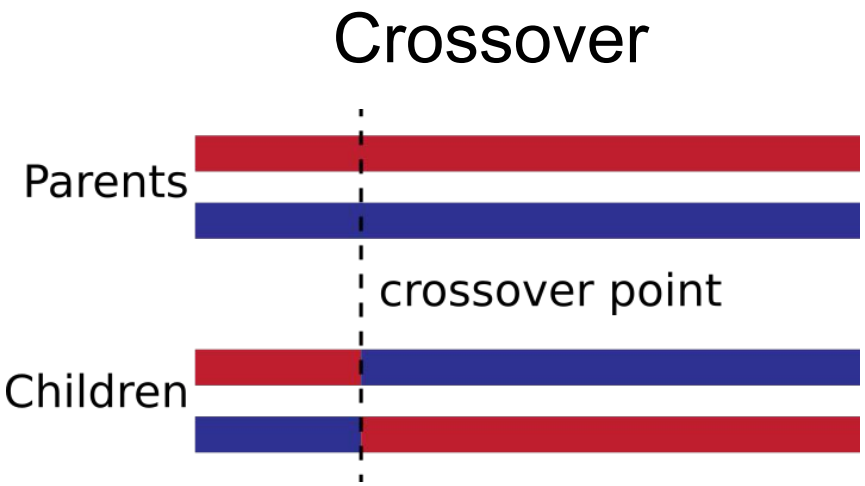
Genetic Algorithm

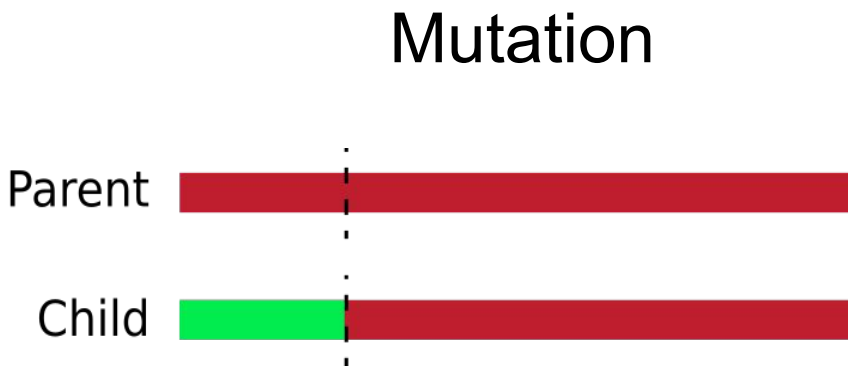
$\{\chi, \eta\}$

Let's see how the GA is made

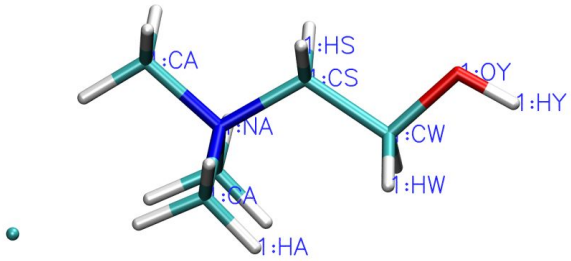
How does a a Genetic Algorithm works

1. **Initialization**: Create an initial population of individuals (chromosomes).
2. **Evaluation**: Assign a fitness value to each individual based on how well it solves the problem.
3. **Selection**: Select individuals from the population for reproduction based on their fitness.
4. **Crossover**: Exchange genetic material (genes) between parents to produce new chromosomes.
5. **Mutation**: Introduce random changes to the offspring's chromosomes.
6. **Replacement**: Replace some individuals in the current population with the newly created offspring.
7. **Iteration**: Repeat the process until the algorithm converges or a termination condition is satisfied.





How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

0-th Generation

parent 1

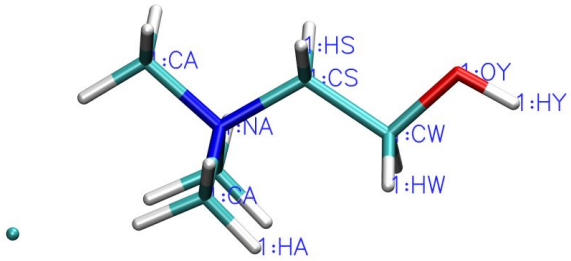
parent 2

.
.
.

parent N

Each generation is a set of individuals (parents) having different chromosomes (i.e. different values for at leas one gene)

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

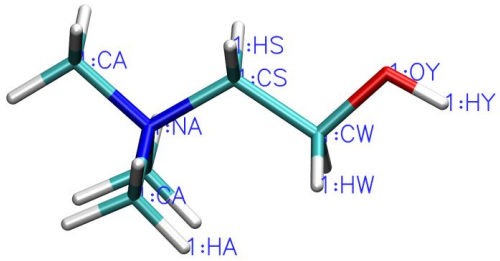
parent 2

.
.
.

parent N

Generation exploitation

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

1st parent

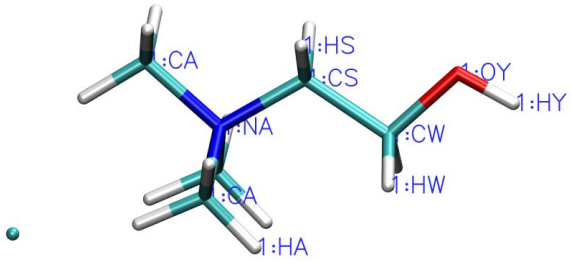
Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

2nd parent

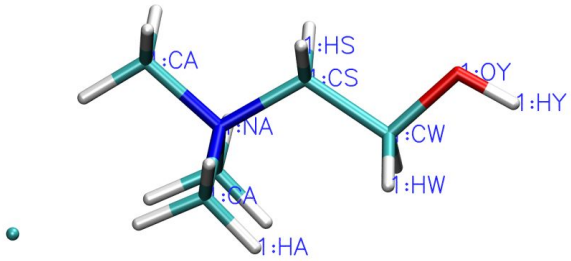
Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

N-th parent

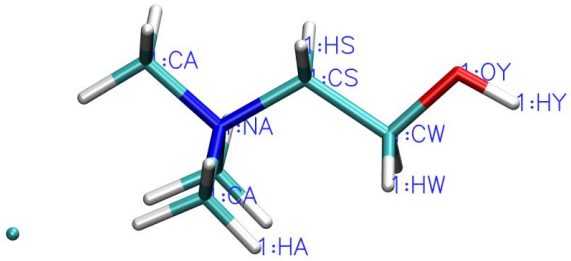
Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

How does a cycle of the GA look like?



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i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

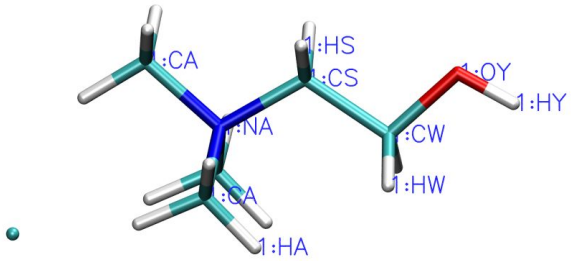
parent 2

.
.
.

parent N

Generation exploitation

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

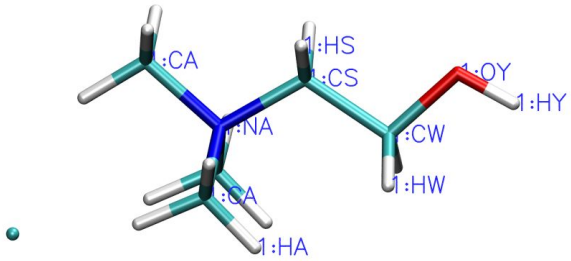
.
.
.

parent N

Generation exploitation

Parents selection (select fittest individuals)

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

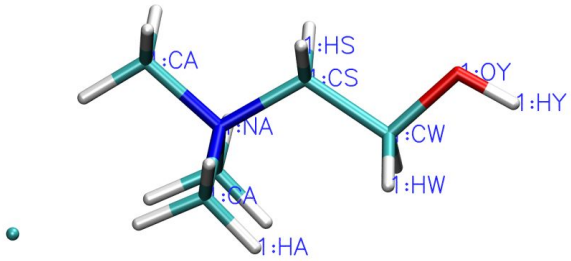
Generation exploitation

Parents selection (select fittest individuals)

Cross-over and mutation

New individuals

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

(M+1)-th Generation

parent 1

parent 2

.
.
.

parent N

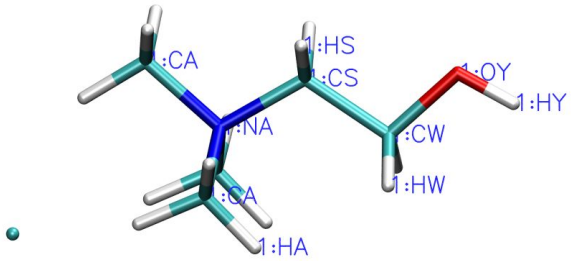
Generation exploitation

Parents selection (select fittest individuals)

Cross-over and mutation

New individuals

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

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M-th Generation

parent 1

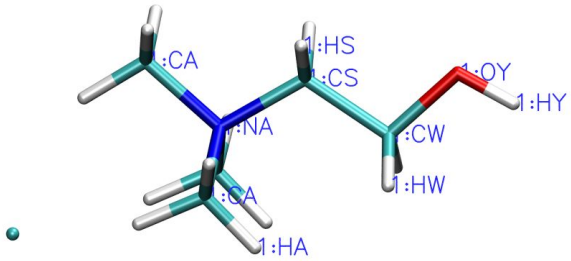
parent 2

.
.
.

parent N

Generation exploitation

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

i-th parent

Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

FQ/EE model

FQ/EE model

$q_{\alpha i}$ = Charge of the i-th atom of the □-th molecule

$$E^{tot}(\mathbf{q},\lambda) = \sum_{\alpha,i} q_{\alpha i}\chi_{\alpha i} + \frac{1}{2}\sum_{\alpha,i}\sum_{\beta,j} q_{\alpha i}J^{qq}_{\alpha i,\beta j}q_{\beta j} + \sum_{\alpha}\lambda_{\alpha}\left(\sum_{i} q_{\alpha i} - Q^{tot}_{\alpha}\right) + \sum_{\alpha,i}\sum_{k} q_{\alpha i}T^{qq}_{\alpha i,k}q^{EE}_{k}$$

$$= \mathbf{q}^{\dagger}\chi + \frac{1}{2}\mathbf{q}^{\dagger}\mathbb{T}^{qq}\mathbf{q} + \lambda^{\dagger}\mathbf{q} + \mathbf{q}^{\dagger}\mathbb{T}^{qq}\mathbf{q}^{EE}$$

$$\begin{bmatrix} \mathbb{J} & \mathbf{1}_{\lambda} \\ \mathbf{1}^{\dagger}_{\lambda} & 0 \end{bmatrix} \cdot \begin{bmatrix} \mathbf{q} \\ \lambda \end{bmatrix} = \begin{bmatrix} -\chi - \mathbf{T}^{qq}\mathbf{q}^{EE} \\ \mathbf{Q} \end{bmatrix}$$

$$\mathbf{T}^{qq}_{ij} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

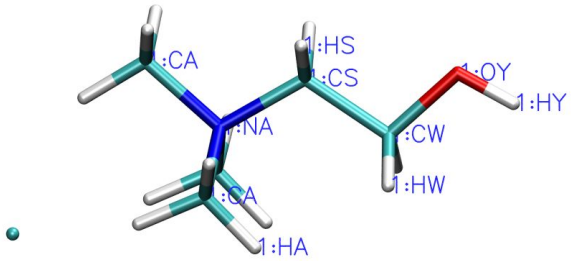
$$J^{qq}_{ij} = \frac{\eta_{ij}}{\left[1 + \eta^2_{ij}r^2_{ij}\right]^{\frac{1}{2}}}$$

Ohno form

$$\eta_{ij} = \frac{\eta_i + \eta_j}{2}$$

$$J^{qq}_{ii} = 2\eta_i$$

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

i-th parent

Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

How do we perform the FQ calculations?

How do we perform FQ calculations?

FQ, and FQFμ calculation

Frequency dependent Molecular Mechanics calculations using ωFQ and ωFQFμ models

How do we perform FQ calculations?

FQ, and FQFμ calculation

Frequency dependent Molecular Mechanics calculations using ωFQ and ωFQFμ models

How do we perform FQ calculations?

ADVERTISEMENT TIME!

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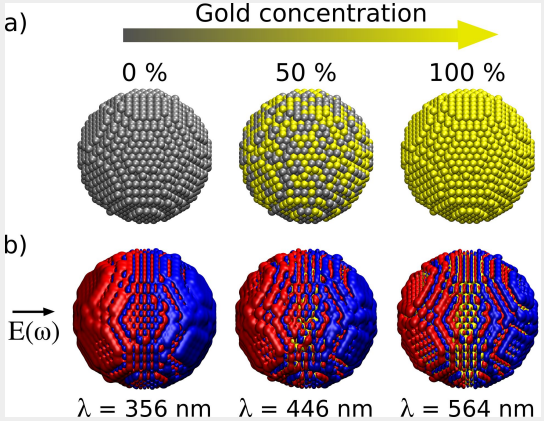
FQ, and FQFμ calculation

Frequency dependent Molecular Mechanics calculations using ωFQ and ωFQFμ models

ωFQ and ωFQFμ models

Capable to describe at the MM level the localized plasmon oscillations in metals, i.e. the collective excitation of conduction electrons.



Each atom is endowed with a charge that responds to:

1) Other charges
2) External monochromatic electric fields

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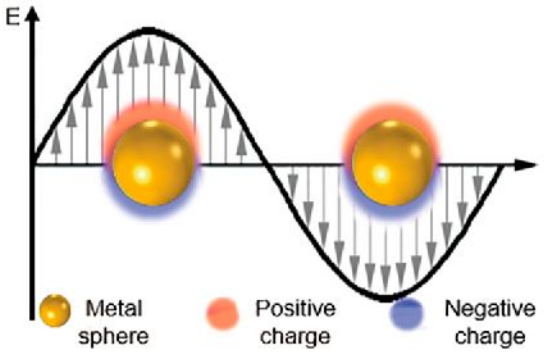
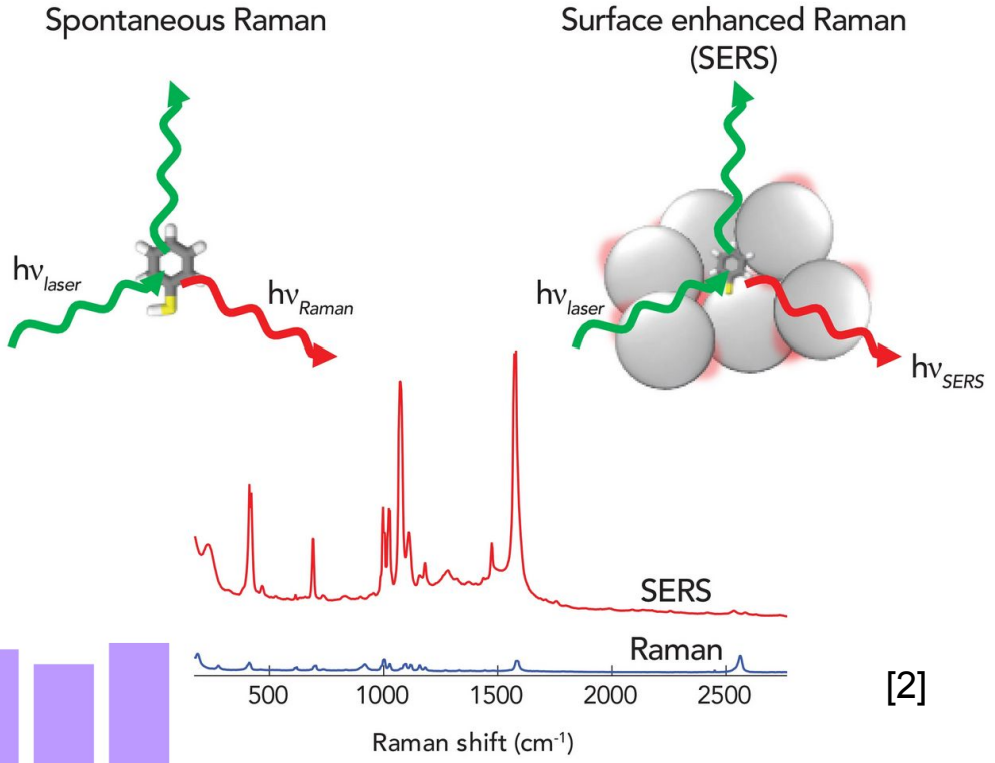
Surface Enhanced Raman Spectroscopy (SERS)

Localized Surface Plasmon Resonance (LSPR)

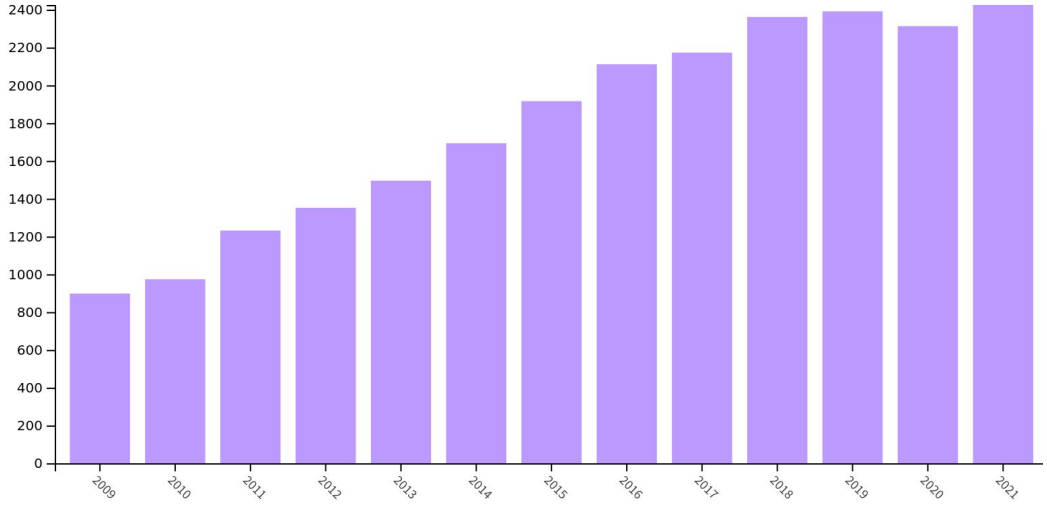


[1]



[2]

Publications with SERS keyword per year



[3]

[1] Zong, Cheng, et al. Chem. rev. 118.10 (2018): 4946-4980.
[2] https://www.spectroscopyonline.com/view/sers-and-ters
[3] Data taken from *Web of science*

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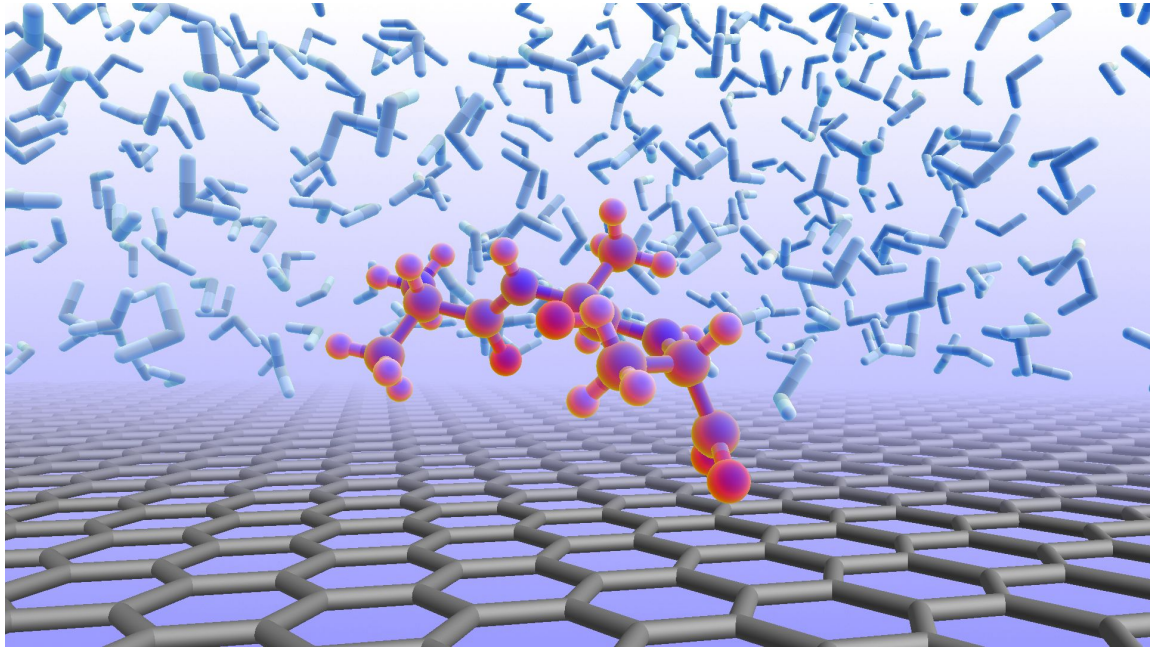
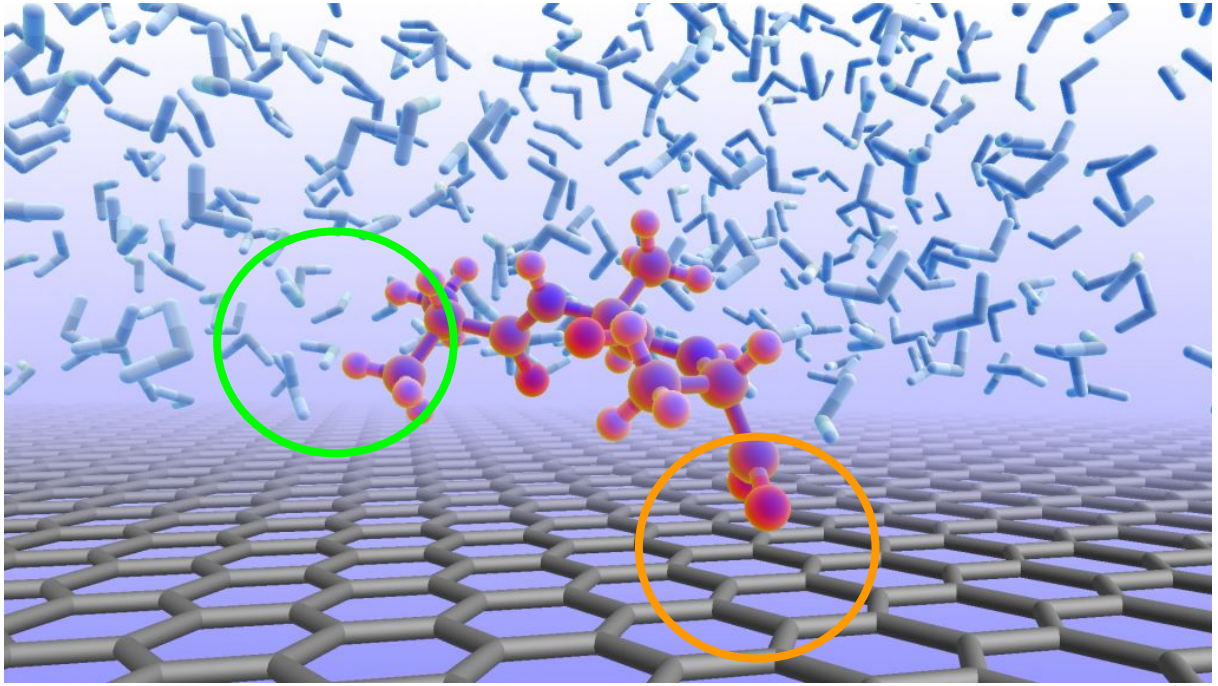
FQ, and FQFμ calculation

Frequency dependent Molecular Mechanics calculations using ωFQ and ωFQFμ models

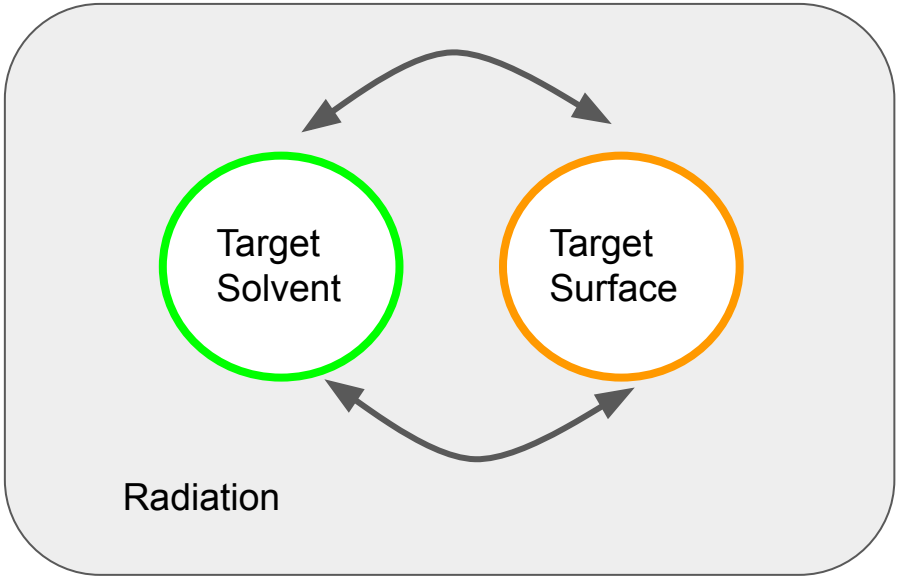


Advertisement time



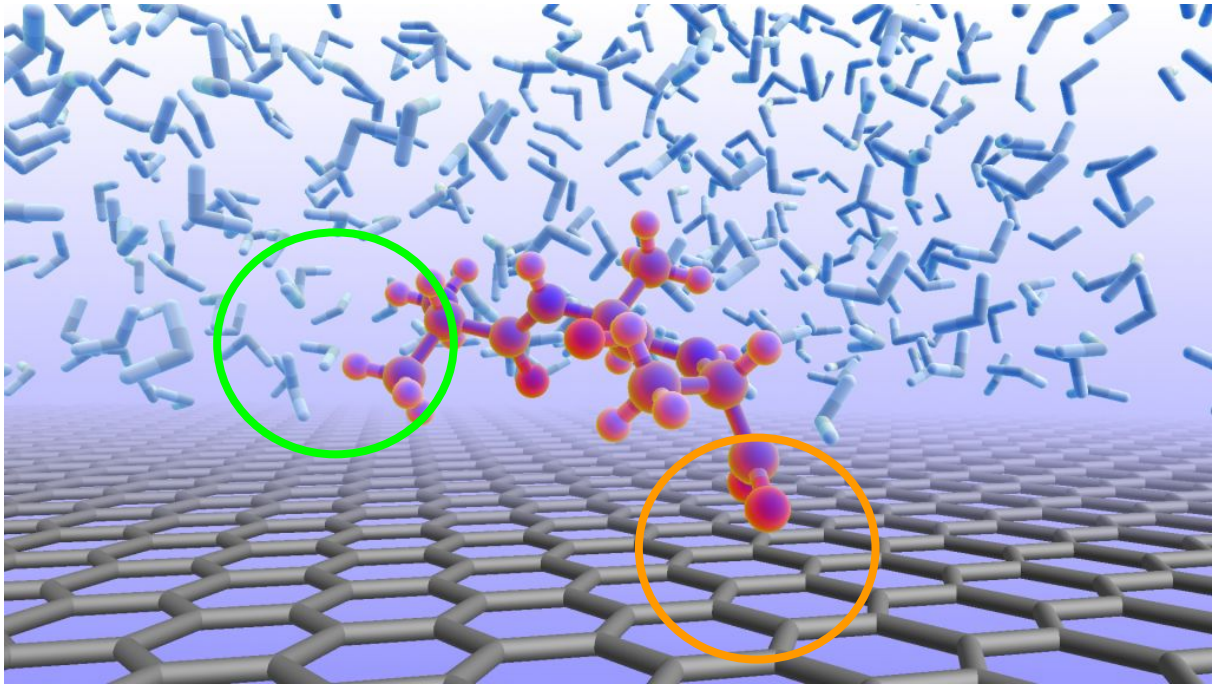
[4]

SERS:



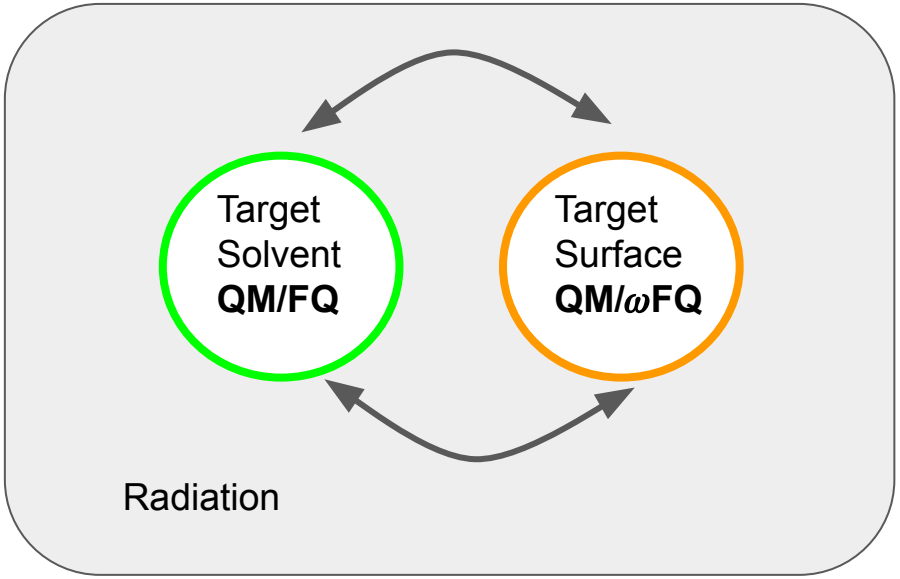
[4] Image taken from https://gems.sns.it/

Advertisement time



[4]

SERS:



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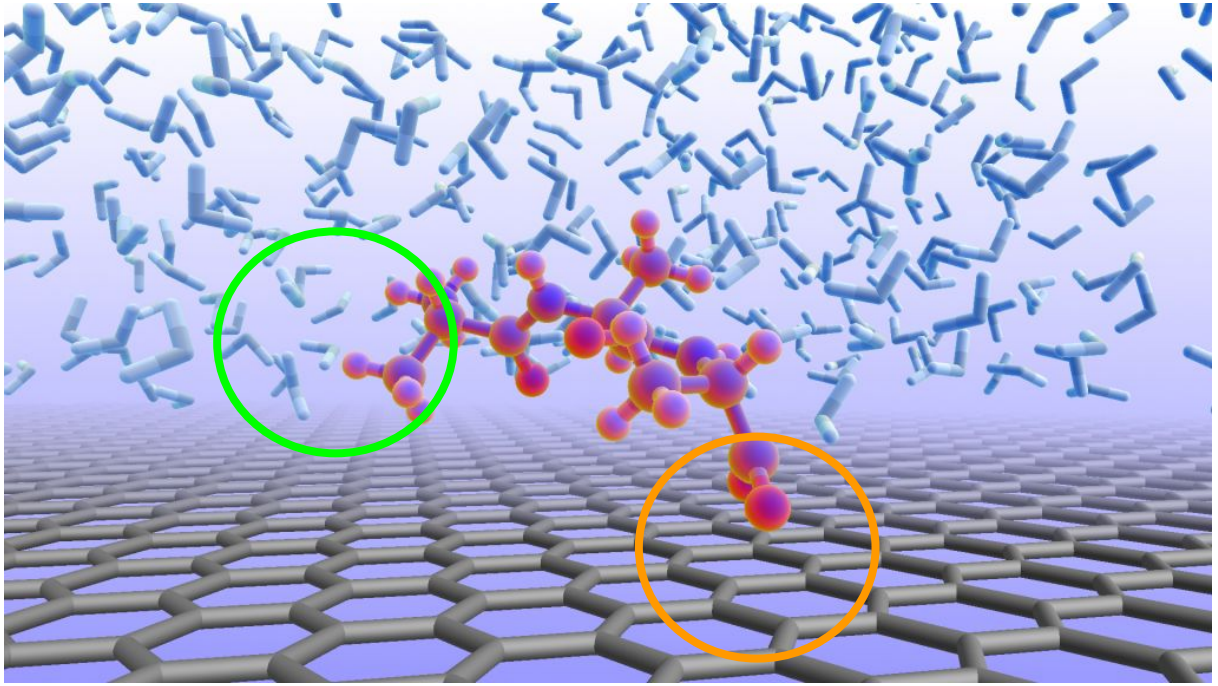
Advertisement time



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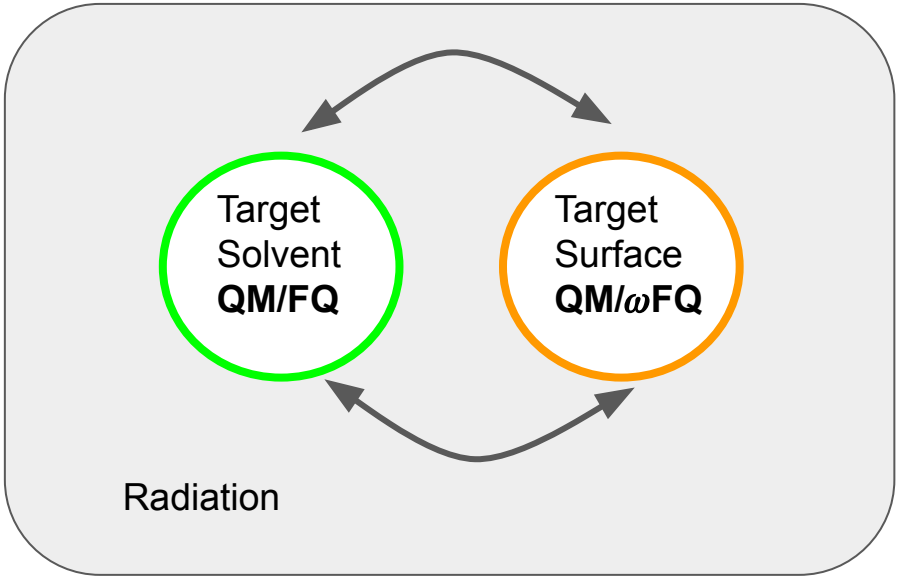

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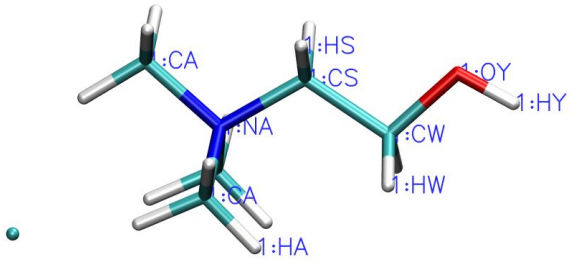
How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

i-th parent

Create FQ/EE calculation from each translated dipole geometry

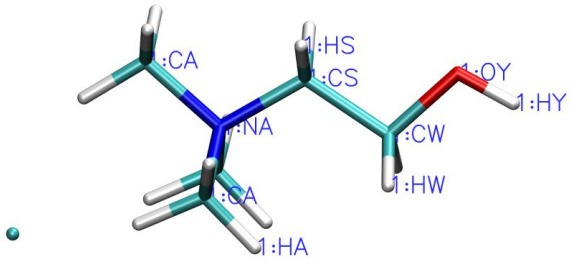
Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

How do we perform the FQ calculations?

Some useful objects



You got used to the ***molecule_class*** and ***dipoles_class*** objects.

Today we will see two new classes which will be useful.

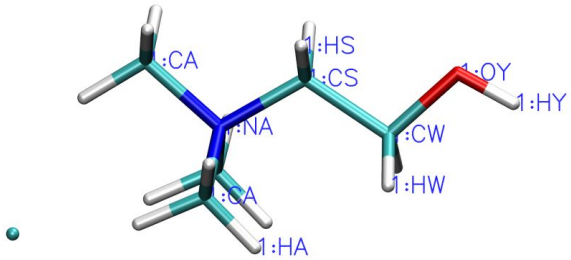
polarizable_embedding_class: gathers information about

1) Type of the force field (FQ in our case)
2) atomtypes of the system
3) electronegativity of each atomtype
4) chemical hardness of each atomtype
5) Some other stuff for other polarizable embedding models different from FQ

Run ***ga_cycle/help_scripts/setup_pe.py*** to see how does an initialized forcefield object look like

```
python3 setup_pe.py
---polarizable force field---
 force_field : fq
 atomtypes   : 'CS'      , 'HS'      , 'NA'      , 'CW'      , 'HW'      , 'OY'      , 'HY'      , 'CA'      , 'HA'      , 'Cl'
 chi         : 0.02900   , 0.47900   , 0.05400   , 0.96100   , 0.84800   , 0.72400   , 0.95400   , 0.34900   , 0.84500   , 0.58900
 eta         : 0.30600   , 0.24500   , 0.52100   , 0.80200   , 0.10000   , 0.70500   , 0.24000   , 0.48200   , 0.50500   , 0.29500
```

Some useful objects



You got used to the ***molecule_class*** and ***dipoles_class*** objects.

Today we will see two new classes which will be useful.

nanofq_class: gathers information about

1) Path towards the nanoFQ exectuable
2) Polarizable model used in the FQ calculation
3) FQ molecule or molecules (molecule_class or cluster_class)
4) EE dipole (dipoles_class)
5) Where is the input file (.mfq)
6) Where is the output file (.log)
7) Some other stuff

Run ***ga_cycle/help_scripts/setup_nanofq.py*** to see how does an initialized nanofq object look like.

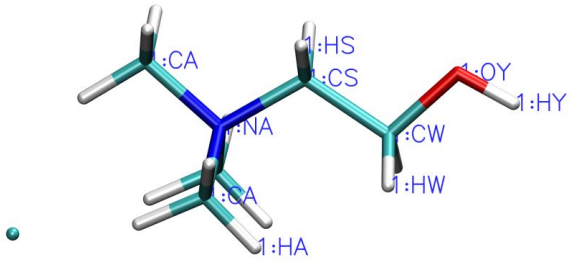
NanoFQ object

```
**********************************************************
nanoFQ object:
path          :/home/luca/programmi/nanofq/build_ee_master/nanoFQ

System        : cluster
----------------------
Molecule with 21 atoms, and charge 1.0
CS     1.60755     0.57454     0.00045
HS     1.81207     1.18388     0.88830
HS     1.81252     1.18377    -0.88737
NA     0.13201     0.27206     0.00015
CW     2.54211    -0.63366     0.00060
HW     2.38871    -1.25659    -0.89325
HW     2.39020    -1.25516     0.89571
OY     3.84828    -0.05959    -0.00090
HY     4.50583    -0.76457    -0.00093
CA    -0.28214    -0.50312     1.22858
HA    -1.38074    -0.60047     1.18569
HA     0.19165    -1.48797     1.20453
HA     0.04252     0.05607     2.11251
CA    -0.62027     1.58405     0.00078
HA    -0.33560     2.14145     0.89917
HA    -0.33530     2.14243    -0.89691
HA    -1.69553     1.33864     0.00045
CA    -0.28202    -0.50176    -1.22920
HA     0.04283     0.05832    -2.11247
HA     0.19149    -1.48676    -1.20609
HA    -1.38064    -0.59902    -1.18642
----------------------
Molecule with 1 atoms, and charge -1.0
Cl    -3.39716    -0.30601    -0.00024
----------------------

EE dipoles      : 1
----------------------
Dipole |      Pos X      Pos Y      Pos Z |      Dir X      Dir Y      Dir Z |   Sign
0      |    2.37184    2.85167    3.31835 |    0.18659    0.55593    0.81002 |     +-
PE          :
---polarizable force field---
 force_field : fq
 atomtypes   : 'CS'       , 'HS'       , 'NA'       , 'CW'       , 'HW'       , 'OY'       , 'HY'       , 'CA'       , 'HA'       , 'Cl'
 chi         : 0.79900    , 0.00000    , 0.60600    , 0.91200    , 0.33300    , 0.21000    , 0.43200    , 0.40000    , 0.50800    , 0.89100
 eta         : 0.85300    , 0.63700    , 0.16400    , 0.55800    , 0.18300    , 0.14100    , 0.34100    , 0.21800    , 0.81300    , 0.21100
**********************************************************
```

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

i-th parent

Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

Task 1: Send a FQ/EE calculation and extract the energy

You are given:
1) A polarizable embedding object (initialized)
2) A translated dipole object

In this task, the code ***run_nanofq.py*** generates a nanofq_object associated to:
1) The executable of nanoFQ
2) A choline chloride .clust file
3) A dipole object
4) a specific dipole to insert in the FQ/EE

Given all this, it generates the FQ/EE calculation and then it runs it.

You are asked to extract the FQ/EE interaction energy in a.u. from the .log file in the calculations folder

To do so, you need to modify ***new_nanofq.get_energy()*** in ***des_param_code/classes/nanofq_class***

NOTE WELL: get_energy() will use the path towards the .log file. This is already initialized when the calculation is ran, so you don't have to do it

Task 2

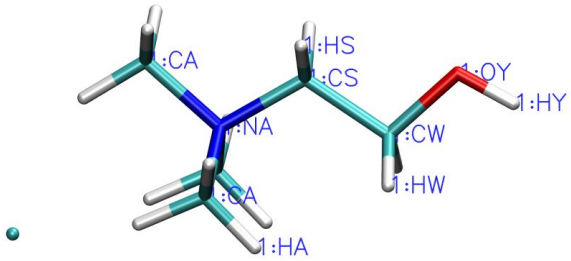
You are given:
1) A set of reference QM/EE calculations computed with eT
2) A set of FQ/EE calculations already computed with nanoFQ and a set of FQ parameters (a single individual)

You need to compute a metrics to evaluate the fitness of this individual

Fitness = 1/Loss

To do so, you need to run ***compute_fitness.py*** after having properly modified ***fitness_evaluator.py*** in ***des_param_code/genetic_algorithm/ga_core.py***

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

i-th parent

Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

Task 3

We will now send all the nanofq calculations needed to evaluate the fitness of an individual.

You will need to run ***run_pe_calculations.py***. This code will run all the calculations for a single individual. We will split the training set in train and test and use the training set to perform the FQ/EE calculations.

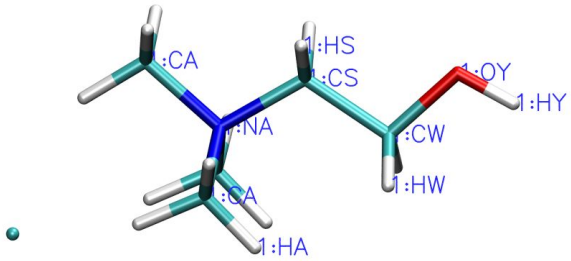
To do so, you have to work on ***des_param_code/genetic_algorithm/ga_core.run_single_individual***(nanofq_seed,reference,dip_files_train ,current_dir)

-nanofq_seed: is a nanofq_object where you have information about the path of the nanofq executable, the system, the polarizable embedding of the individual to evaluate,
-reference: is the set of training QM/EE energies (a dictionary)
-dip_files: the set of training .dip files
-current _dir: the current directory

You are asked to work on *ga_core.run_single_individual*:
For each of the dip_files, generate a nanofq object associated to the system, executable, correct dipole, correct polarizable embedding.
Launch the calculation with nanoFQ and extract its energies as a dictionary.
Compute and return fitness. *Use the other tasks to get yourself inspired and use the two lines of code I provided you as a comment.*

Then run ***run_pe_calculations.py*** to test it.

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

M-th Generation

parent 1

parent 2

.
.
.

parent N

i-th parent

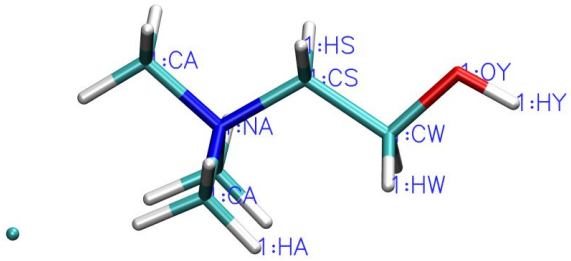
Create FQ/EE calculation from each translated dipole geometry

Send the FQ/EE calculation

Collect the FQ/EE interaction energy

Compare to QM/EE interaction energy: compute a fitness value

How does a cycle of the GA look like?



genes: χHS, ηHS, χOY, ηOY, …

i-th parent= [χHS, ηHS, χOY, ηOY, …]$_i$

(M+1)-th Generation

parent 1

parent 2

.
.
.

parent N

Generation exploitation

Parents selection (select fittest individuals)

Cross-over and mutation

New individuals