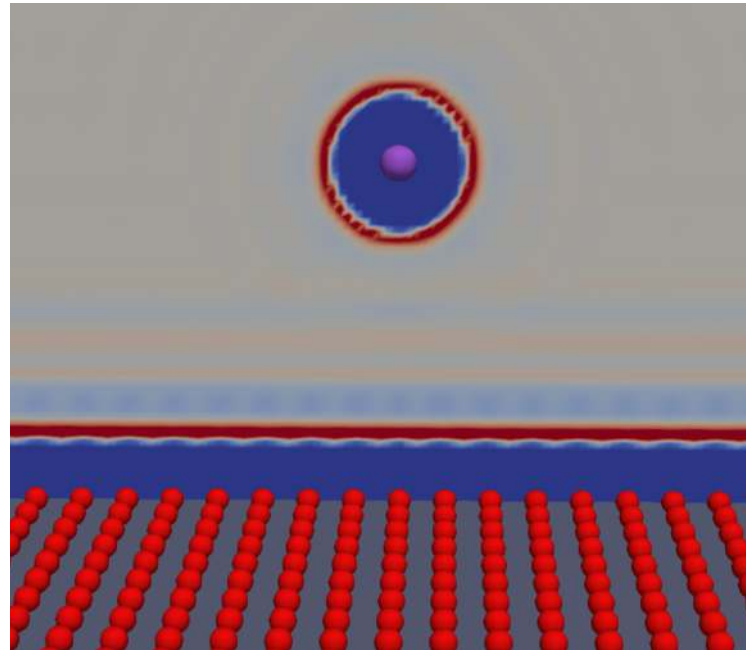


Molecular Density Functional Theory and its coupling with the N body quantum problem

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GDR NBODY – 10 janvier 2019

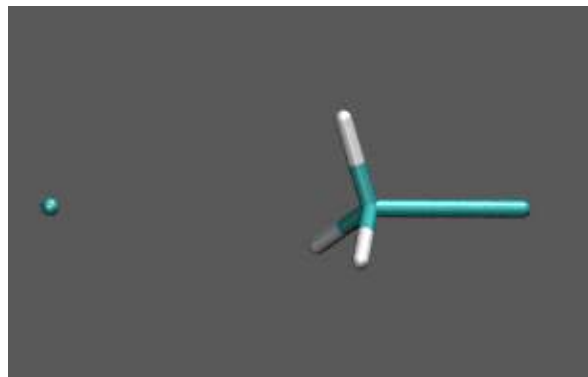


Quantum Chemistry and Solvation

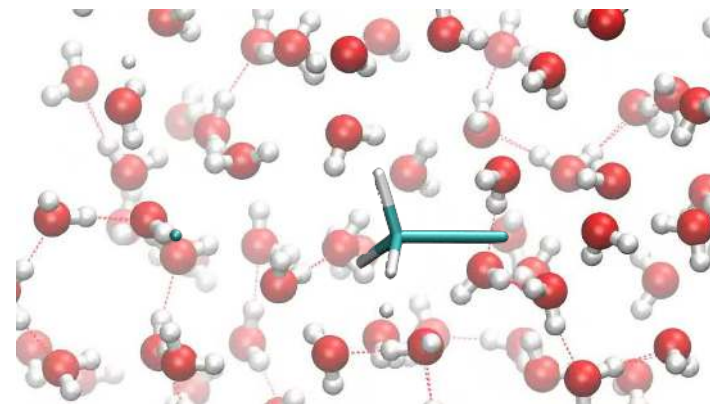
QM calculations are **expansive** (when there are a lot of electrons).

There are (almost always) done in vacuum

Number of (Valence) electrons: 22



Number of (Valence) electrons: 470



1 mol/L \approx 56 water molecules

And things get even worse: **T > 0 K**, **Free Energy** (or entropy) matters...

Solvation: MM and QM/MM

To compute free energies: **Statistical Physics**

Generate **a lot of configurations** + ensemble average

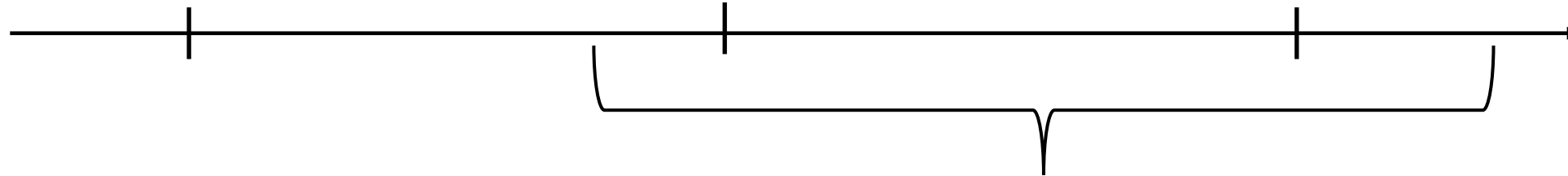


Monte Carlo or **Molecular dynamics** (forces needed).

Full Quantum: **ab-initio MD**

Classical FF: all atoms

Classical FF: coarse-grained



Computational cost
accuracy

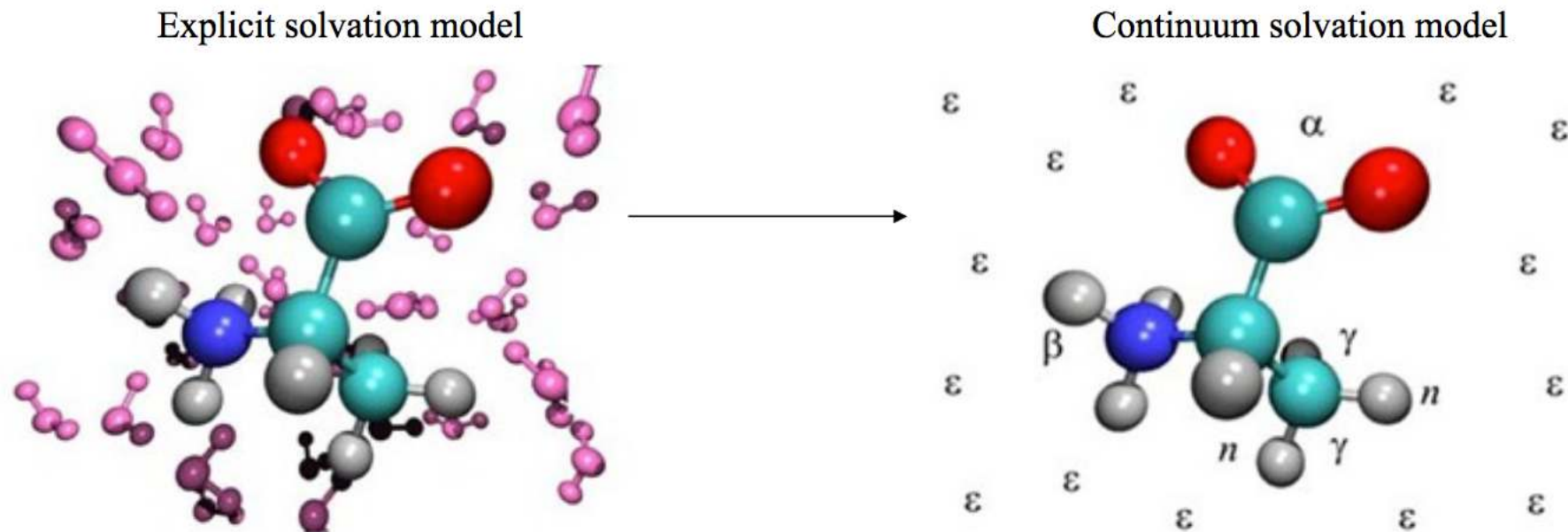
Pros: precise, molecular description

Cons: Expansive, parametrization

QM/MM

Solvation: Continuum methods

The idea is to average the solvent degrees of freedom prior to the calculation



Solvent is model by a dielectric continuum and several parameters modelling: polarizability, cavity, etc...

Pros: Fast (almost free)

Cons: Highly parametrized, lack molecular description (H bonding...)

Molecular Density Functional Theory in brief

PHYSICAL REVIEW

VOLUME 137, NUMBER 5A

1 MARCH 1965

Thermal Properties of the Inhomogeneous Electron Gas*

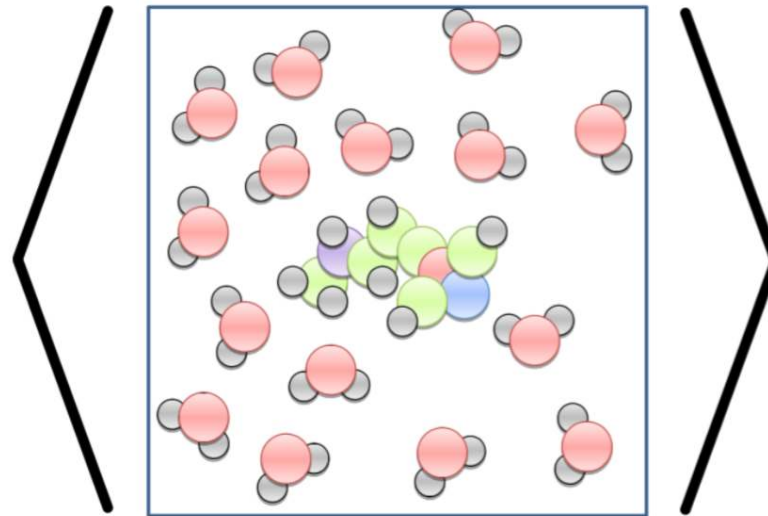
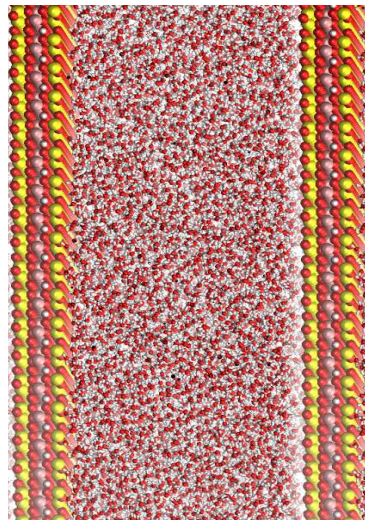
N. DAVID MERMIN†

Department of Physics, University of California, San Diego, La Jolla, California

(Received 8 October 1964)

A variational property of the ground-state energy of an electron gas in an external potential $v(\mathbf{r})$, derived by Hohenberg and Kohn, is extended to nonzero temperatures. It is first shown that in the grand canonical ensemble at a given temperature and chemical potential, no two $v(\mathbf{r})$ lead to the same equilibrium density. This fact enables one to define a functional of the density $F[n(\mathbf{r})]$ independent of $v(\mathbf{r})$, such that the quantity $\Omega = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ is at a minimum and equal to the grand potential when $n(\mathbf{r})$ is the equilibrium density in the grand ensemble in the presence of $v(\mathbf{r})$.

$$F[\rho] = \Omega[\rho] - \Omega_0$$



$$\left. \frac{\partial \mathcal{F}[\rho(\mathbf{r}, \Omega)]}{\partial \rho(\mathbf{r}, \Omega)} \right|_{\rho=\rho_{\text{eq}}} = 0$$

Structure
i.e. **solvent configurations**

Free Energy

MDFT in details

$\rho(\mathbf{r}, \boldsymbol{\Omega})$ Solute and solvent are **molecular** (rigid entities with multiple sites) thus the solvent density depends on **position** and **orientation**

$$F[\rho] = F_{\text{id}}[\rho] + F_{\text{exc}}[\rho] + F_{\text{ext}}[\rho]$$

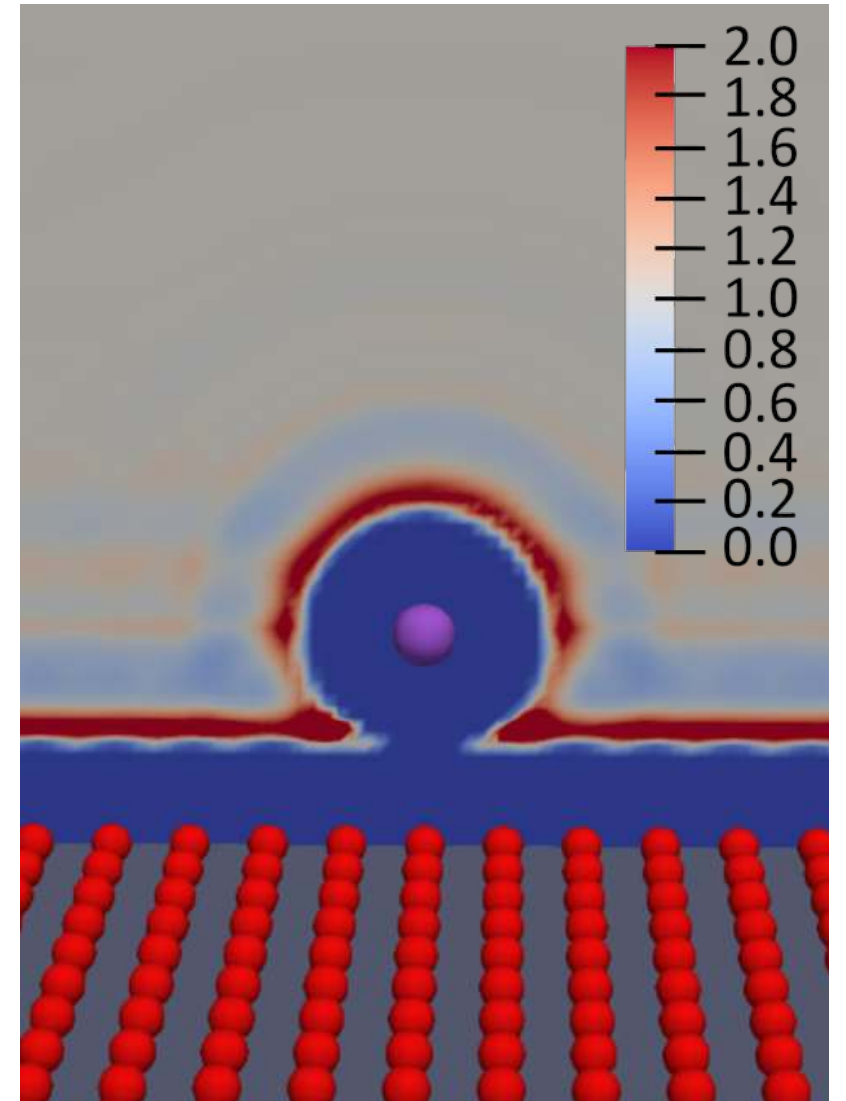
total *ideal entropy* *solute-solvent* *solvent-solvent*

The ideal term is the one of the non-interacting fluid

$$F_{\text{id}}[\rho] = k_B T \iint \left(\rho \ln \frac{\rho(\mathbf{r}, \boldsymbol{\Omega})}{\rho_0} - \rho(\mathbf{r}, \boldsymbol{\Omega}) + \rho_0 \right) d\mathbf{r} d\boldsymbol{\Omega}$$

The solute is represented by an **external potential**

$$F_{\text{ext}}[\rho] = \int \rho(\mathbf{r}, \boldsymbol{\Omega}) V(\mathbf{r}, \boldsymbol{\Omega}) d\mathbf{r} d\boldsymbol{\Omega}$$



MDFT in details

The hard part is the **excess** one (as in eDFT).

The most advanced expression is done within the homogenous reference fluid approximation and is equivalent to HNC and corresponds to the hyper-netted chain approximation [1].

$$F_{\text{exc}}[\rho] = -\frac{k_B T}{2} \iiint \Delta\rho(\mathbf{r}_1, \boldsymbol{\Omega}_1) c(r_{12}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) \Delta\rho(\mathbf{r}_2, \boldsymbol{\Omega}_2) d\mathbf{r}_1 d\boldsymbol{\Omega}_1 d\mathbf{r}_2 d\boldsymbol{\Omega}_2$$

In practice:

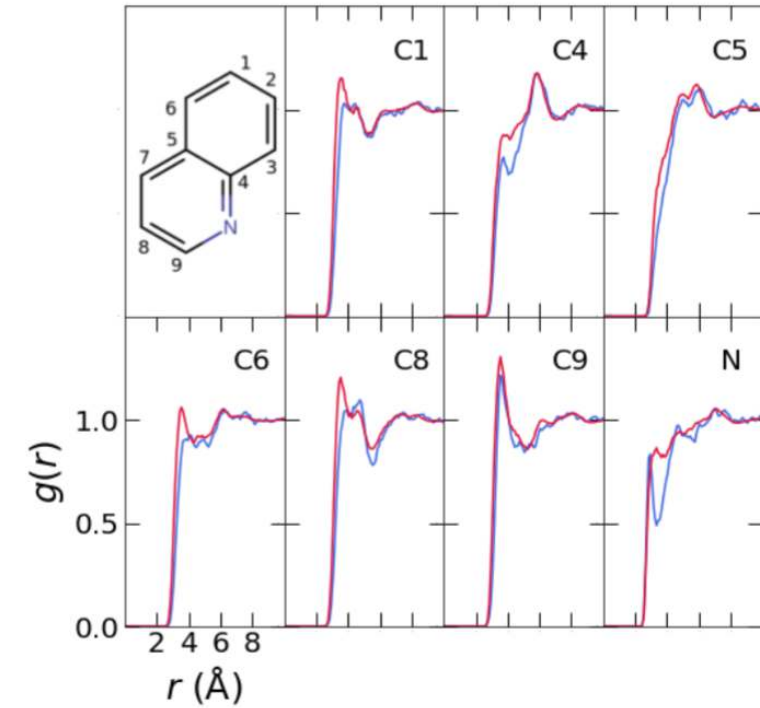
- Input: -solvent dcf and homogenous density (scalar)
- solute: choice of classical FF: LJ, charges,...

Minimization on a 6D grid.

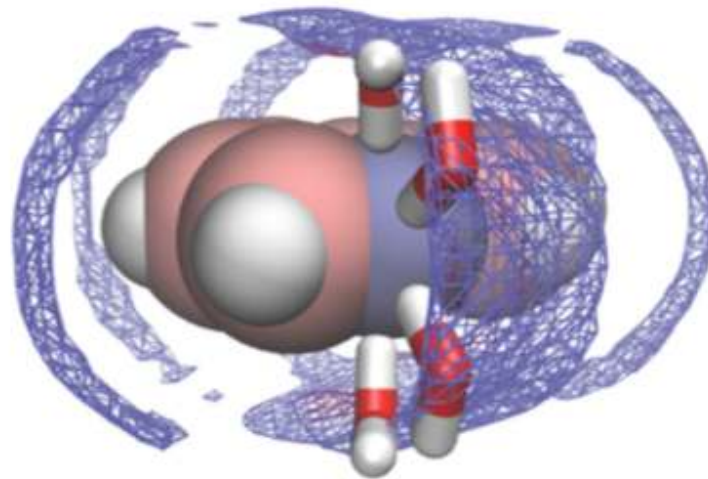
[1]Ding, L, Levesque, M, Borgis, D, & Belloni, L. (2017) Efficient molecular density functional theory using generalized spherical harmonics expansions. *The Journal of Chemical Physics* **147**, 094107.

Some example on classical systems

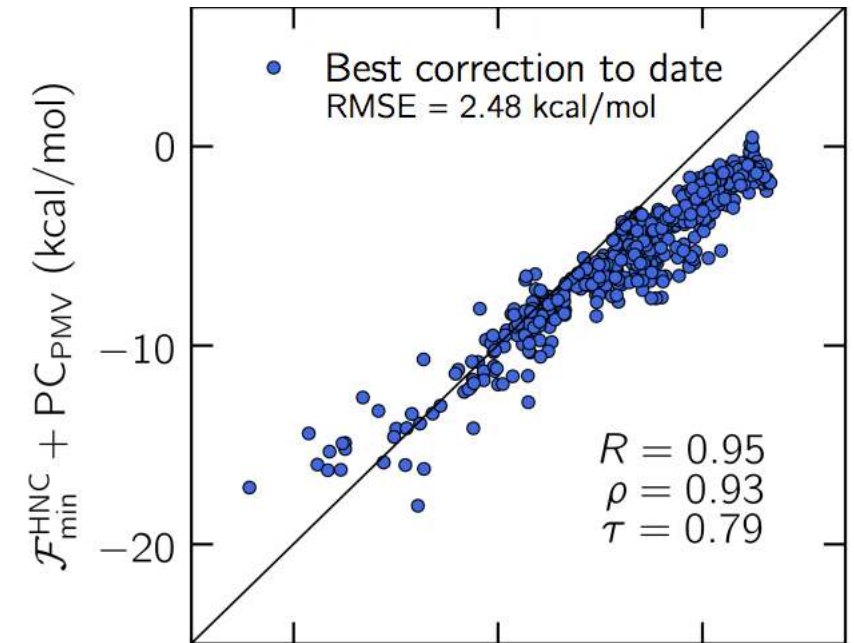
Structure



Luukkonen et al, in prep



Free energies



Robert, A, Luukkonen, S and Levesque, M
[arXiv:1908.10720](https://arxiv.org/abs/1908.10720)

$$F_{\text{ext}}[\rho] = \int \rho(\mathbf{r}, \boldsymbol{\Omega}) V(\mathbf{r}, \boldsymbol{\Omega}) d\mathbf{r} d\boldsymbol{\Omega}$$

Now **the external potential** of MDFT comes from a **QM** calculation

$$V = V_{\text{ES}} + V_{\text{disp}}$$

Electrostatic part comes from solving Poisson equation for the electronic density

$$\Delta V_{\text{ES}}(\mathbf{r}) = -\frac{n(\mathbf{r})}{4\pi\epsilon_0}$$

V_{disp} We keep a LJ description

$$F_{\text{tot}}[\rho] = F[\rho] + E_{\text{QM}} - \int V_{\text{ES}}(\mathbf{r}, \boldsymbol{\Omega}) \rho(\mathbf{r}, \boldsymbol{\Omega}) d\mathbf{r} d\boldsymbol{\Omega}$$

QM/MDFT (preliminary work)

Water in water:

QM package is GPAW (not the best choice...)



Functional: PBE

Box size 5 Å, h=0.2 Å

Dipole moment $\mu=1.9$ D

Dipole moment μ (D)	Experience	QM	QM-CSM [1]	QM/MDFT
Vaccum	1.85	1.9	/	/
Solution	2.3/2.4	/	2.3	2.2

The agreement is not so bad considering I did not parametrize anything

[1] A. Held and M. Walter, Simplified continuum solvent model with a smooth cavity based on volumetric data, *J. Chem. Phys.* **141**, 174108 (2014).

QM/MDFT (preliminary work)

So far the QM is not perturbed by the classical part, let's do it!

Compute the solvent charge density $\rho_c(\mathbf{r}) = \int \sigma(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') d\mathbf{r}' d\Omega$

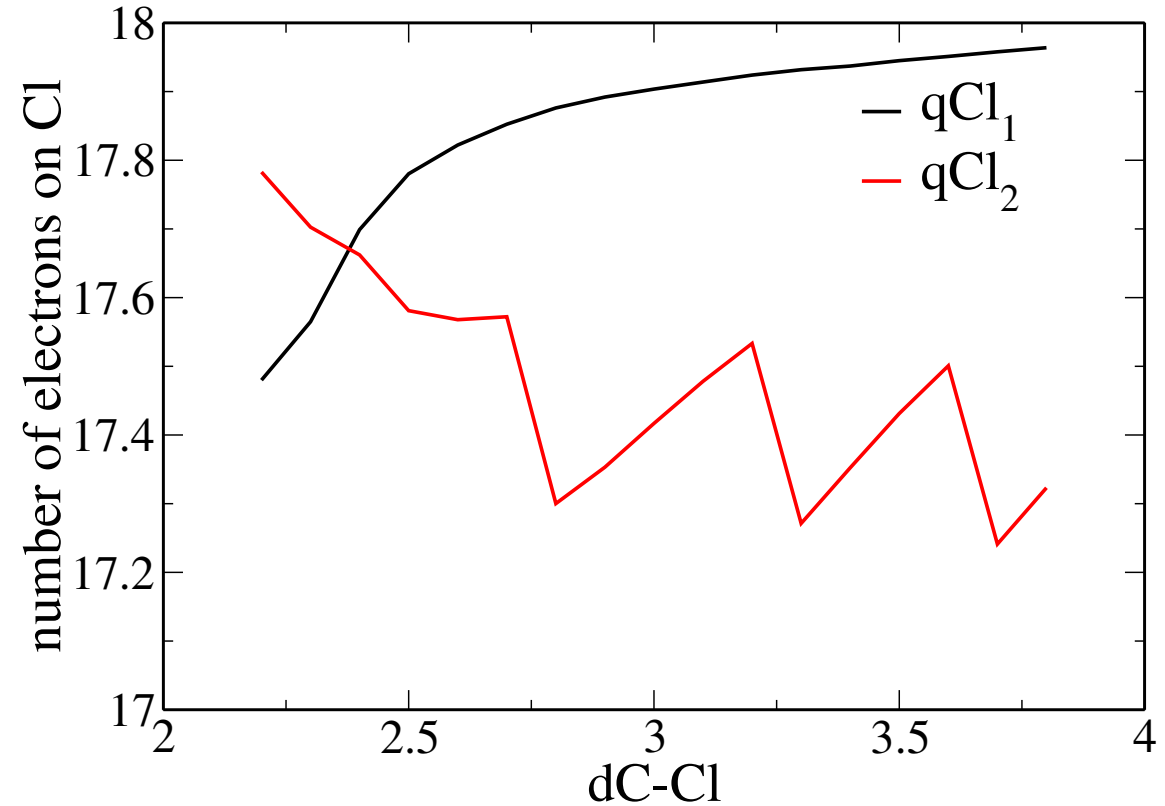
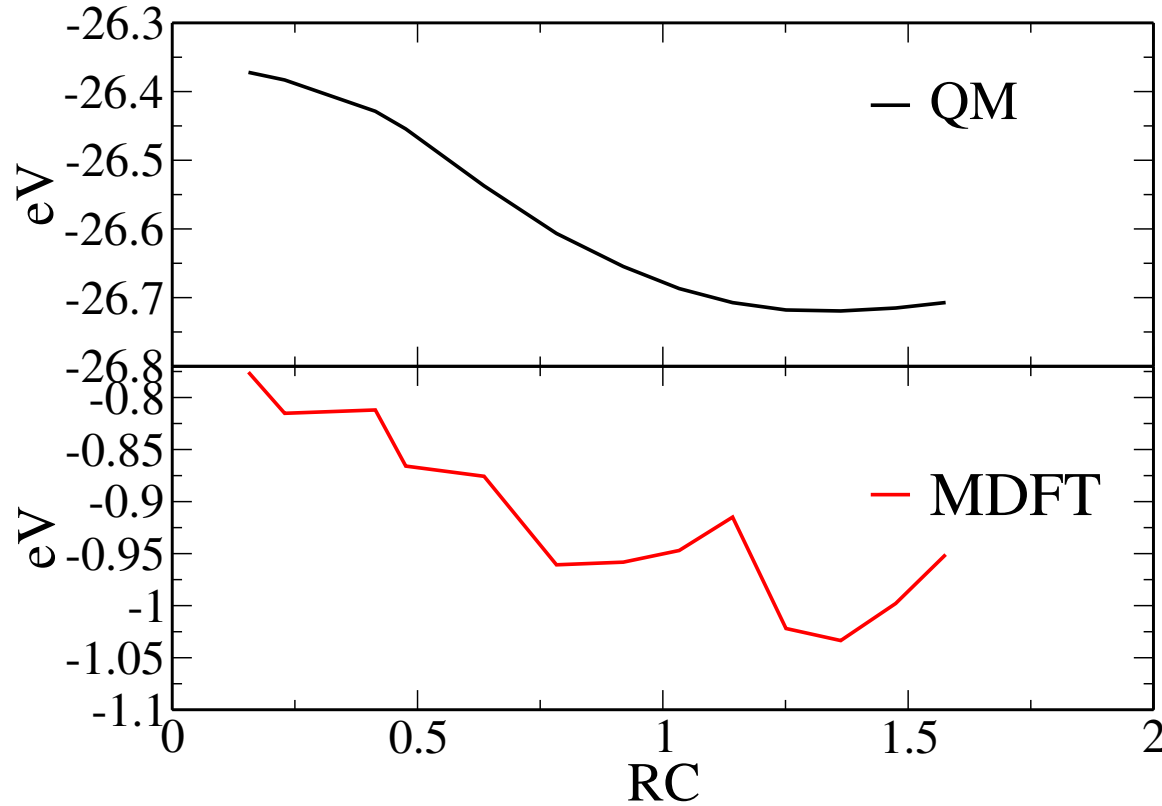
Compute an external electrostatic potential acting on the QM part $\Delta V_{\text{ext}}(\mathbf{r}) = -\frac{\rho_c(\mathbf{r})}{4\pi\epsilon_0}$

Redo the QM calculation / MDFT calculation sequentially until convergence (4 cycles).

Dipole moment μ (D)	Experience	QM	QM-CSM [1]	QM/MDFT	QM/MDFT with interactions
Vaccum	1.85	1.9	/	/	/
Solution	2.3/2.4	/	2.3	2.2	2.3

QM/MDFT SN/2 reaction

Using the same approach I tried to study the $\text{Cl-CH}_3 \cdots \cdots \text{Cl}^-$ SN₂ reaction.



Conclusions/Perspectives

MDFT is a powerful technique to study solvation problems

It may be a good compromise for taking into account solvent effects in QM calculation (computational cost + molecular description)

It clearly needs further development

When coupled with eDFT, it should be possible to simultaneous optimization of the two density fields

Thank you all for listening !

Guillaume Jeanmairat

Collaborators:



Maximilien Levesque (ENS)



Daniel Borgis (ENS)