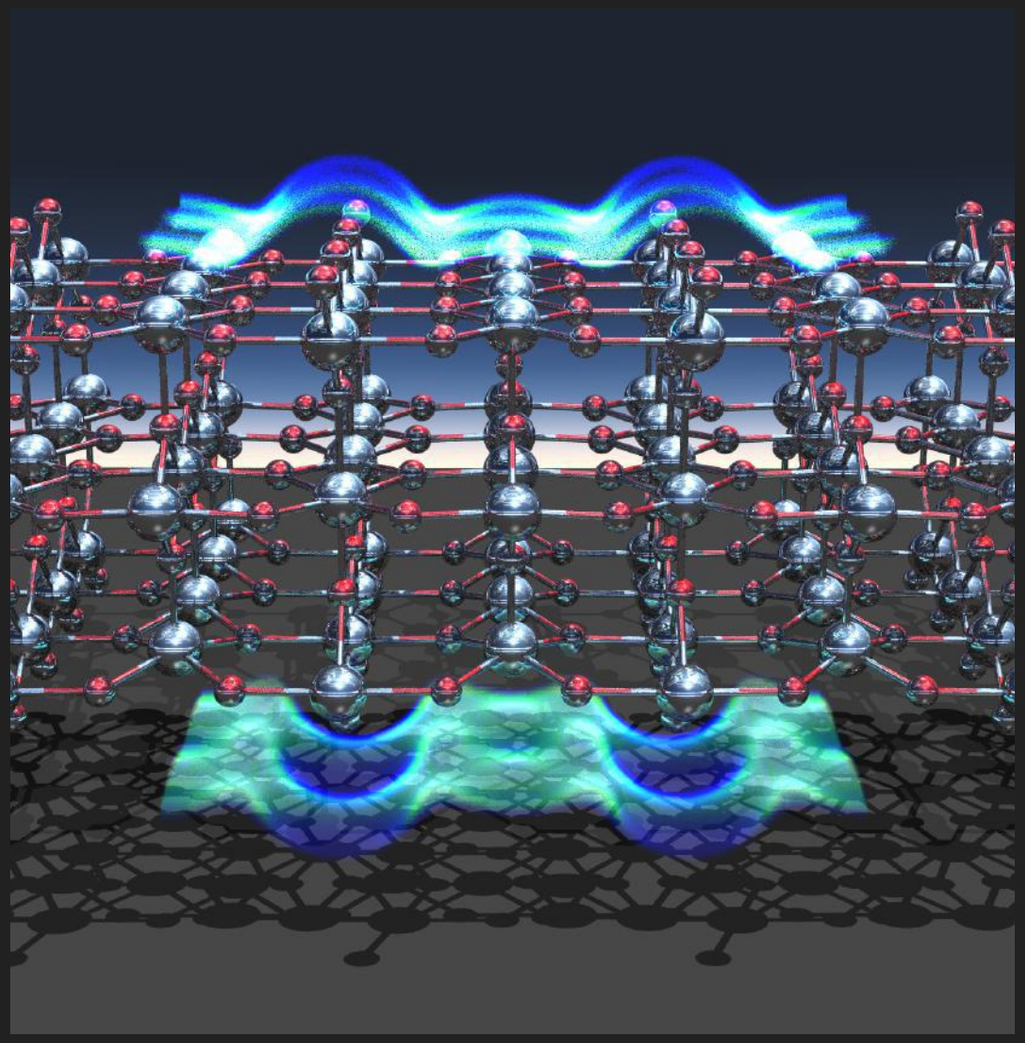


OLIVIERO ANDREUSSI

UNIVERSITY OF NORTH TEXAS

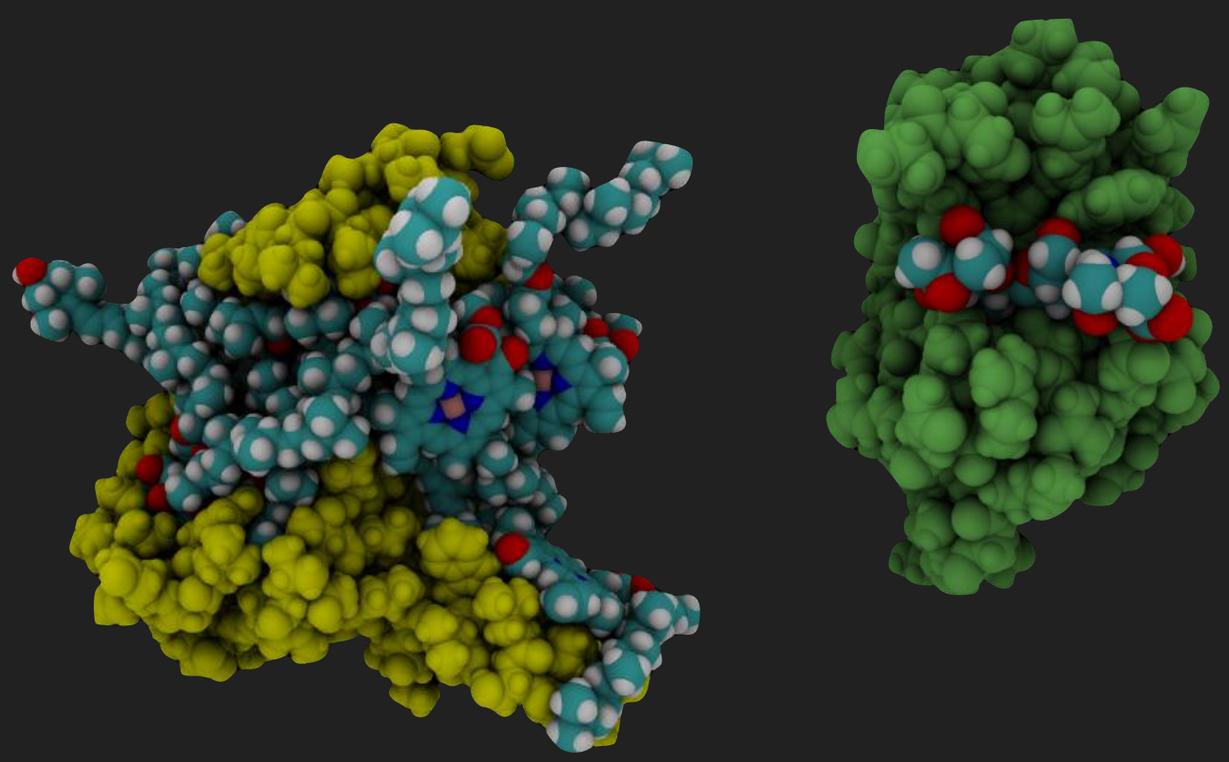
ENVIRON: CONTINUUM EMBEDDINGS IN QUANTUM-ESPRESSO

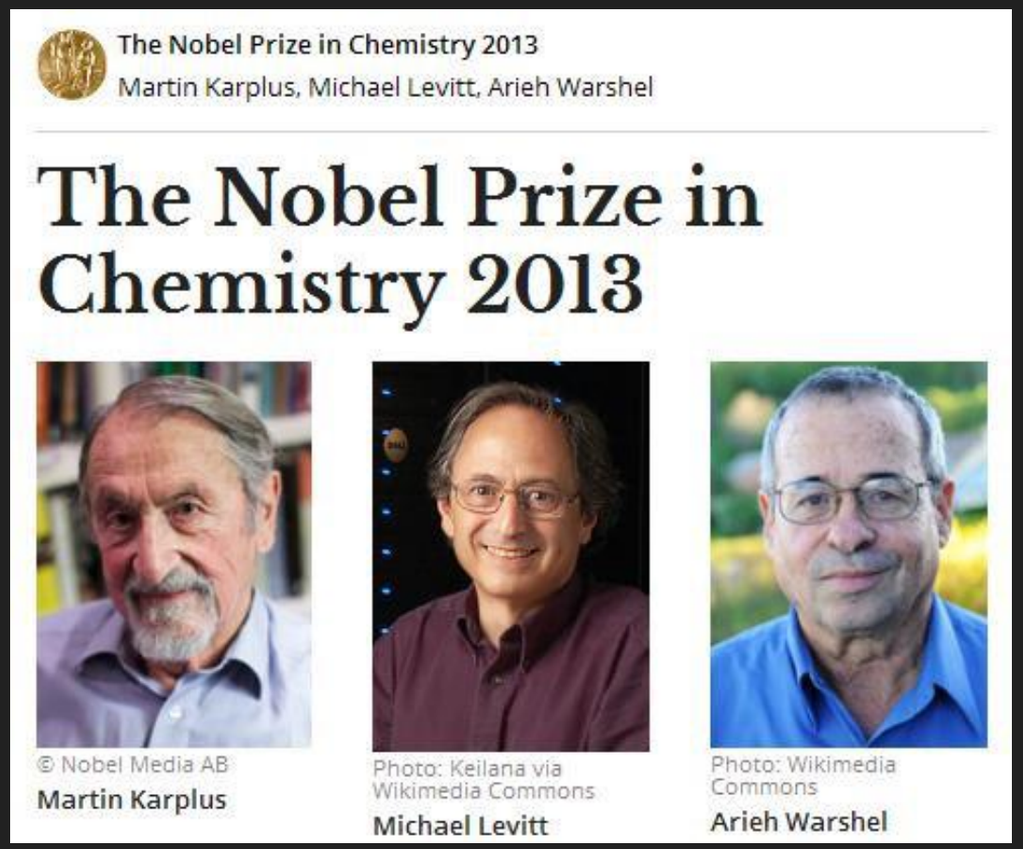
OUTLINE

- Introduction to Continuum Embedding
- Ingredients
  - Continuum
  - Interface
  - Interactions
    - Numerical Solvers
- Recipes

DEALING WITH COMPLEXITY

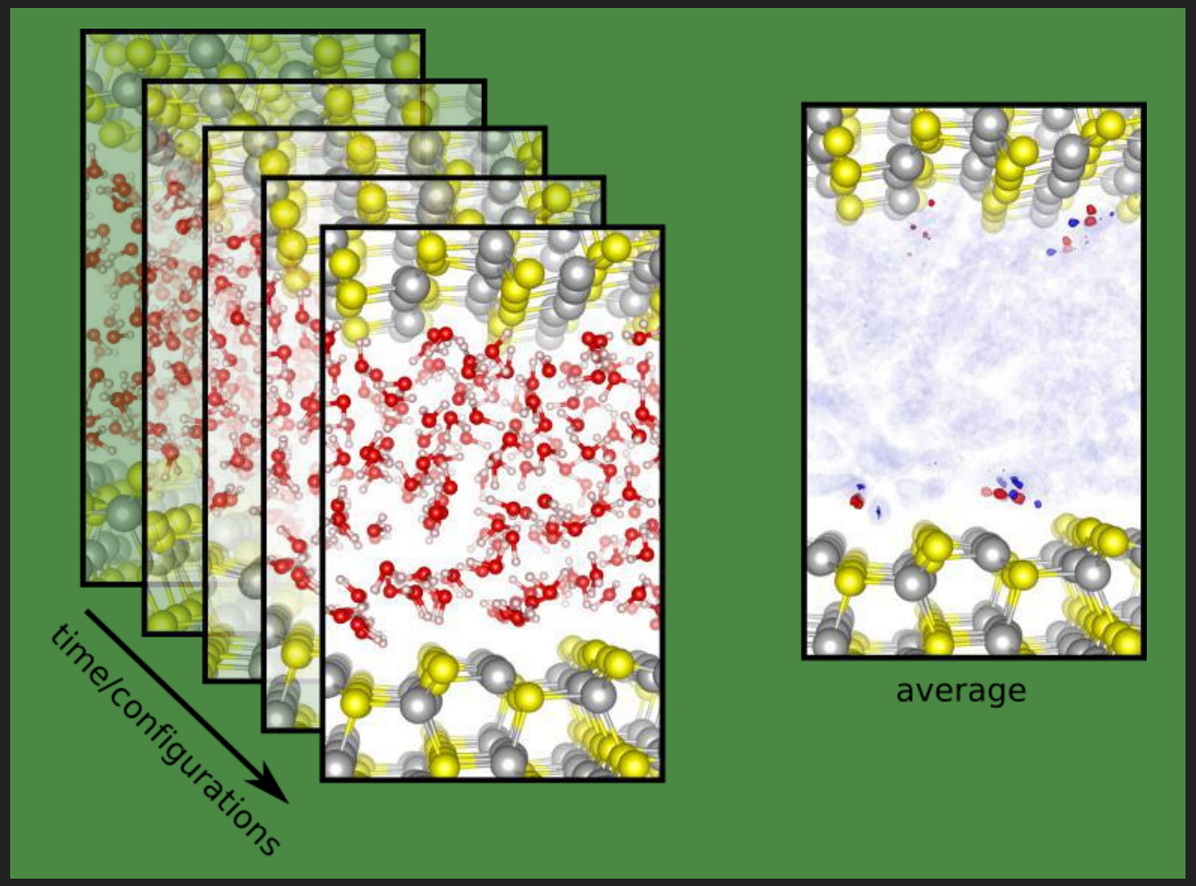
- Democratic approaches (see tomorrow's session)
- Hierarchical approaches
- Atomistic (QM/MM, DE, ONIOM, …)





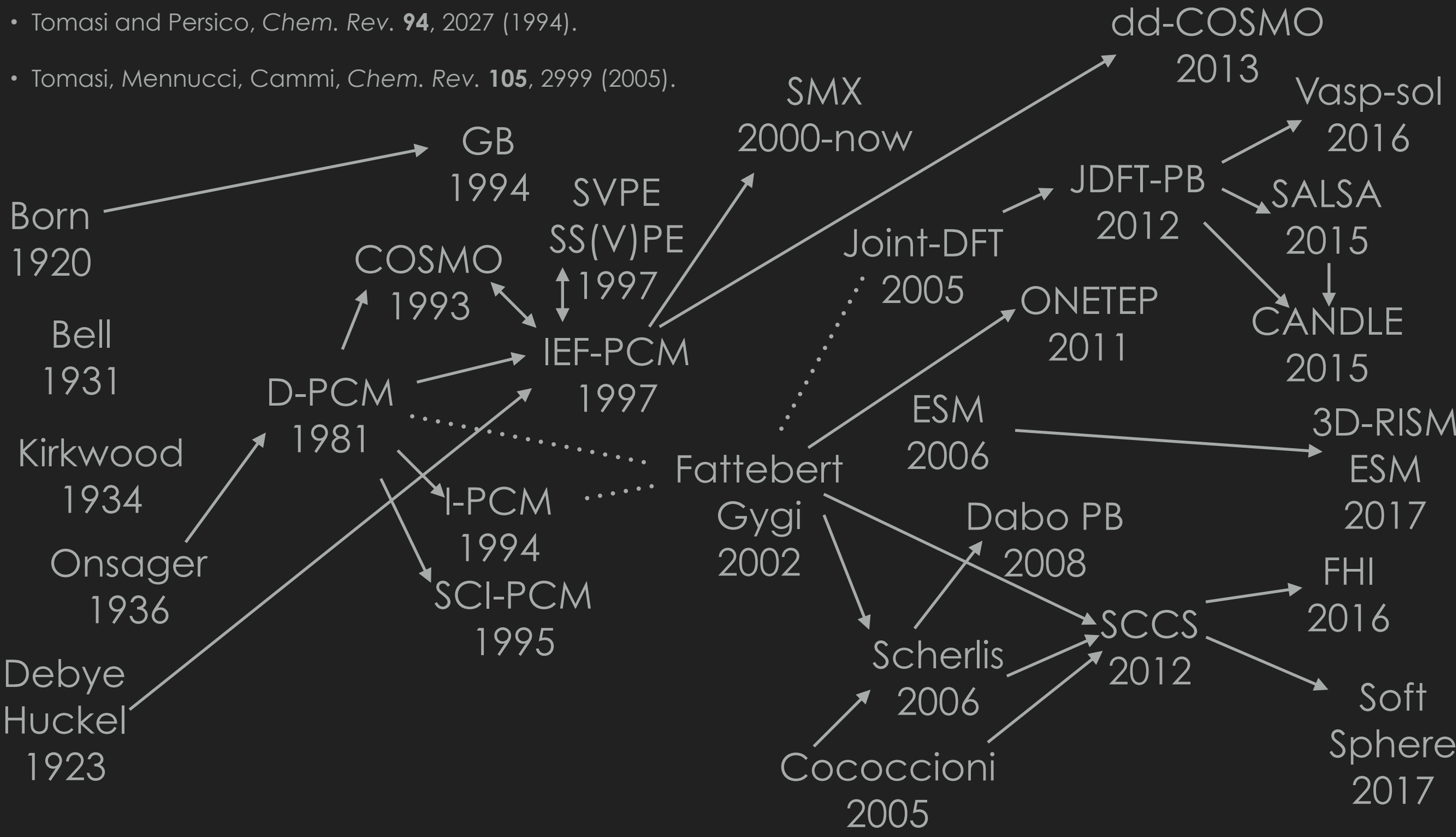
DEALING WITH COMPLEXITY

- Hierarchical approaches
  - Continuum (PCM, COSMO, etc.)
- Fast (high-throughput)
- Versatile
- Accurate (in the right conditions)



CONTINUUM GENEALOGY

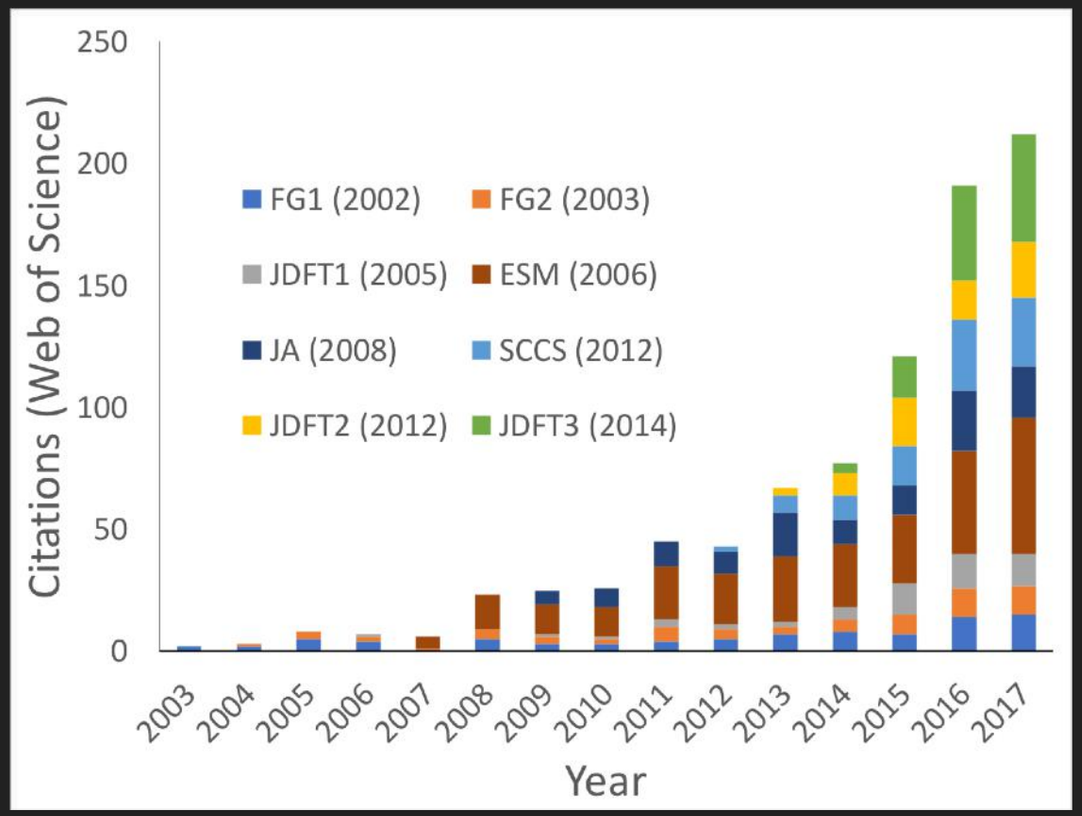
- Tomasi and Persico, *Chem. Rev.* **94**, 2027 (1994).
- Tomasi, Mennucci, Cammi, *Chem. Rev.* **105**, 2999 (2005).



CONTINUUM EMBEDDINGS IN CONDENSED-MATTER

- Very active energy-related topic: catalysis, electro-catalysis, electro-chemistry, super-capacitors, batteries, solar, etc.
- In Quantum ESPRESSO (Environ), Big-DFT, FHI-AIMS, VASP (VaspSol), ONETEP (DL_MG), CP2K, GPAW, JDFT-x

Andreussi and Fisicaro, *tutorial review accepted on Int. J. Quantum Chem. (2018)*. Open Access!

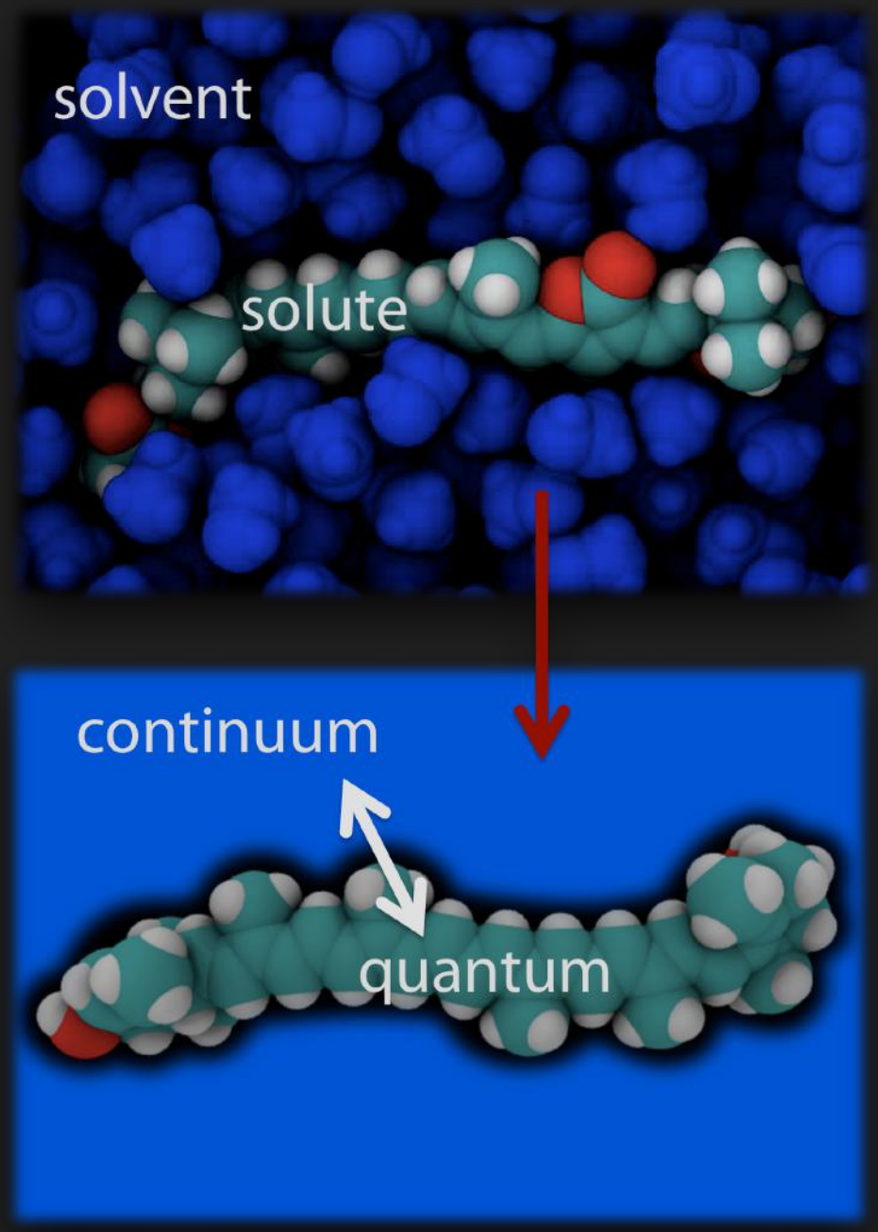


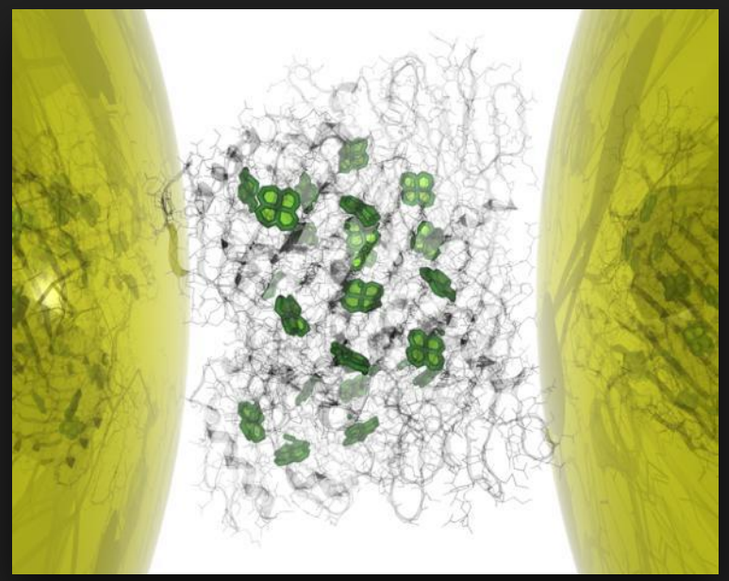
INGREDIENTS

- Continuum
- Interface
- Interactions
  - Numerical Solver

CONTINUUM

- Liquid
- Pressure medium
- Electrolyte
- Nanoparticle
- …



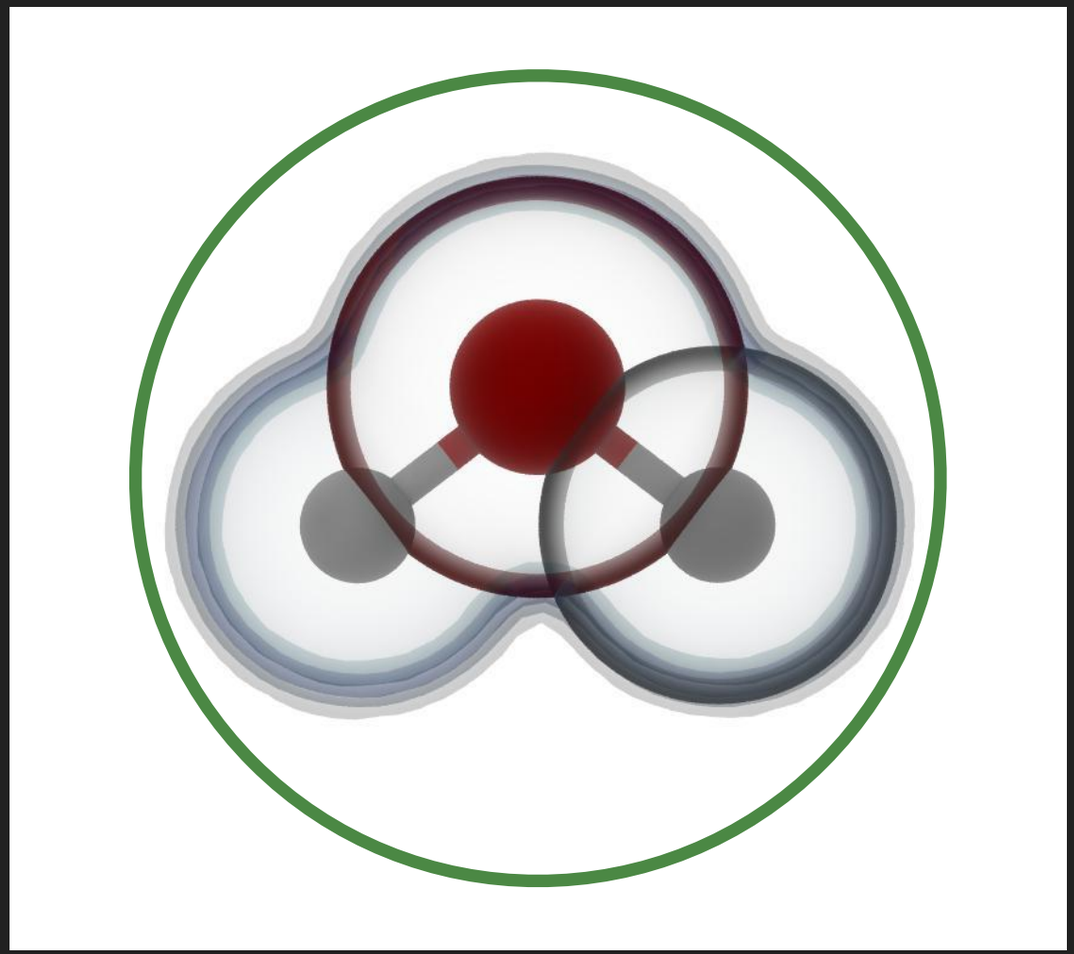


O. Andreussi, A. Biancardi, S. Corni and B. Mennucci, *Nano Lett.* **13**, 4475 (2013)

INTERFACE

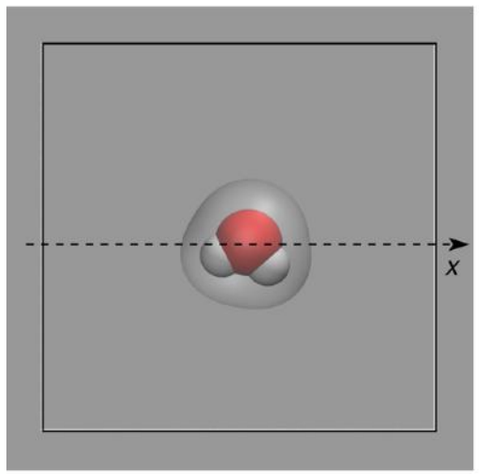
- Simple or complex
- Sharp or smooth
- Fixed or based on electrons or ions or both
- Local or non-local
- Single or multiple
- …

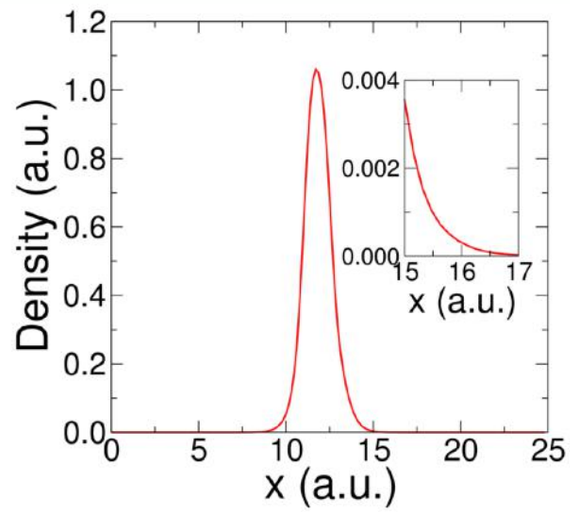
$$s(\mathbf{r}) = \begin{cases} 1 & \mathbf{r} \in \text{system} \\ 0 & \mathbf{r} \in \text{continuum} \end{cases}$$

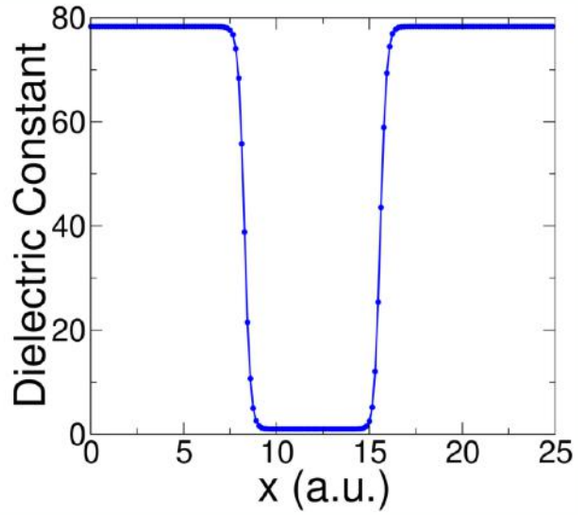


ELECTRONIC INTERFACE

$$s\left(\mathbf{r}\right) \equiv s\left(\rho^{el}\left(\mathbf{r}\right)\right)$$







$$s\left(\rho^{el}\left(\mathbf{r}\right)\right) = \frac{1}{2}\left(1 - \frac{1 - \left(\rho^{el}\left(\mathbf{r}\right)/\rho_0\right)^{2\beta}}{1 + \left(\rho^{el}\left(\mathbf{r}\right)/\rho_0\right)^{2\beta}}\right)$$

2 parameters

J.-L. Fattebert and F. Gygi, *J. Comput. Chem.* **23**, 662, (2002)
J.-L. Fattebert and F. Gygi, *Int. J. Quantum Chem.* **93**, 139 (2003)

O. Andreussi, I. Dabo and N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)

$$s\left(\mathbf{r}\right) = \begin{cases} 1 & \rho^{el}\left(\mathbf{r}\right) > \rho_{max} \\ t\left(\ln\left(\rho^{el}\left(\mathbf{r}\right)\right)\right) & \rho_{max} > \rho^{el}\left(\mathbf{r}\right) > \rho_{min} \\ 0 & \rho^{el}\left(\mathbf{r}\right) < \rho_{min} \end{cases}$$

2 parameters

IONIC INTERFACE

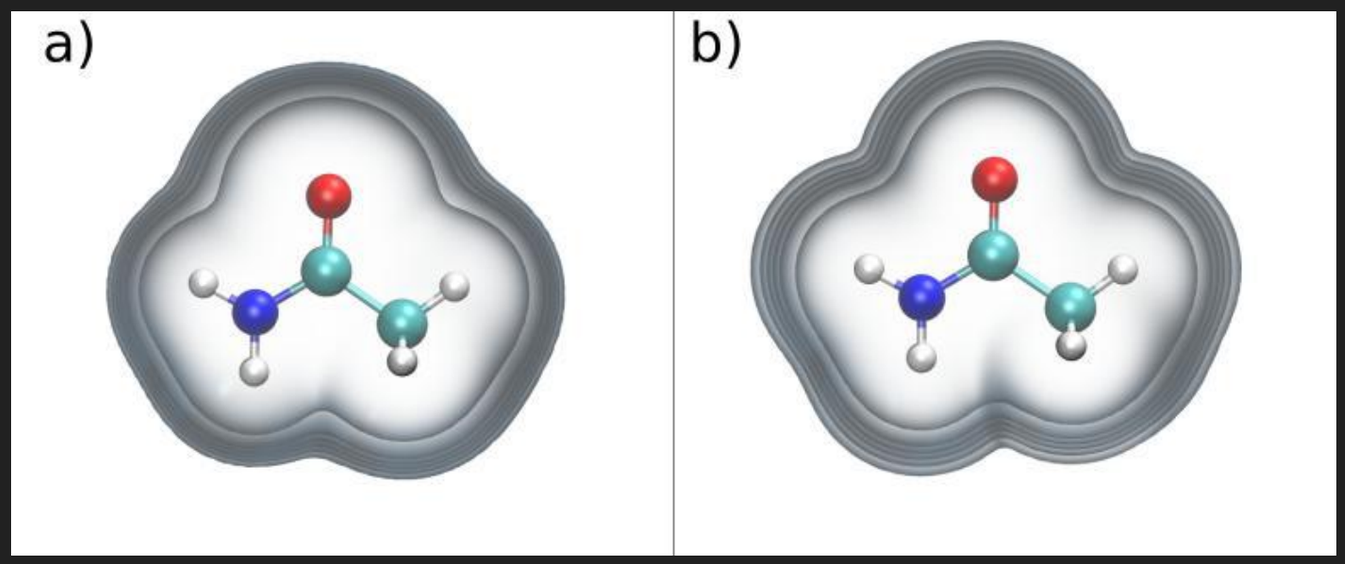
- Analytic derivatives
- Stable
- Atom-dependent parametrization
  - UFF atomic radii
  - Uniform scaling
  - Smoothing

$$s\left(\mathbf{r}\right) \equiv s\left(\left\{\left|\mathbf{r}-\mathbf{R}_i\right|\right\}\right)$$

$$s\left(\mathbf{r}\right) = 1 - \prod_i h_i\left(\left|\mathbf{r}-\mathbf{R}_i\right|\right),$$

$$h_i\left(\left|\mathbf{r}\right|\right) = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{\left|\mathbf{r}\right| - \alpha R_i^{vdW}}{\Delta}\right)\right]$$

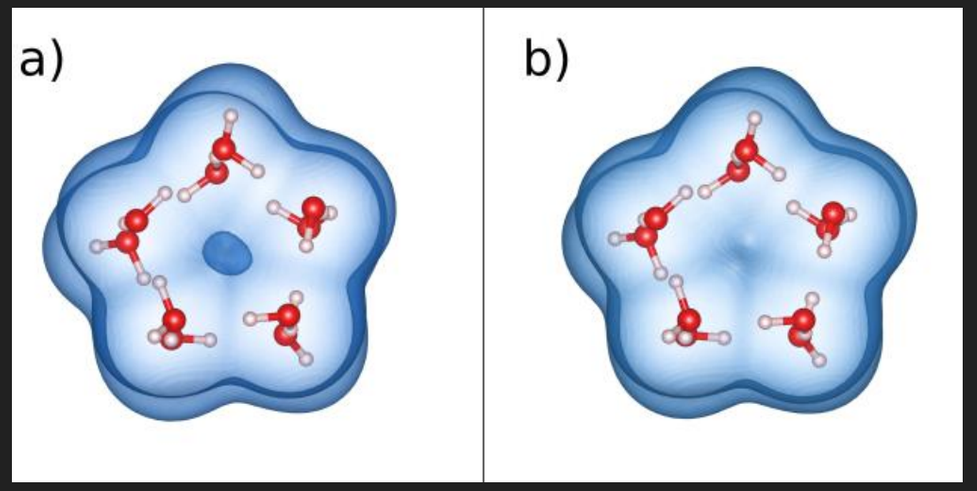
Giuseppe Fisicaro, et al. *J. Chem. Theory Comput.* **13**, 3829 (2017)



Electronic Ionic

SOLVENT-AWARE INTERFACE

- Augment the solute interface by a non-local term, that contains information on how much empty volume is around



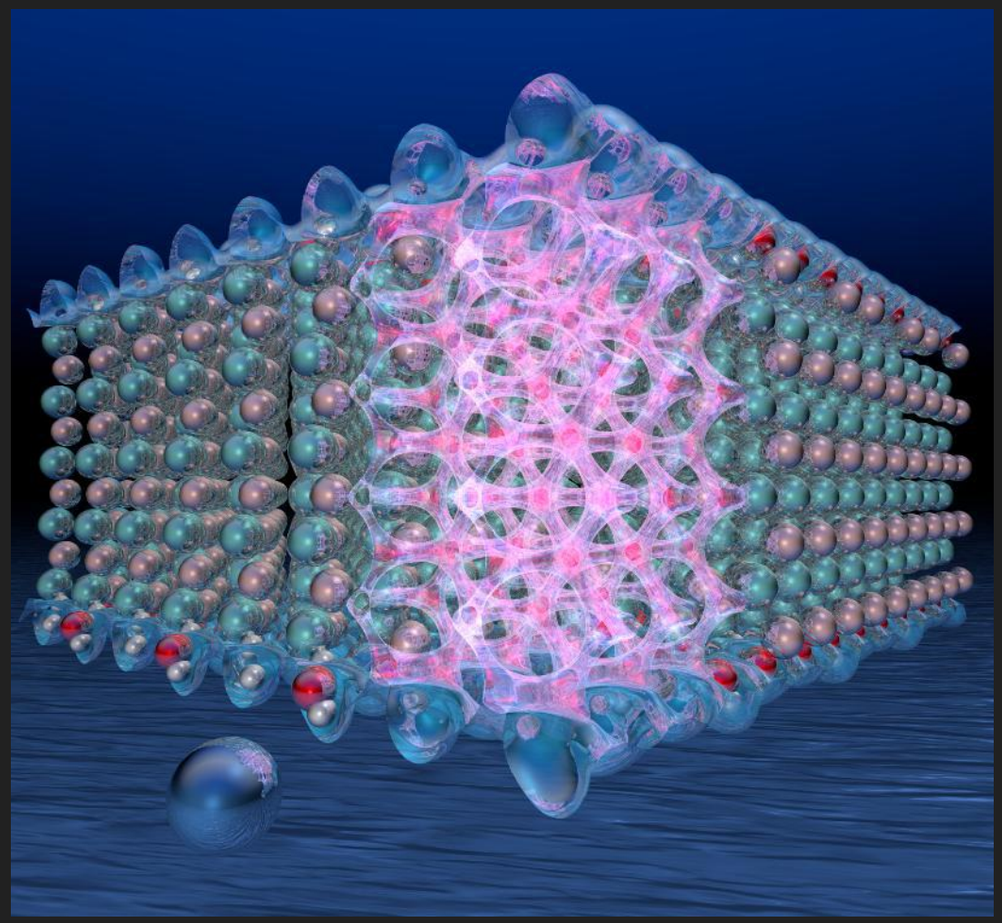
smooth function

$$\hat{s}(\mathbf{r}) = s(\mathbf{r}) + (1 - s(\mathbf{r}))\, t\left(f^{ff}(\mathbf{r})\right)$$

$$f^{ff}\left[s(\mathbf{r}')\right](\mathbf{r}) \equiv \int s(\mathbf{r}')\, h(|\mathbf{r} - \mathbf{r}'|)\, \mathrm{d}\mathbf{r}' = s * h(\mathbf{r})$$

filled fraction

smooth spherical function

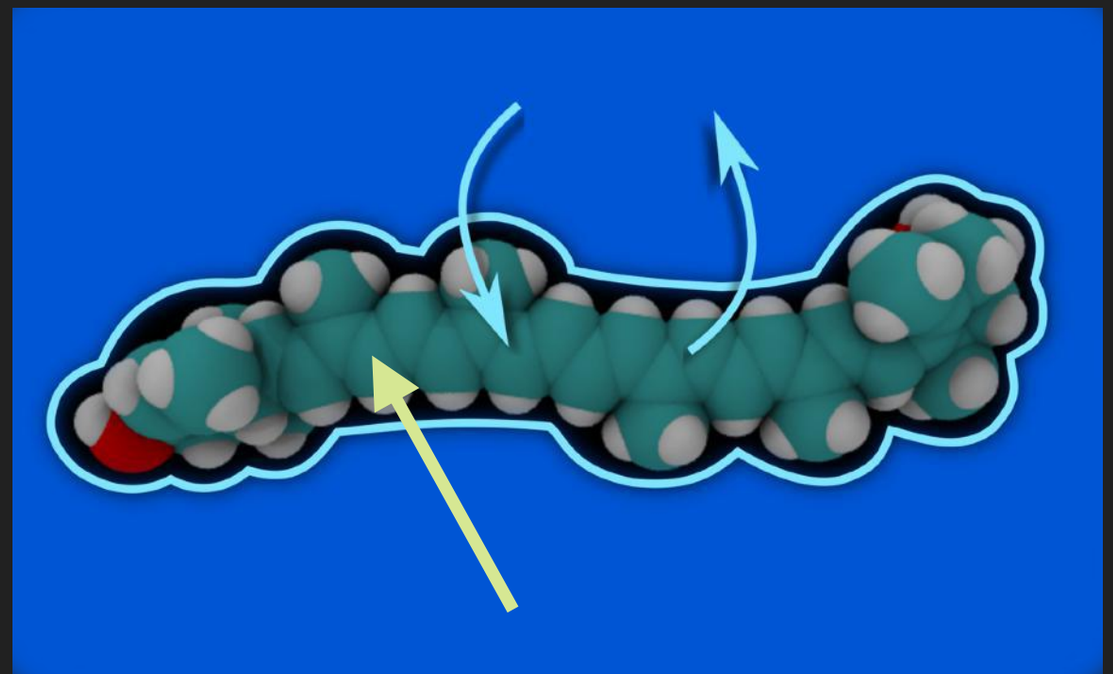


- Smooth differentiable expression
- Extra parameters: from geometrical considerations or tuned to experiments

Andreussi et al. *JCTC* (2019)

INTERACTIONS

- Electrostatic
  - Dielectric screening (dipolar)
  - Coulomb interaction (monopole)
- Pressure
- Cavitation
- Dispersion
- Repulsion
- Specific (hydrogen bonds, chemical bonds, etc.)
- …



$$\Delta G^{sol} = \Delta G^{el} + G^{cav} + G^{dis} + G^{rep} + \Delta G^{tm} + P\Delta V$$

$$V_{KS}^{interface}(\mathbf{r}) = \int \frac{\delta s(\mathbf{r}')}{\delta \rho^{el}(\mathbf{r})} \frac{\delta G[s]}{\delta s(\mathbf{r}')} \mathrm{d}\mathbf{r}'$$

$$\mathbf{f}_i^{interface} = -\int \frac{\partial s(\mathbf{r})}{\partial \mathbf{R}_a} \frac{\delta G[s]}{\delta s(\mathbf{r})} \mathrm{d}\mathbf{r}$$

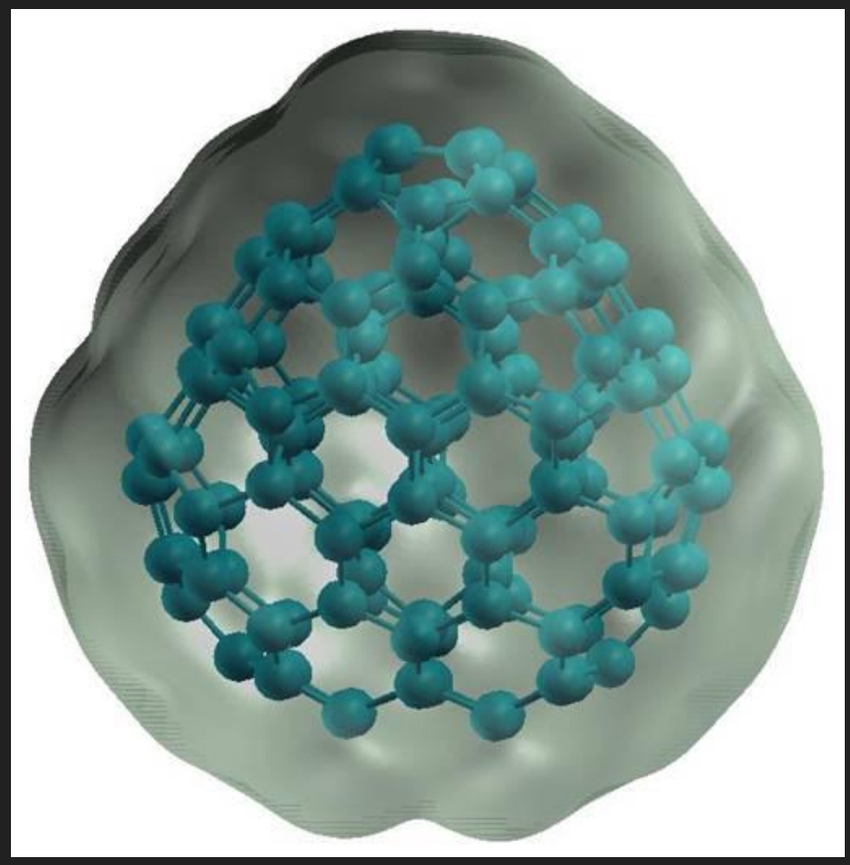
VOLUME

- Pressurizing medium (Enthalpy functional)

$$V \equiv V[s] = \int s(\mathbf{r})\,\mathrm{d}\mathbf{r}.$$

$$G^{PV}[s] = P^{ext} V[s]$$

$$\frac{\delta G^{PV}[s]}{\delta s}(\mathbf{r}) = 1$$



M. Cococcioni, et al. *PRL* **94**, 145501 (2005)

SURFACE

- Cavitation, repulsion

$$G^{cav}[s] = \gamma S[s]$$

$$S[s] = \int |\nabla s(\mathbf{r})| \, \mathrm{d}\mathbf{r}$$

$$\frac{\delta G^{cav}[s]}{\delta s}(\mathbf{r}) = -\nabla \cdot \left(\frac{\nabla s(\mathbf{r})}{|\nabla s(\mathbf{r})|} \right)$$

M. Cococcioni, et al. *PRL* **94**, 145501 (2005)
D. Scherlis, et al. *J. Chem. Phys.* **124**, 74103 (2006)

DIELECTRIC SCREENING

- Polarizable dielectric medium

$$G\left[\rho^{el},\{\mathbf{R}_i\}\right]=\int\rho^{sys}\left(\mathbf{r}\right)\phi\left(\mathbf{r}\right)\mathrm{d}\mathbf{r}-\int\frac{1}{8\pi}\epsilon\left(\mathbf{r}\right)\left|\nabla\phi\left(\mathbf{r}\right)\right|^2\mathrm{d}\mathbf{r}$$

$$\rho^{sys}\left(\mathbf{r}\right)=\left(\rho^{el}\left(\mathbf{r}\right)+\sum_i z_i\delta\left(\left|\mathbf{r}-\mathbf{R}_i\right|\right)\right)$$

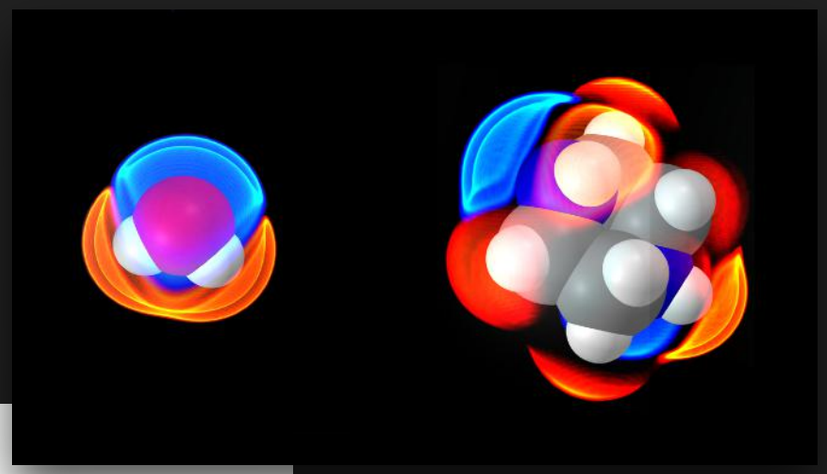
$$\frac{\delta G}{\delta\phi}=0\rightarrow\nabla\cdot\epsilon\left(\mathbf{r}\right)\nabla\phi\left(\mathbf{r}\right)=-4\pi\rho^{sys}\left(\mathbf{r}\right)$$

Generalized Poisson Equation (GPE)

$$\epsilon\left(\mathbf{r}\right)\equiv\epsilon\left(s\left(\mathbf{r}\right)\right)=1+\left(\epsilon_0-1\right)\left(1-s\left(\mathbf{r}\right)\right)$$

J.-L. Fattebert and F. Gygi, *J. Comput. Chem.* **23**, 662, (2002)
J.-L. Fattebert and F. Gygi, *Int. J. Quantum Chem.* **93**, 139 (2003)

POLARIZATION CHARGE



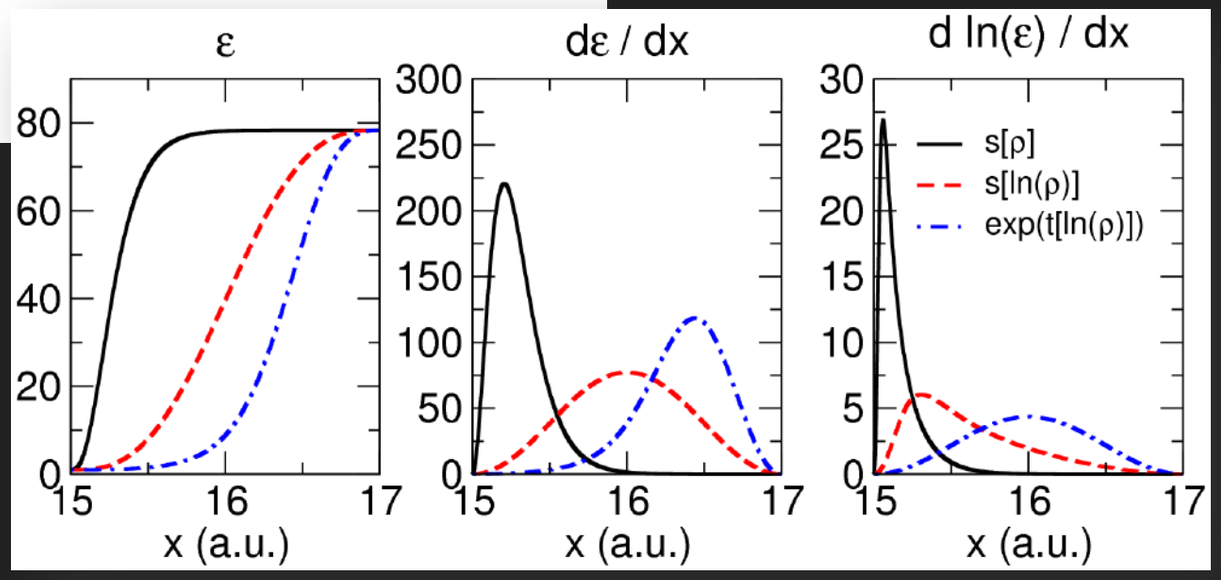
- Reshuffling of GPE

$$\nabla^2\phi(\mathbf{r}) = -4\pi\left(\rho^{sys}(\mathbf{r}) + \rho^{pol}(\mathbf{r})\right)$$

$$\rho^{pol}(\mathbf{r}) = \frac{1}{4\pi}\nabla\ln\epsilon(\mathbf{r})\cdot\nabla\phi(\mathbf{r}) - \frac{\epsilon(\mathbf{r})-1}{\epsilon(\mathbf{r})}\rho^{sys}(\mathbf{r})$$

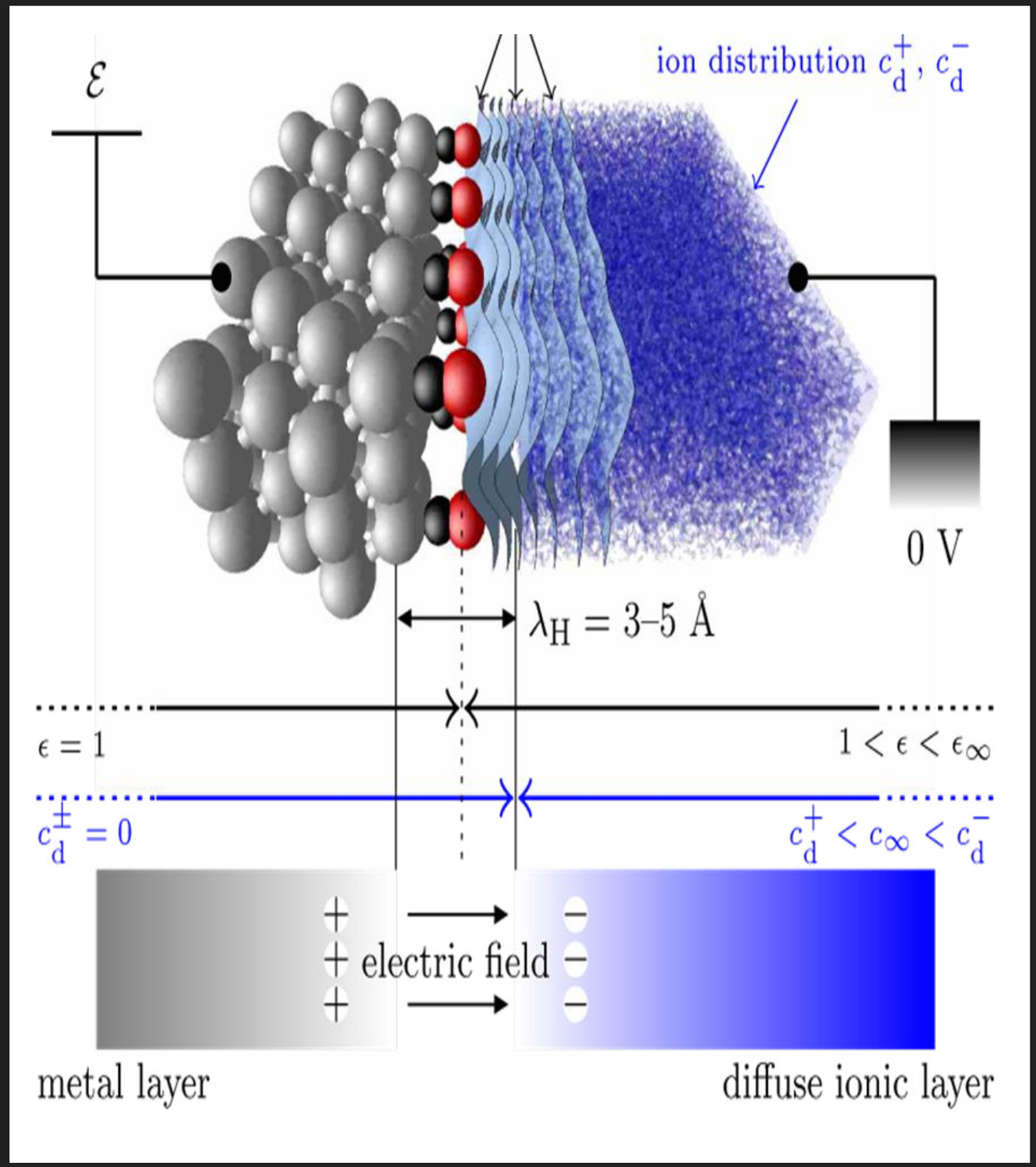
$$\epsilon(\mathbf{r}) = e^{\log\epsilon_0[1-s(\mathbf{r})]}$$

O. Andreussi, I. Dabo and N. Marzari,
J. Chem. Phys. **136**, 064102 (2012)



ELECTROLYTE

- Separate interface
- Neutralizing distribution of counter-ions in solution:
  - Study of charged slabs
  - Study of applied electrochemical potentials



I. Borukov, D. Adelman and H. Orland *PRL* **79**, 435 (1997)
Dabo et al. *arXiv:0901.0096* (2008)
R. Jinnouchi and A.B. Andreson, *PRB* **77**, 245417 (2008)

ELECTROLYTE

- Ionic species in solution $\rho^{\pm}(\mathbf{r}) = z^{\pm} c^{\pm}(\mathbf{r})$

$$G\left[\rho^{el}, \{\mathbf{R}_i\}, c^+, c^-\right] = \int \left\{ \left[\rho^{sys}(\mathbf{r}) + \rho^+(\mathbf{r}) + \rho^-(\mathbf{r})\right] \phi(\mathbf{r}) - \frac{\epsilon(\mathbf{r})}{8\pi} |\nabla\phi(\mathbf{r})|^2 + \right.$$
$$\left. -\mu^+ c^+(\mathbf{r}) - \mu^- c^-(\mathbf{r}) - Ts\left[c^+(\mathbf{r}), c^-(\mathbf{r})\right] \right\} \mathrm{d}\mathbf{r}$$

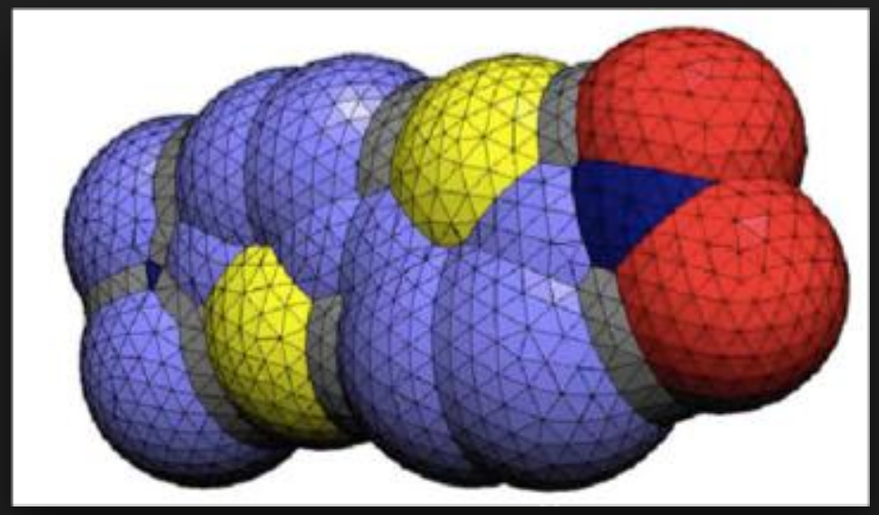
$$s\left[c^+, c^-\right] = -k_B \left[c^+(\mathbf{r}) \ln\left(c^+(\mathbf{r})\right) + c^-(\mathbf{r}) \ln\left(c^-(\mathbf{r})\right)\right]$$

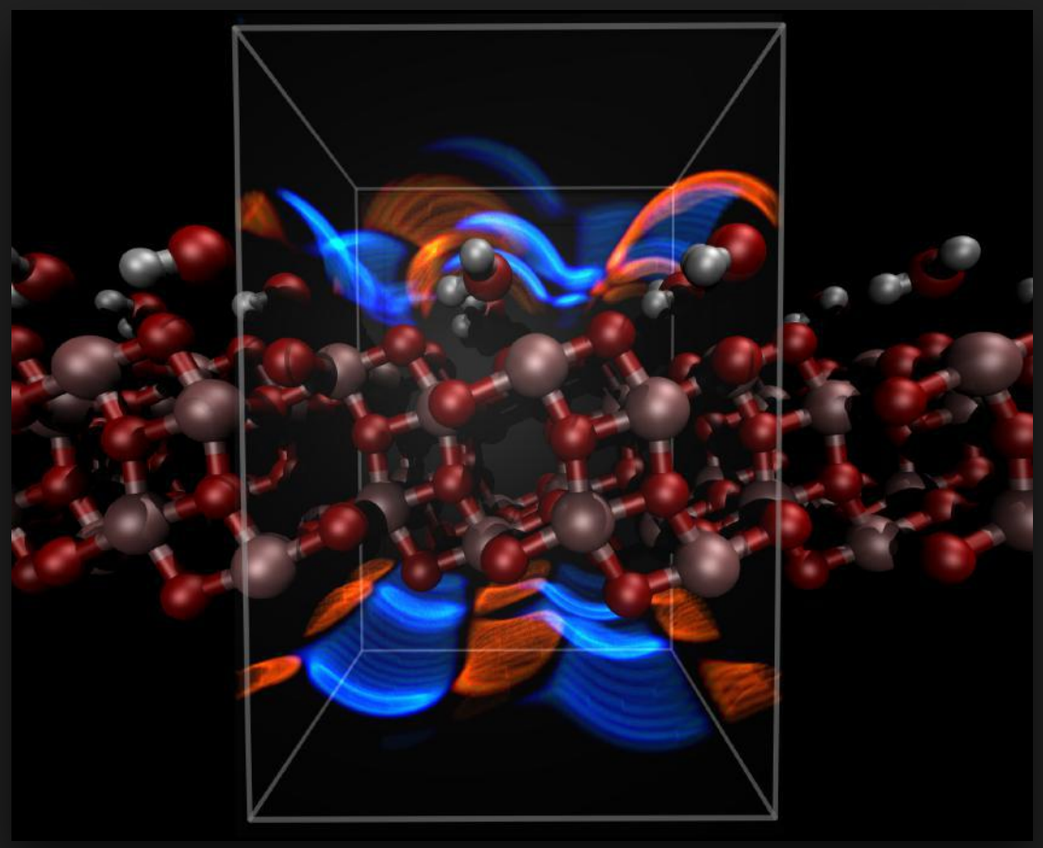
$$\frac{\delta G}{\delta c^{\pm}} = 0 \rightarrow c^{\pm}(\mathbf{r}) = c_B(\mathbf{r})\, e^{\frac{-z^{\pm}\phi(\mathbf{r})}{k_B T}}$$

$$\frac{\delta G}{\delta \phi} = 0 \rightarrow \nabla \cdot \epsilon(\mathbf{r}) \nabla\phi(\mathbf{r}) = -4\pi \left(\rho^{sys}(\mathbf{r}) + \rho^+(\mathbf{r}) - \rho^-(\mathbf{r})\right)$$

NUMERICAL SOLVER

- Bi-directional interactions are usually associated with non-analytic partial differential equations (GPE, PBE, MPBE, LPBE, etc.)
  - Boundary Element Methods
  - Domain decomposition
  - Multigrid
  - Gradient descent coupled with vacuum Poisson solver (FFT, wavelets, etc.)
  - …

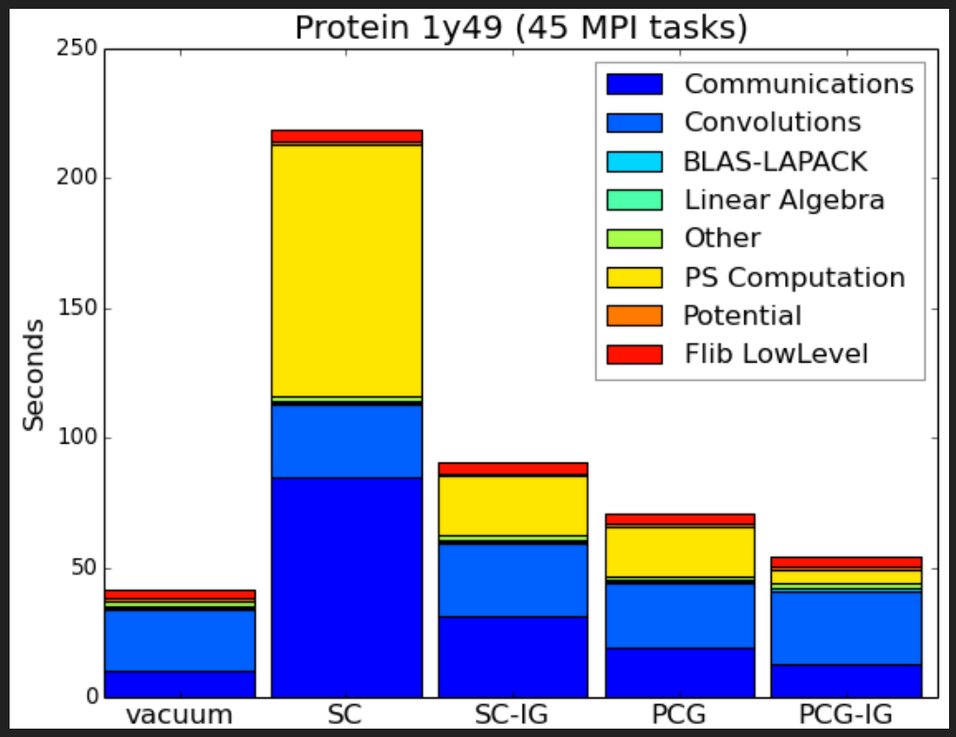


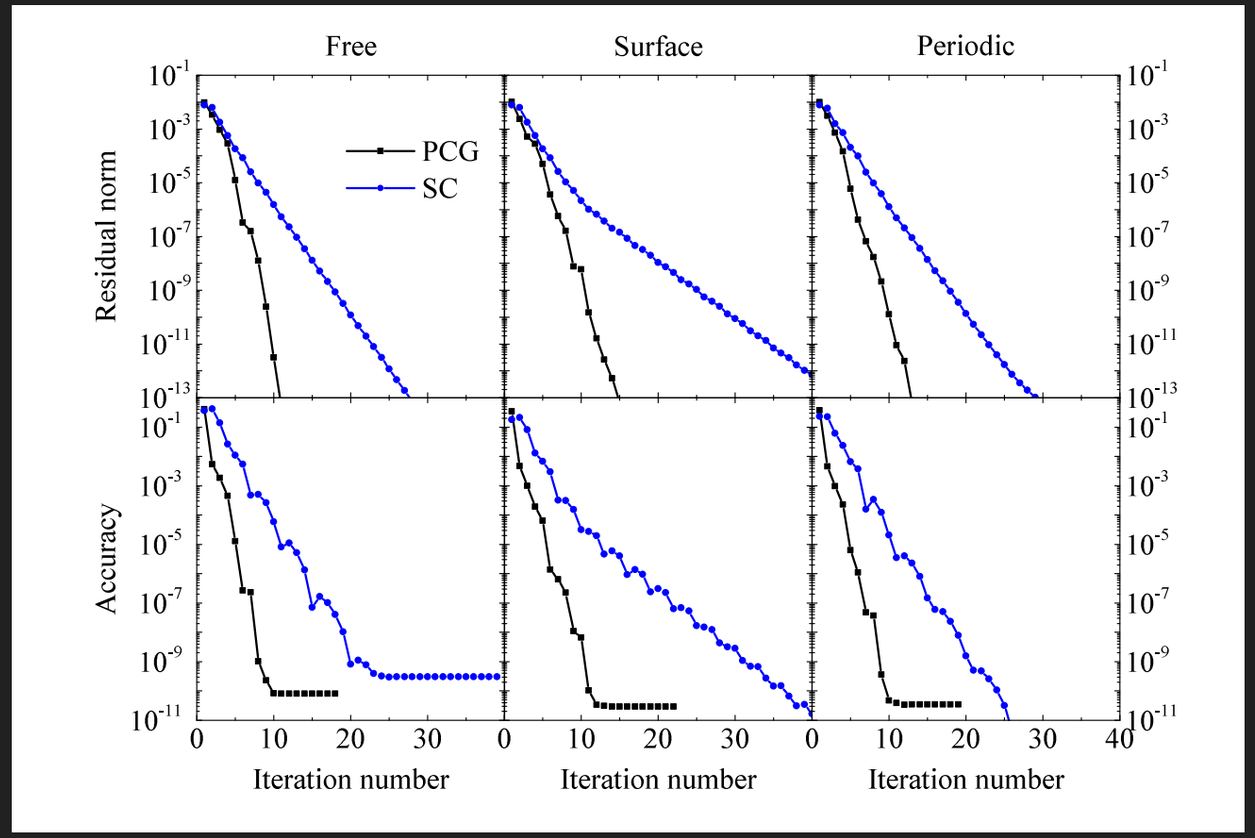


IMPROVED PRECONDITIONED SCHEME

$$\mathcal{P}^{CG} v_k(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})}\nabla^2[v_k(\mathbf{r})\sqrt{\epsilon(\mathbf{r})}] = -4\pi r_k(\mathbf{r}).$$

$$\begin{aligned}\mathcal{A} v_k(\mathbf{r}) &= \nabla \cdot \epsilon(\mathbf{r})\nabla v_k(\mathbf{r}) \\ &= -v_k(\mathbf{r})q(\mathbf{r}) - 4\pi r_k(\mathbf{r}),\end{aligned}$$



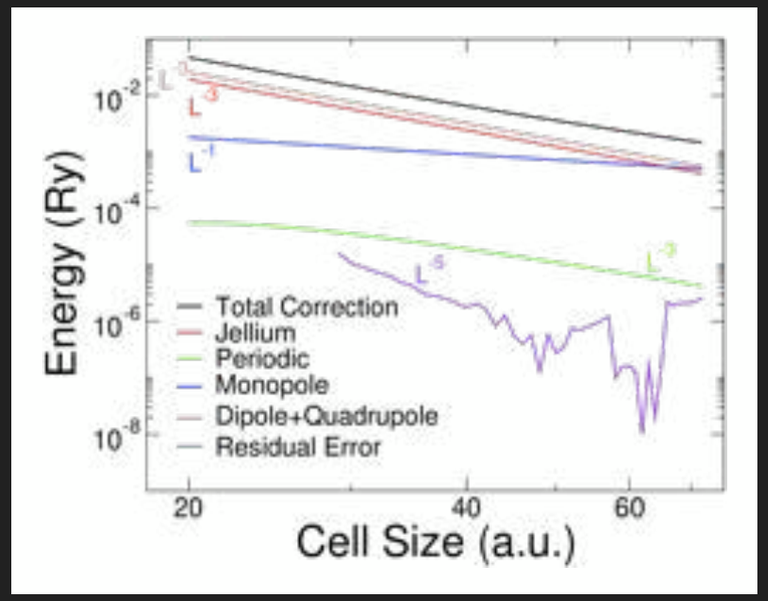


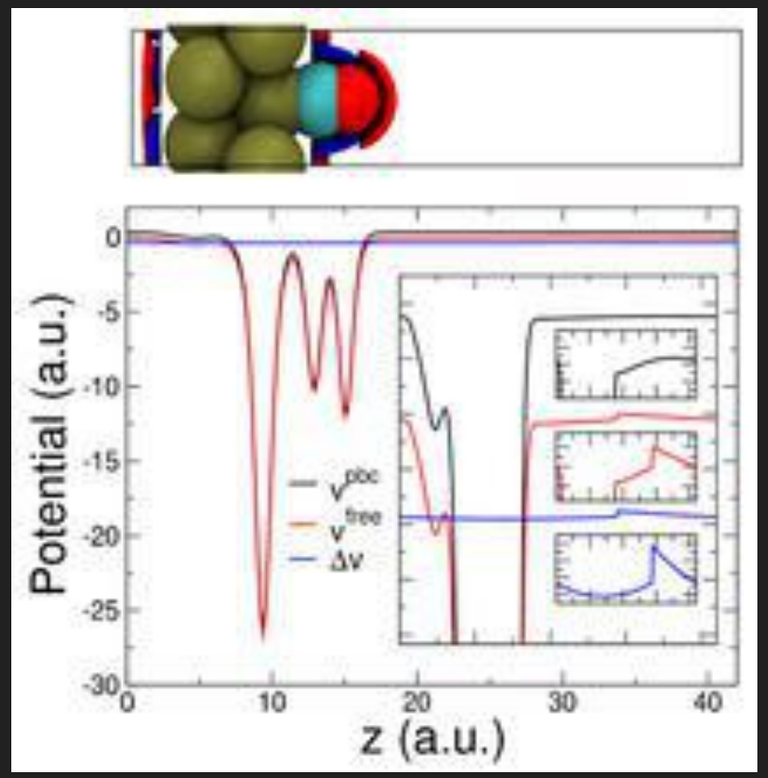
G. Fisicaro, L. Genovese, O. Andreussi, N. Marzari and S. Goedecker, *J. Chem. Phys.* **144**, 014103 (2016).

FFTS

- Fast, parallel, widespread
- Periodic boundary conditions (PBC) artifacts
- Makov-Payne
- Point-countercharge
- Martyna-Tuckerman

O. Andreussi and N. Marzari, *PRB* **90**, 245101 (2014)





RECIPES

- Model development level
  - Choose the continuum, choose the interface, choose the interactions
  - Tune the parameters
- User level
  - Choose the solver
  - Choose an application (compatible with the parameters)

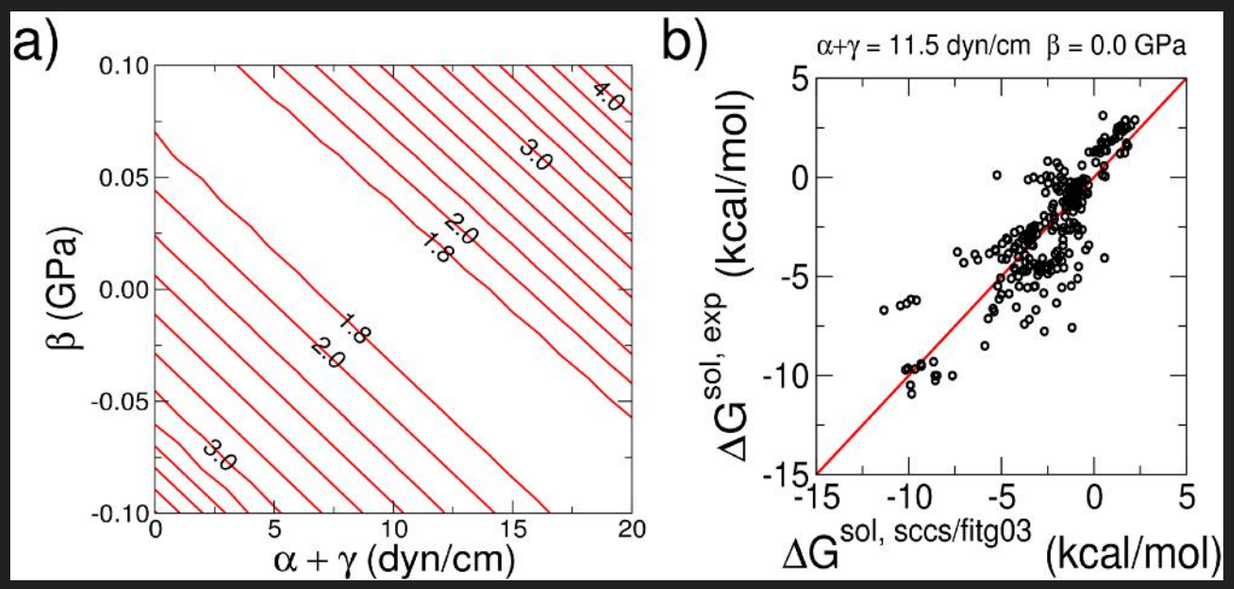
SELF-CONSISTENT CONTINUUM SOLVATION (SCCS)

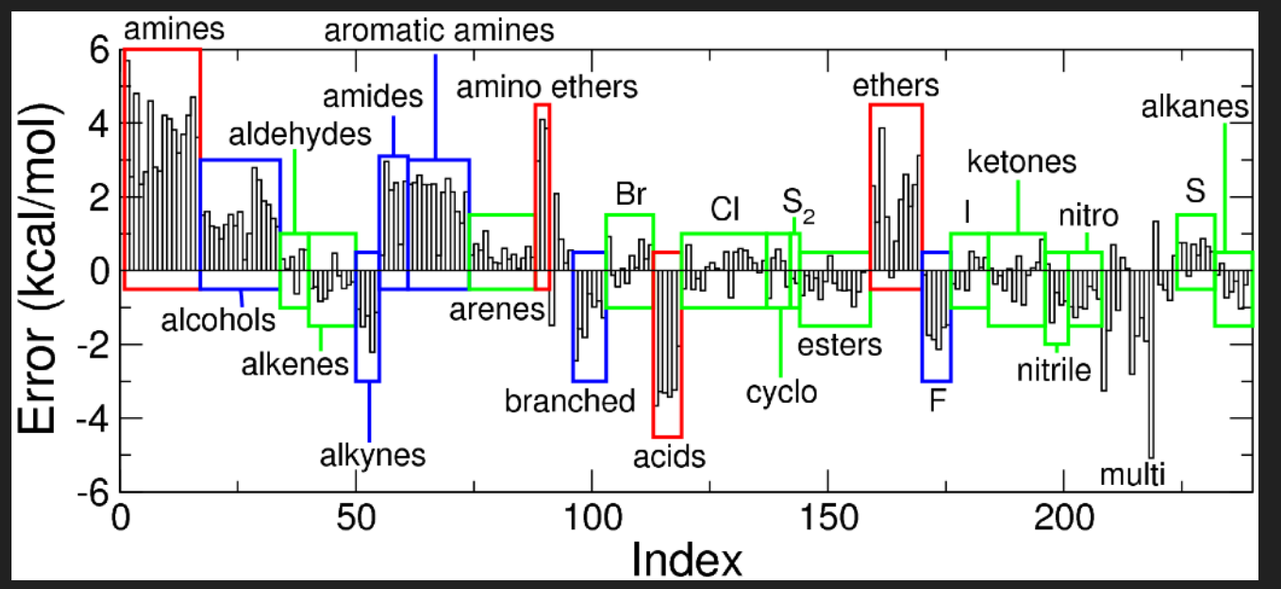
- Aqueous solutions
- Electronic interface
- Dielectric + Surface + Volume
- Or Dielectric + Surface (2D systems)

$$s(\mathbf{r}) = \begin{cases} 1 & \rho^{el}(\mathbf{r}) > \rho_{max} \\ t\left(\ln\left(\rho^{el}(\mathbf{r})\right)\right) & \rho_{max} > \rho^{el}(\mathbf{r}) > \rho_{min} \\ 0 & \rho^{el}(\mathbf{r}) < \rho_{min} \end{cases}$$

$$\epsilon(\mathbf{r}) = e^{\log \epsilon_0 [1 - s(\mathbf{r})]}$$

$$\Delta G = \Delta G^{el}\left(\epsilon\left(s(\mathbf{r})\right)\right) + \alpha S\left[s(\mathbf{r})\right] + \beta V\left[s(\mathbf{r})\right]$$

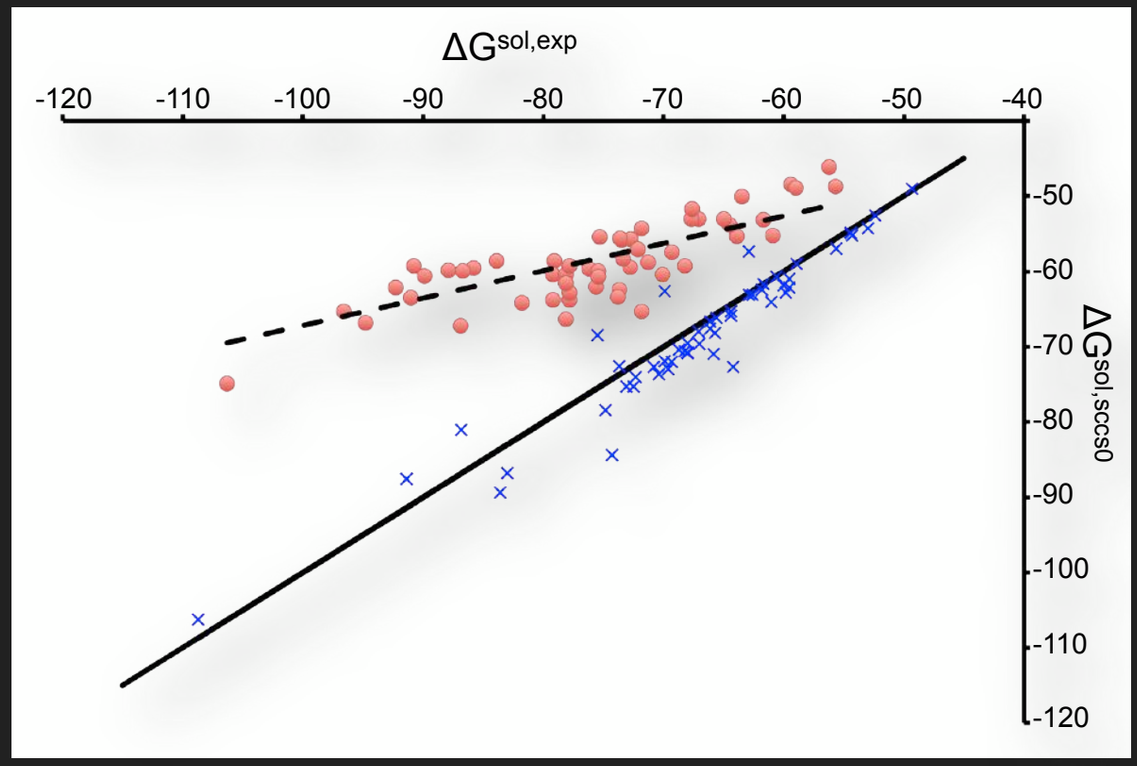


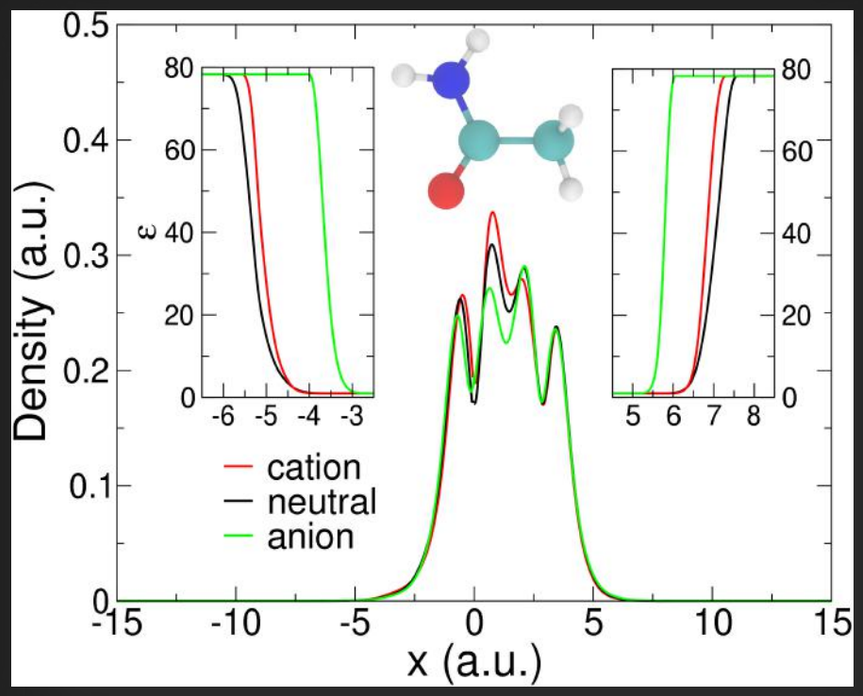


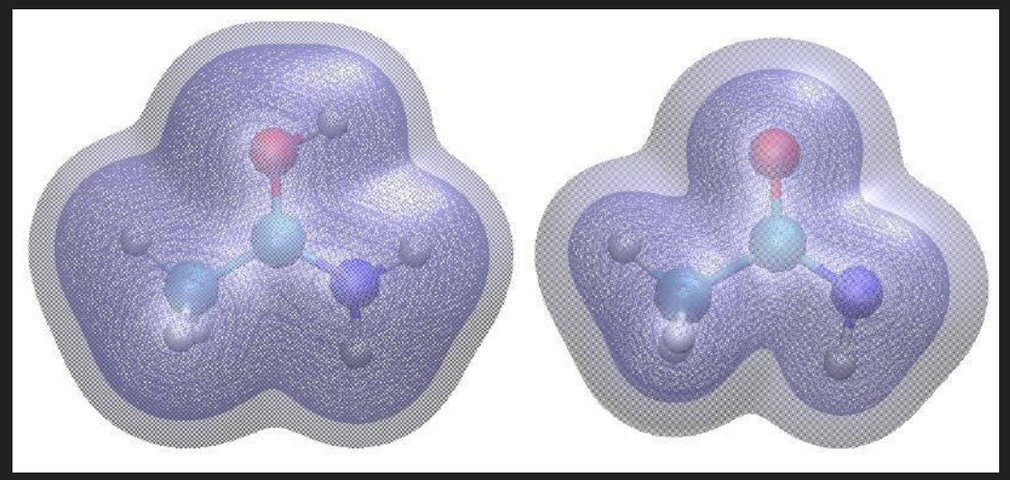
O. Andreussi, I. Dabo and N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)

SCCS FOR CHARGED SPECIES

- Anions need a separate parameterization



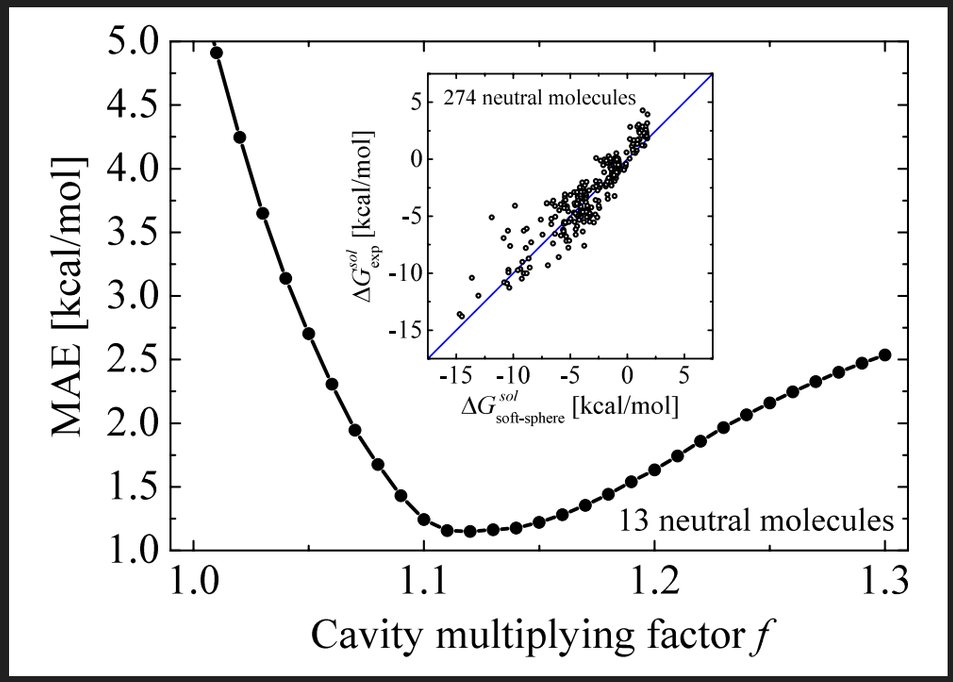




C. Dupont, O. Andreussi and N. Marzari, *J. Chem. Phys.* **139**, 214110 (2013)

SOFT-SPHERE CONTINUUM SOLVATION

- Aqueous solutions
- Ionic interface
- Dielectric + Surface + Volume



- Or Dielectric + Surface (2D systems)

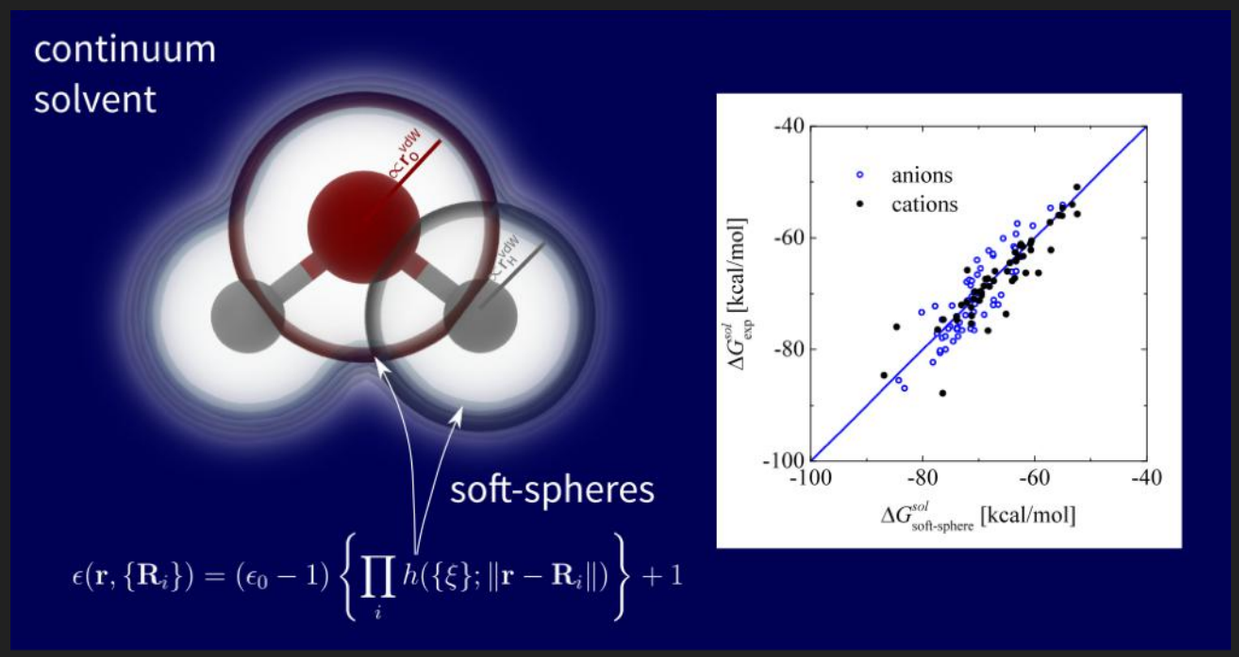


Table 2. MAEs in Aqueous Solvation Free Energies (kcal/mol) for Several Solvation Models (MAEs from ref 38)[a]

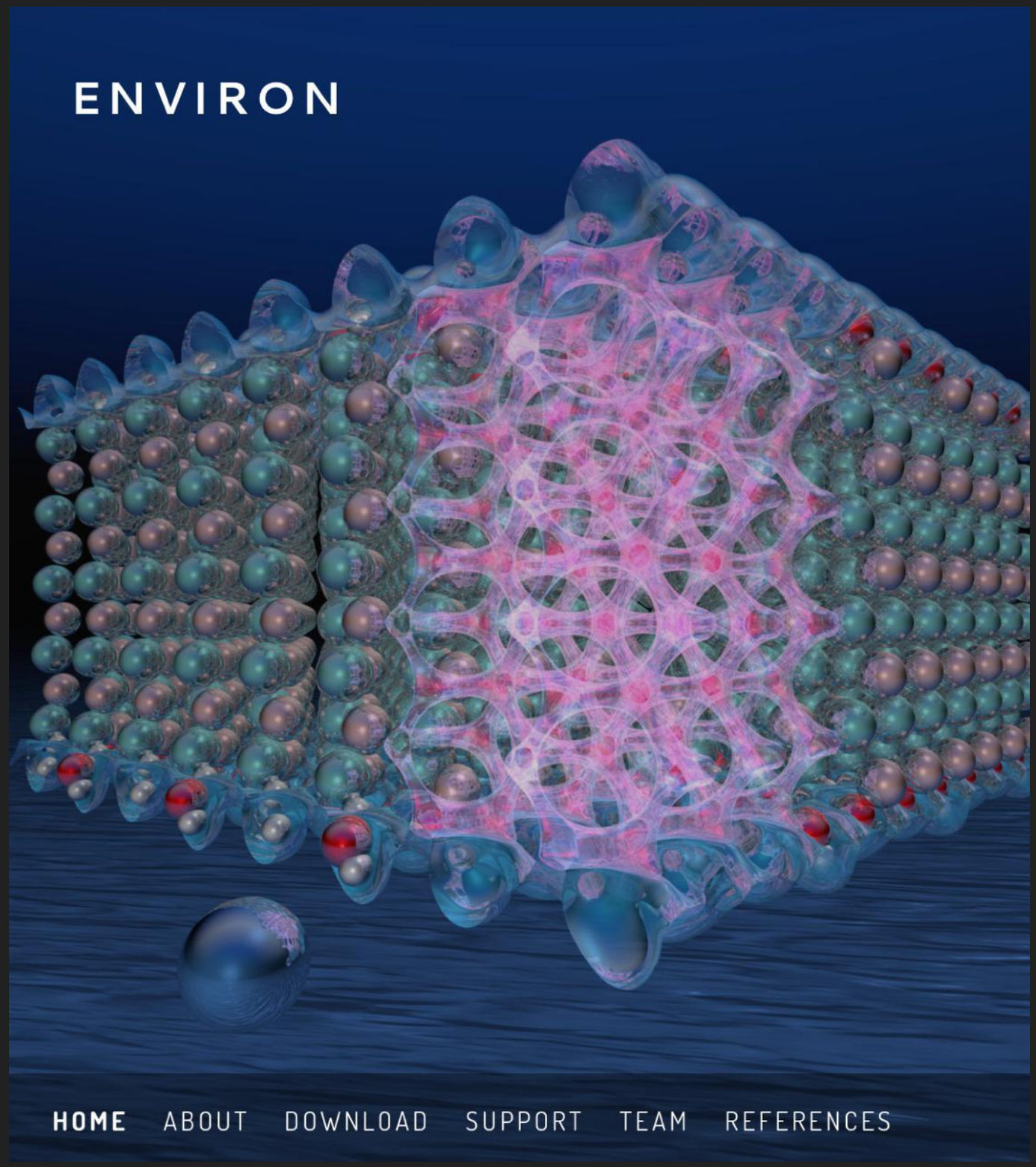
method	neutrals	cations	anions
soft-sphere[b]	1.12	2.13	2.96
sccs[23]	1.14[c]	2.27[d]	5.54[d]
SM8[38]	0.55	2.70	3.70
SM12[39]	0.59	2.90	2.90
PB/Jaguar[38]	0.86	3.10	4.80
IEF-PCM[38]	1.18	3.70	5.50
C-PCM/GAMESS[38]	1.57	7.70	8.90
GCOSMO/NWChem[38]	8.17	11.00	7.00

[a]Model benchmarks refer to same set of 274 neutrals, 60 anions, and 52 cations of the Minnesota Solvation Database, version 2012.[28] [b]Parametrization of row 2 Table 1. [c]The sccs implemented in BigDFT. [d]The sccs for ions corresponds to a reduced set of 55 anions and 51 cations[23] of the same Minnesota data set.

Giuseppe Fisicaro, et al. *J. Chem. Theory Comput.* **13**, 3829 (2017)

THE CODE

- Basic information
- Download and installation
- Input and Output
- Testing and examples



AN OPEN SOURCE PROJECT

- Website: www.quantum-environ.org
- Documentation: https://environ.readthedocs.io
- Public Q&A group: quantum-environ-users@googlegroups.com
- Public GitHub mirror: https://github.com/environ-developers/Environ

- Five releases:
  - Environ 0.1 in February 2015
  - Environ 0.2 in February 2016
  - Environ 1.0 in February 2018
  - Environ 1.1 in April 2019
  - Environ 2.0 in October 2021

ENVIRON 2.0

- A modular library written in Fortran 90/95/2003 (Object-Oriented Code)
- It relies on Quantum Espresso to perform reciprocal-space operations (gradients, Poisson potential, and related stuff)
  - Compiled as a stand-alone library
  - Currently only coupled with QE
- New features w.r.t Environ 1.1:
  - Internally generated G-vectors and FFT grids
  - Decoupled cells for DFT system and embedding Environment
  - Semiconductor embedding
- Extended use of object-oriented principles

DOWNLOAD AND INSTALLATION

- For news and releases, check out
  - www.quantum-environ.org
- For installation instructions, theoretical overview, and more, check out
  - https://environ.readthedocs.io/en/latest/
- Instructions are also available in the README file
- Once installed:
  1. Run the test-suite to check for consistency
  2. Run the examples to get familiarized with the tools
  3. Input keywords are also in Doc/INPUT_Environ.html

INPUT FILE

- Environ requires one additional input file
- It must be named **environ.in** and located in the directory where pw.x is running
- environ.in is composed of three namelists (two optional) and two optional cards

ENVIRON NAMELISTS

&ENVIRON (REQUIRED)

The global properties of the calculation

- The strength of the different environment effects
- Basic control keywords (verbosity)

&BOUNDARY (OPTIONAL)

The definition of the continuum boundaries

&ELECTROSTATIC (OPTIONAL)

The parameters for the electrostatic solvers

ENVIRON CARDS

EXTERNAL_CHARGES (OPTIONAL)

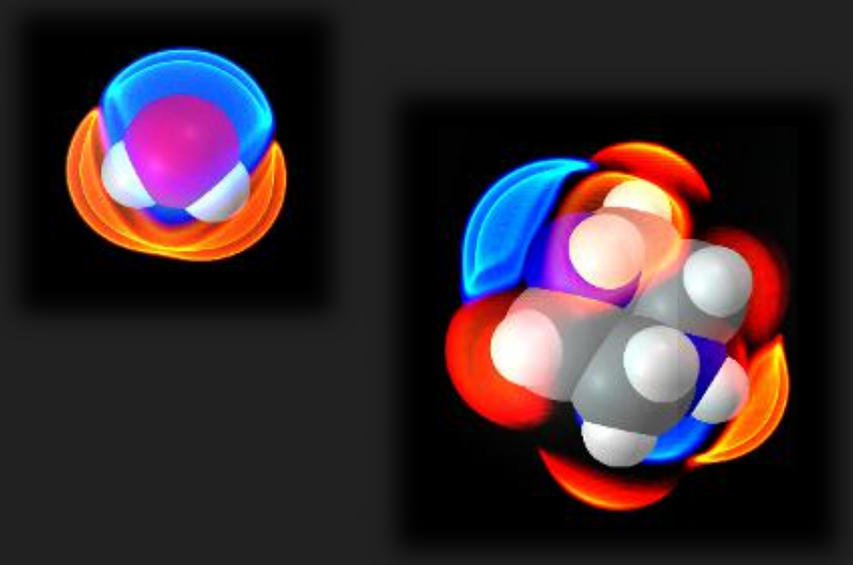
- Defines additional charge densities included in the electronic structure calculation (must be activated by env_external_charges = N>0)

DIELECTRIC_REGIONS (OPTIONAL)

- Defines non-homogenous dielectric regions inside the simulation cell
- (must be activated by env_dielectric_regions = N>0)

THREE LEVELS OF OUTPUT

1. verbose=0 (default)
   - only print minimal information to standard output (inside the QE output file)
2. verbose>0
   - generate an additional readable text file named environ.debug
   - contains information of the Environ calculations
3. verbose>1
   - generate additional cube files
   - contains values of specific physical quantities on the simulation grid



Cube files may be useful for debugging or rendering purposes; they can be viewed with molecular visualization software, such as VMD

RUNNING TESTS

- Environ comes with a test-suite to allow for consistency checks
- To run the tests in serial, switch over to Environ/tests and run
- make run-tests

...or in parallel

- make run-tests-parallel

NOTE: a few tests may give some small errors and reported as failed

RUNNING EXAMPLES

- Summarized in Environ/examples/README
- To run, switch over to Environ/examples

1. Change directory into one of the examples
   - cd example01/
2. Run the script
   - ./run_example.sh
3. Make sure the script to run the example is executable. If not, run
   - chmod a+x run_example.sh
4. Compare results against the available references

COUPLING WITH QE

- Environ is coupled with the following QE sub-packages:
  - PW & NEB
  - CP
  - TDDFPT
  - XSPECTRA
- To run environ with these codes, run (e.g. PW)
  - $QEPATH/bin/pw.x –environ < filename.in > filename.out
  - On the VM you can just run pw.x –environ …

USERS & ENVIRON

- If you use the code and it works…
  - please cite the main references
  - full list available online and in the calculation output
- If you use the code and it doesn’t work…
  - Bug – NO WORRIES!… we’ll fix it
  - Numerical problems - GREAT!… Try tweaking the parameters
  - Physical problem – NOT SO GREAT! May require development of new features
- In any case, please:
  - Check out the FAQ online or the Q&A group
  - Contact us (oliviero.andreussi@unt.edu)