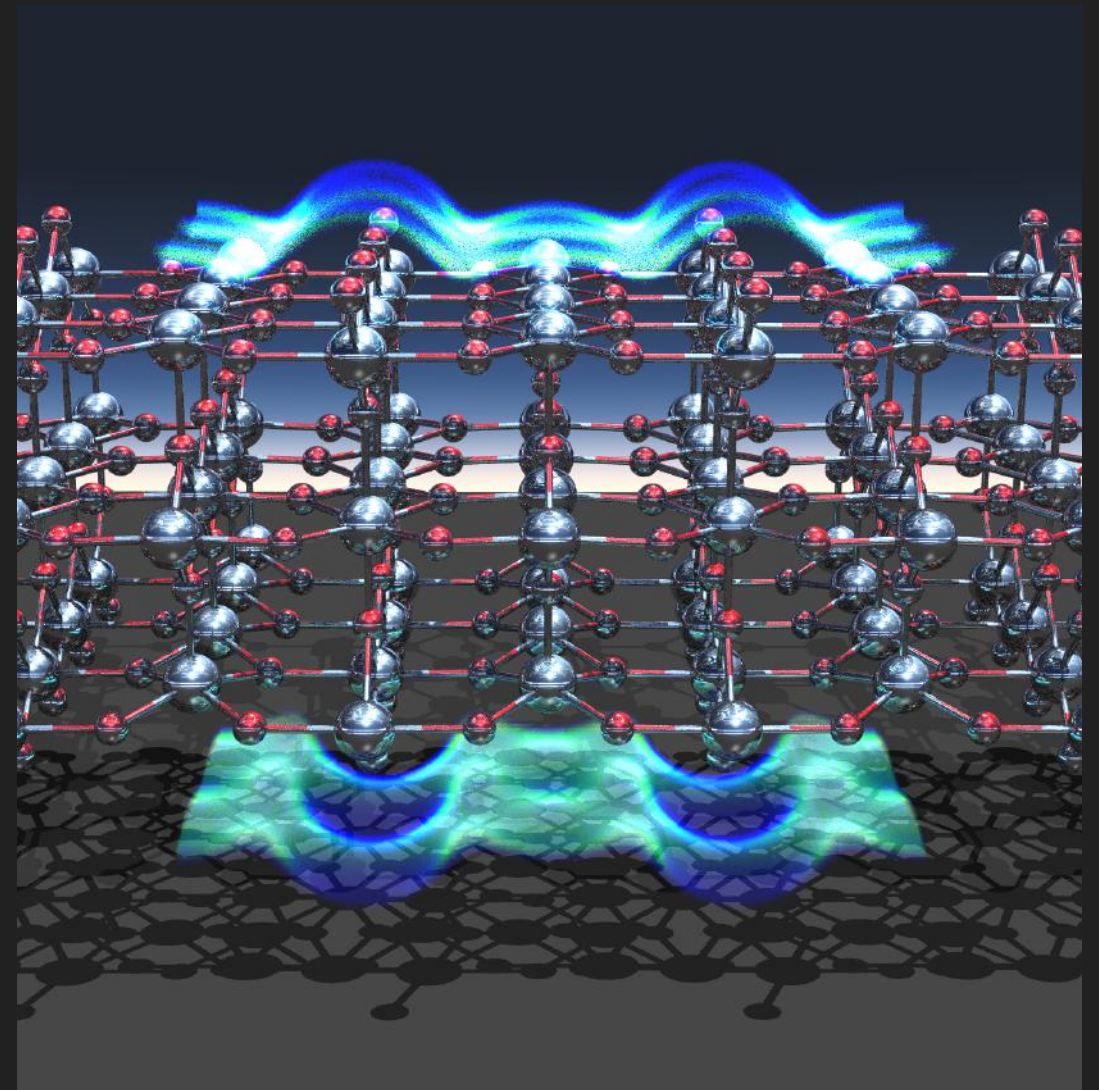




OLIVIERO ANDREUSSI
UNIVERSITY OF NORTH TEXAS

ENVIRON: CONTINUUM EMBEDDINGS IN QUANTUM-ESPRESSO

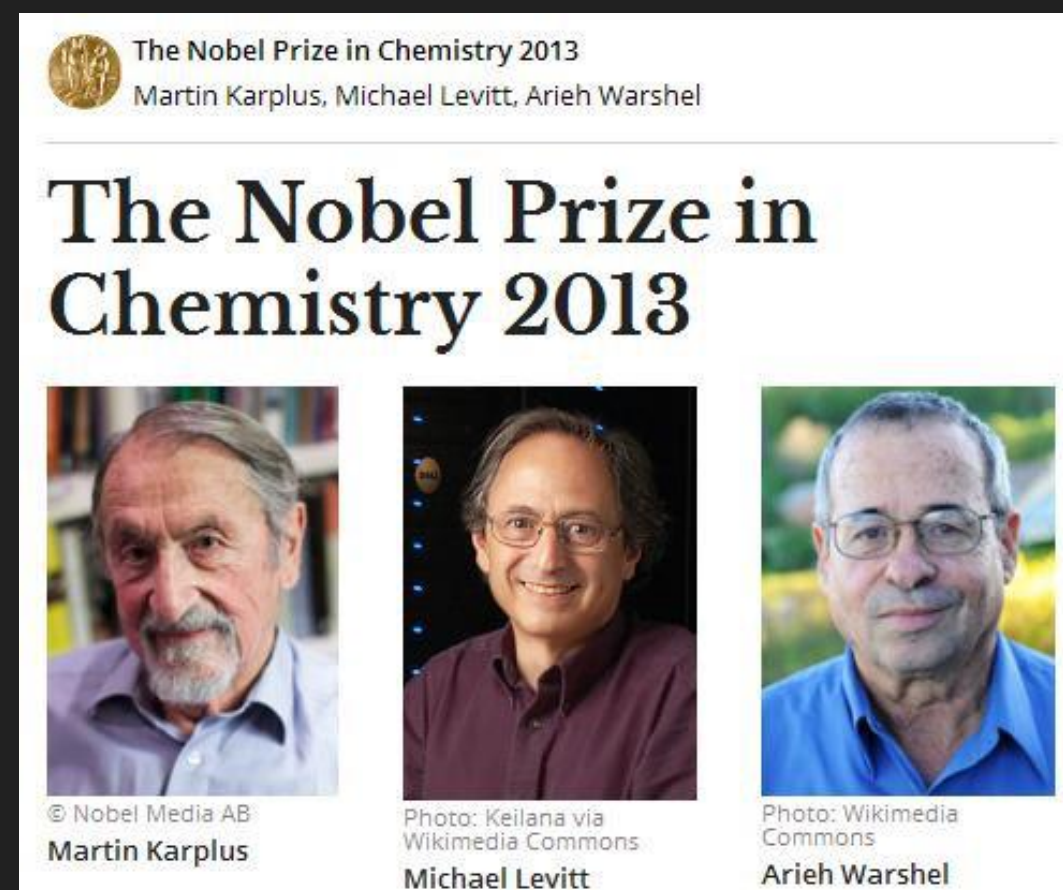
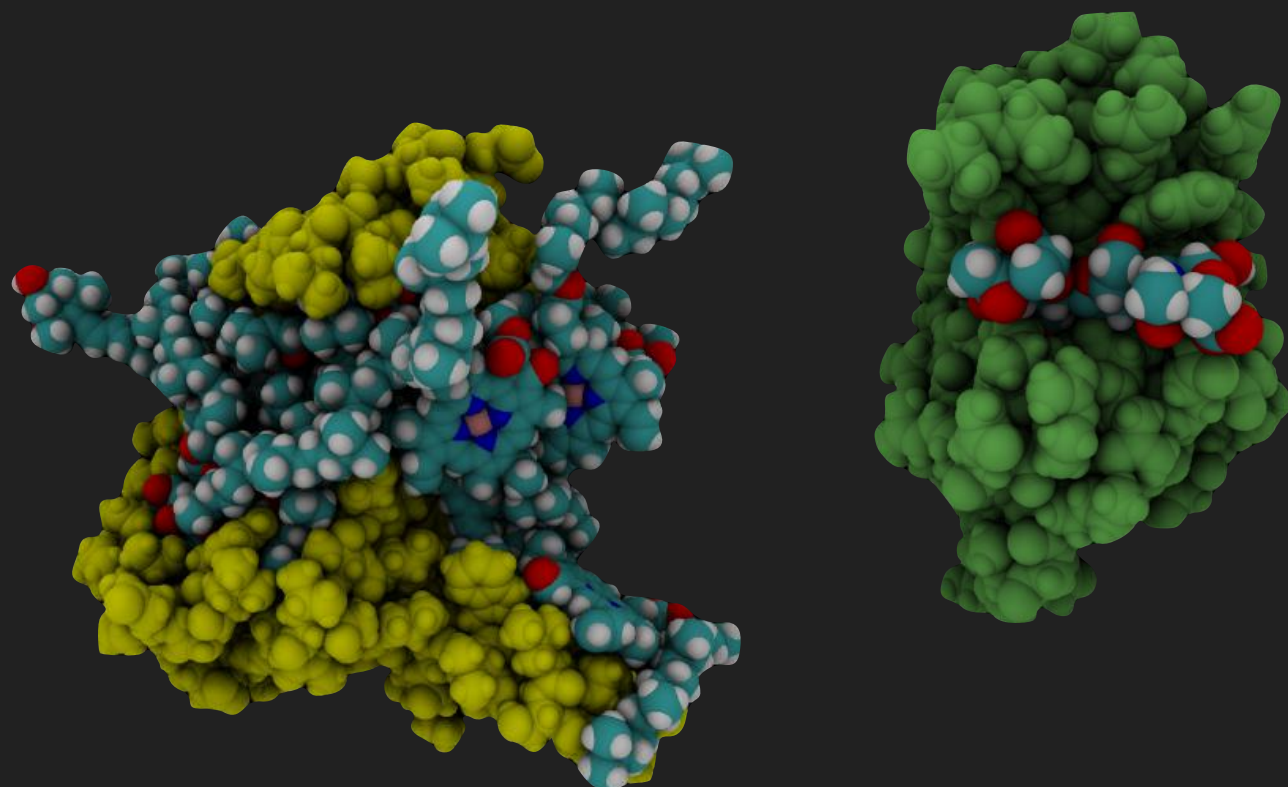


OUTLINE

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

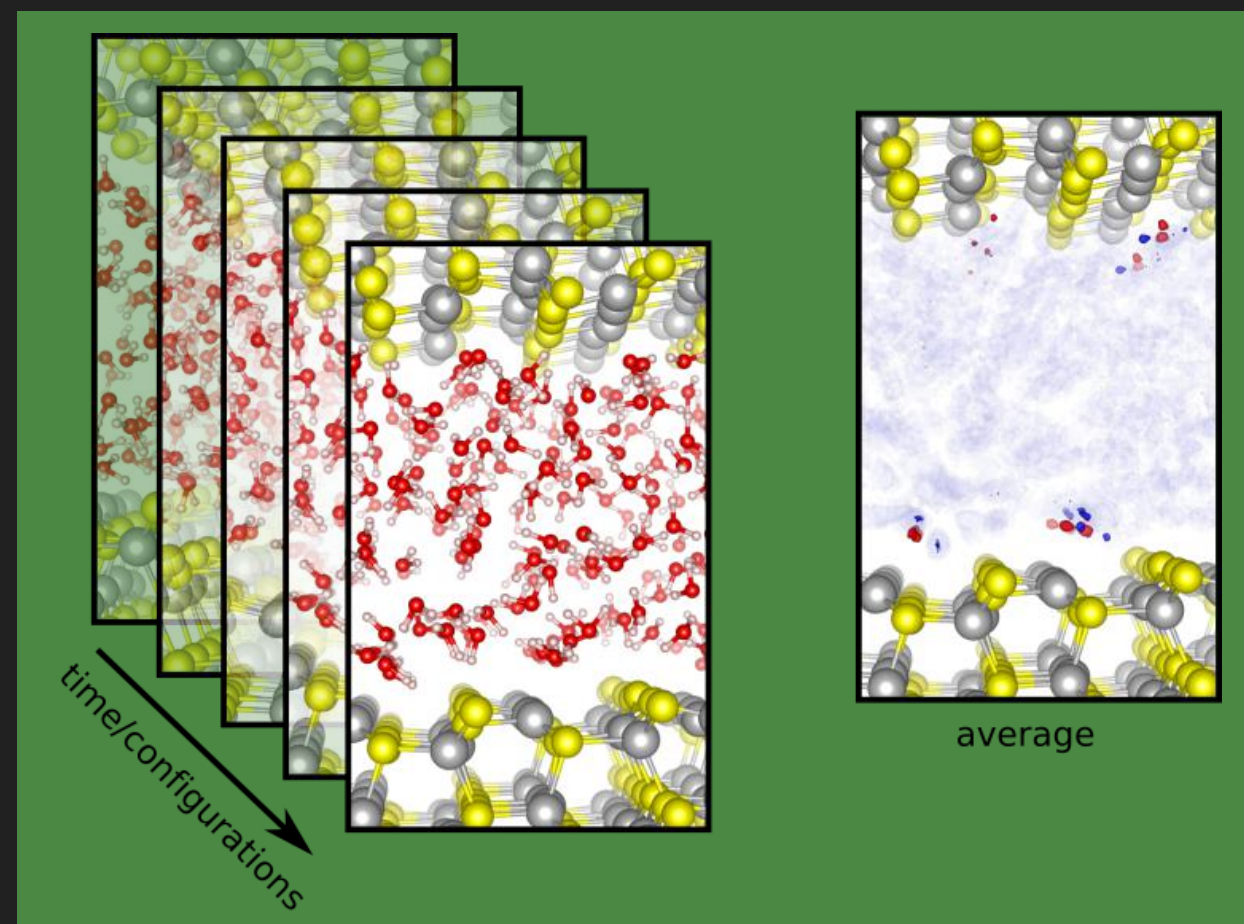
DEALING WITH COMPLEXITY

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



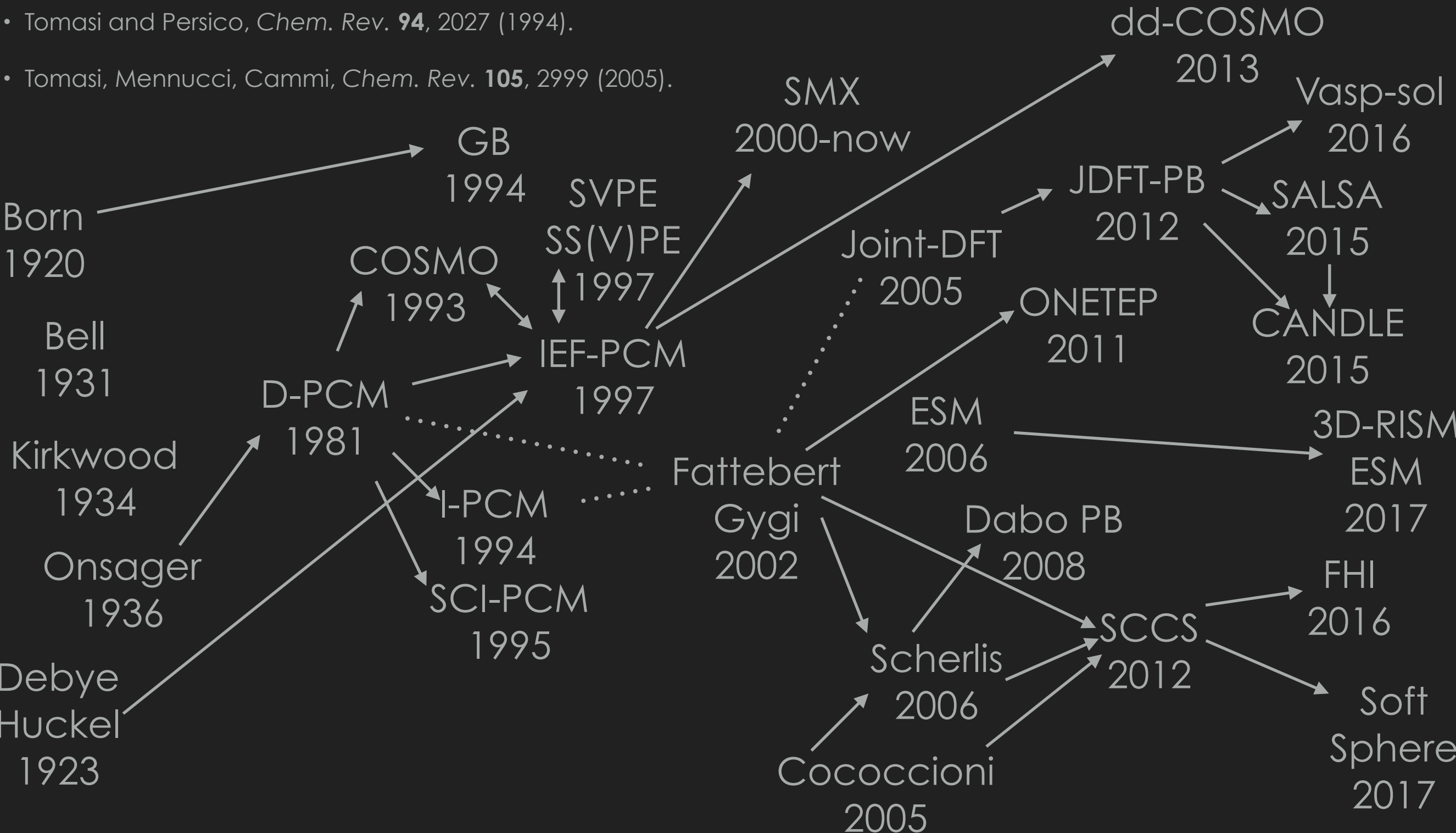
DEALING WITH COMPLEXITY

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

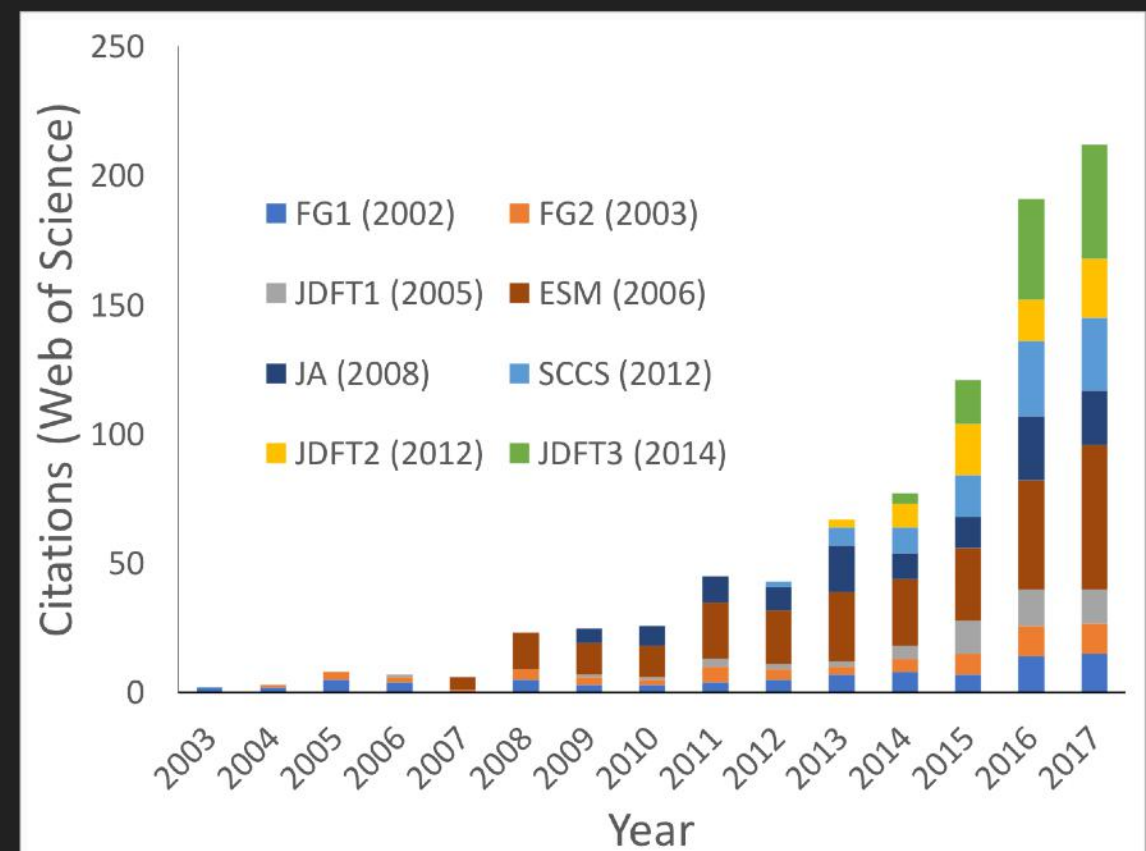


CONTINUUM GENEALOGY

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



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



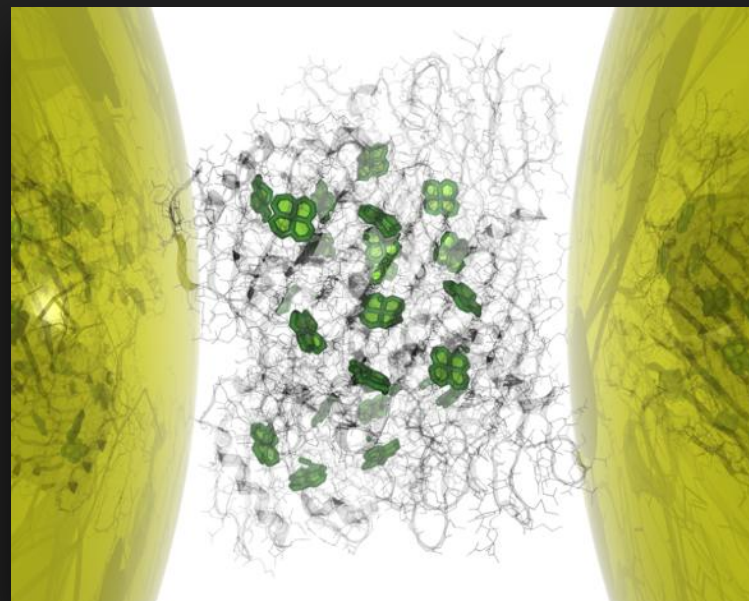
INGREDIENTS

- ▶ Continuum
- ▶ Interface
- ▶ Interactions
 - ▶ Numerical Solver

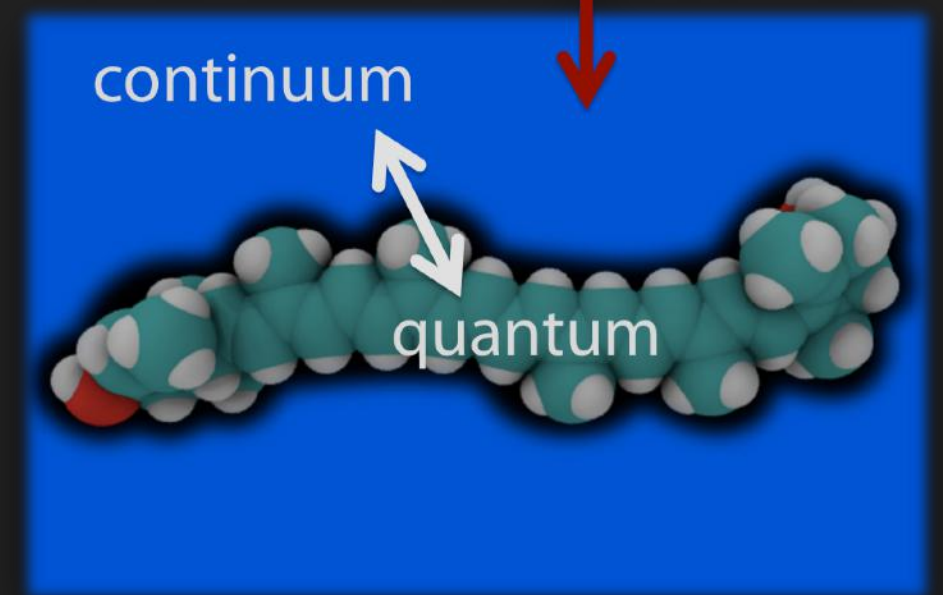
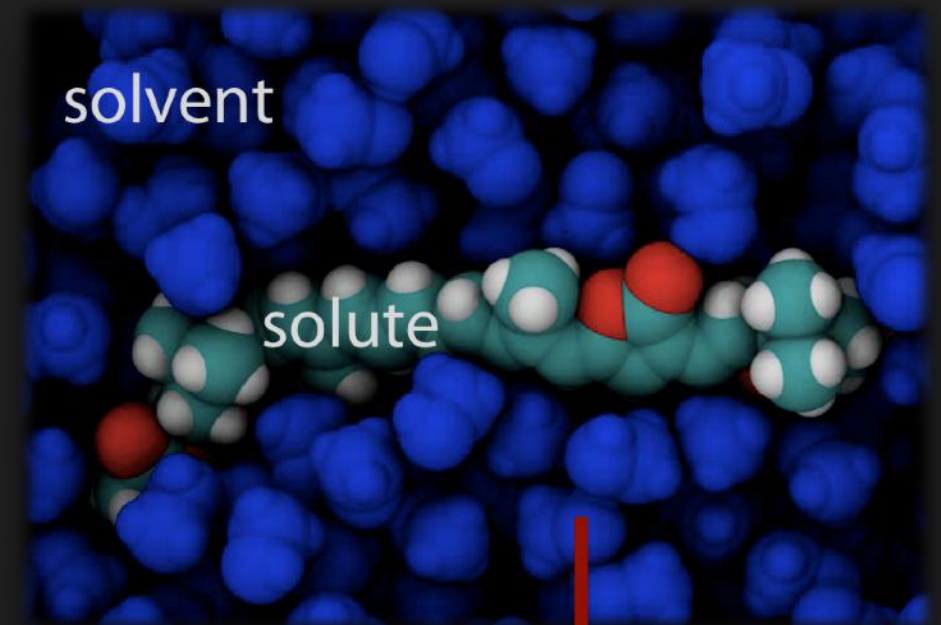


CONTINUUM

- ▶ Liquid
- ▶ Pressure medium
- ▶ Electrolyte
- ▶ Nanoparticle
- ▶ ...



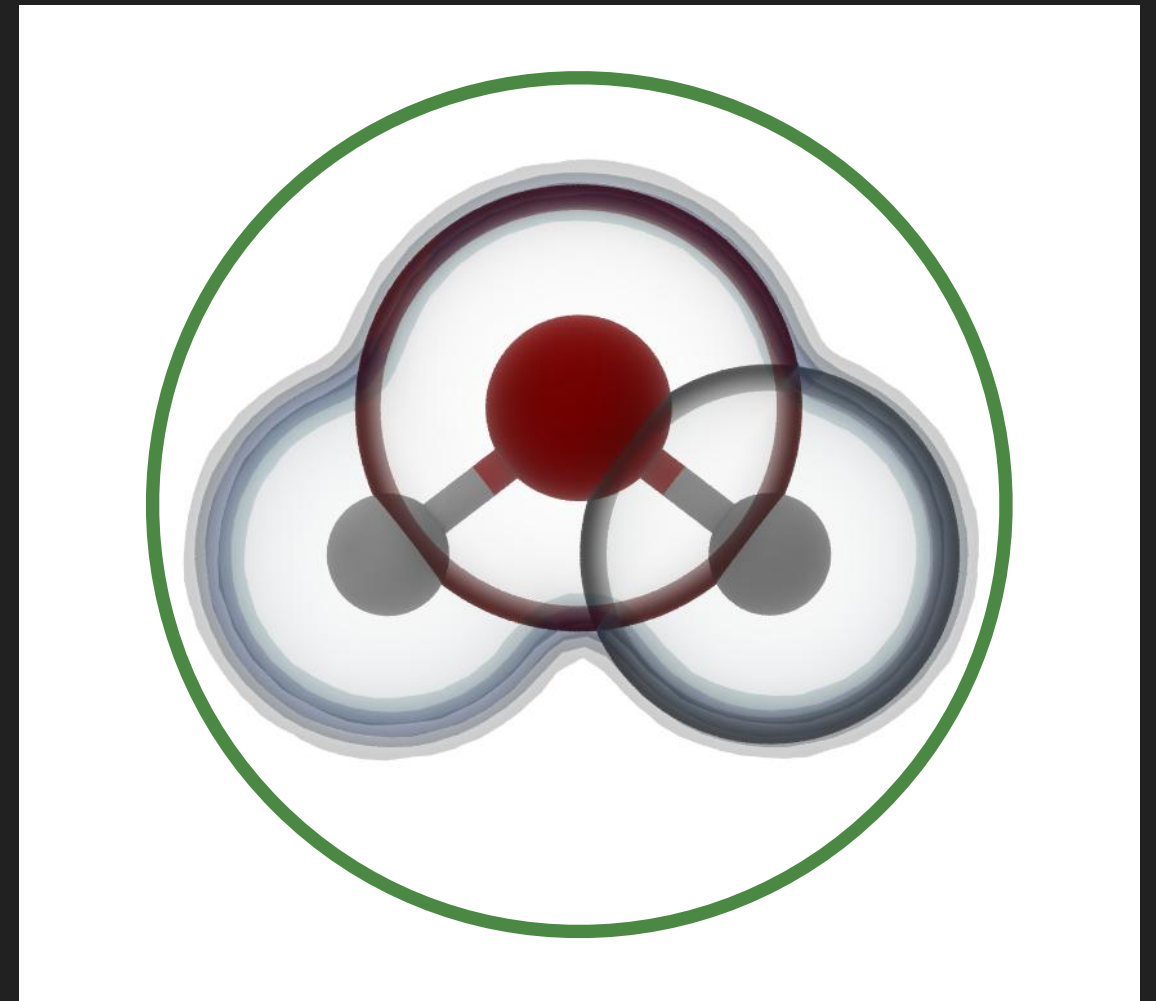
O. Andreussi, A. Biancardi, S. Corni and
B. Mennucci, *Nano Lett.* **13**, 4475 (2013)



INTERFACE

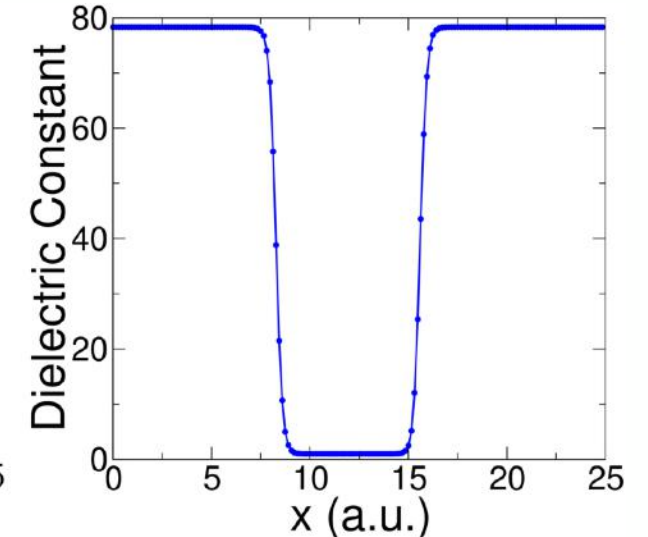
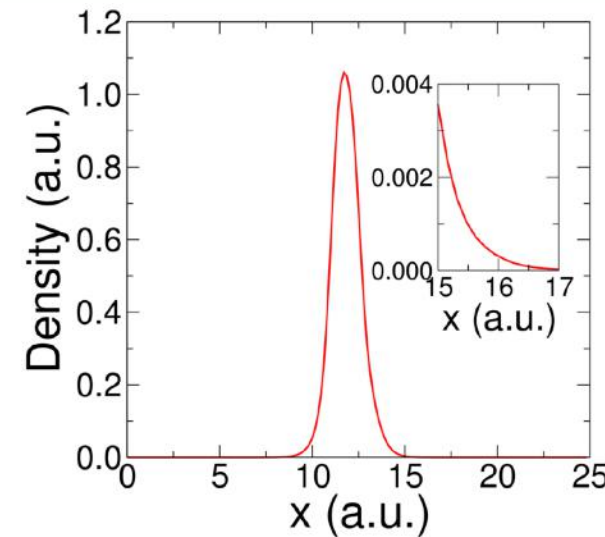
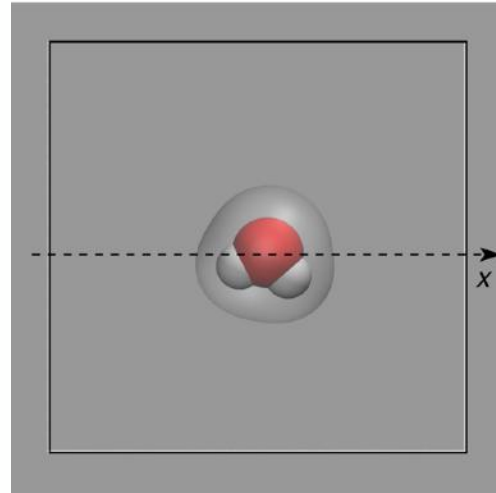
- ▶ Simple or complex
- ▶ Sharp or smooth
- ▶ Fixed or based on electrons or ions or both
- ▶ Local or non-local
- ▶ Single or multiple
- ▶ ...

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



ELECTRONIC INTERFACE

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



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

2 parameters

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

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)

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

2 parameters

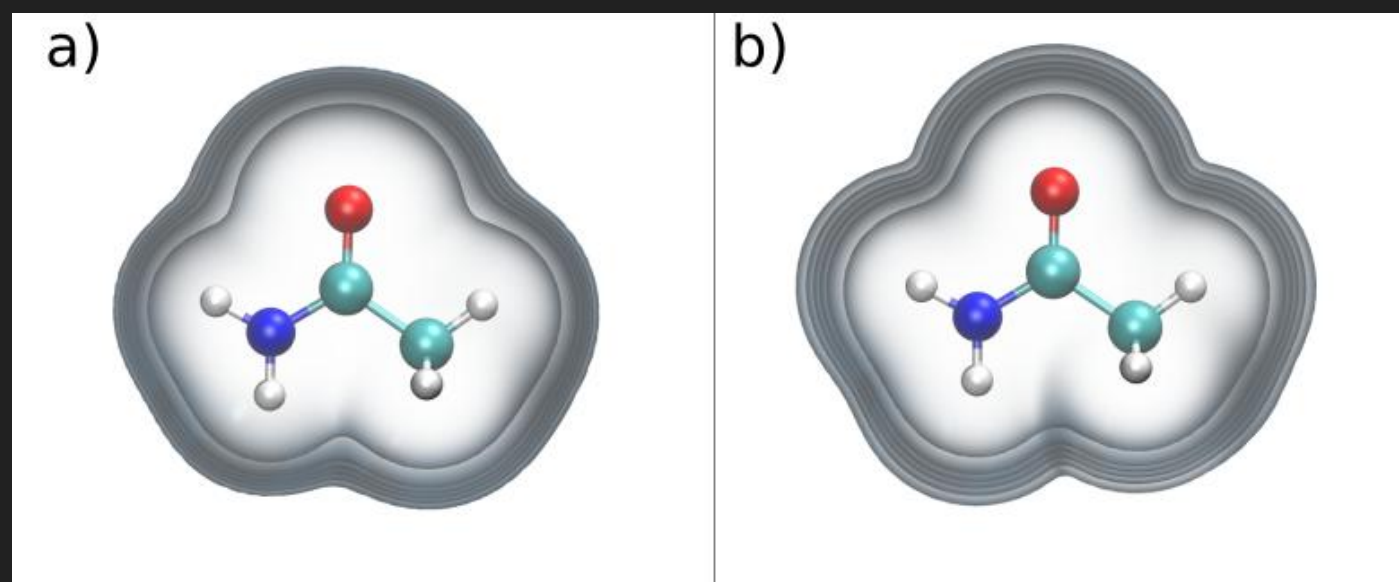
IONIC INTERFACE

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

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

$$s(\mathbf{r}) = 1 - \prod_i h_i(|\mathbf{r} - \mathbf{R}_i|),$$
$$h_i(|\mathbf{r}|) = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{|\mathbf{r}| - \alpha R_i^{vdW}}{\Delta} \right) \right]$$

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

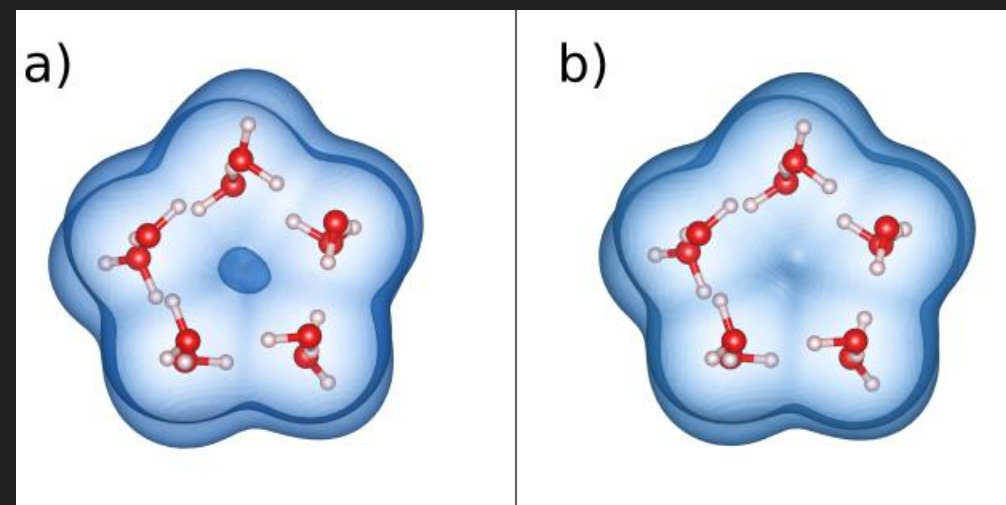


Electronic

Ionic

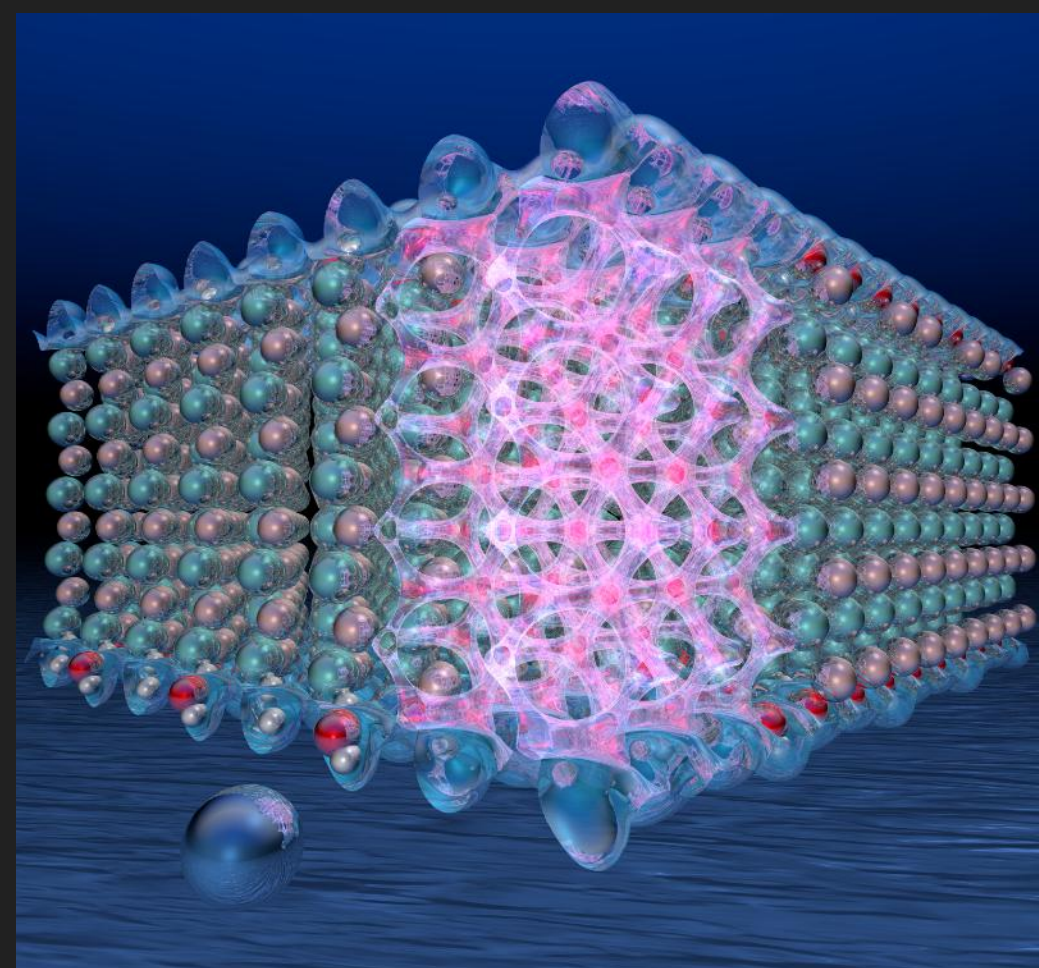
SOLVENT-AWARE INTERFACE

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



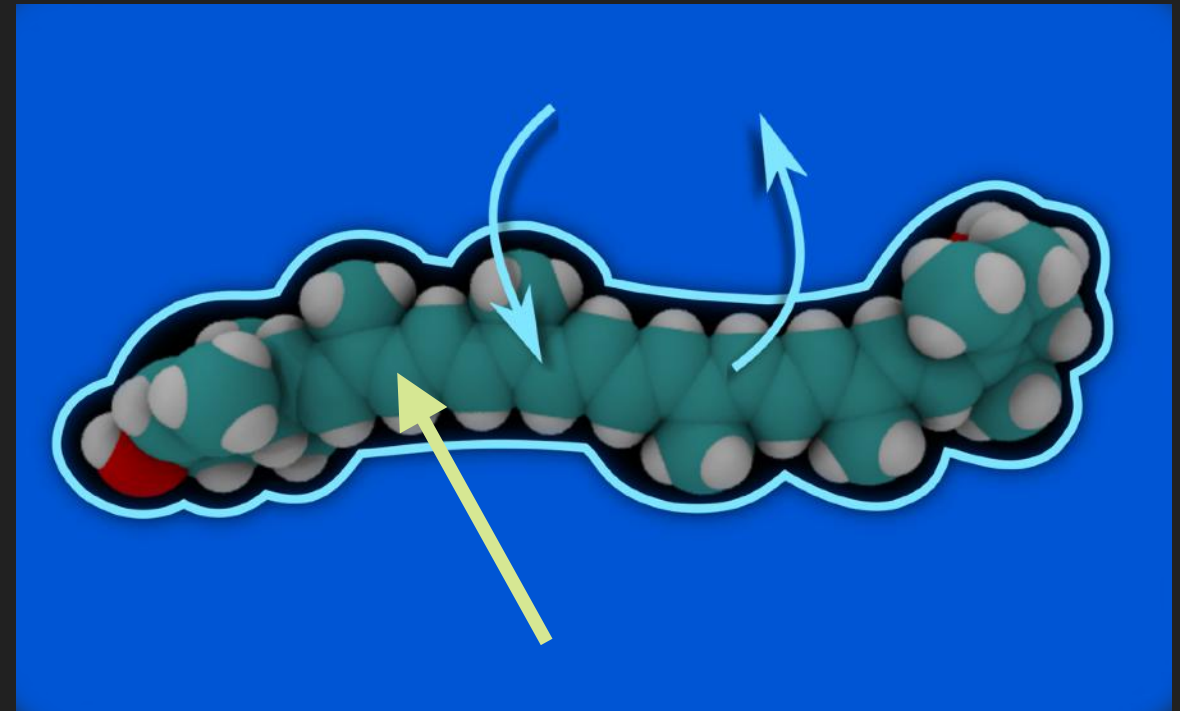
$$\hat{s}(\mathbf{r}) = s(\mathbf{r}) + (1 - s(\mathbf{r})) \overset{\text{smooth function}}{t(f^{ff}(\mathbf{r}))}$$
$$\underset{\text{filled fraction}}{f^{ff}[s(\mathbf{r}')]}(\mathbf{r}) \equiv \int \underset{\substack{\text{smooth} \\ \text{spherical function}}}{s(\mathbf{r}') h(|\mathbf{r} - \mathbf{r}'|)} d\mathbf{r}' = s * h(\mathbf{r})$$

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



INTERACTIONS

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



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

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

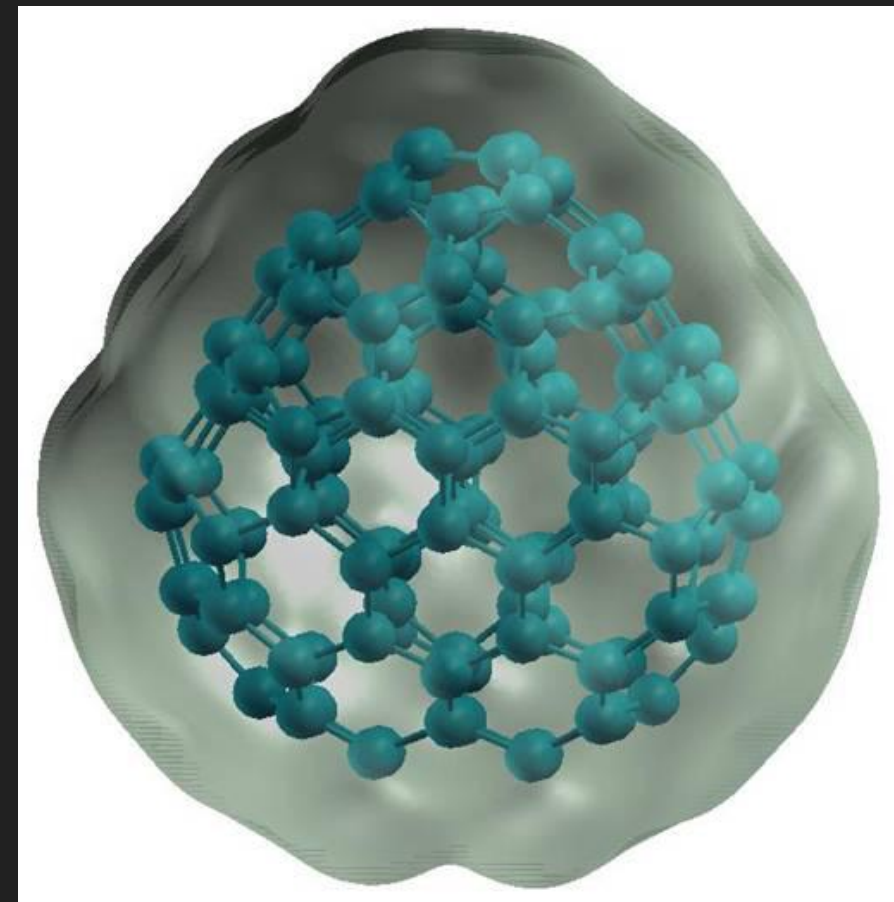
VOLUME

- Pressurizing medium (Enthalpy functional)

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

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

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



SURFACE

► Cavitation, repulsion

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

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

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



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

DIELECTRIC SCREENING

► Polarizable dielectric medium

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

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

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

Generalized Poisson Equation (GPE)

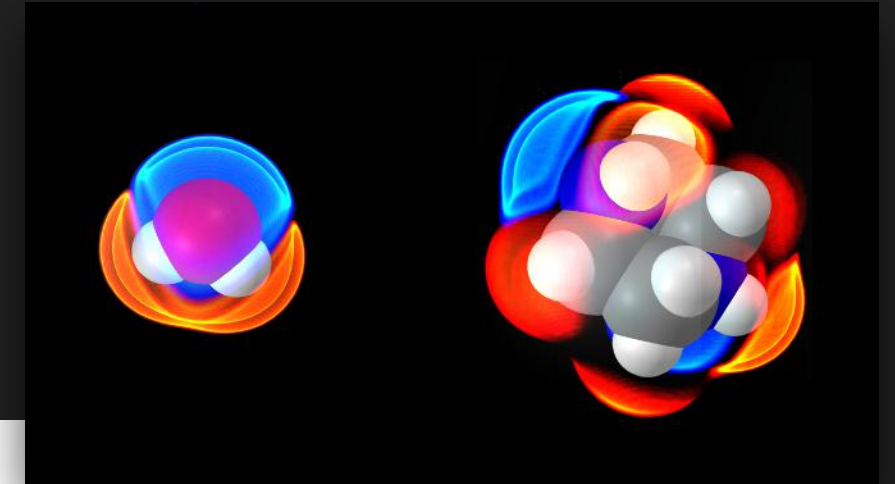
$$\epsilon(\mathbf{r}) \equiv \epsilon(s(\mathbf{r})) = 1 + (\epsilon_0 - 1)(1 - s(\mathbf{r}))$$

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

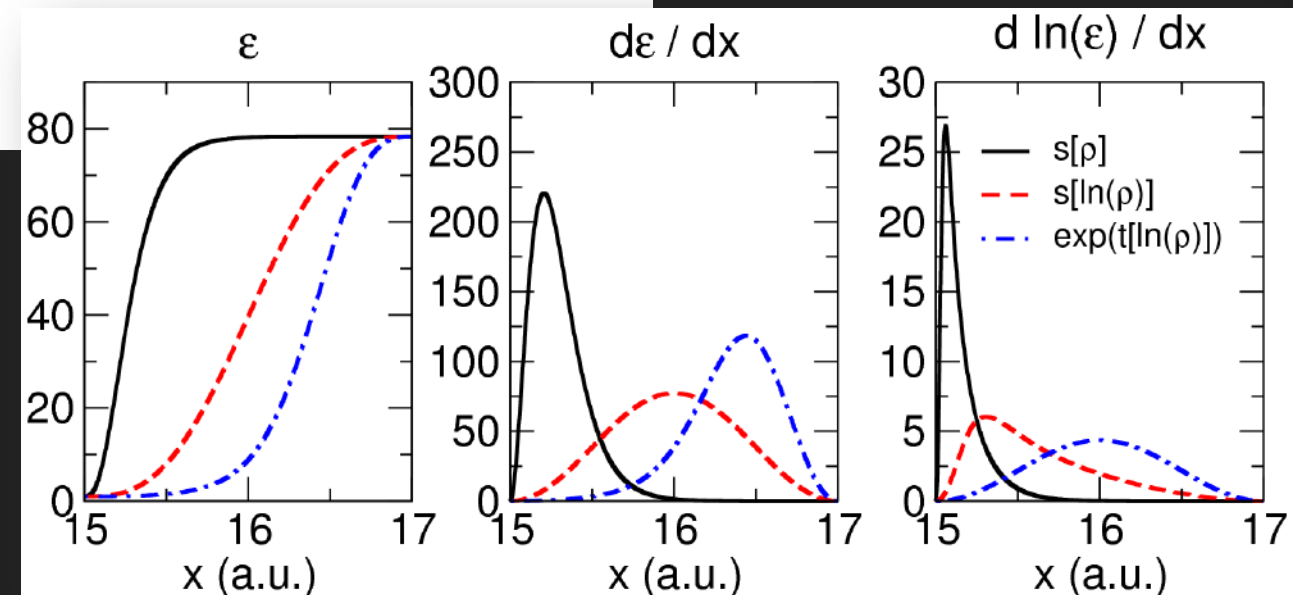


$$\nabla^2 \phi(\mathbf{r}) = -4\pi (\rho^{sys}(\mathbf{r}) + \rho^{pol}(\mathbf{r}))$$

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

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

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



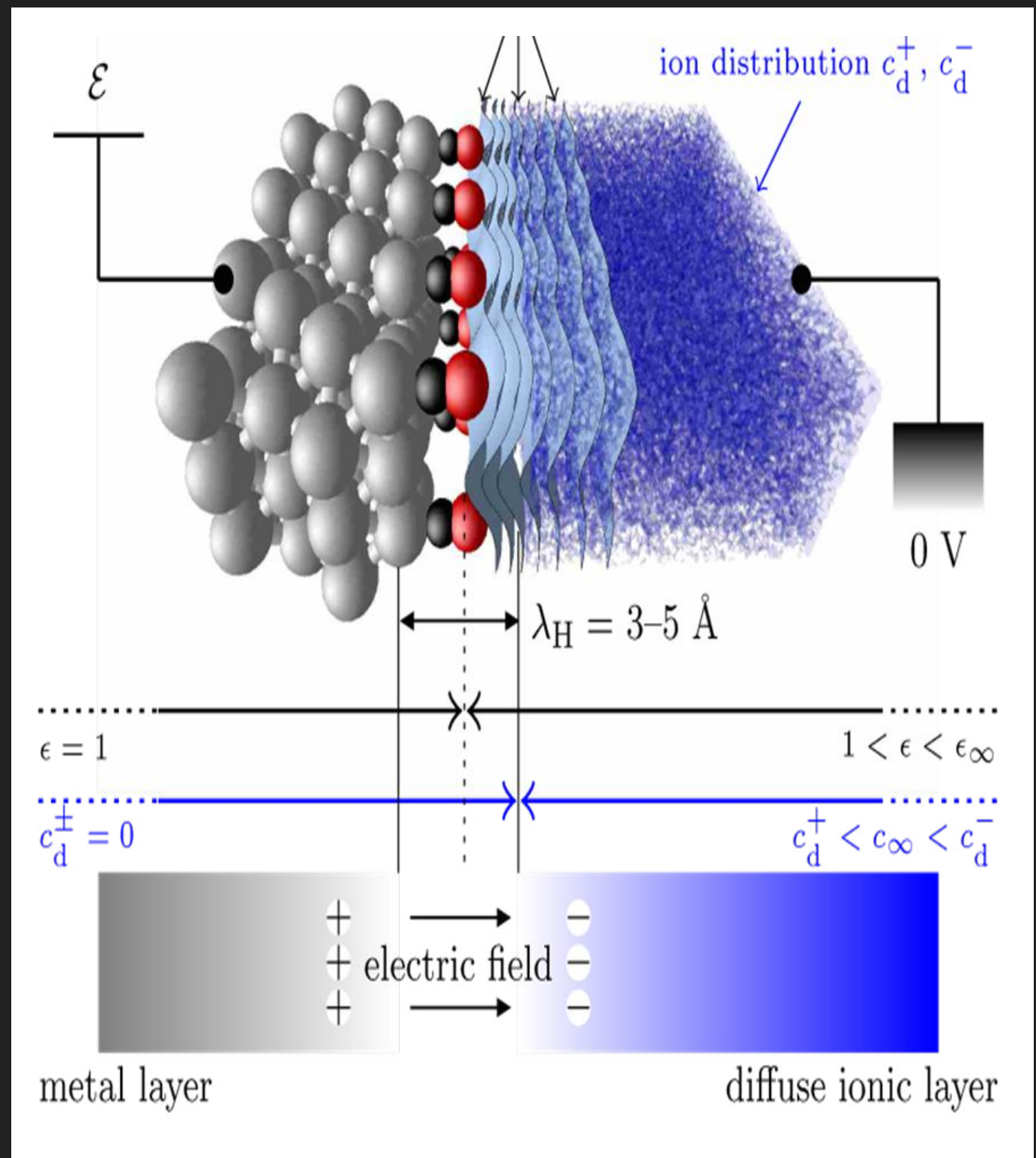
ELECTROLYTE

- ▶ 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

$$\rho^{\pm}(\mathbf{r}) = z^{\pm} c^{\pm}(\mathbf{r})$$

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

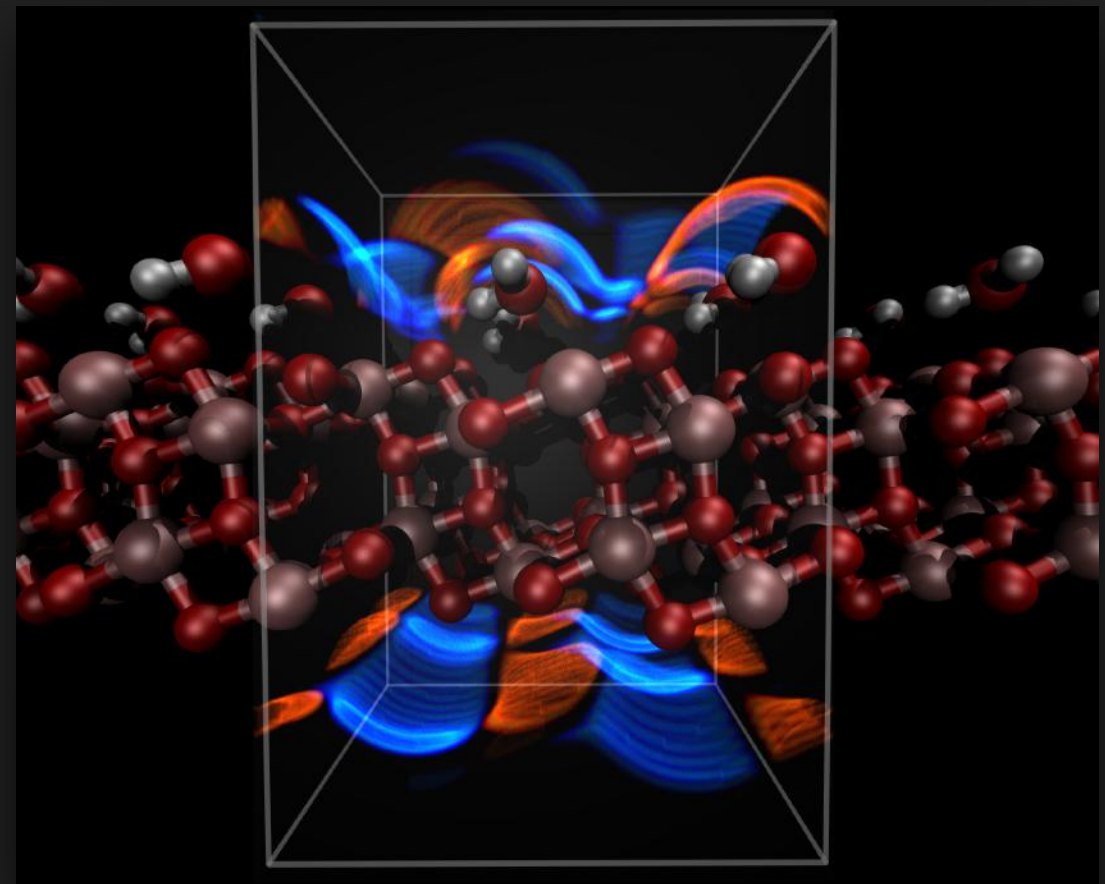
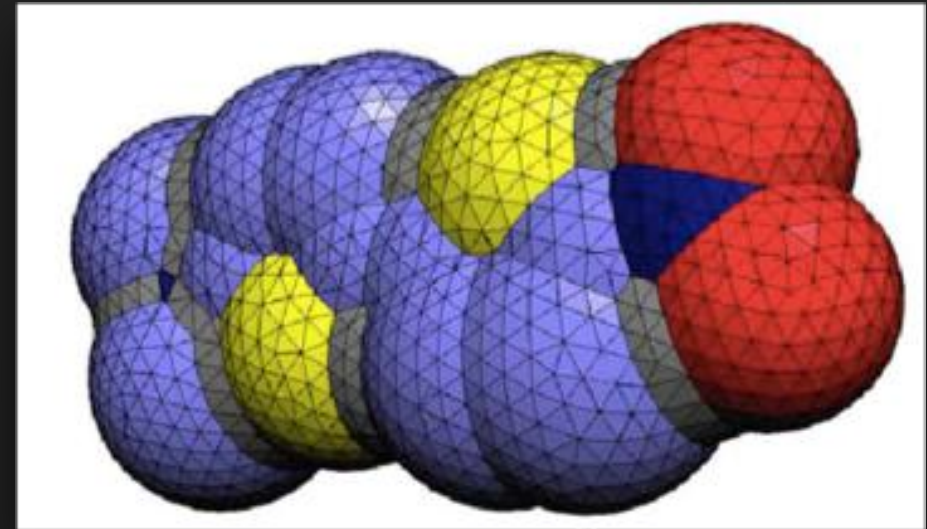
$$s[c^+, c^-] = -k_B [c^+(\mathbf{r}) \ln(c^+(\mathbf{r})) + c^-(\mathbf{r}) \ln(c^-(\mathbf{r}))]$$

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

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

NUMERICAL SOLVER

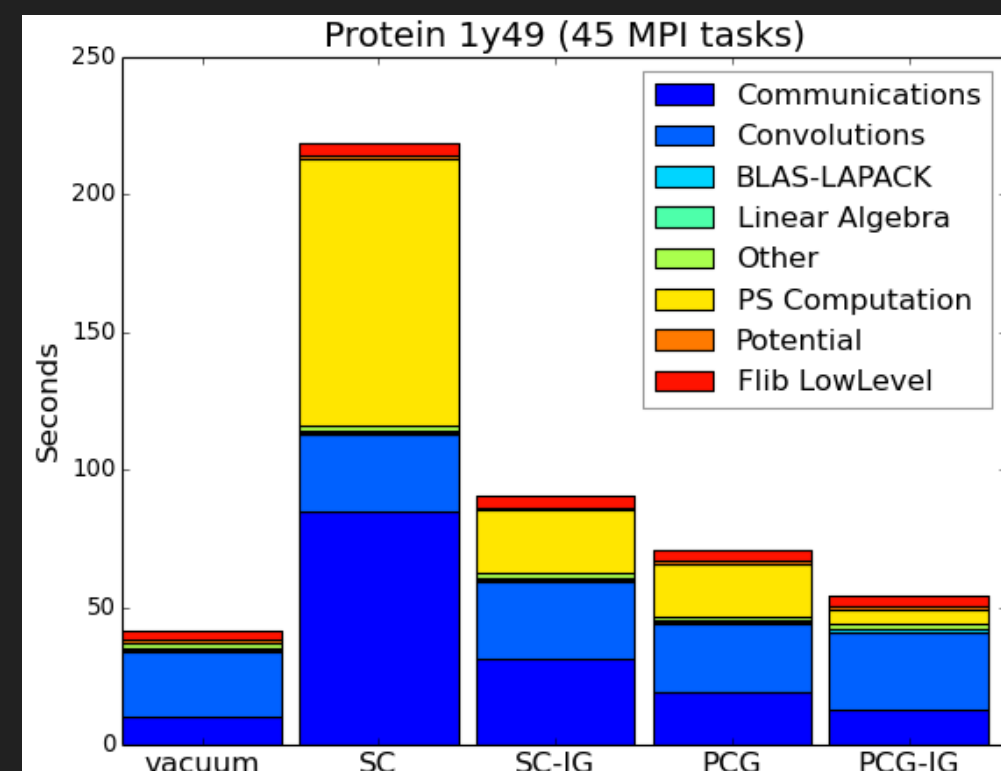
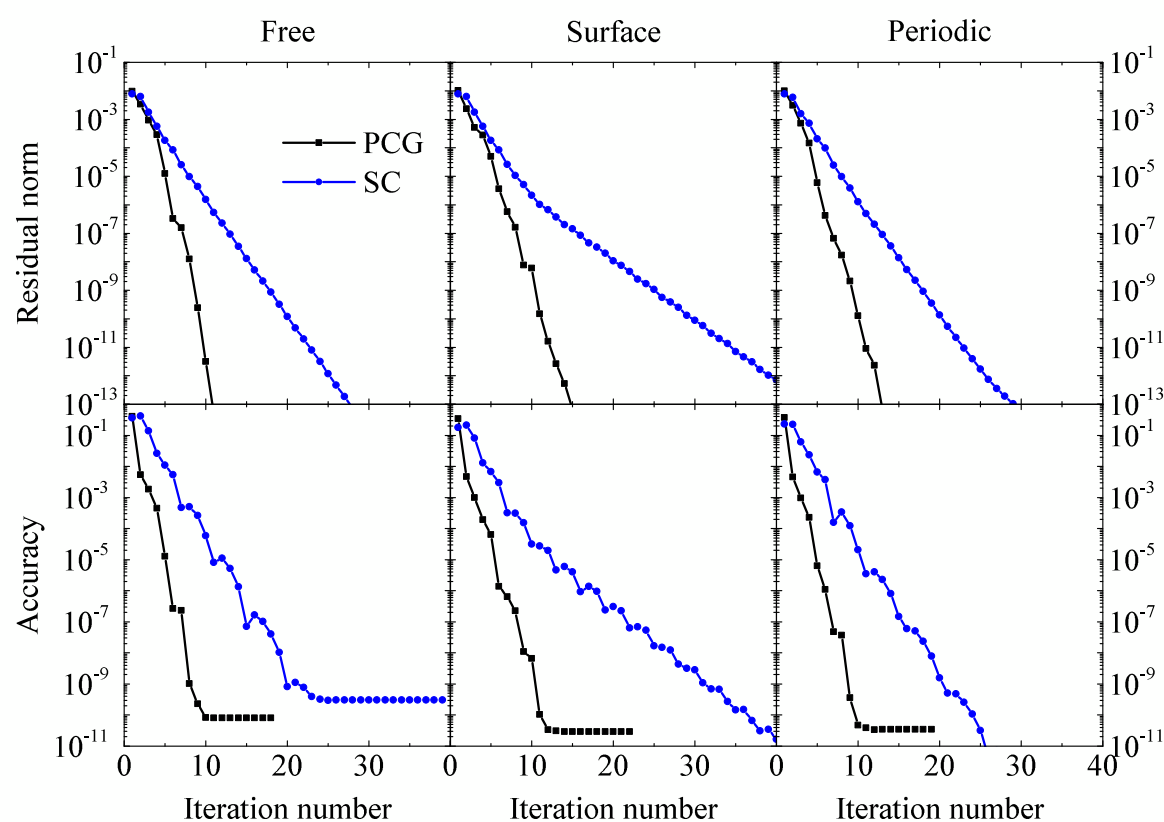
- ▶ Bi-directional interactions are usually associated with non-analytic partial differential equations (GPE, PBE, MPBE, LPBE, etc.)
- ▶ Boundary Element Methods
- ▶ Domain decomposition
- ▶ Multigrid
- ▶ Gradient descent coupled with vacuum Poisson solver (FFT, wavelets, etc.)
- ▶ ...



IMPROVED PRECONDITIONED SCHEME

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

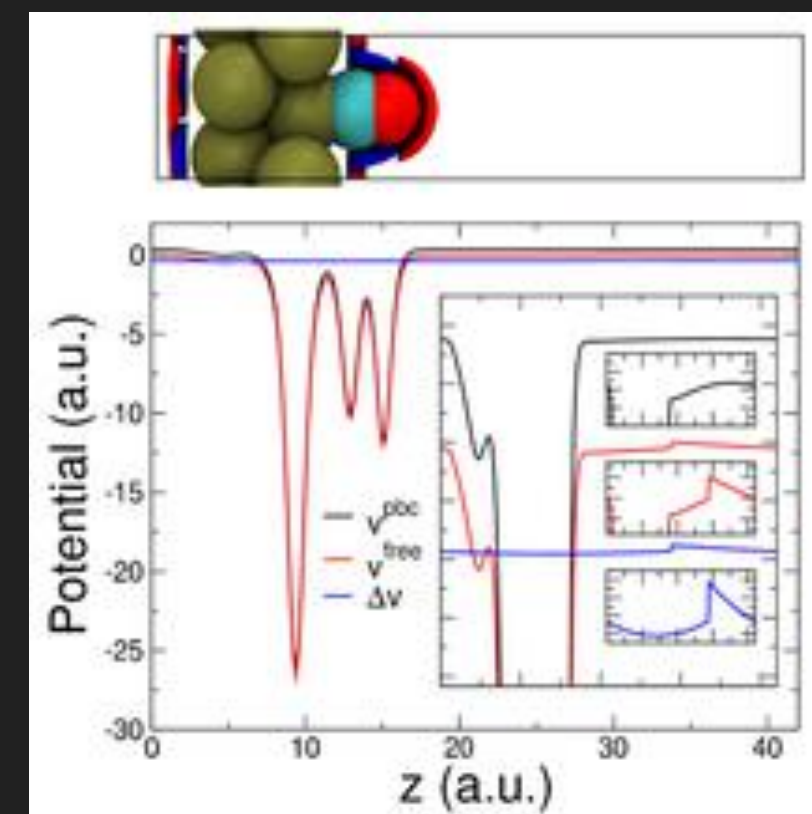
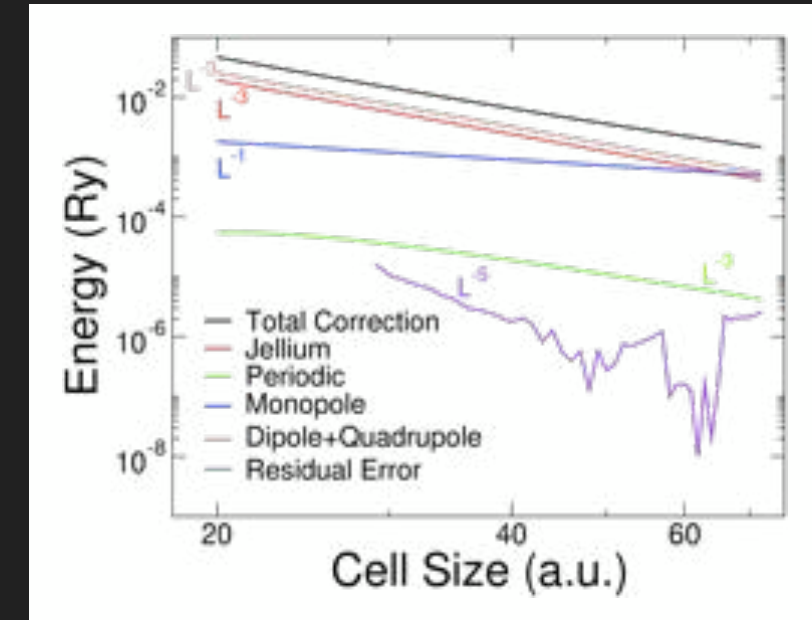
$$\begin{aligned} \mathcal{A} v_k(\mathbf{r}) &= \nabla \cdot \epsilon(\mathbf{r}) \nabla v_k(\mathbf{r}) \\ &= -v_k(\mathbf{r}) q(\mathbf{r}) - 4\pi r_k(\mathbf{r}), \end{aligned}$$



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



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)



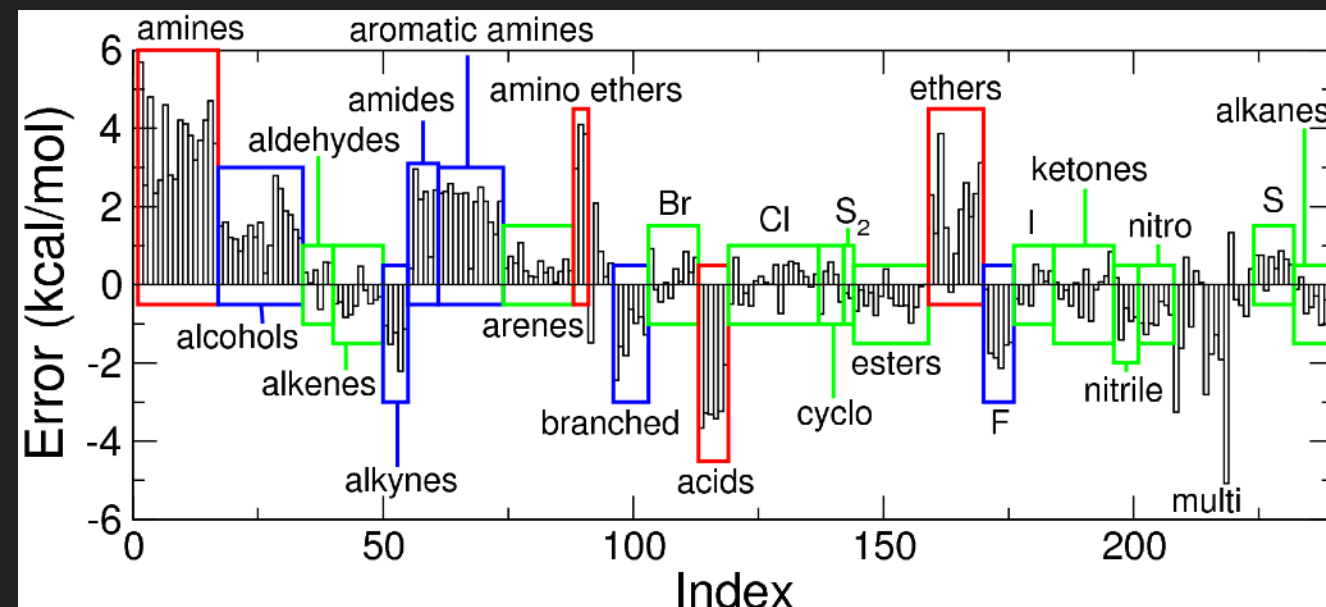
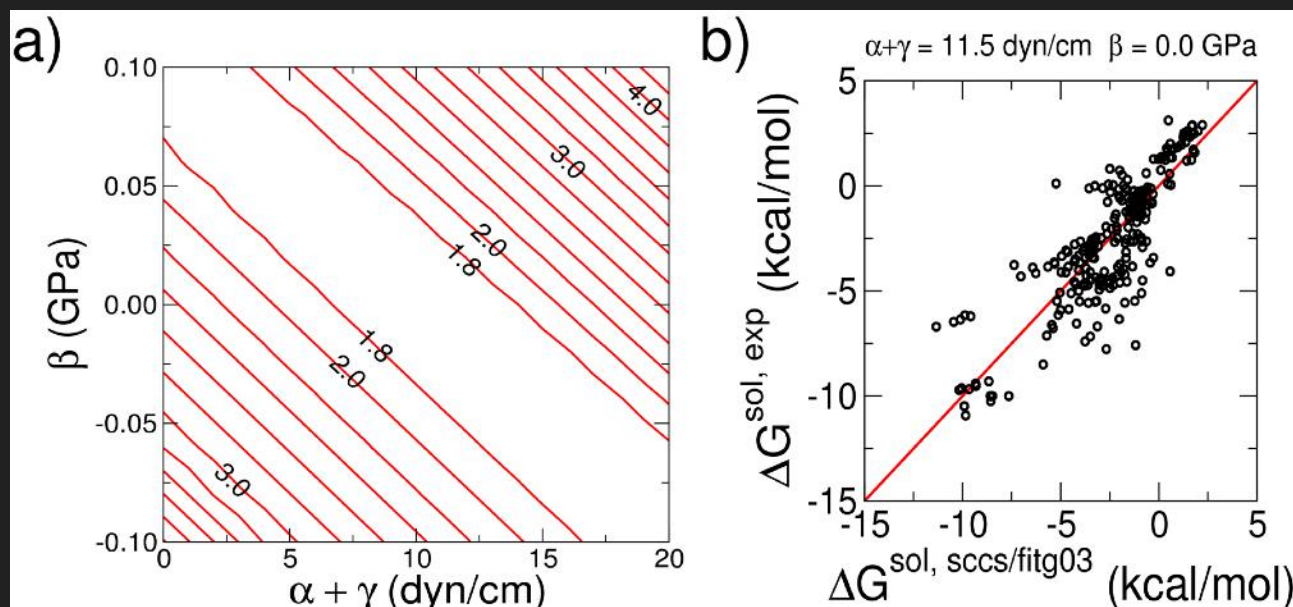
SELF-CONSISTENT CONTINUUM SOLVATION (SCCS)

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

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

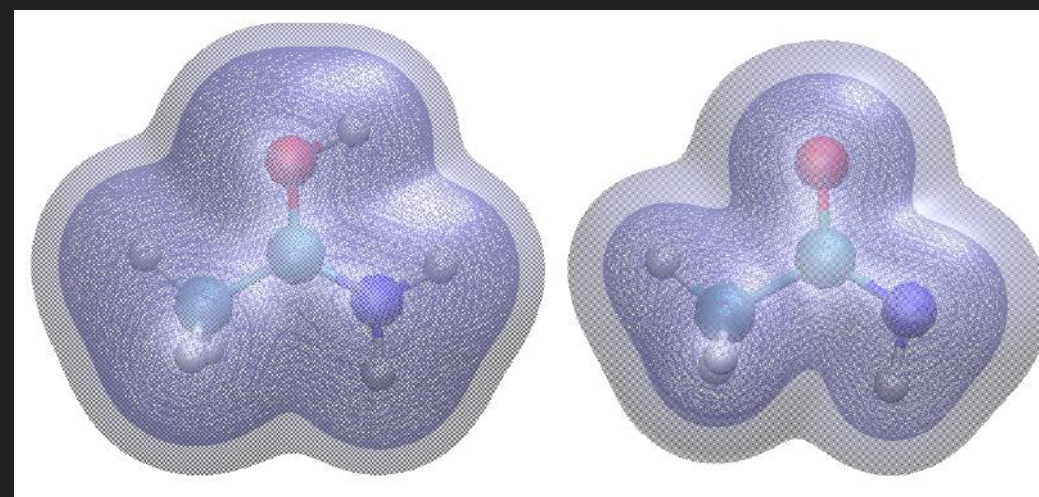
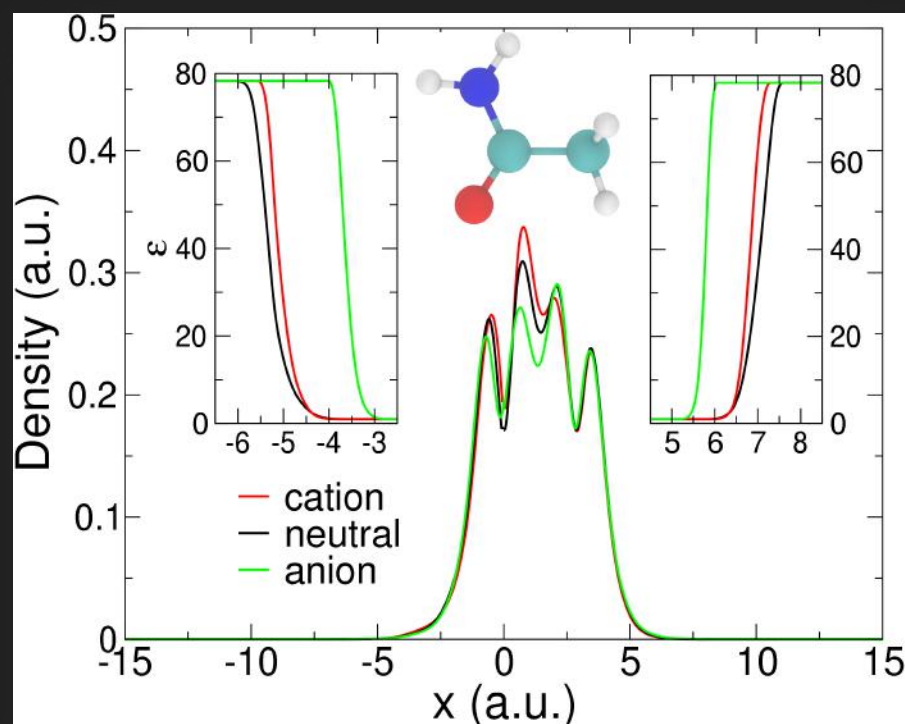
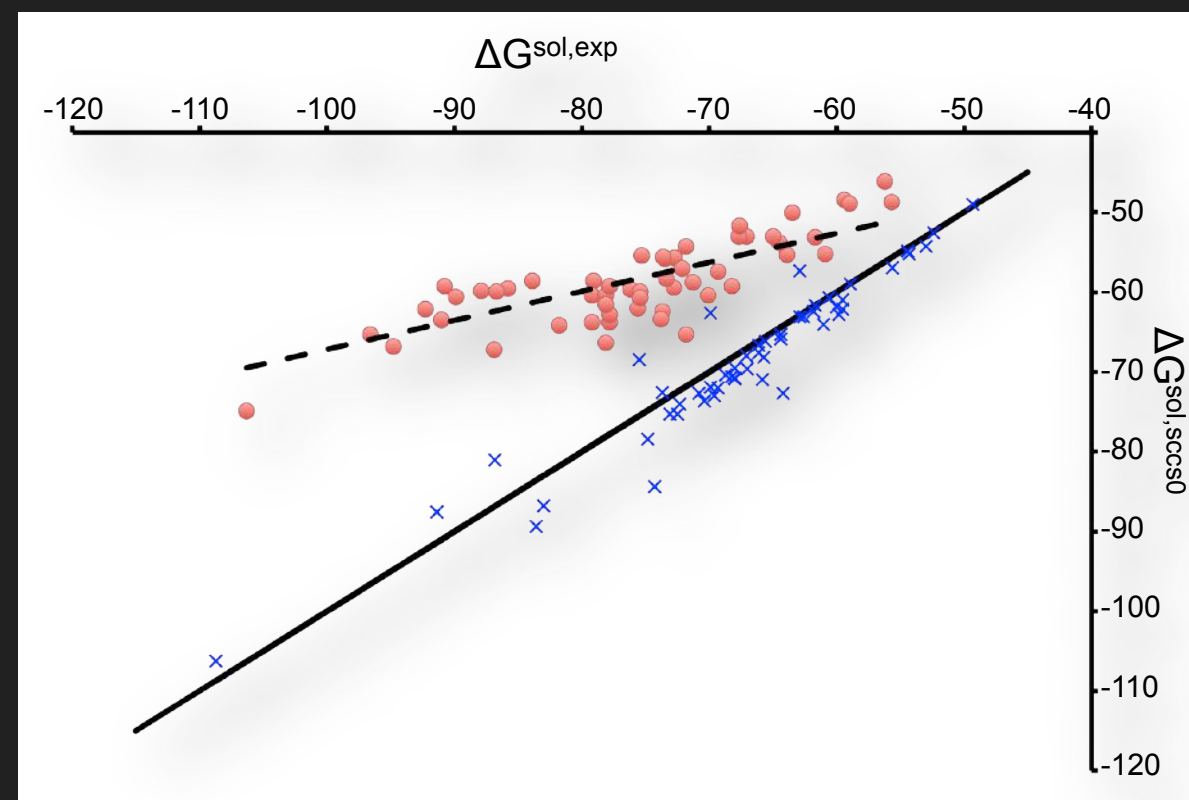
$$\epsilon(\mathbf{r}) = e^{\log \epsilon_0 [1 - s(\mathbf{r})]}$$

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



SCCS FOR CHARGED SPECIES

- Anions need a separate parameterization



SOFT-SPHERE CONTINUUM SOLVATION

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

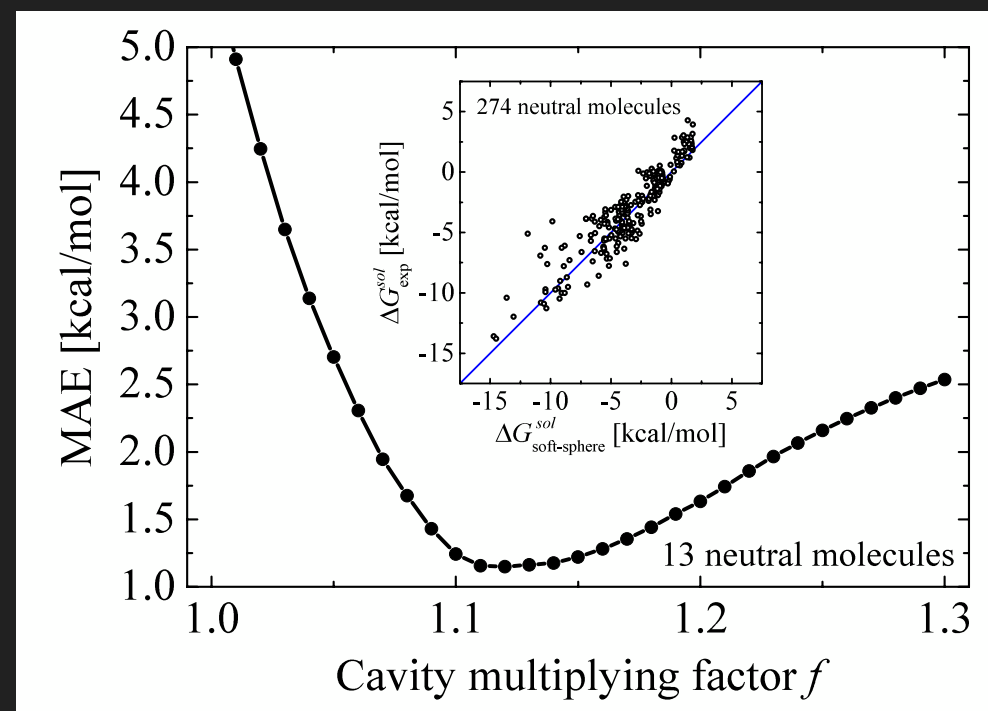


Table 2. MAEs in Aqueous Solvation Free Energies (kcal/mol) for Several Solvation Models (MAEs from ref 38)^a

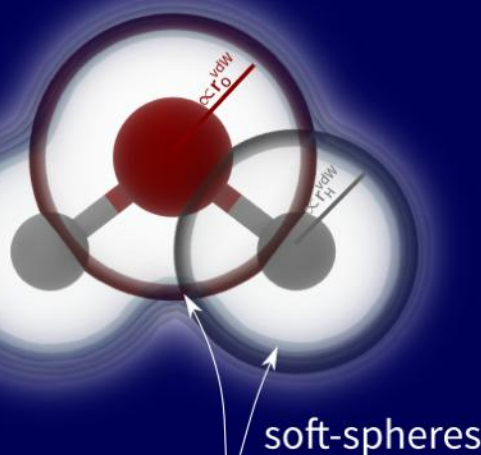
method	neutrals	cations	anions
soft-sphere ^b	1.12	2.13	2.96
sccs ²³	1.14 ^c	2.27 ^d	5.54 ^d
SM8 ³⁸	0.55	2.70	3.70
SM12 ³⁹	0.59	2.90	2.90
PB/Jaguar ³⁸	0.86	3.10	4.80
IEF-PCM ³⁸	1.18	3.70	5.50
C-PCM/GAMESS ³⁸	1.57	7.70	8.90
GCOSMO/NWChem ³⁸	8.17	11.00	7.00

^aModel benchmarks refer to same set of 274 neutrals, 60 anions, and 52 cations of the Minnesota Solvation Database, version 2012.²⁸

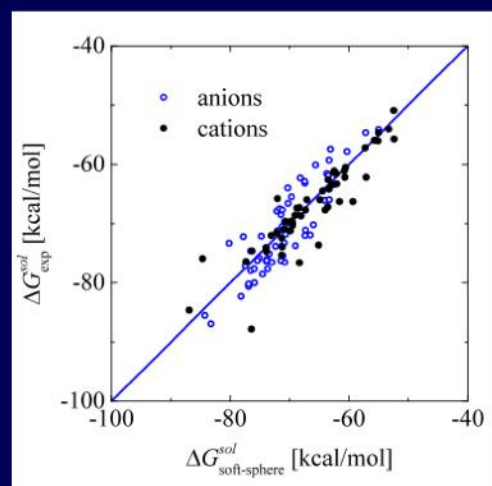
^bParametrization of row 2 Table 1. ^cThe sccs implemented in BigDFT.

^dThe sccs for ions corresponds to a reduced set of 55 anions and 51 cations²³ of the same Minnesota data set.

continuum
solvent

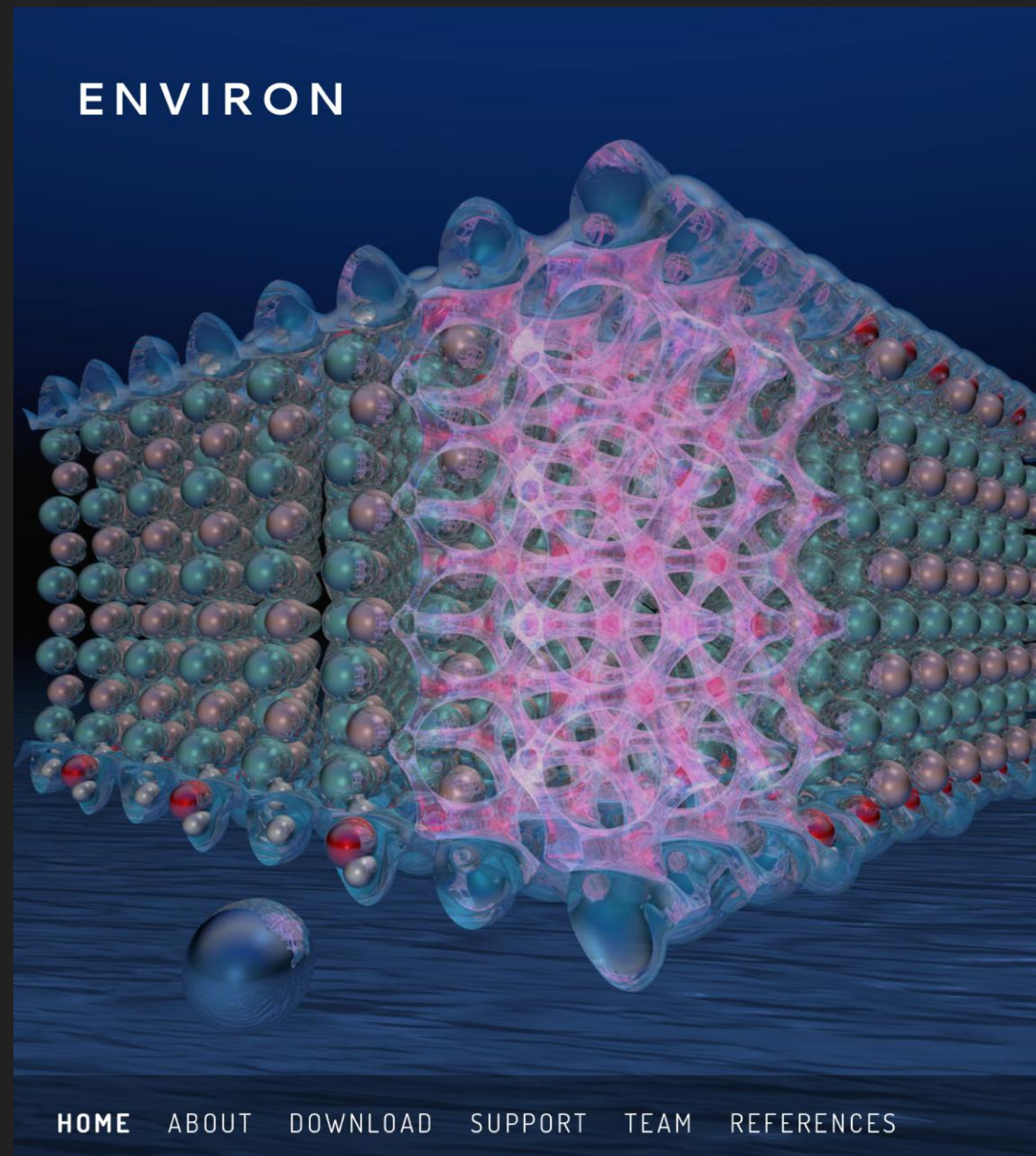


$$\epsilon(\mathbf{r}, \{\mathbf{R}_i\}) = (\epsilon_0 - 1) \left\{ \prod_i h(\{\xi\}; \|\mathbf{r} - \mathbf{R}_i\|) \right\} + 1$$



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)

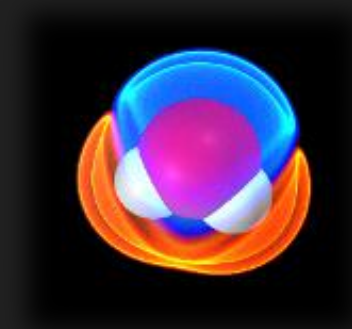
- ▶ only print minimal information to standard output (inside the QE output file)

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)