Solvation and environment effects: Continuum models via the Environ plugin

Quantum-ESPRESSO School

Trieste 24/01/2017

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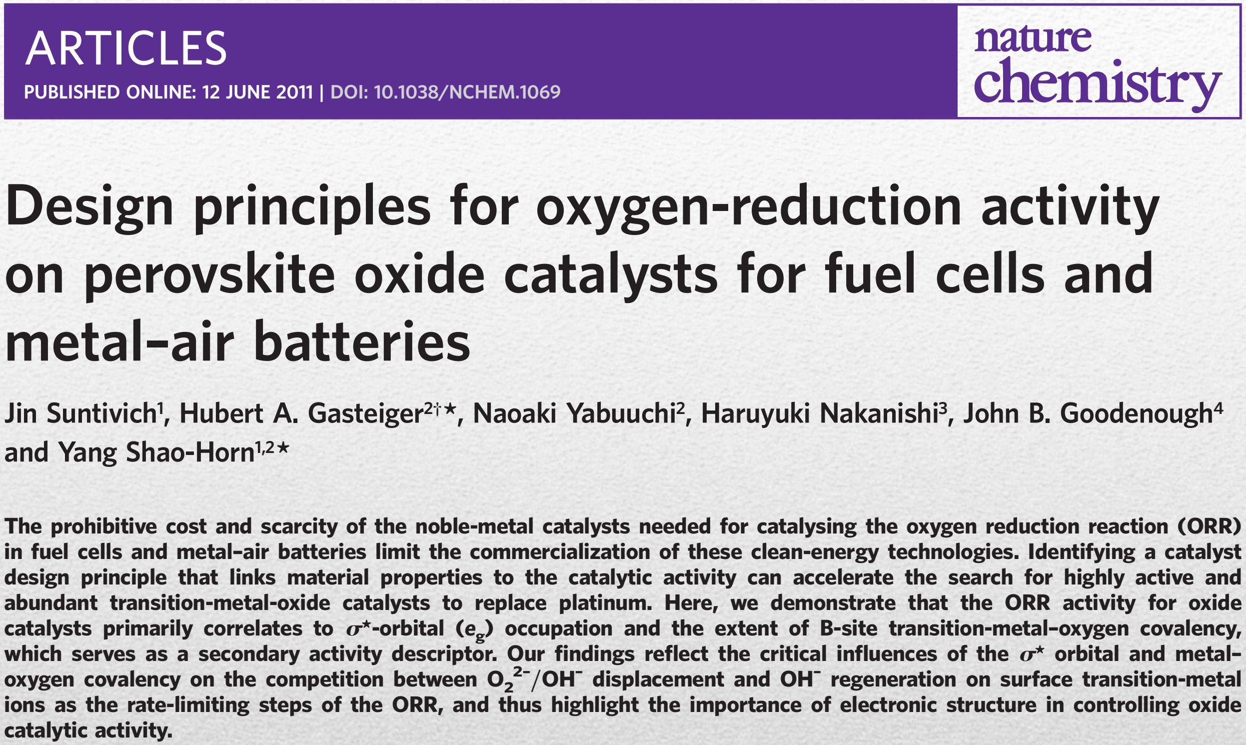
- Multiscale models: motivations and choices
  - Continuum models of solvation: from quantum-chemistry to condensed matter
- Self-consistent continuum solvation
  - Dielectric model
  - Pressure and Surface-tension
  - Periodic boundary corrections
  - Electrochemistry
- The Environ module for Quantum-ESPRESSO
  - PW, CP, NEB, TDDFpT

Outline

Motivation



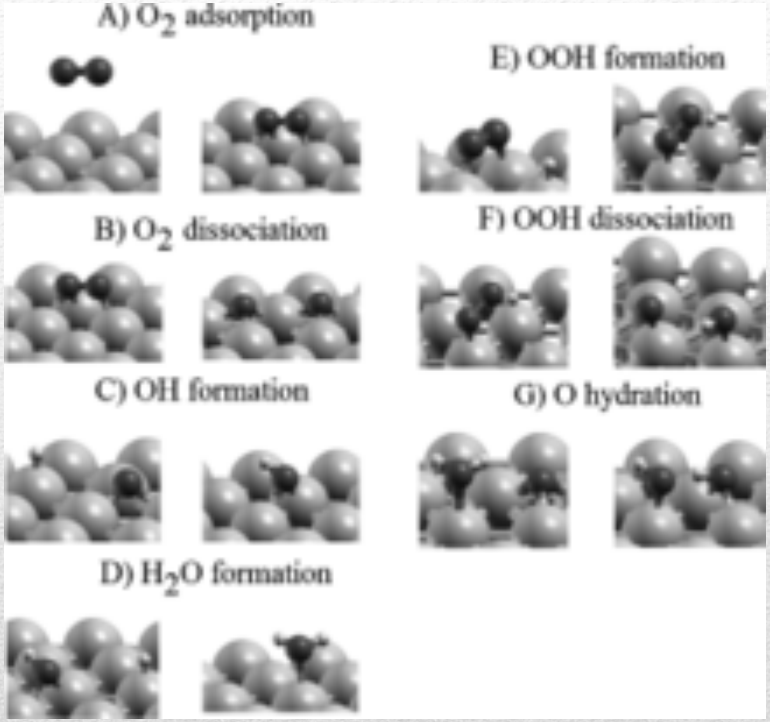
ARTICLES
PUBLISHED ONLINE: 12 JUNE 2011 | DOI: 10.1038/NCHEM.1069
nature chemistry

Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries

Jin Suntivich[1], Hubert A. Gasteiger[2†*], Naoaki Yabuuchi[2], Haruyuki Nakanishi[3], John B. Goodenough[4] and Yang Shao-Horn[1,2*]

The prohibitive cost and scarcity of the noble-metal catalysts needed for catalysing the oxygen reduction reaction (ORR) in fuel cells and metal–air batteries limit the commercialization of these clean-energy technologies. Identifying a catalyst design principle that links material properties to the catalytic activity can accelerate the search for highly active and abundant transition-metal-oxide catalysts to replace platinum. Here, we demonstrate that the ORR activity for oxide catalysts primarily correlates to σ^*-orbital (e_g) occupation and the extent of B-site transition-metal–oxygen covalency, which serves as a secondary activity descriptor. Our findings reflect the critical influences of the σ^* orbital and metal–oxygen covalency on the competition between O_2^{2-}/OH^- displacement and OH^- regeneration on surface transition-metal ions as the rate-limiting steps of the ORR, and thus highlight the importance of electronic structure in controlling oxide catalytic activity.

- Bulk calculations of bands
- NEB calculations of transition states
- BO/CP calculations of reactions (maybe biased MD)



Motivation

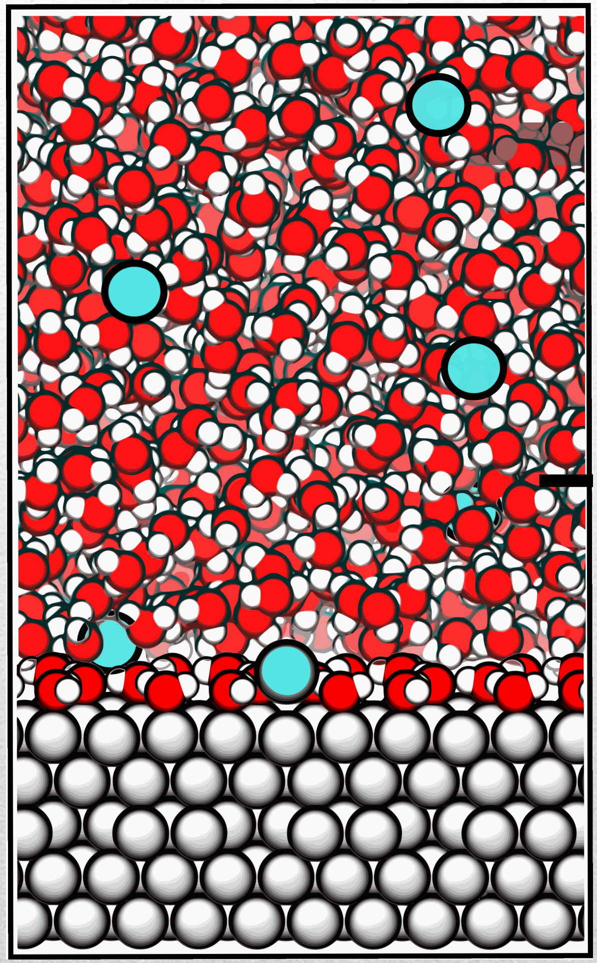
Realistic calculations, which allow to predict, need to be:

- More accurate
- More complex

Ideally they should not cost more and/or be more cumbersome than standard calculations, so that we can go high-throughput on them.

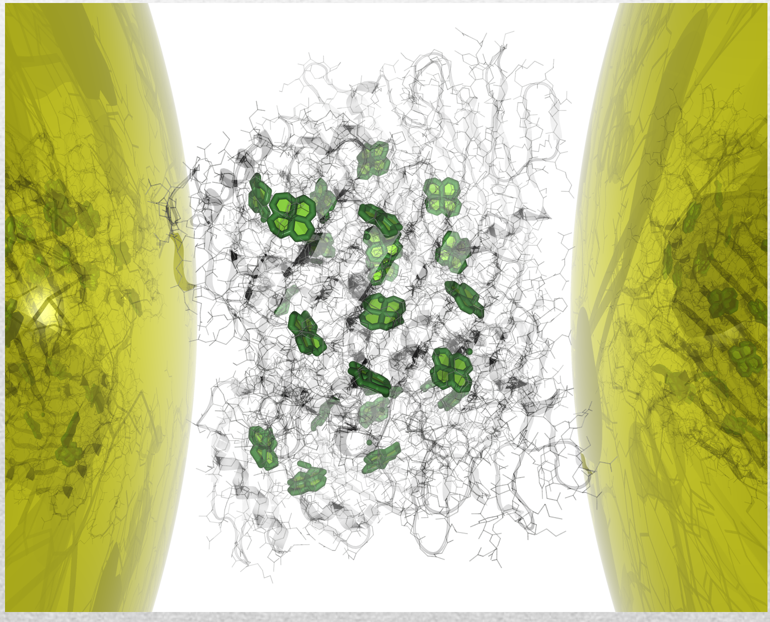
Motivation

- How large a simulation cell
- How many water molecules
    - How many electrons
- Sampling
- Is the result ‘correct’?



Full atomistic QM

- Focus on part of the system, treated at the highest level
- Use some fast, maybe approximate model to handle the rest (aka the environment)
  - Atomistic (lower level ab-initio, semiemprical, classical QM/MM)
  - Coarse-grained
  - Continuum



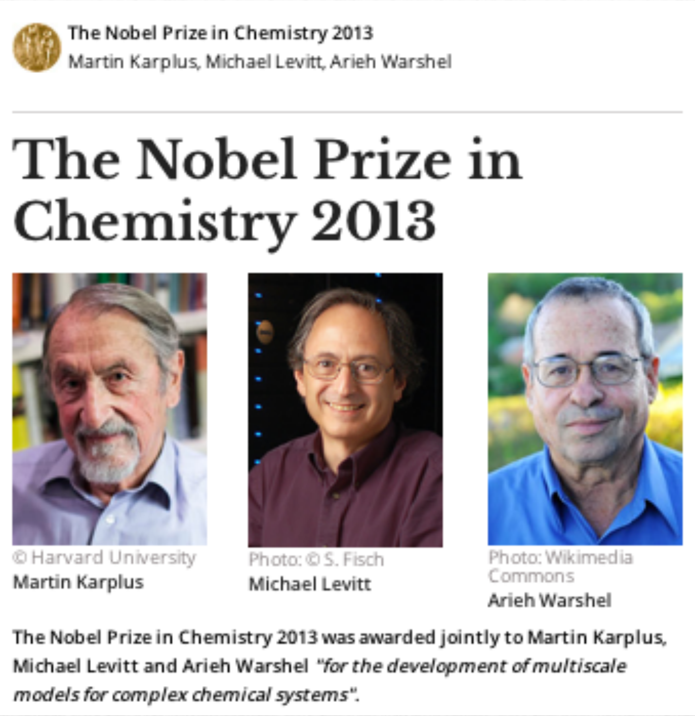
Chlorophyll pigments (QM)
in the FMO protein (MM/MMPol)
near metal nanoparticles (Continuum)

O. Andreussi, et al. *J. Phys. Chem. A* **119**, 5197 (2015).

Hierarchical models

Hierachical models

The importance of the work of the laureates is independent of what strategy is used for the choice of the studied configuration(s). The prize focuses on how to evaluate the variation in the energy of the real system in a accurate and efficient way for systems where relatively large geometry changes or changes in electronic configuration in a smaller part of the studied system is strongly coupled to a surrounding that is only weakly perturbed. One way to address this problem is to develop an efficient computer code based on the Schrödinger equation that makes it possible to handle systems of the size that is required. The Car – Parrinello approach[13] is the leading strategy along this line. It is however still too demanding with respect to computer resources to be able to handle the large systems necessary for biomolecular modelling or extended supra-molecular systems with the required accuracy. The solution to the problem is instead to combine classical modelling of the larger surrounding, along the line suggested by Westheimer[4], Allinger[7], Némety and Scheraga[8], with quantum chemical modelling of the core region, where the chemically interesting action takes place.



The Nobel Prize in Chemistry 2013
Martin Karplus, Michael Levitt, Arieh Warshel

The Nobel Prize in Chemistry 2013

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Martin Karplus

Photo: © S. Fisch
Michael Levitt

Photo: Wikimedia Commons
Arieh Warshel

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems"*.

Continuum models of solvation

From qauntum-chemistry to condensed matter

Why using a continuum?

- Hierarchical approach, solute with full details, solvent simplified:
- take advantage of statistical averaging: isotropic continuum.
- only focuses on effects of interest: electrostatics;

Intrinsically high-throughput

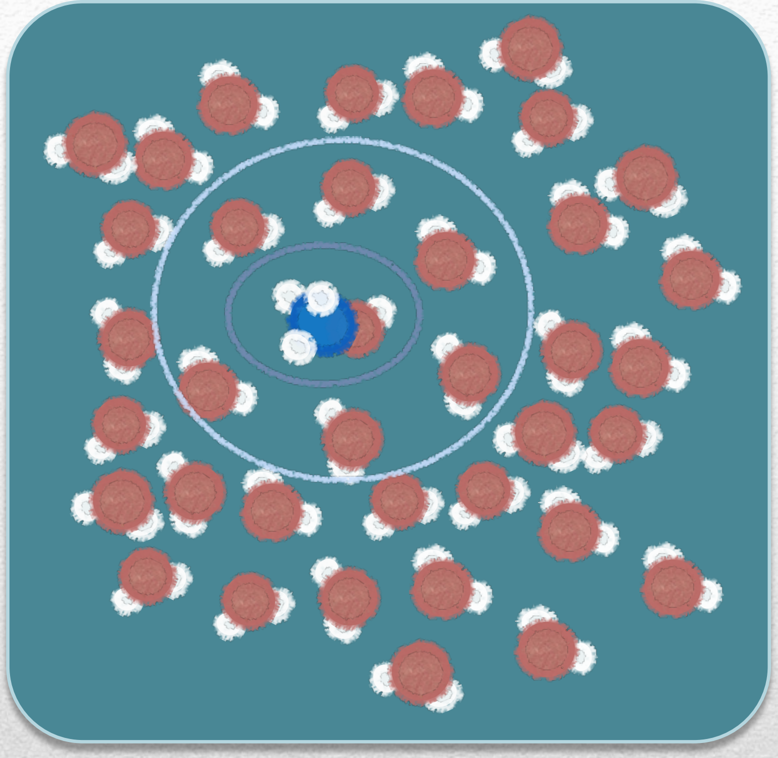
Reduced number of molecules and implicit average

Sometimes solvent is 'structural'

Experimental dielectric constant

Biased selection, sometimes all interactions are important

- Cavity
  - Rigid, soft
  - Sharp or smooth
  - Atomic/electronic
- Interactions
  - Electrostatic
  - Cavitation
  - Dispersion/Repulsion
  - H-bonds



Continuum models: the main ingredients

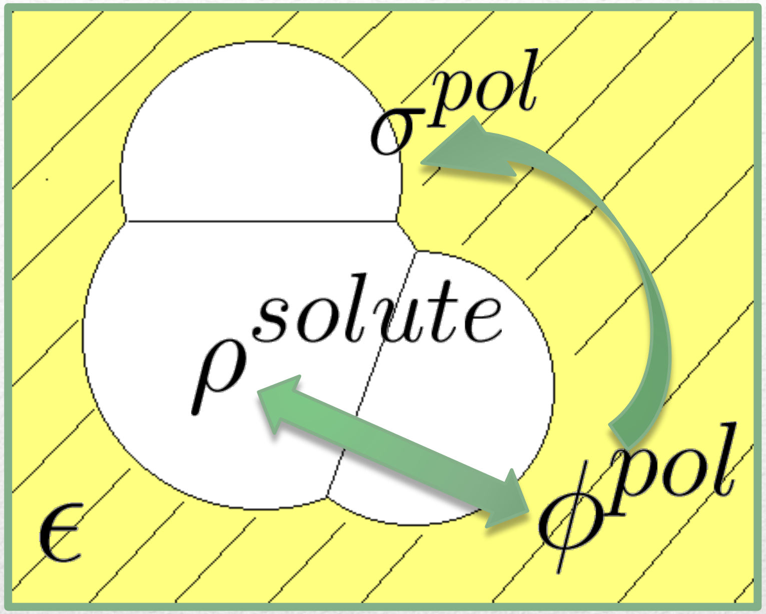
Continuum Models: PCM

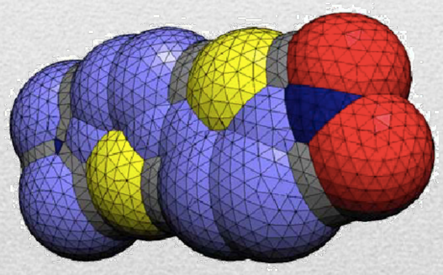
Polarizable Continuum Model

$$\sigma^{pol} = A^{-1}\phi[\rho^{solute}]$$

$$G^{el} = \langle\Psi|\, H^0 + \frac{1}{2}\phi^{pol}\, |\Psi\rangle$$

- Molecular shaped cavity
- Usually atom-defined cavity
- Sharp 2D interface
- Numerically solved via Boundary Elements Methods (BEM)





J. Tomasi and M. Persico, *Chem. Rev.* **94** 2027 (1994)
J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* **105** 2999 (2005)

PCM: Pros and Cons

of its most common flavor

PROs

- Fast
- Reasonably parameterized and well tested
- Its electrostatic component gives reliable results (spectroscopy, reactions, etc.)

CONs

- Sharp atom-centered interface: possible problems with forces
- Arbitrary and possibly parameter intensive definition of cavity
- Does not account cavity softness

- IEF-PCM by Tomasi, Mennucci et al.
- COSMO by Klamt et al.
- Isodensity PCM and Self-Consistent Isodensity PCM (SCI-PCM) by Scalmani et al.
- SMx (x=1,8) methods by Cramer, Truhlar et al.
- SVPE or SSVPE by Chipman et al.

Implemented in Gaussian, GAMESS, Molpro, NWChem, QChem, ADF, Dalton, etc.

PCM-related methods

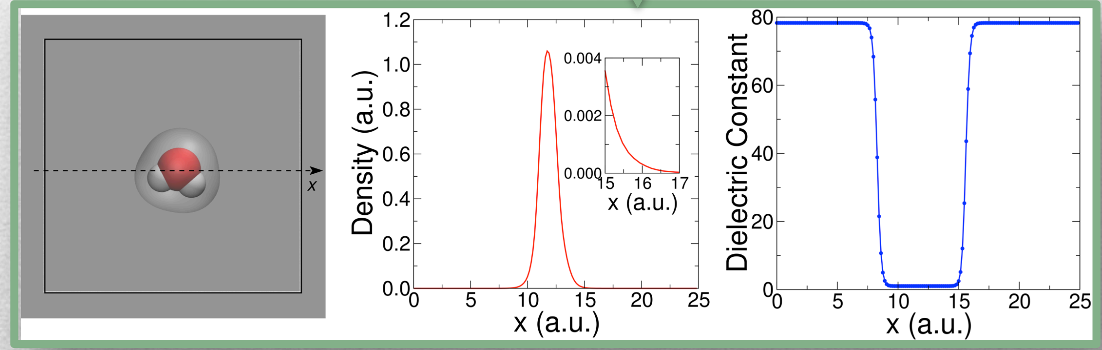
Continuum Models: FG

$$F[\rho^{solute},\phi^{tot}] = \int \phi^{tot}(\mathbf{r})\rho^{solute}(\mathbf{r})d\mathbf{r} - \int \frac{\boxed{\epsilon[\rho^{el}(\mathbf{r})]}}{8\pi}\left|\nabla\phi^{tot}(\mathbf{r})\right|^2 d\mathbf{r}$$

$$\frac{\delta F}{\delta\phi^{tot}} = 0 \rightarrow \nabla\cdot\epsilon[\rho^{el}(\mathbf{r})]\nabla\phi^{tot}(\mathbf{r}) = -4\pi\rho^{solute}(\mathbf{r})$$

$$\frac{\delta F}{\delta\rho^{el}} = \left(\frac{\delta E^{hartree}}{\delta\rho^{el}}\right) + v_{pol} + v_{\epsilon}$$

- Fully variational approach
- Smooth (3D) self-consistent dielectric function
- Numerically solved via multigrid



J. Fattebert and F. Gygi, *J. Comput. Chem.* **23** 662 (2002)

FG Model: Pros and Cons

of its original formulation

PROs

- Elegant variational formulation
- Soft self-consistent cavity
- Limited number of parameter

CONs

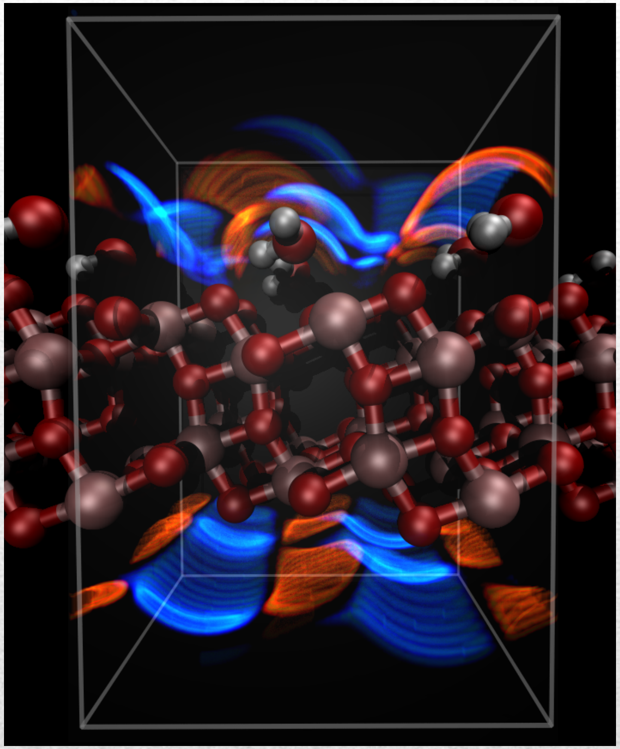
- More computational expensive
- Choice of dielectric function can lead to convergence problems
- Limited parameterization
- Missing non-electrostatic terms

- Self-consistent Continuum Solvation (SCCS) by Andreussi et al.
- Vasp-sol by Mattew and Hennig
- Salsa by Tomas Arias et al.
- CANDLE by Goddard et al.

Other tools/modules developed by Skylaris et al. Reuter, Oberhofer et al., Vandevondelee et al.

Implemented in QE, VASP, BigDFT, CP2K, ONETEP, CASTEP, etc.

Derived or analogous to FG



- Electrostatics based on a **redefined** version of Fattebert-Gygi model
- Non-electrostatics based on quantum **surface and** quantum **volume**
- Changed the numerical approach, from multigrid to **FFT-based**
- **Reparametrized** for neutral and charged compounds

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

Self-consistent Continuum Solvation (SCCS)

Revising FG: electrostatics

Poisson Equation in dielectric medium

$$\nabla \cdot \epsilon\left(\rho^{el}(\mathbf{r})\right)\nabla\phi^{tot}(\mathbf{r}) = -4\pi\rho^{solute}(\mathbf{r})$$

Polarization charge

$$\rho^{pol}(\mathbf{r}) \equiv -\nabla\cdot\mathbf{P}(\mathbf{r}) = \nabla\cdot\left(\frac{\epsilon(\rho^{el}(\mathbf{r}))-1}{4\pi}\nabla\phi^{tot}(\mathbf{r})\right)$$

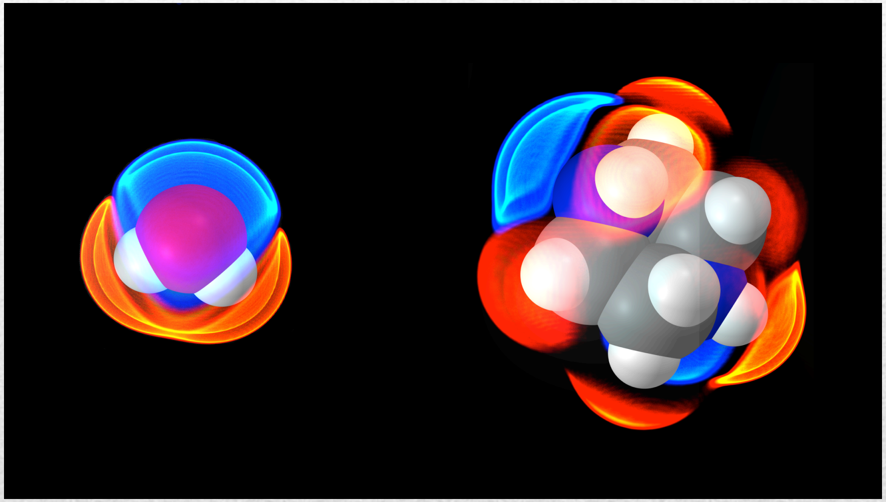
Vacuum-like Poisson Equation

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

Polarization charge

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

$$\rho^{iter}(\mathbf{r}) = \frac{1}{4\pi}\nabla \ln \epsilon(\rho^{el}(\mathbf{r})) \cdot \nabla \phi^{tot}(\mathbf{r})$$



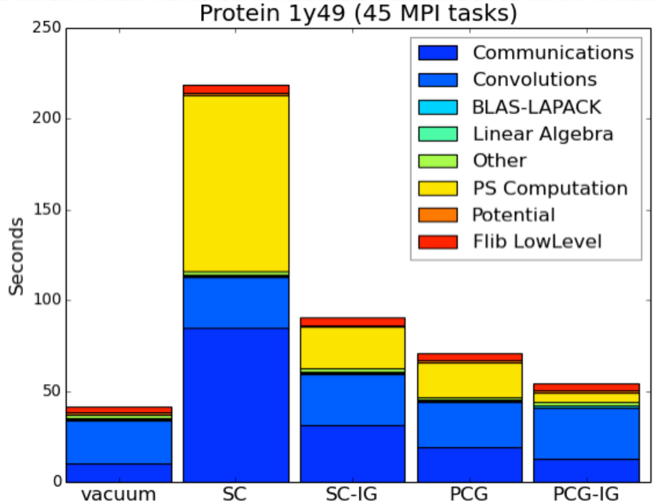
Computationally robust and easy to implement

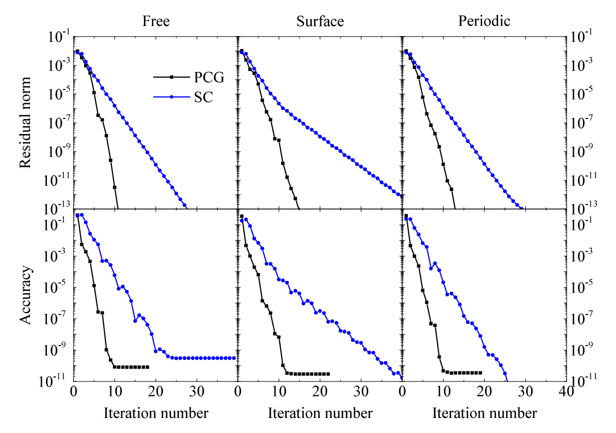
Naturally parallel and fully periodic

Iterative Solver via FFT

Even better solvers

- Iterative solution on polarization charge can be shown to be equivalent to a preconditioned steepest-descent algorithm on the potential.
- A more efficient preconditioned conjugate-gradient algorithm with a smart preconditioner was recently developed.



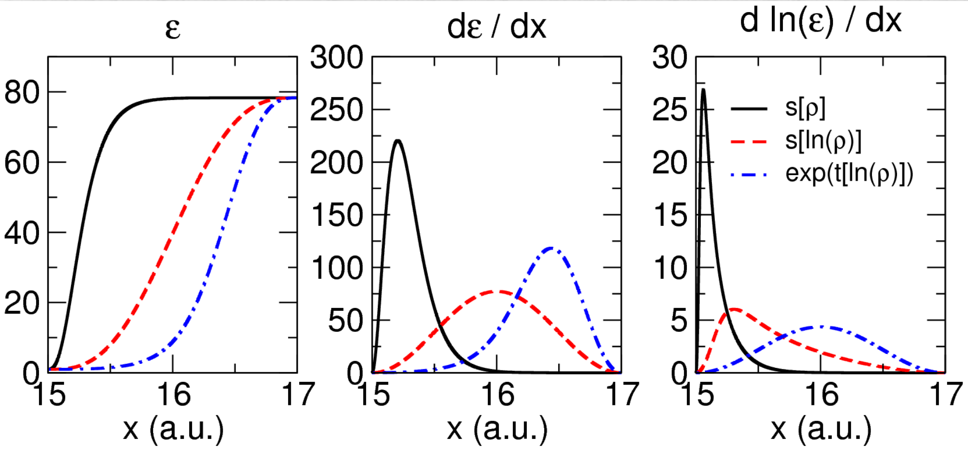


G. Fisicaro, L. Genovese, O. Andreussi, N. Marzari, and S. Goedecker, *J. Chem. Phys.* **144**, 014103 (2016)

Novel dielectric function

$$\epsilon_{\epsilon_0,\rho_{min},\rho_{max}}\left(\rho^{elec}\right) = \begin{cases} 1 & \rho^{elec} > \rho_{max} \\ \exp\left(t\left(\ln \rho^{elec}\right)\right) & \rho_{min} < \rho^{elec} < \rho_{max} \, , \\ \epsilon_0 & \rho^{elec} < \rho_{min} \end{cases}$$

$$t(x) = \frac{\ln \epsilon_0}{2\pi}\left[2\pi \frac{(\ln \rho_{max} - x)}{(\ln \rho_{max} - \ln \rho_{min})} - \sin\left(2\pi \frac{(\ln \rho_{max} - x)}{(\ln \rho_{max} - \ln \rho_{min})}\right)\right]$$



- Ideally flat in important regions
- Adapted to an exponentially decaying electronic density
- Optimally smooth polarization charge

Cavitation model

- Quantum Volume

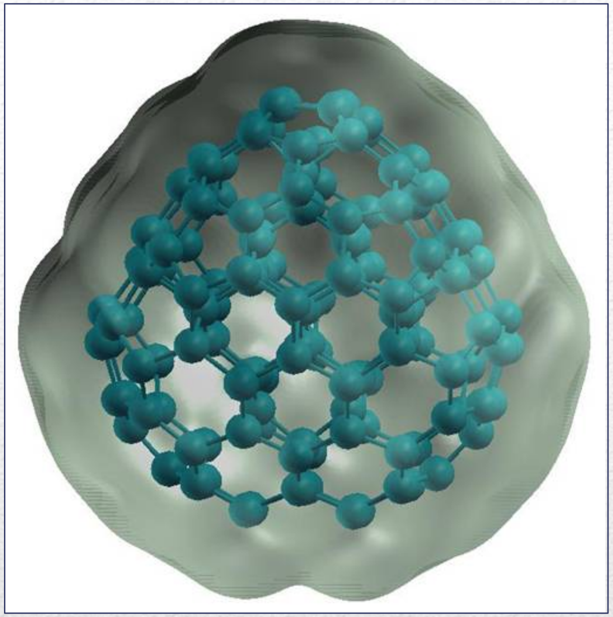
$$H = E + P^{ext}V$$

$$V = \int d\mathbf{r}\vartheta\left(\rho^{elec}(\mathbf{r})\right)$$

- Quantum Surface

$$G^{cav} = \gamma S$$

$$S = \int d\mathbf{r}\left\{\vartheta_{\rho_0-\frac{\Delta}{2}}\left(\rho^{elec}(\mathbf{r})\right) - \vartheta_{\rho_0+\frac{\Delta}{2}}\left(\rho^{elec}(\mathbf{r})\right)\right\} \times \frac{\left|\nabla\rho^{elec}(\mathbf{r})\right|}{\Delta}$$



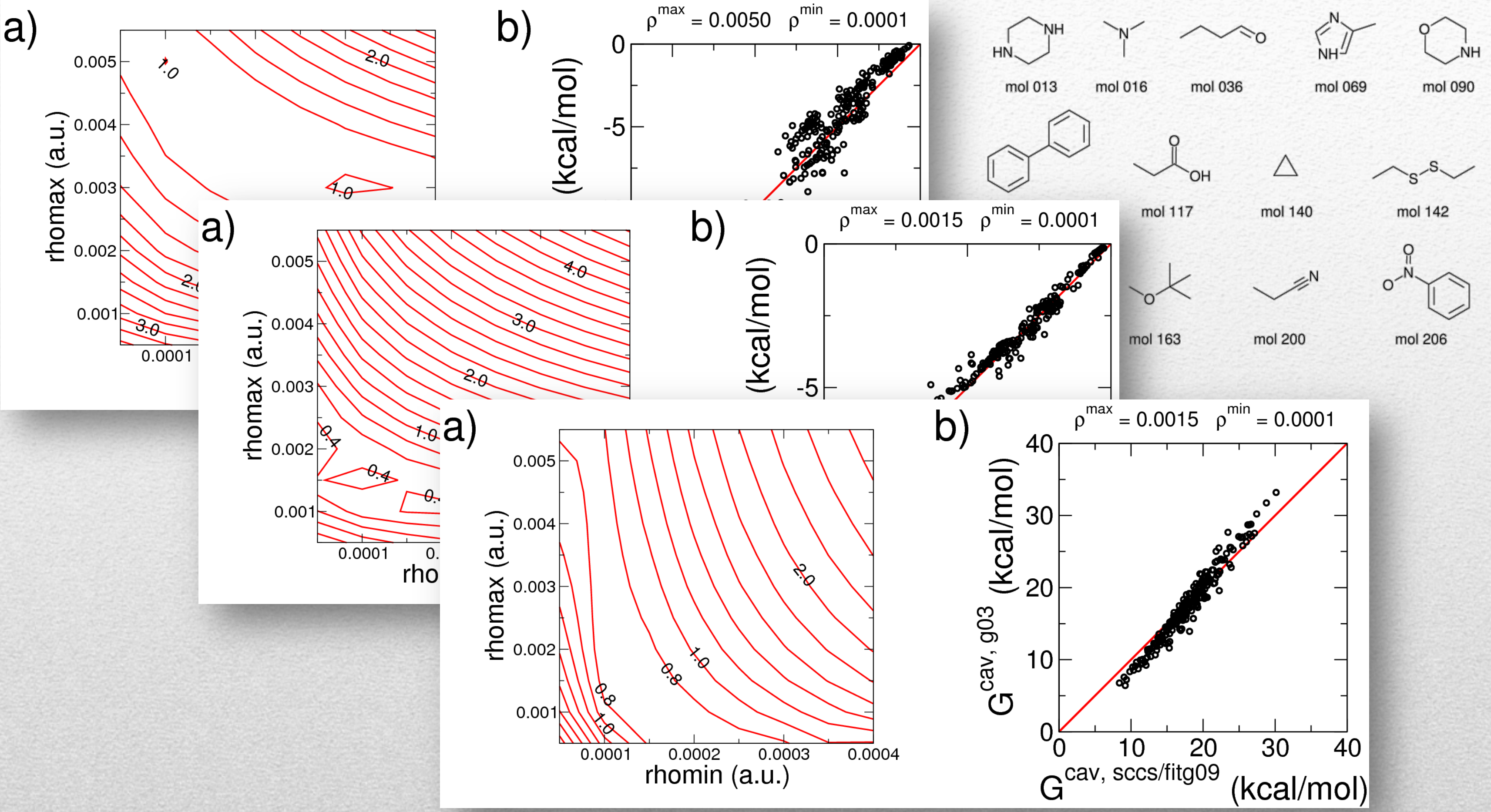
M. Cococcioni, F. Mauri, G. Ceder and N. Marzari, *PRL* **94**, 145501 (2005)
D. Scherlis, M. Coccocioni et al., *J. Chem. Phys.***124** 074103 (2006)

$$\Delta G^{sol} = \Delta G^{el}(\epsilon_0, \rho_{min}, \rho_{max}) + (\alpha + \gamma)S + \beta V$$

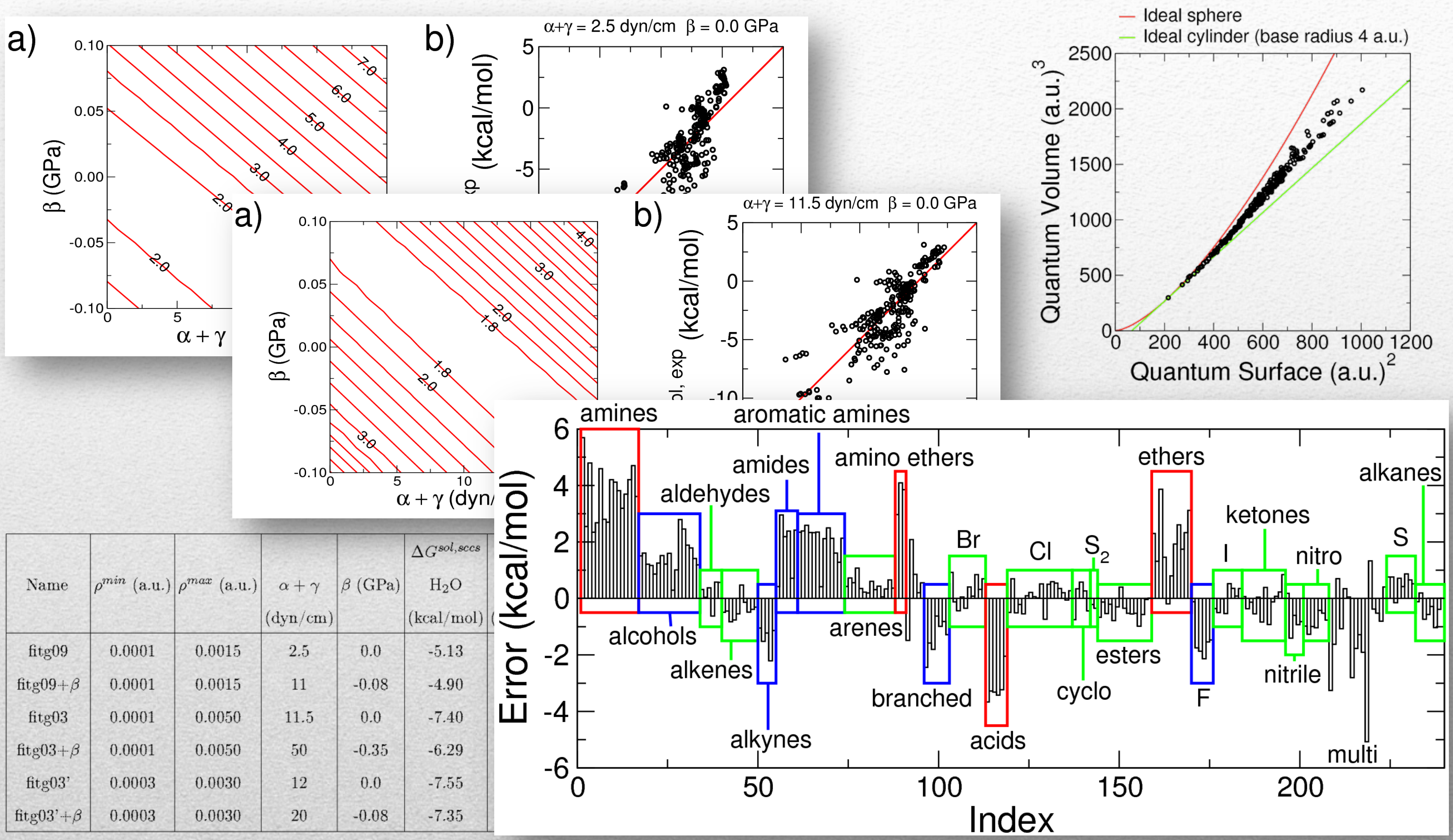
Up to six parameters:

- Up to two experimental quantities (static dielectric constant and surface tension)
- Just two parameters to define the cavity (dielectric function)
- Up to two solvent-dependent parameters to fit experimental results

Parameterize SCCS: Free Energies of Solvation

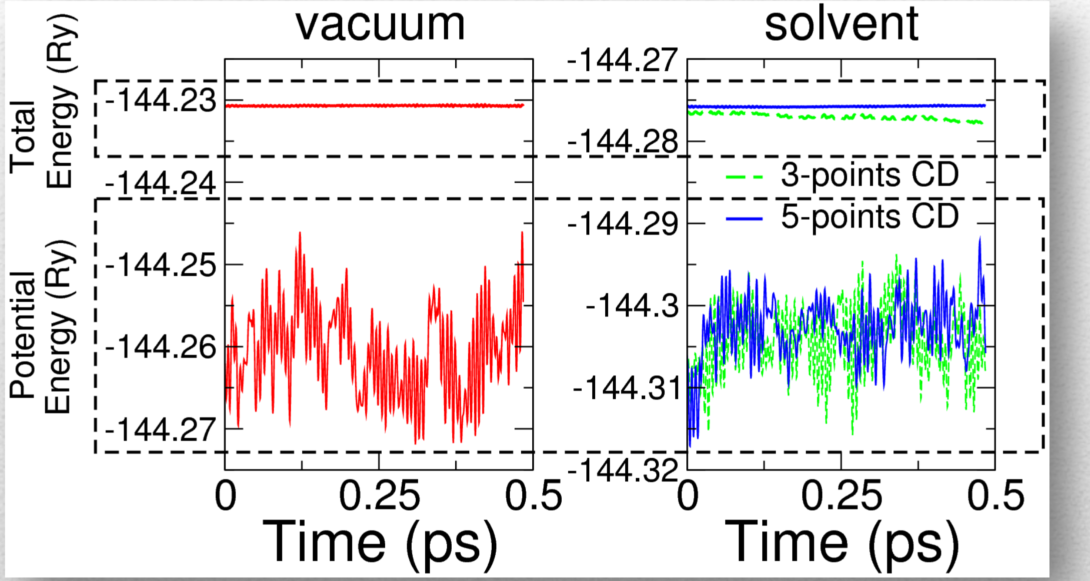


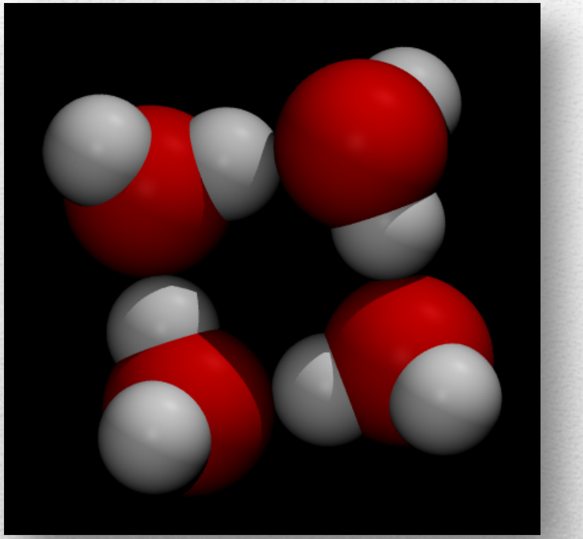
Fit of the cavity parameters



Name	ρ^{min} (a.u.)	ρ^{max} (a.u.)	$\alpha + \gamma$ (dyn/cm)	β (GPa)	$\Delta G^{sol,sccs}$ H_2O (kcal/mol)
fitg09	0.0001	0.0015	2.5	0.0	-5.13
fitg09+β	0.0001	0.0015	11	-0.08	-4.90
fitg03	0.0001	0.0050	11.5	0.0	-7.40
fitg03+β	0.0001	0.0050	50	-0.35	-6.29
fitg03'	0.0003	0.0030	12	0.0	-7.55
fitg03'+β	0.0003	0.0030	20	-0.08	-7.35

Fit of the experiments

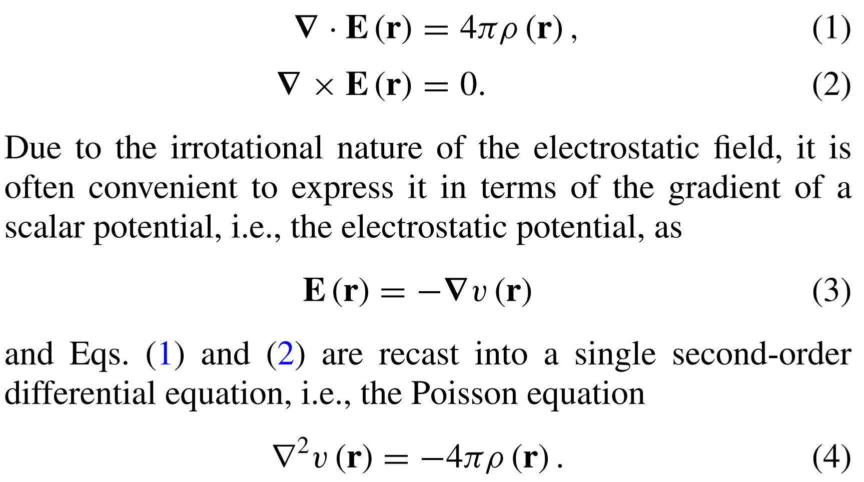




Test on Molecular Dynamics

Charged Systems: new problems

- Periodic Boundary Conditions (PBC)
- DFT convergence of Anions’ Electronic Structure
- Much stronger solvent-solute interaction



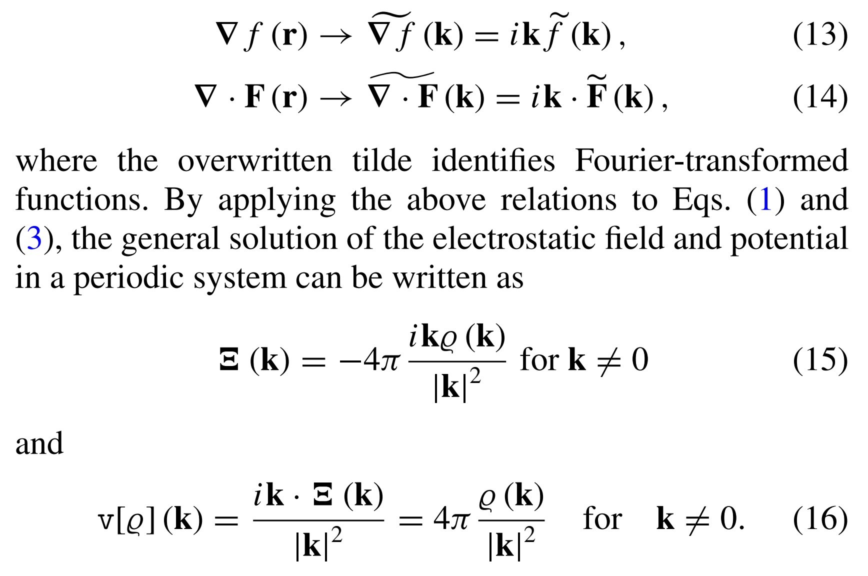
$$\nabla \cdot \mathbf{E}(\mathbf{r}) = 4\pi\rho(\mathbf{r}), \tag{1}$$
$$\nabla \times \mathbf{E}(\mathbf{r}) = 0. \tag{2}$$

Due to the irrotational nature of the electrostatic field, it is often convenient to express it in terms of the gradient of a scalar potential, i.e., the electrostatic potential, as

$$\mathbf{E}(\mathbf{r}) = -\nabla v(\mathbf{r}) \tag{3}$$

and Eqs. (1) and (2) are recast into a single second-order differential equation, i.e., the Poisson equation

$$\nabla^2 v(\mathbf{r}) = -4\pi\rho(\mathbf{r}). \tag{4}$$



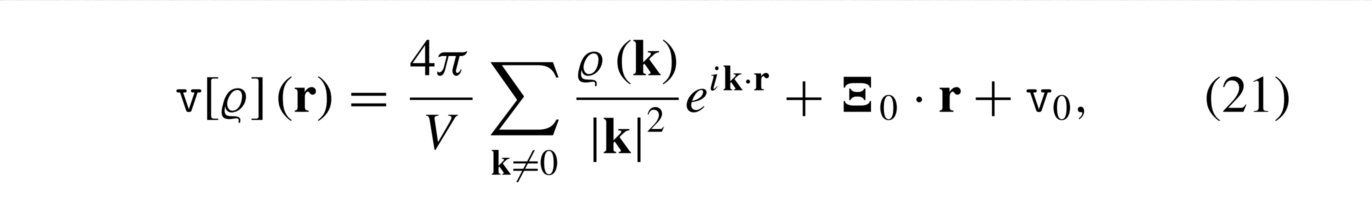
$$\nabla f(\mathbf{r}) \rightarrow \widetilde{\nabla f}(\mathbf{k}) = i\mathbf{k}\tilde{f}(\mathbf{k}), \tag{13}$$
$$\nabla \cdot \mathbf{F}(\mathbf{r}) \rightarrow \widetilde{\nabla \cdot \mathbf{F}}(\mathbf{k}) = i\mathbf{k} \cdot \tilde{\mathbf{F}}(\mathbf{k}), \tag{14}$$

where the overwritten tilde identifies Fourier-transformed functions. By applying the above relations to Eqs. (1) and (3), the general solution of the electrostatic field and potential in a periodic system can be written as

$$\boldsymbol{\Xi}(\mathbf{k}) = -4\pi\frac{i\mathbf{k}\varrho(\mathbf{k})}{|\mathbf{k}|^2} \text{ for } \mathbf{k} \neq 0 \tag{15}$$

and

$$\mathrm{v}[\varrho](\mathbf{k}) = \frac{i\mathbf{k}\cdot\boldsymbol{\Xi}(\mathbf{k})}{|\mathbf{k}|^2} = 4\pi\frac{\varrho(\mathbf{k})}{|\mathbf{k}|^2} \quad \text{for} \quad \mathbf{k} \neq 0. \tag{16}$$



$$\mathrm{v}[\varrho](\mathbf{r}) = \frac{4\pi}{V}\sum_{\mathbf{k}\neq 0}\frac{\varrho(\mathbf{k})}{|\mathbf{k}|^2}e^{i\mathbf{k}\cdot\mathbf{r}} + \boldsymbol{\Xi}_0\cdot\mathbf{r} + \mathrm{v}_0, \tag{21}$$

FFTs and PBC artifacts

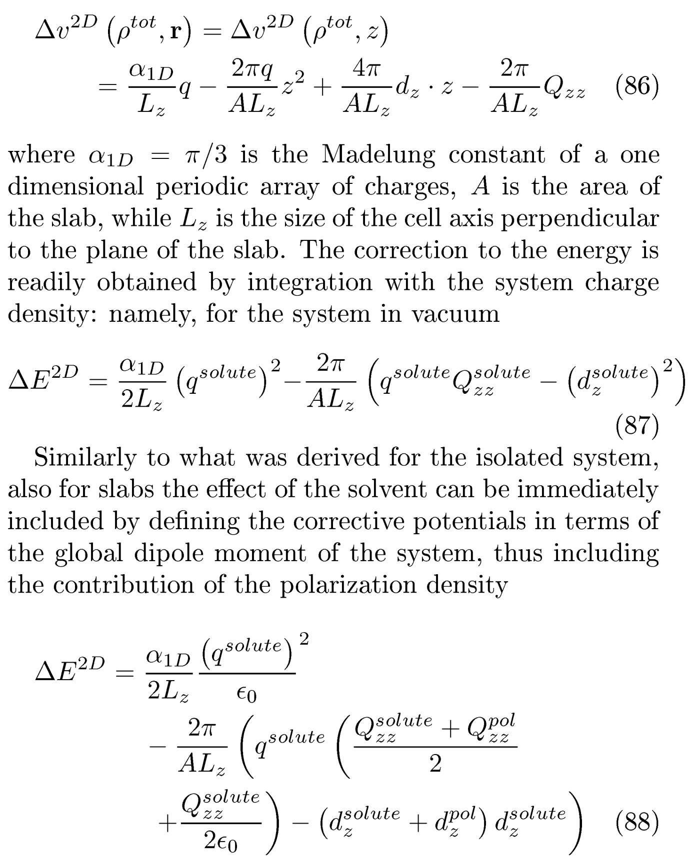
O. Andreussi and N. Marzari, *Phys. Rev. B* **90**, 245101 (2014)

- Periodically replicated charge distribution
- Only neutral charge distributions (or neutralized background)
- Only zero average electric field
- Zero average potential (tin-foil boundary conditions)

- Different strategies to solve the problem in vacuum:
  - Makov-Payne (post-processing, cubic cells, errors up to L^{-3})
  - Martyna-Tuckerman (reciprocal space, perfect if cell twice as big as system)
  - Parabolic correction (Point-Countercharge PCC)

FFTs and PBC artifacts

O. Andreussi and N. Marzari, *Phys. Rev. B* **90**, 245101 (2014)



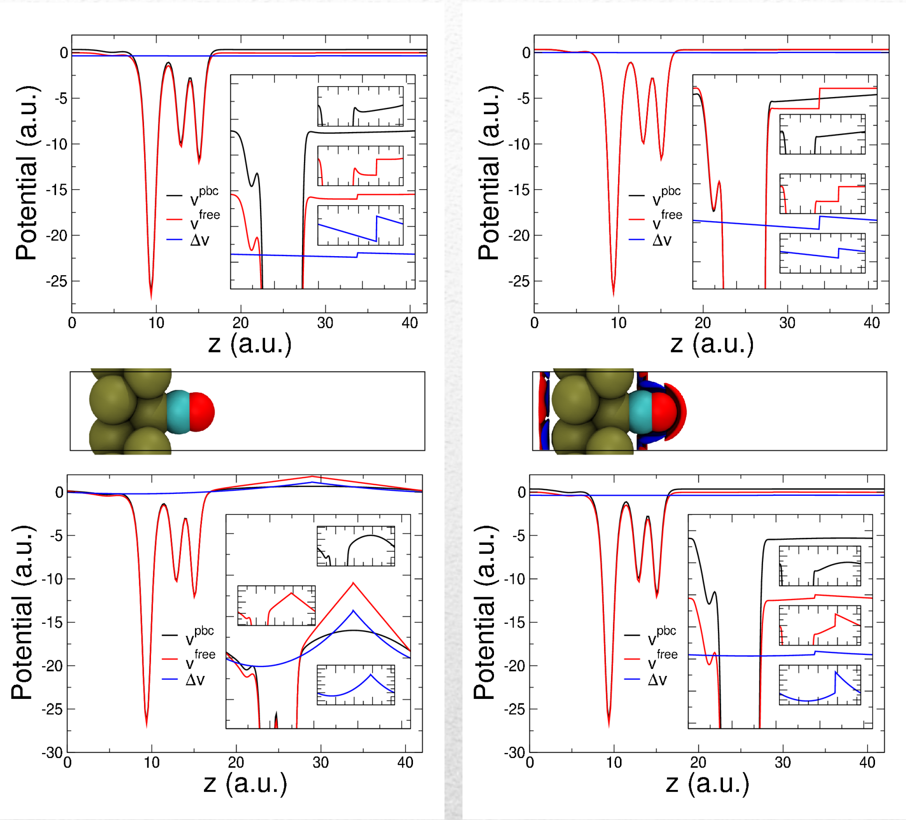
$$\Delta v^{2D}\left(\rho^{tot},\mathbf{r}\right) = \Delta v^{2D}\left(\rho^{tot},z\right) = \frac{\alpha_{1D}}{L_z}q - \frac{2\pi q}{AL_z}z^2 + \frac{4\pi}{AL_z}d_z \cdot z - \frac{2\pi}{AL_z}Q_{zz} \qquad (86)$$

where $\alpha_{1D} = \pi/3$ is the Madelung constant of a one dimensional periodic array of charges, A is the area of the slab, while L_z is the size of the cell axis perpendicular to the plane of the slab. The correction to the energy is readily obtained by integration with the system charge density: namely, for the system in vacuum

$$\Delta E^{2D} = \frac{\alpha_{1D}}{2L_z}\left(q^{solute}\right)^2 - \frac{2\pi}{AL_z}\left(q^{solute}Q_{zz}^{solute} - \left(d_z^{solute}\right)^2\right) \qquad (87)$$

Similarly to what was derived for the isolated system, also for slabs the effect of the solvent can be immediately included by defining the corrective potentials in terms of the global dipole moment of the system, thus including the contribution of the polarization density

$$\Delta E^{2D} = \frac{\alpha_{1D}}{2L_z}\frac{\left(q^{solute}\right)^2}{\epsilon_0} - \frac{2\pi}{AL_z}\left(q^{solute}\left(\frac{Q_{zz}^{solute}+Q_{zz}^{pol}}{2} + \frac{Q_{zz}^{solute}}{2\epsilon_0}\right) - \left(d_z^{solute}+d_z^{pol}\right)d_z^{solute}\right) \qquad (88)$$



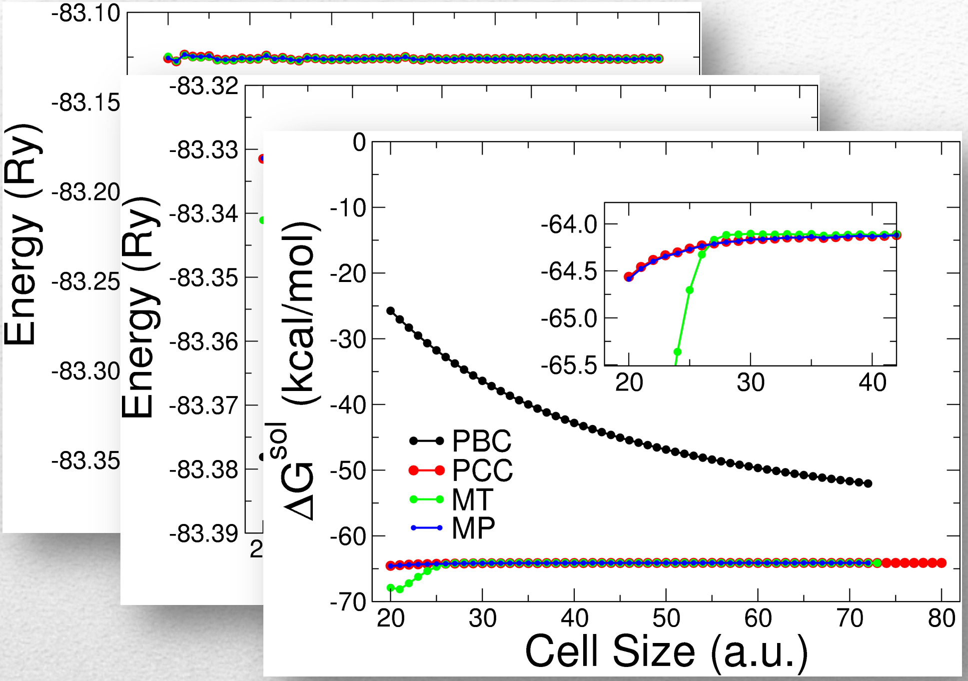
vacuum

continuum solvent

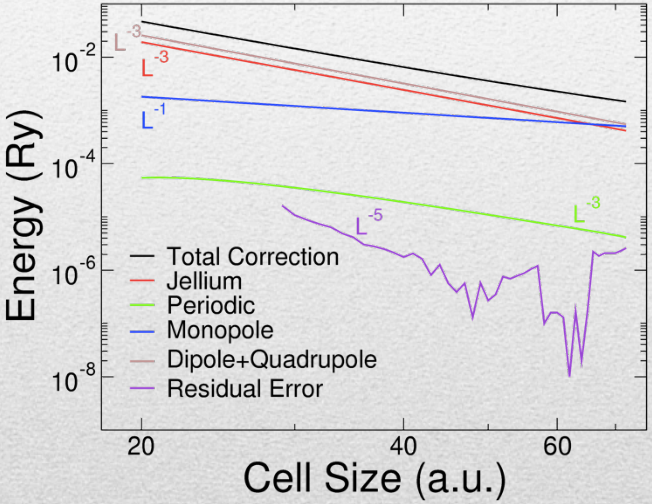
Parabolic correction in 2d systems

O. Andreussi and N. Marzari, *Phys. Rev. B* **90**, 245101 (2014)

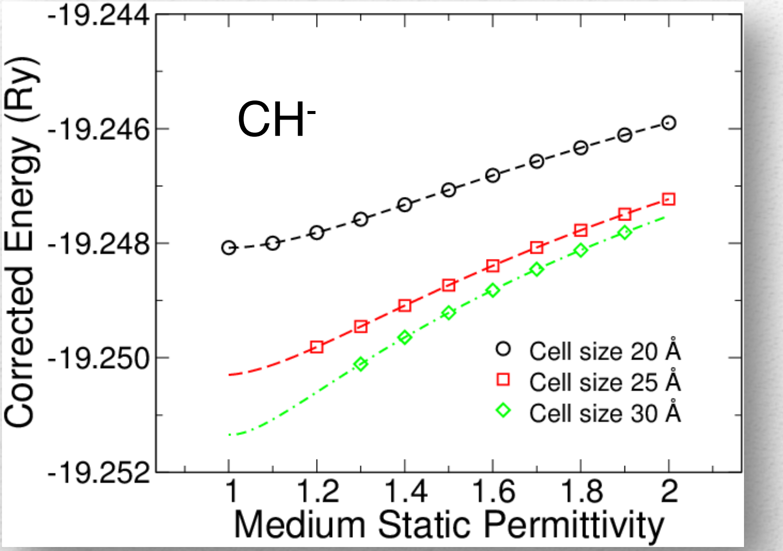
PBC Correction: extension to continuum environments

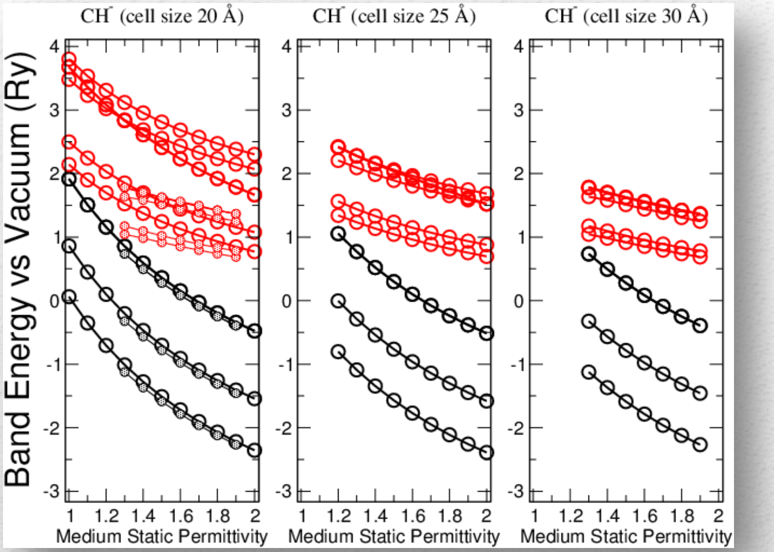


- Makov-Payne
- Martyna-Tuckermann
- Point Counter-Charge (0D and 2D)



O. Andreussi and N. Marzari, *Phys. Rev. B* **90**, 245101 (2014)





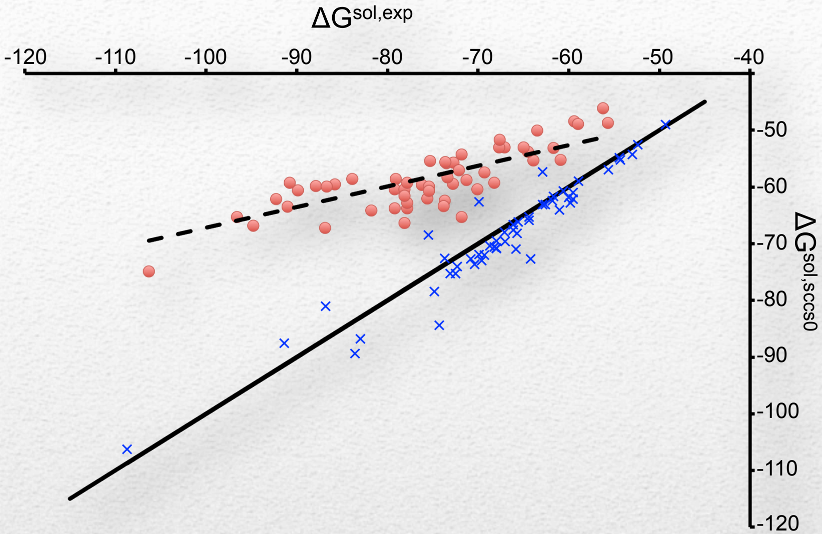
(eV)	Experimental	Burke [1]	Extrapolated [2]
CH	1.24	1.53	1.57
CH2	0.65	0.78	0.78
CH3	0.08	0.08	0.15
NH	0.38	0.55	0.64
NH2	0.77	0.83	0.93
OH	1.83	1.95	2.02

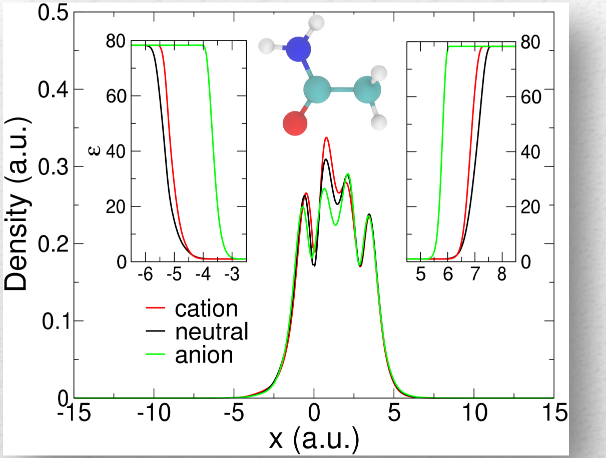
(eV)	Experimental	Burke [1]	Extrapolated [2]
SiH	1.28	1.4	1.38
SiH2	1.12	1.29	1.24
SiH3	1.41	1.42	1.36
PH	1.03	1.07	1.06
PH2	1.27	1.25	1.23
HS	2.36	2.33	2.30

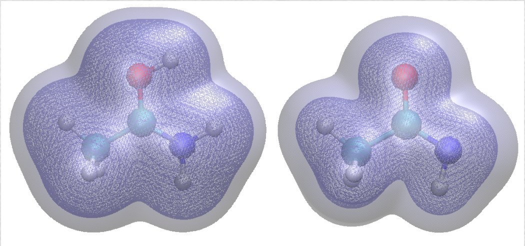
[1] M.C. Kim, E. Sim and K. Burke, *J. Chem. Phys.* **134**, 171103 (2011)
[2] O. Andreussi, C. Dupont and N. Marzari, *in preparation* (2017)

Converging Anions in vacuum

Stronger solvent-solute interaction: refitting



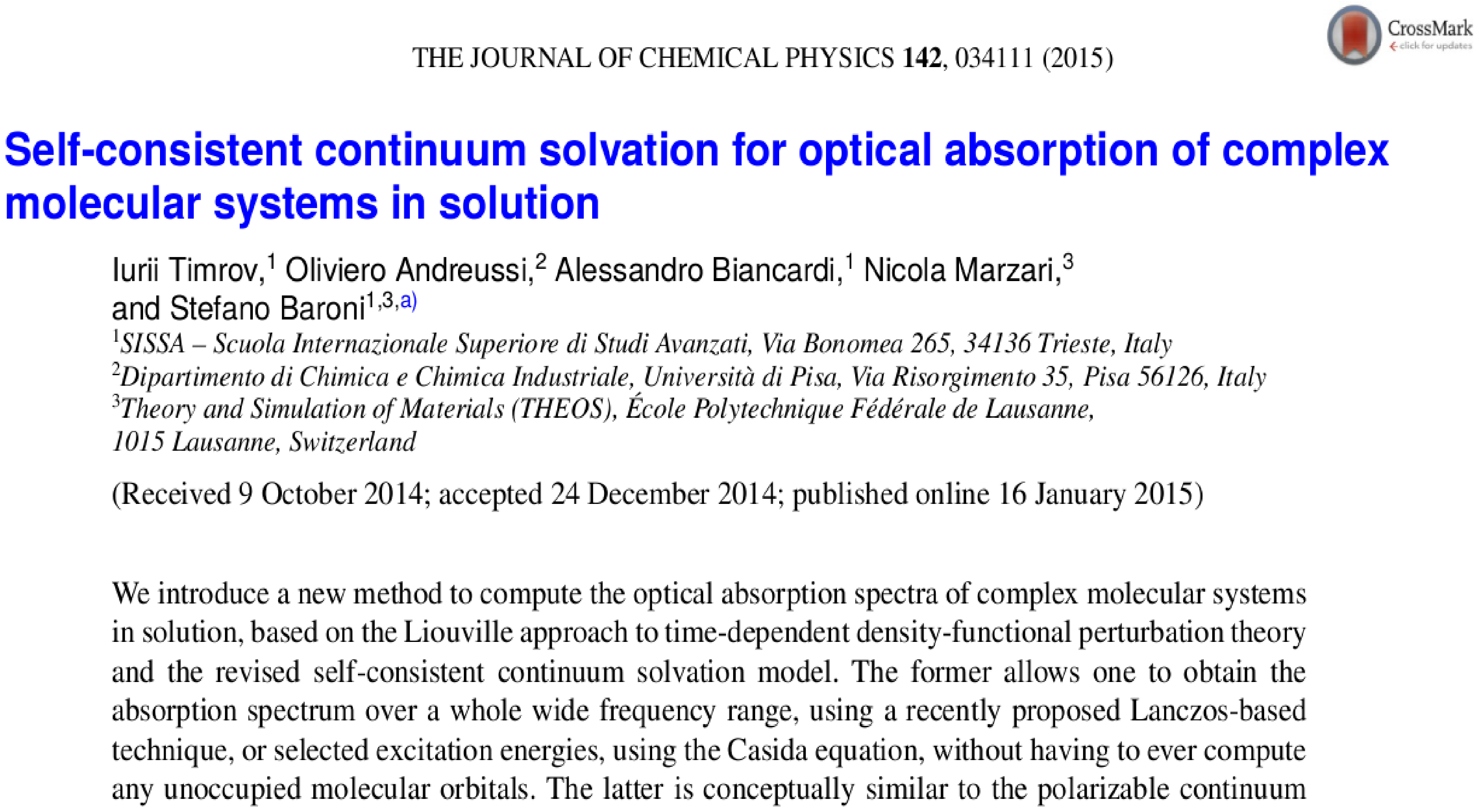




- Very good results on cations (MAE of ~2 kcal/mol)
- Poor results on anions, improve after re-parametrization (MAE of ~7 kcal/mol)

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

Revised self-consistent continuum solvation (SCCS) model for the excited state (TDDFpT)



THE JOURNAL OF CHEMICAL PHYSICS **142**, 034111 (2015)

Self-consistent continuum solvation for optical absorption of complex molecular systems in solution

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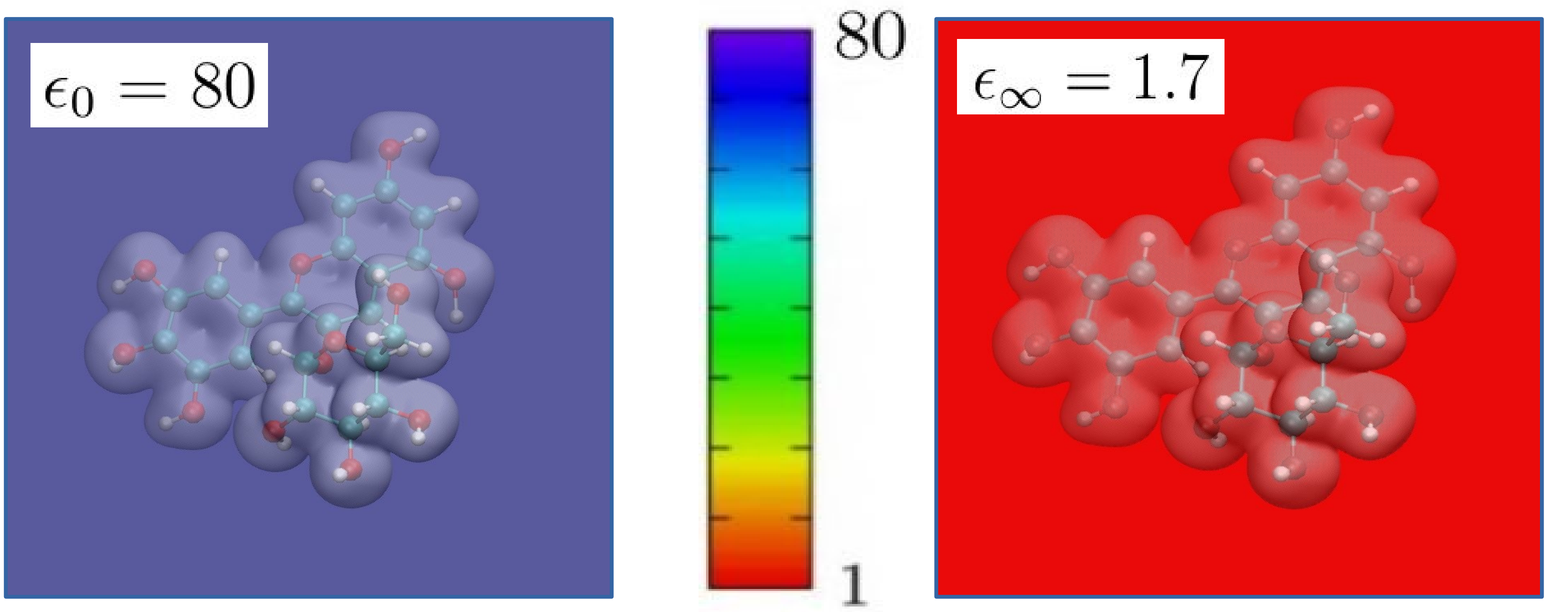
We introduce a new method to compute the optical absorption spectra of complex molecular systems in solution, based on the Liouville approach to time-dependent density-functional perturbation theory and the revised self-consistent continuum solvation model. The former allows one to obtain the absorption spectrum over a whole wide frequency range, using a recently proposed Lanczos-based technique, or selected excitation energies, using the Casida equation, without having to ever compute any unoccupied molecular orbitals. The latter is conceptually similar to the polarizable continuum

From ground state to excited state

What happens when we excite the system (irradiation by light)?

The dielectric constant of the solvent (water in this case) changes from 80 to 1.7. This fact is taken into account in the TDDFPT equations.

Ground state → **Excited state**



Approximation for the optical response:

$$\epsilon(\omega) = \epsilon_\infty$$

TDDFPT + SCCS equations in a nutshell

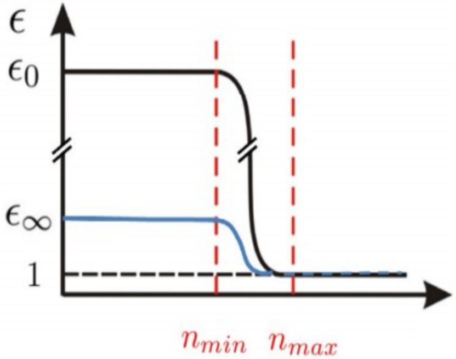
To 1st order in the perturbation, the frequency-dependent Kohn-Sham equation reads:

$$\left(\hat{H}^\circ - \varepsilon_v - \omega\right)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\hat{V}_{\mathrm{int}}(\omega)\varphi^\circ_v(\mathbf{r}) = -\hat{P}_c\hat{V}'_{\mathrm{ext}}(\omega)\varphi^\circ_v(\mathbf{r})$$

where

$$\hat{H}^\circ = -\frac{1}{2}\nabla + \hat{V}^\circ_{\mathrm{XC}} + \hat{V}^\circ_{\mathrm{ext}} + \hat{V}^\circ_{\mathrm{H,solute}} + \hat{V}^\circ_{\mathrm{H,solvent}} + \hat{V}^\circ_{\epsilon}$$

$$\hat{V}_{\mathrm{int}}(\omega) = \hat{V}'_{\mathrm{XC}}(\omega) + \hat{V}'_{\mathrm{ext}}(\omega) + \hat{V}'_{\mathrm{H,solute}}(\omega) + \hat{V}'_{\mathrm{H,solvent}}(\omega) + \hat{V}'_{\epsilon}(\omega)$$



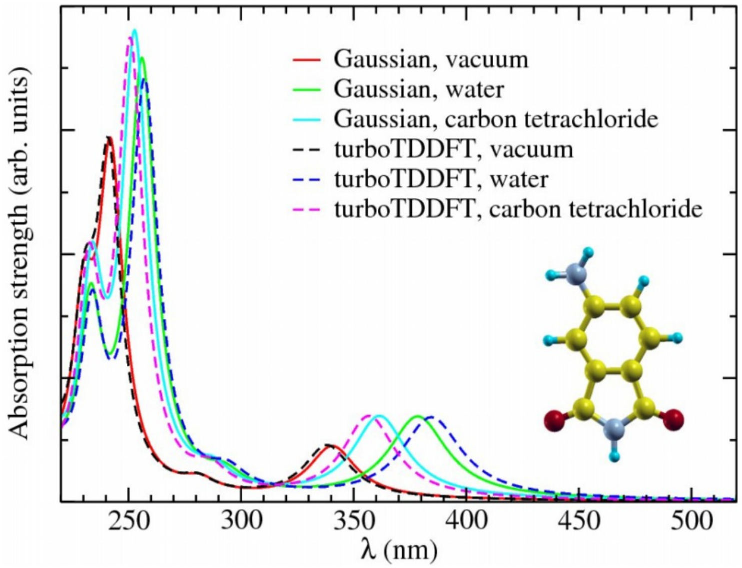
The solute and solvent response charge densities read:

$$\tilde{n}'_{\mathrm{solute}}(\mathbf{r},\omega) = 2\sum_v \varphi^\circ_v(\mathbf{r})\left[\tilde{\varphi}'_v(\mathbf{r},\omega) + \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)\right] \quad\longrightarrow\quad \hat{V}'_{\mathrm{H,solute}}(\omega)$$

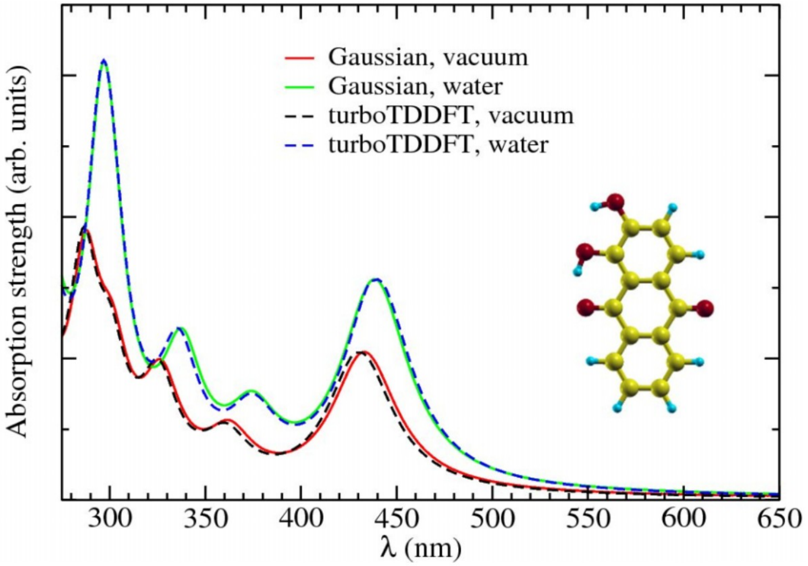
$$\tilde{n}'_{\mathrm{solvent}}(\mathbf{r},\omega) = \frac{1}{4\pi}\nabla\ln\epsilon(\mathbf{r})\cdot\nabla\left(\hat{V}'_{\mathrm{H,solute}}(\omega) + \hat{V}'_{\mathrm{H,solvent}}(\omega)\right) - \frac{\epsilon(\mathbf{r})-1}{\epsilon(\mathbf{r})}\tilde{n}'_{\mathrm{solute}}(\mathbf{r},\omega) \quad\longrightarrow\quad \hat{V}'_{\mathrm{H,solvent}}(\omega)$$

Examples (using B3LYP hybrid functional)

4-aminophthalimide (4-AP)



alizarin

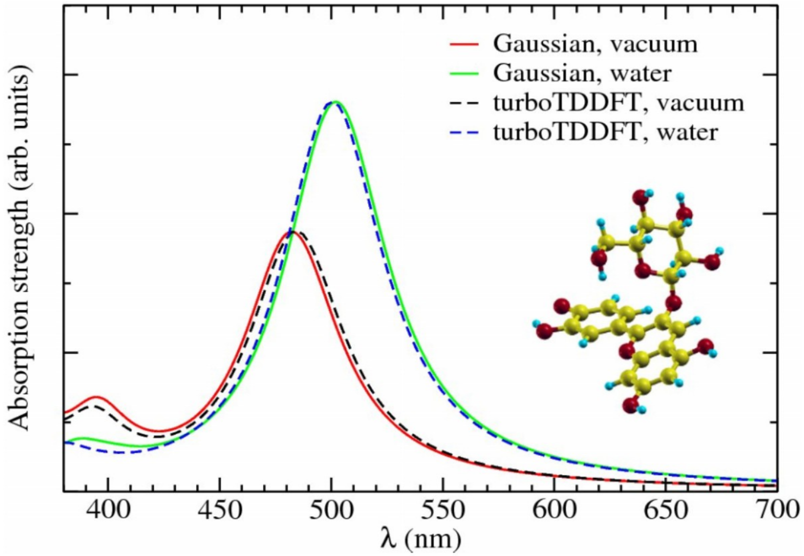


The solvatochromic shifts of the absorption peaks in the spectra are due to two effects:

- *geometrical* (relaxation in vacuum VS solvent);

- *dielectric screening* (electronic excitations are screened by the solvent)

cyanin



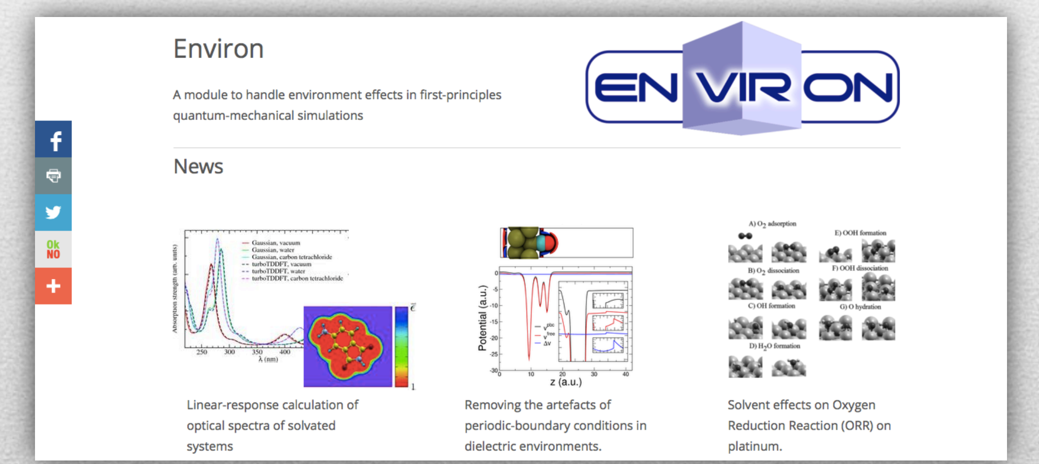
I. Timrov, O. Andreussi, A. Biancardi, N. Marzari, S. Baroni,
J. Chem. Phys. ***142****, 034111 (2015).*

The Environ module

A library for continuum environments in QE

Environ as a plugin of QE

- Interfaced with PW, NEB, CP, and TDDFpT
- Planned extension to PHonon, (and Yambo)
- Available on QE-Forge
  http://qe-forge.org/gf/project/electroemb/
- Official release, infos, news, etc. on
  www.quantum-environ.org



Environ

A module to handle environment effects in first-principles quantum-mechanical simulations

News

Linear-response calculation of optical spectra of solvated systems

Removing the artefacts of periodic-boundary conditions in dielectric environments.

Solvent effects on Oxygen Reduction Reaction (ORR) on platinum.

- Plugins activated by the `"exe.x --plugin"` (e.g. `pw.x --environ`) command-line option
- Handling of input keywords:
  - Independent input file (environ.in)
- Print outs: summary, timing, debug
  - Internal debug with an internal verbose=integer keyword
  - Not (yet) interfaced with the post-processing (PP) code

Interfaced with QE via plugins

- Designed for arbitrary “external” potentials which need to be computed along the SCF (may depend on electronic density)
- Each physical embedding requires up to three ingredients:
  - Contribution to the Kohn-Sham potential (in real-space)
  - Contribution to the total energy
  - Contribution to the inter-atomic forces

Environ as a self-standing library

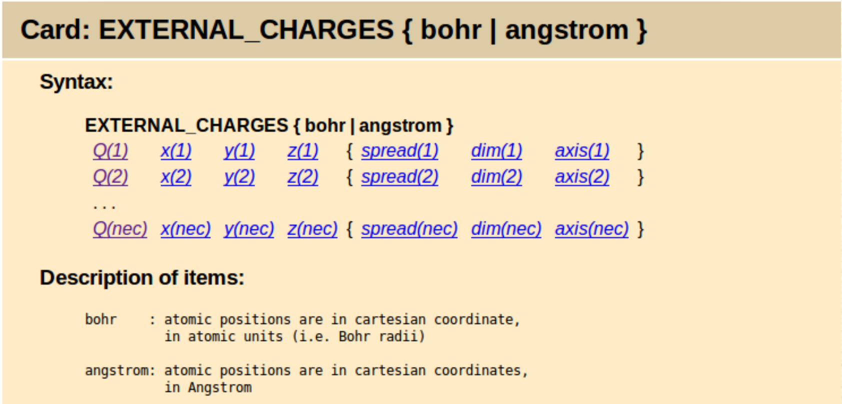
- Continuum dielectric
- External pressure
- Surface tension
- Periodic-boundary-conditions corrections in real-space (especially useful for slabs)

- Fixed user-defined distributions of charges
- Fixed user-defined dielectric regions

- Electrochemical diffuse-layer (in progress)

Available Embeddings

External Charges



Card: EXTERNAL_CHARGES { bohr | angstrom }

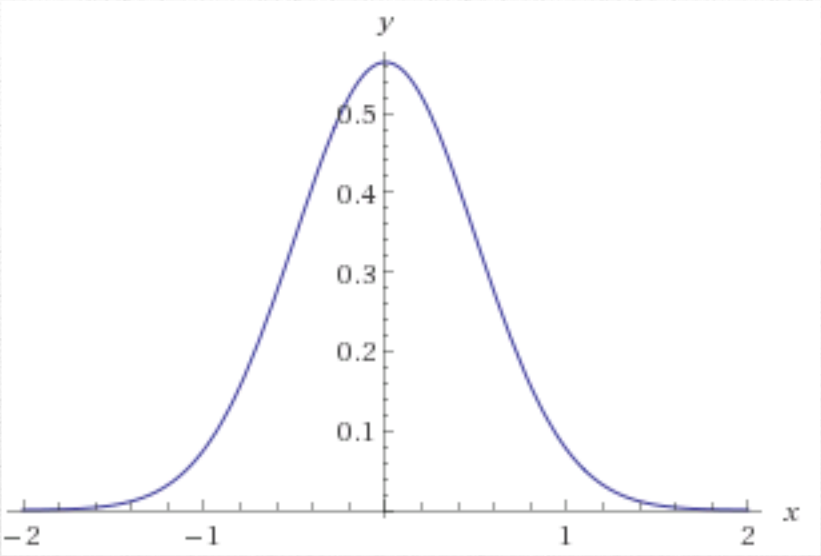
Syntax:

```
EXTERNAL_CHARGES { bohr | angstrom }
 Q(1)    x(1)    y(1)    z(1)    { spread(1)    dim(1)    axis(1)    }
 Q(2)    x(2)    y(2)    z(2)    { spread(2)    dim(2)    axis(2)    }
 . . .
 Q(nec)  x(nec)  y(nec)  z(nec)  { spread(nec)  dim(nec)  axis(nec)  }
```

Description of items:

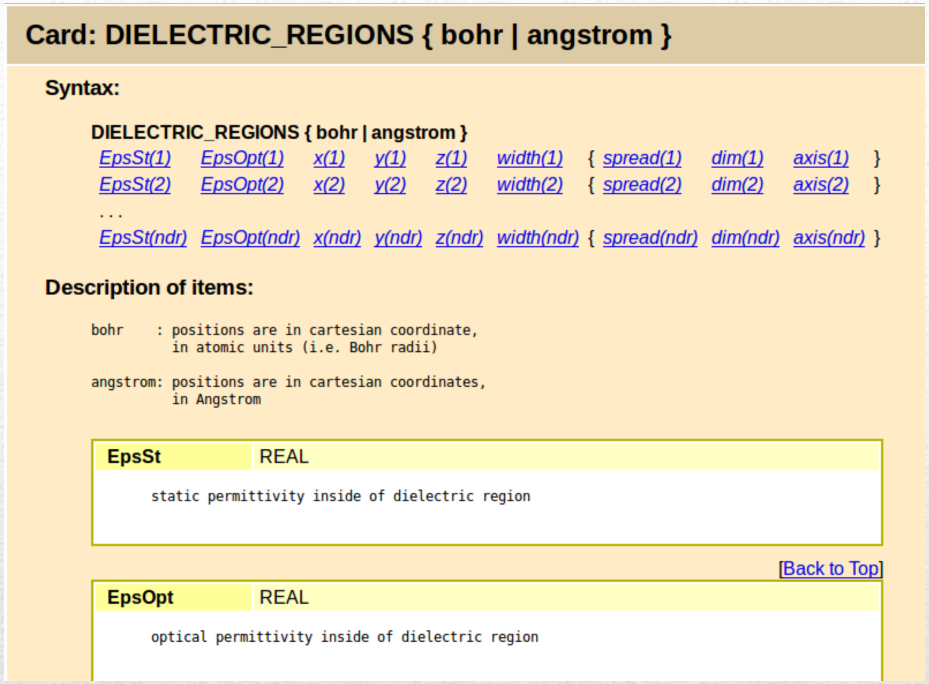
```
bohr    : atomic positions are in cartesian coordinate,
          in atomic units (i.e. Bohr radii)

angstrom: atomic positions are in cartesian coordinates,
          in Angstrom
```

- Classical (fixed) charge distributions
- Compensate extra charge in simulation cell
- QM/MM (only electrostatics up to now)



- Shape given by Gaussian function exp($||x-x_0||^2/\text{spread}^2$)
- Possibility to define multiple 0D-1D-2D charges

Dielectric regions



Card: DIELECTRIC_REGIONS { bohr | angstrom }

Syntax:

```
DIELECTRIC_REGIONS { bohr | angstrom }
EpsSt(1)   EpsOpt(1)   x(1)   y(1)   z(1)   width(1)   { spread(1)   dim(1)   axis(1)   }
EpsSt(2)   EpsOpt(2)   x(2)   y(2)   z(2)   width(2)   { spread(2)   dim(2)   axis(2)   }
. . .
EpsSt(ndr) EpsOpt(ndr) x(ndr) y(ndr) z(ndr) width(ndr) { spread(ndr) dim(ndr) axis(ndr) }
```

Description of items:

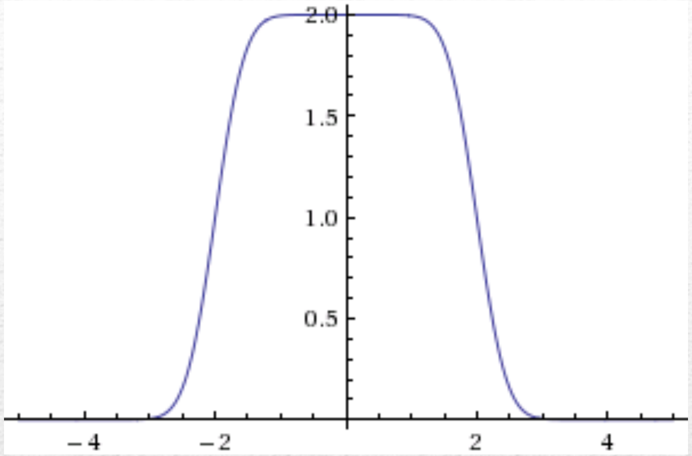
```
bohr    : positions are in cartesian coordinate,
          in atomic units (i.e. Bohr radii)

angstrom: positions are in cartesian coordinates,
          in Angstrom
```

EpsSt	REAL
	static permittivity inside of dielectric region

[Back to Top]

EpsOpt	REAL
	optical permittivity inside of dielectric region

- Solvent exclusion regions
- Reduce complexity of systems (substrates effects, interfaces, etc.)



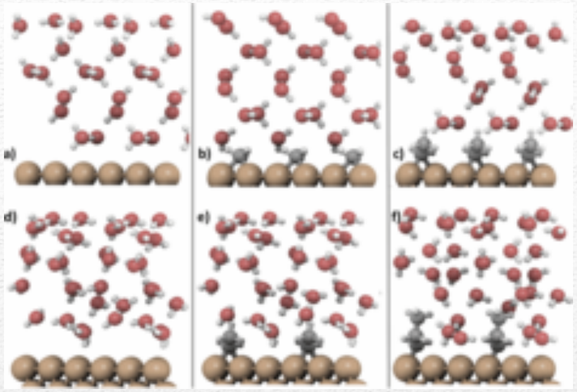
- Shape given by complementary error function: erfc((||x-x_0||-width)/spread)
- Possibility to define multiple 0D-1D-2D regions
- At the intersection, input orders count

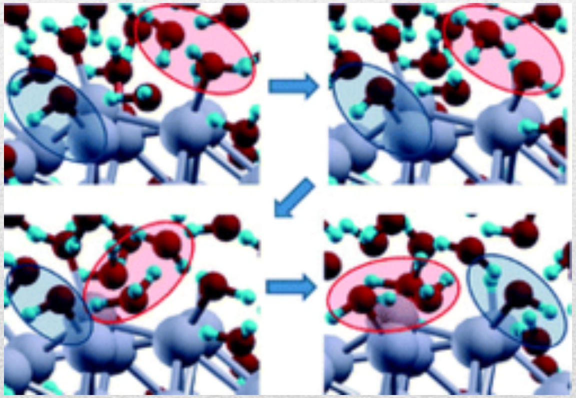
Environ References

- G. Fisicaro, L. Genovese, O. Andreussi, N. Marzari, and S. Goedecker, "A generalized Poisson and Poisson-Boltzmann solver for electrostatic environments", *J. Chem. Phys.* **144**, 014103 (2016)
- I. Timrov, O. Andreussi, A. Biancardi, N. Marzari and S. Baroni, "Self-consistent continuum solvation for optical absorption of complex molecular systems in solution", *J. Chem. Phys.* **142,** 034111 (2015)
- O. Andreussi and N. Marzari, "Electrostatics of solvated systems in periodic boundary conditions", *Phys. Rev. B* **90**, 245101 (2014)
- C. Dupont, O. Andreussi and N. Marzari, "Self-consistent continuum solvation (SCCS): The case of charged systems", *J. Chem. Phys.* **139**, 214110 (2013)
- O. Andreussi, I. Dabo and N. Marzari, "Revised self-consistent continuum solvation in electronic structure calculations", *J. Chem. Phys.* **136**, 064102 (2012).

Using SCCS

- Alkyl-growth catalysis (M. Montemore, O. Andreussi, J. Medlin, "Hydrocarbon Adsorption in an Aqueous Environment: A Computational Study of Alkyls on Cu(111)", *J. Chem. Phys.* **145**, 074702 (2016)
- Oxygen reduction reaction on Pt nanoparticles (L. Sementa, O. Andreussi, W.A. Goddard, and A. Fortunelli, "Catalytic activity of Pt_38 in the oxygen reduction reaction from first-principles", *Catal. Sci and Tech.* **6**, 6901 (2016)) and clean surfaces (A. Fortunelli, W.A. Goddard, Y. Sha, T.H. Yu, L. Sementa, G. Barcaro and O. Andreussi, "Dramatic Increase in the Oxygen Reduction Reaction for Platinum Cathodes from Tuning the Solvent Dielectric Constant", *Angew. Chem. Int. Ed.* **53**, 1 (2014)
- Charge transfer in Cu-amyloids (G. La Penna, C. Hureau, O. Andreussi and P. Faller, "Identifying, by First-Principles Simulations, Cu[Amyloid-beta] Species Making Fenton-Type Reactions in Alzheimer's Disease", *J. Phys. Chem. B* **117**, 16455 (2013))





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- Iuri Timrov, SISSA – EPFL
- Alessandro Biancardi, SISSA

- Alessandro Fortunelli & Luca Sementa, CNR-Pisa
- Mattew Montemore, University of Colorado
- Giovanni la Penna, CNR-Firenze

EPFL
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

THEOS
THEORY AND SIMULATION
OF MATERIALS