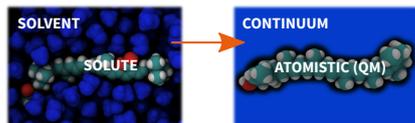


# Solvent -aware Interfaces in Continuum Solvation

 O. Andreussi<sup>1,2</sup>, G. Fisicaro<sup>3</sup>, S. Goedecker<sup>3</sup>, N. Marzari<sup>2</sup>

## MOTIVATIONS

Continuum models of solvation are multiscale approaches that are used to model complex systems, where a distinction can be made between an important component and its environment.



Key ingredient is the definition of **the interface** between the two regions:

- It should only be defined on the degrees of freedom of the important component.
- It should be defined so as to provide clean derivatives with respect to the degrees of freedom of the system, in order to allow optimizations.
- It should only describe the region of space that is accessible to the environment.

This last feature is usually neglected, but it is crucial in many applications and in hybrid atomistic/continuum approaches.

## CONTINUUM SOLVATION

Continuum models of solvation have long played a key role in quantum-chemistry calculations [1], but have only recently started to appear in the condensed matter and materials communities [2-3]. By integrating out all the environment degrees of freedom, a finer control on the physical important aspects of the problem can be achieved, together with a substantial reduction of the computational burden. This will allow the high-throughput modeling of wet interfaces, which is crucial in searching for novel materials in electrochemistry and catalysis.

The ingredients of our recently developed approaches are the following:

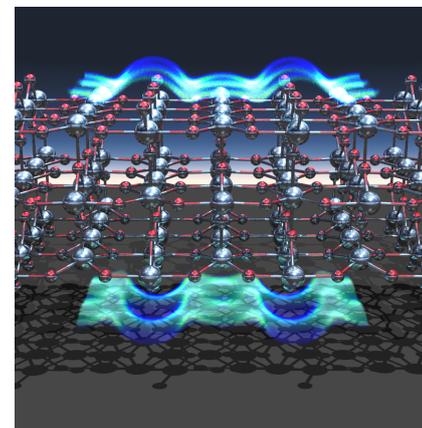
- **Electrostatic:** the continuum has an associated dielectric screening, which modifies electrostatic interactions in the system

$$\nabla \cdot \epsilon(s(\mathbf{r})) \nabla \phi = -4\pi \rho(\mathbf{r})$$

- **Non-Electrostatic:** short range interactions are assumed to be proportional to the surface and volume of the interface.

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

Interface function  
 $s(\rho^{\text{el}}(\mathbf{r}); \{\mathbf{R}_a^{\text{ion}}\}; \mathbf{r})$   
 Continuous and smooth function that goes from 1 to 0 in passing from the system region to the continuum environment

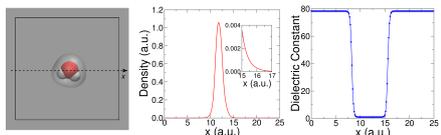


Polarization charge surrounding a TiO2 slab. Despite being inaccessible to the solvent molecules, low-density regions inside the crystal may be filled by the continuum environment.

## SELF-CONSISTENT CONTINUUM SOLVATION (SCCS) [2-7,9]

The interface function is defined in terms of the electronic density of the system

$$s(\rho^{\text{el}}(\mathbf{r}); \mathbf{r}) = \begin{cases} 1 & \rho > \rho^{\text{max}} \\ s(\log(\rho^{\text{el}}(\mathbf{r}))) & \\ 0 & \rho < \rho^{\text{min}} \end{cases}$$



The continuum embedding (right) starts at the outskirts of the quantum-mechanical electronic density of the studied system (left and central central)

- **PROs:** compact formulation that relies on a minimal number of global parameters ( $\rho^{\text{max}}$  and  $\rho^{\text{min}}$ ), automatically adapt to electronic degrees of freedom; no direct contributions to interatomic forces.
- **CONs:** more computationally demanding, less flexible to improve accuracy (anions require separate parameterization), electronic optimization may be hindered

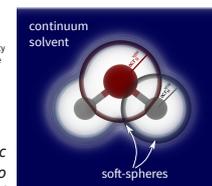
## SOFT-SPHERES CONTINUUM SOLVATION (SSCS) [7-9]

The interface function is built as the product of atom-centered smooth differentiable functions

$$s(\{\mathbf{R}_a^{\text{ion}}\}; \mathbf{r}) = 1 - \prod_a h_a(\{\xi\}; \|\mathbf{r} - \mathbf{R}_a^{\text{ion}}\|)$$

Soft-spheres parameters  
 - softness: global, fixed for stability  
 - steric radii: specific, literature  
 - scaling factor: global, tunable

Go from 0 to 1 as the argument goes through the soft-sphere radius

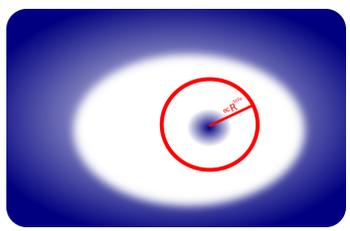


Soft-spheres interface for a solvated water molecule, soft-sphere radii are built by uniform scaling of atomic van der Waals radii

- **PROs:** more flexible parameterization, individual spheres on specific atomic types can be adjusted, providing a remarkable accuracy also for charged systems; less computationally demanding; analytical contributions to interatomic forces.
- **CONs:** larger number of parameters requires more careful tuning and validation

## SOLVENT-AWARE INTERFACES

A non-local contribution to the interface function: for each point in space a spherical region is sampled and the continuum is allowed only if its volume fraction in the sphere is larger than the volume of a solvent molecule. The new interface is built in terms of smooth differentiable functions, keeping the overall approach well-behaved for optimizations over the solute degrees of freedom



$$f(\mathbf{r}) = \frac{1}{V_{\text{solvent}}} \int s(\mathbf{r}') h(\{\xi\}; \|\mathbf{r} - \mathbf{r}'\|) d\mathbf{r}'$$

$$\hat{s}(\mathbf{r}) = s(\mathbf{r}) + (1 - s(\mathbf{r})) r(\{\eta\}; f(\mathbf{r}))$$

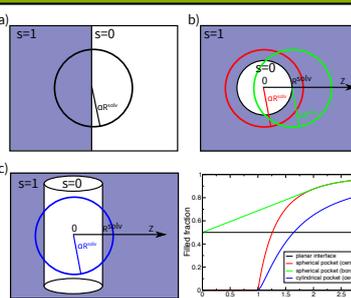
$$F[\hat{s}(\mathbf{r})] = \int g(\hat{s}(\rho^{\text{el}}(\mathbf{r}), \{\mathbf{R}_a\}; \mathbf{r})) d\mathbf{r}$$

$$\frac{\delta F[\hat{s}(\mathbf{r})]}{\delta \hat{s}} = \frac{\delta F[s(\mathbf{r})]}{\delta s} (1 - r(f(\mathbf{r}))) + \int \frac{\delta F[s(\mathbf{r}')] }{\delta s} (1 - s(\mathbf{r}')) \hat{r}(f(\mathbf{r}')) h(\mathbf{r} - \mathbf{r}') d\mathbf{r}'$$

## CHOICE OF THE PARAMETERS

The new formulation of the interface introduces five new parameters. Of these, the solvent radius has a well-defined physical and can be obtained from the literature or from simple simulations. Two parameters are introduced to smoothen the definition of the interface, thus improving numerical stability; these parameters can be tuned on performances.

- scaling factor: controls the total size of the sampled space, must be larger than 1, but not too large.
- filled fraction threshold: depends on the kind of artefacts one needs to correct, may be tuned to improve accuracy.



Simple geometrical reasons provide some boundaries for the undefined parameters: a) the new interface should not change at a sharp planar boundary, thus the threshold should be larger than 0.5; b) in order to completely fill a spherical cavity the size of a solvent molecule, the threshold should be lower than the red curve; c) filling elongated cavities requires even lower thresholds.

## IMPLEMENTATION IN EXISTING CODES

### BigDFT [9,10]

Implementation of SCCS and SSCS versions of the continuum dielectric

- **Advanced Poisson solver:** based on a Green's function formalism, to handle periodic systems, surfaces and isolated systems without boundary conditions artifacts.
- **Linear scaling DFT:** massively parallel code using a wavelet basis set, able to treat large atomistic systems from first-principles [6].
- **Minima Hopping:** for global minimum search and reaction path investigation.

### Quantum ESPRESSO [11]

Environ module, last official release Environ\_0.2 in Feb 2016, next release Environ\_1.0 in Jul 2017. Interfaced with

- **PW:** single-point calculations, geometry optimization, cell relaxation, Born-Oppenheimer molecular dynamics, with pseudo-potentials, plane-waves basis set, reciprocal zone sampling for metallic systems, hybrid functionals and Hubbard U corrections.
- **NEB:** calculation of transition states and reaction rates via the Nudged Elastic Band method.
- **TDDFT:** calculation of excitations energies and optical spectra via Time-Dependent DFT.
- **CP:** Car-Parrinello and damped molecular dynamics simulations on large systems.

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## FUTURE DEVELOPMENTS

- **Applications:** parametrization, tuning and validation on electrochemical systems and reactions. Applications to noble metal surfaces and transition metal oxides for batteries and fuel cells.
- **Properties:** coupling with the calculation of magnetic resonance (NMR and EPR) and infra-red (IR) spectroscopies.
- **HPC:** Optimization for large systems on parallel and hybrid (CPU/GPU) architectures.

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