

Soft-sphere continuum solvation in electronic structure calculations

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Leeds (and remotely), England

Overview

1 Motivation

- Complex electrostatic environments

2 Electrostatic solvers

- Generalized Poisson equation
- Poisson-Boltzmann equation

3 Soft-sphere solvation model

- Build up the dielectric cavity
- Non-electrostatic terms to the total energy
- Model parametrization

4 Structure predictions in vacuum and wet environments

5 Conclusions

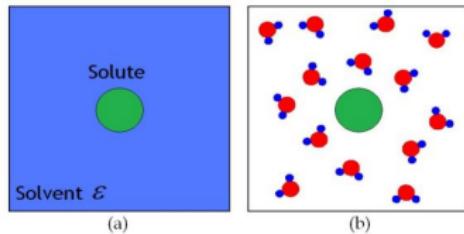
Motivation

- Experimental processes take place in neutral and ionic solutions
- Synthesis and growth, solar-energy harvesting or electro-catalytic water splitting
- Chemical reactions
- Extend vacuum-based *ab-initio* simulations to complex wet environments

¹B. Schaefer *et al.* J. Chem. Phys. **140**, 214102 (2014)

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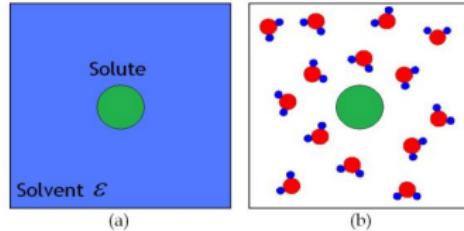


Continuum solvation

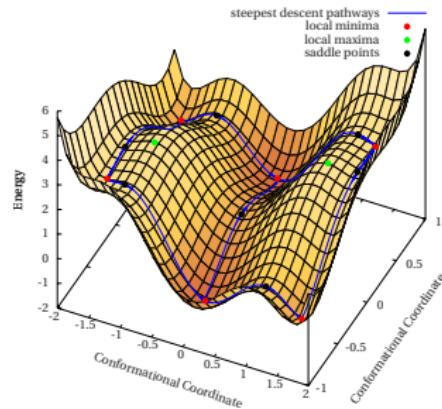
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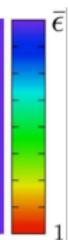
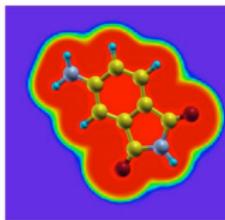


Born-Oppenheimer energy surface¹
(~ 10^4 DFT runs!)

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From vacuum to complex wet environments

Dielectric cavity $\epsilon(\mathbf{r})$



Generalized Poisson equation

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

Model for non electrostatic terms to the energy

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

From vacuum to complex wet environments

Kohn-Shan energy in vacuum read

$$E[\rho] = T[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \rho\phi[\rho]d\mathbf{r} + E_{xc}[\rho]$$

where ϕ is the electrostatic potential, solution of the **Standard Poisson equation** in vacuum

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

Neutral or ionic wet environments

Generalized Poisson equation (GPe)

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

Poisson-Boltzmann equation (PBe)

$$\nabla \cdot \epsilon(\mathbf{r})\nabla\phi(\mathbf{r}) = -4\pi \left[\rho(\mathbf{r}) + \rho^{ions}[\phi](\mathbf{r}) \right]$$

- Electrostatic solvers
- Analytical dielectric cavity
 - Soft-sphere (atomic coordinates)
 - Self-consistent (electronic density)
- Model for the non-electrostatic terms to the total energy

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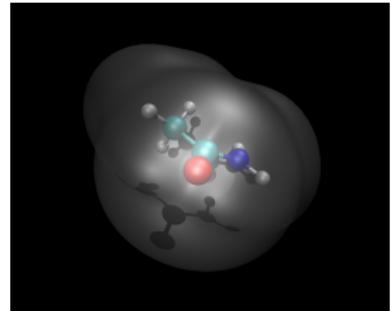
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Self-consistent iterative procedure for GPe

Generalized Poisson equation

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Vacuum-like problem²

$$\nabla^2 \phi(\mathbf{r}) = -4\pi \left[\frac{\rho(\mathbf{r})}{\epsilon(\mathbf{r})} + \rho^{\text{iter}}(\phi(\mathbf{r})) \right]$$

Algorithm Self-Consistent iterative procedure (SC)

- 1: set ρ_0^{iter}
- 2: **for** $k = 0, 1, \dots$ **do**
- 3: $\rho_k^{\text{tot}} = \rho/\epsilon + \rho_k^{\text{iter}}$
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- 5: $\rho_{k+1}^{\text{iter}} = \frac{1}{4\pi} \nabla \ln \epsilon \cdot \nabla \phi_k$
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- 7: $r_{k+1} = \rho_{k+1}^{\text{iter}} - \rho_k^{\text{iter}}$
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where

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

Action integral \rightarrow Minimization problem

$$\mathcal{I} = \int \left[\frac{1}{2} \nabla \phi(\mathbf{r}) \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) - 4\pi \rho(\mathbf{r}) \phi(\mathbf{r}) \right] d\mathbf{r}.$$

Preconditioned steepest descent (PSD)

Iteration number $N_{\text{iter}} \propto k$

$k = \frac{d_{\max}}{d_{\min}} \implies$ condition number

²O. Andreussi *et al.* J. Chem. Phys. 136, 064102 (2012)

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Preconditioned conjugate gradient algorithm for GPe⁴

Iteration number $N_{\text{iter}} \propto \sqrt{k}$

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Algorithm Preconditioned conjugate gradient (PCG)

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1:  $r_0 = b - A\phi_0$ 
2: for  $k = 0, 1, \dots$  do
3:    $v_k = P^{-1}r_k$ 
4:   if  $k = 0$  then
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Preconditioner³:

$$1. \quad r'_k(\mathbf{r}) = \frac{r_k(\mathbf{r})}{\sqrt{\epsilon(\mathbf{r})}}$$

$$2. \quad \nabla^2 v'_k(\mathbf{r}) = -4\pi r'_k(\mathbf{r})$$

$$3. \quad v_k(\mathbf{r}) = \frac{v'_k(\mathbf{r})}{\sqrt{\epsilon(\mathbf{r})}}$$

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

Change of variable $v'_k(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} v_k(\mathbf{r})$

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Operator:

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

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³L. Genovese *et al.* J. Chem. Phys. **125**, 074105 (2006)

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

Change of variable $v'_k(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} v_k(\mathbf{r})$

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla v_k(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} \nabla^2 v'_k(\mathbf{r}) - v'_k(\mathbf{r}) \nabla^2 \sqrt{\epsilon(\mathbf{r})}$$

Operator:

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

where

$$q(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} \nabla^2 \sqrt{\epsilon(\mathbf{r})}$$

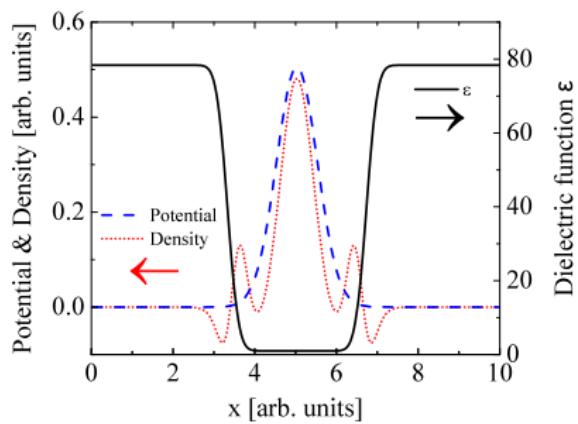
³L. Genovese *et al.* J. Chem. Phys. **125**, 074105 (2006)

⁴G. Fisicaro *et al.* J. Chem. Phys. **144**, 014103 (2016)

Numerical solutions of the GPe

Finite difference discretization on a orthorhombic grid

- $\phi(\mathbf{r})$ → electrostatic potential
- $\rho(\mathbf{r})$ → input charge density
- $\epsilon(\mathbf{r})$ → dielectric function



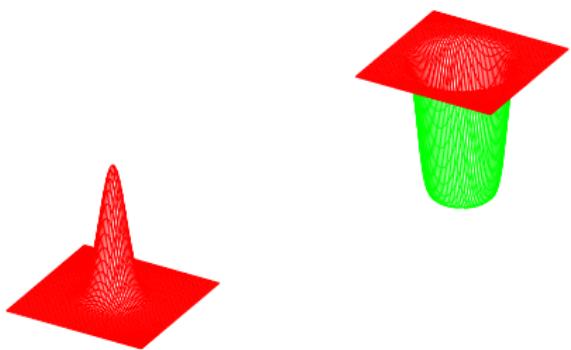
Operator

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



$$\mathcal{A}\phi = b$$

$$b = -4\pi\rho(\mathbf{r})$$



Numerical solutions of the GPe

Boundary conditions

- free
- surface
- periodic

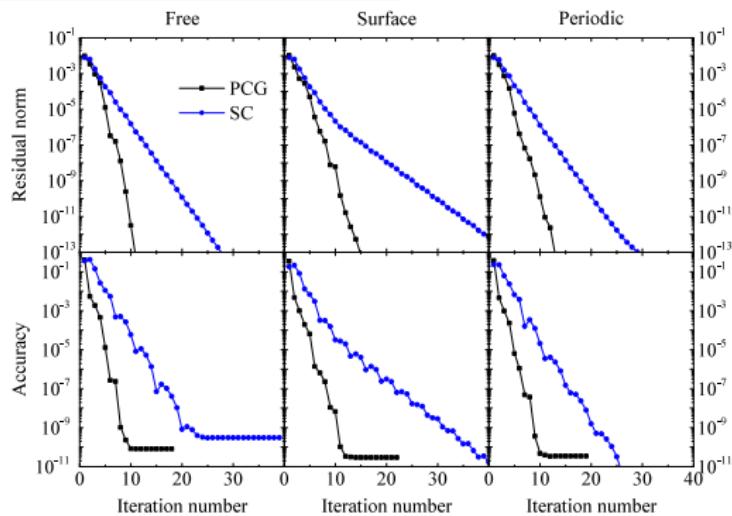
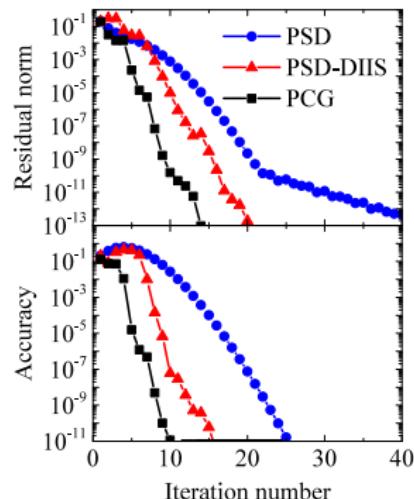


Figure: Euclidean norm of the residual vector r_k and accuracy of the solution (BigDFT Poisson solver).

Free boundary conditions



Accuracy $\sim 10^{-10}$
in ~ 10 iterations!

Poisson-Boltzmann equation

Electrostatic problem with ionic solvent:

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \phi(\mathbf{r}) = -4\pi \left[\rho(\mathbf{r}) + \rho^{ions}[\phi](\mathbf{r}) \right]$$

$$\rho^{ions}[\phi](\mathbf{r}) = eN_A \sum_{i=1}^m Z_i c_i[\phi](\mathbf{r})$$

Adding finite ion size effects

Steric force

$$F_i^S = -kT \nabla \ln \left(\frac{1}{1 - \sum_{j=1}^m \frac{c_j}{c_j^{\max}}} \right)$$

Imposing equilibrium between

Thermal force

$$F_i^T = -kT \nabla \ln(c_i)$$

Electric force

$$F_i^E = -Z_i e \nabla \phi$$

Modified Poisson-Boltzmann equation

$$c_i[\phi](\mathbf{r}) = \frac{c_i^\infty \exp\left(-\frac{Z_i e \phi(\mathbf{r})}{kT}\right)}{1 + \sum_{j=1}^m \frac{c_j^\infty}{c_j^{\max}} \left[\exp\left(-\frac{Z_j e \phi(\mathbf{r})}{kT}\right) - 1 \right]}$$

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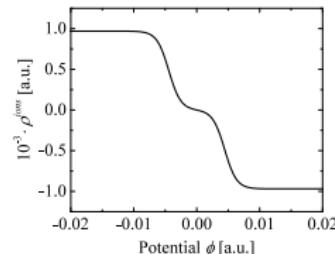
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PCG for linear Poisson-Boltzmann equation

Iteration number $N_{iter} \propto \sqrt{k}$
 $k \implies$ condition number

Algorithm Preconditioned Conjugate Gradient (PCG)

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1:  $r_0 = b - A\phi_0$ 
2: for  $k = 0, 1, \dots$  do
3:    $v_k = P^{-1}r_k$ 
4:   if  $k = 0$  then
5:      $p_0 = v_0$ 
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7:      $p_k = v_k + \beta_k p_{k-1}$  (where  $\beta_k = \frac{(v_k, r_k)}{(v_{k-1}, r_{k-1})}$ )
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Preconditioner⁵:

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

Linear PB operator:

$$\begin{aligned}\mathcal{A}v_k(r) &= \nabla \cdot \epsilon(r) \nabla v_k(r) + 4\pi \rho^{ions}[\phi](r) \\ &= -v_k(r) \sqrt{\epsilon(r)} \nabla^2 \sqrt{\epsilon(r)} - 4\pi r_k(r) - v_k(r) \frac{4\pi e^2 N_A}{kT} \sum_{i=1}^m Z_i^2 c_i^\infty\end{aligned}$$

⁵L. Genovese et al. J. Chem. Phys. 125, 074105 (2006)

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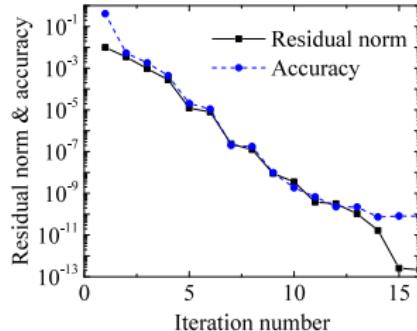
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⇒ Equilibrium between thermal, electric and steric forces

Self-consistent (SC) iterative procedures:

Algorithm SC procedure for (M)PBe

```
1: set  $\rho_0^{\text{ions}}$ 
2: for  $k = 0, 1, \dots$  do
3:    $\rho_k^{\text{tot}} = \rho + \rho_k^{\text{ions}}$ 
4:   solve  $\nabla \cdot \epsilon \nabla \phi_k = -4\pi \rho_k^{\text{tot}}$  (Algorithm SC or PCG)
5:   compute  $\rho_{k+1}^{\text{ions}} = \rho^{\text{ions}}[\phi_k]$ 
6:    $\rho_{k+1}^{\text{ions}} = \eta \rho_{k+1}^{\text{ions}} + (1 - \eta) \rho_k^{\text{ions}}$ 
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8: end for
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Algorithm Improved SC procedure for (M)PBe

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1: set  $\phi_1 = 0$ ,  $\rho_0^{\text{ions}} = 0$ ,  $\rho_1^{\text{ions}}$ ,  $r_0' = \rho$ 
2: for  $k = 1, \dots$  do
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$$c_i[\phi](\mathbf{r}) = \frac{eN_A Z_i c_i^\infty \exp\left(-\frac{Z_i e \phi(\mathbf{r})}{kT}\right)}{1 + \sum_{j=1}^m \frac{c_j^\infty}{c_j^{\max}} \left[\exp\left(-\frac{Z_j e \phi(\mathbf{r})}{kT}\right) - 1 \right]}.$$

⇒ Equilibrium between thermal, electric and steric forces

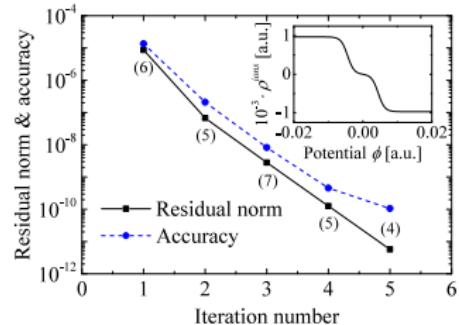
Self-consistent (SC) iterative procedures:

Algorithm SC procedure for (M)PBe

```
1: set  $\rho_0^{ions}$ 
2: for  $k = 0, 1, \dots$  do
3:    $\rho_k^{tot} = \rho + \rho_k^{ions}$ 
4:   solve  $\nabla \cdot \epsilon \nabla \phi_k = -4\pi \rho_k^{tot}$  (Algorithm SC or PCG)
5:   compute  $\rho_{k+1}^{ions} = \rho^{ions}[\phi_k]$ 
6:    $\rho_{k+1}^{ions} = \eta \rho_{k+1}^{ions} + (1 - \eta) \rho_k^{ions}$ 
7:    $r_{k+1} = \rho_{k+1}^{ions} - \rho_k^{ions}$ 
8: end for
```

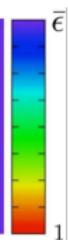
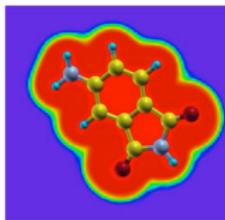
Algorithm Improved SC procedure for (M)PBe

```
1: set  $\phi_1 = 0$ ,  $\rho_0^{ions} = 0$ ,  $\rho_1^{ions}$ ,  $r_0' = \rho$ 
2: for  $k = 1, \dots$  do
3:    $\rho_k^{tot} = r_{k-1}' + \rho_k^{ions} - \rho_{k-1}^{ions}$ 
4:   solve  $\nabla \cdot \epsilon \nabla \phi_k' = -4\pi \rho_k^{tot}$  (Algorithm PCG with  $r_k'$ )
5:    $\phi_k = \phi_k + \phi_k'$ 
6:   compute  $\rho_{k+1}^{ions} = \rho^{ions}[\phi_k]$ 
7:    $\rho_{k+1}^{ions} = \eta \rho_{k+1}^{ions} + (1 - \eta) \rho_k^{ions}$ 
8:    $r_{k+1} = \rho_{k+1}^{ions} - \rho_k^{ions}$ 
9: end for
```



From vacuum to complex wet environments

Dielectric cavity $\epsilon(\mathbf{r})$



Generalized Poisson equation

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

Model for non electrostatic terms to the energy

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

Soft-sphere dielectric cavity⁶

Atomic system of N atoms of coordinates \mathbf{R}_i
(for $i = 1, \dots, N$)

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

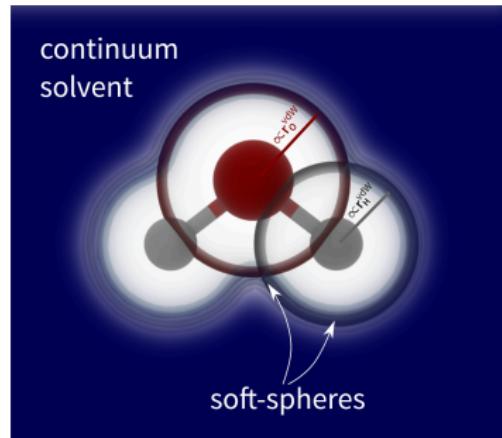
where

- ϵ_0 is dielectric constant of the surrounding medium
- $h(\mathbf{r})$ is an atom centered error functions (radii $r_i = fr_i^{vdW}$ from UFF) varying from 0 inside the cavity to 1 outside

$$h(r_i, \Delta; \|\mathbf{r} - \mathbf{R}_i\|) = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{\|\mathbf{r} - \mathbf{R}_i\| - r_i}{\Delta} \right) \right]$$

being Δ a parameter which controls the transition region ($\approx 4\Delta$ wide)

$$\mathcal{A}v_k(\mathbf{r}) = \nabla \cdot \epsilon(\mathbf{r}) \nabla v_k(\mathbf{r}) = -v_k(\mathbf{r}) \sqrt{\epsilon(\mathbf{r})} \nabla^2 \sqrt{\epsilon(\mathbf{r})} - 4\pi r_k(\mathbf{r})$$



The smooth interface allows for a fast analytic calculation of derivatives and forces

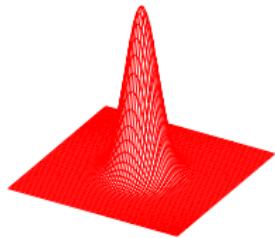
⁶G. Fisicaro *et al.* J. Chem. Theory Comput. **13**, 3829 (2017)

Self-consistent dielectric cavity

Self-consistent cavity mapped by $\rho^{elec}(\mathbf{r})^7$

$$\epsilon(\mathbf{r}) = \epsilon(\rho^{elec}(\mathbf{r}))$$

$$\epsilon(\rho^{elec}) = \begin{cases} 1 & \rho^{elec} > \rho_{max} \\ \exp(t(\rho^{elec})) & \rho_{min} < \rho^{elec} < \rho_{max} \\ \epsilon_0 & \rho^{elec} < \rho_{min} \end{cases}$$

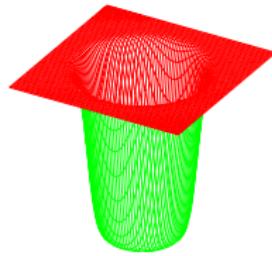


transition between atomistic
vacuum cavity

$$\Downarrow t(x)$$

the full dielectric medium

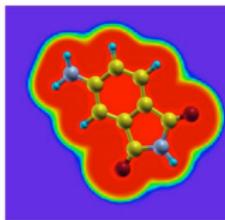
$$t(x) = \frac{\ln \epsilon_0}{2\pi} \left[2\pi \frac{\ln \rho_{max} - x}{\ln \rho_{max} - \ln \rho_{min}} - \sin \left(2\pi \frac{\ln \rho_{max} - x}{\ln \rho_{max} - \ln \rho_{min}} \right) \right]$$



⁷O. Andreussi *et al.* J. Chem. Phys. **136**, 064102 (2012)

From vacuum to complex wet environments

Dielectric cavity $\epsilon(\mathbf{r})$



Generalized Poisson equation

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

Model for non electrostatic terms to the energy

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

Solvation free energy

Electrostatic contribution to the solvation energy

$$\Delta G^{el} = G^{el} - G^0$$

PCM introduced other non-electrostatic terms⁸

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

The non-electrostatic terms G^{cav} , G^{rep} , and G^{dis} can be expressed as linear functions of the “quantum surface” S and “quantum volume” V of the dielectric cavity⁹

$$\Delta G^{sol} = \Delta G^{el} + (\alpha + \gamma)S + \beta V$$

being γ the surface tension of the solvent, α and β solvent-specific tunable parameters.

Introducing the function

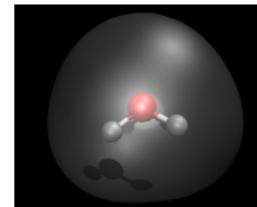
$$\theta[\epsilon](\mathbf{r}) = \frac{\epsilon_0 - \epsilon(\mathbf{r})}{\epsilon_0 - 1},$$

the quantum volume V of the solute can be defined as

$$V[\epsilon] = \int d\mathbf{r} \theta[\epsilon](\mathbf{r}).$$

The associated quantum surface S is

$$S[\epsilon] = \int d\mathbf{r} |\nabla \theta[\epsilon](\mathbf{r})| = \frac{1}{\epsilon_0 - 1} \int d\mathbf{r} |\nabla \epsilon(\mathbf{r})|$$



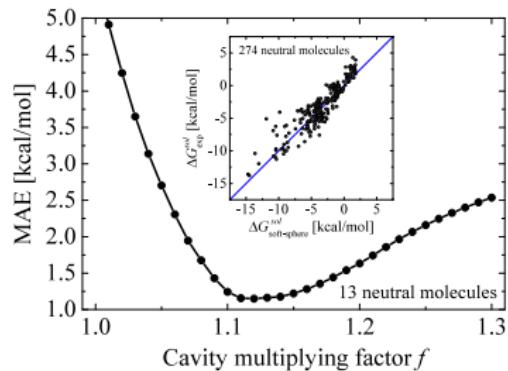
⁸J. Tomasi *et al.* Chem. Rev. **105**, 2999 (2005)

⁹D. A. Scherlis *et al.* J. Chem. Phys. **124**, 074103 (2006)

Soft-sphere model benchmark: solvation free energy results

Calculations for all molecules with:

- Geometry optimization both in vacuum & dielectric environment
- PCG solver for GPe with free BC
- Soft norm-conserving pseudopotentials and PBE functionals
- BigDFT package¹⁰



¹⁰www.bigdft.org

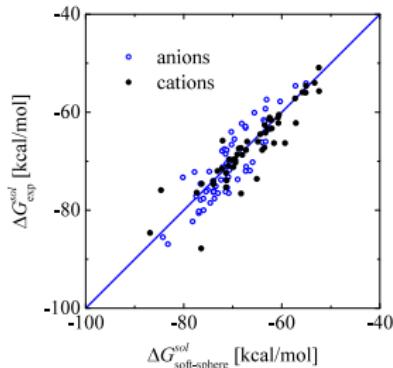


Table: Mean Absolute Errors in aqueous solvation free energies (kcal/mol) for several solvation models (MAEs from Marenich SM8 JCTC (2007)). Model benchmarks refer to same set of 274 neutrals, 60 anions and 52 cations of the Minnesota Solvation Database, version 2012.

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

^a parametrization with UFF radii r_i^{vdW} , $f = 1.16$, $\alpha + \gamma = 11.5$ dyn/cm, $\beta = 0$ GPa.

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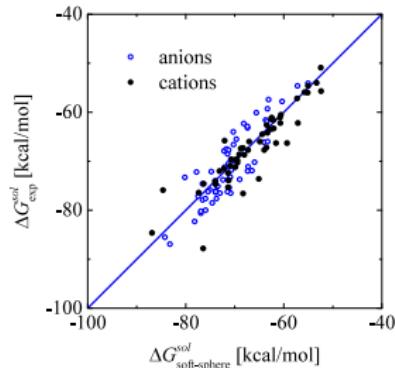
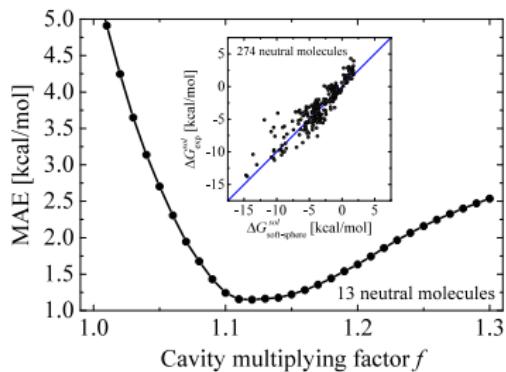


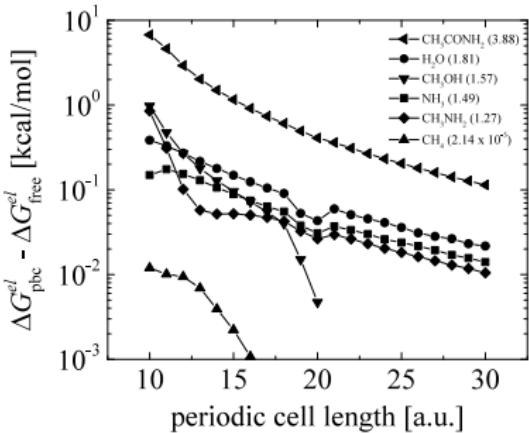
Table: Mean Absolute Errors in nonaqueous solvation free energies (kcal/mol) (SM8 MAE from Marenich SM8 JCTC (2007)). Dataset from Minnesota Solvation Database, version 2012.

Method	mesitylene	ethanol
soft-sphere	0.71	1.28
SM8	0.40	1.53

¹¹www.bigdft.org

Electrostatic solvation energy results

Free vs Periodic boundary conditions

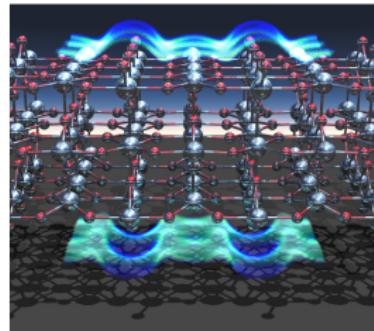


Difference between the electrostatic solvation energy computed with periodic and free boundary conditions as function of the periodic cell length.

Table: Molecule dipole norm in vacuum and water solvent (in Debye).

	Dipole ^{vacuum}	Dipole ^{water}
CH_3CONH_2	3.88	5.76
H_2O	1.81	2.41
CH_3OH	1.57	2.14
NH_3	1.49	1.98
CH_3NH_2	1.27	1.78
CH_4	$2.14 \cdot 10^{-5}$	$1.33 \cdot 10^{-4}$

Surface boundary condition



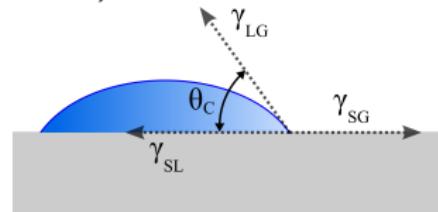
Soft-sphere model benchmark: contact angle and solid-liquid interfaces¹²

The contact angle θ_C quantifies the wettability of a surface

$$\cos \theta_C = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

Interfacial energies

- γ_{SG} = solid-vapor
- γ_{SL} = solid-liquid
- γ_{LG} = liquid-vapor (i.e. the surface tension)



The spreading coefficient S represents the work performed to spread a liquid over a unit surface area:

$$S = \gamma_{SG} - \gamma_{LG} - \gamma_{SL}$$

$S < 0 \Rightarrow$ partial wetting

Table: Simulated spreading coefficient S and contact angle θ_C for several surfaces in contact with implicit water described by the soft-sphere model.

	slab layers	S [mJ/m ²]	θ_C [degree]
silver (001)	8	33	-
SiO ₂ α -quartz cleaved (001)	18	35	-
SiO ₂ α -quartz reconstructed (001)	27	-69	87
Diamond (001)	12	-76	92
Graphene	1	-82	97
CaF ₂ (111)	15	-6.4	24
CaF ₂ (100)	15	121	-

¹²G. Fisicaro *et al.* J. Chem. Theory Comput. **13**, 3829 (2017)

Performances and timings for full SCF runs

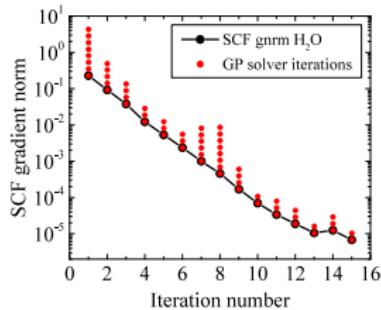
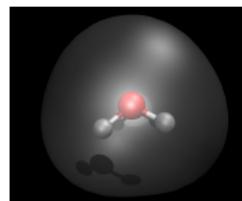
Calculations with

- Soft-sphere model
- PCG solver for GPe with input guess and dynamic exit
- BigDFT package www.bigdft.org

Timings for the protein PDB ID: 1y49 (122 atoms) in water

- Full SCF convergence 49 s
- Solvent/vacuum runtime ratio $\alpha = 1.16$

GP solver performances
for H₂O molecule

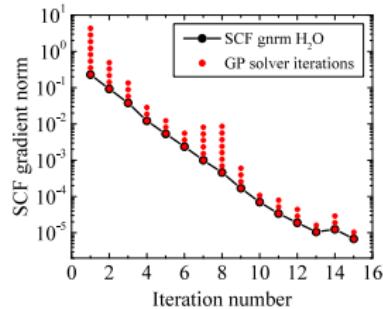
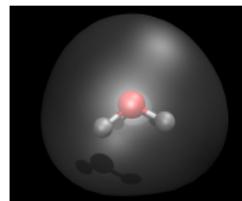


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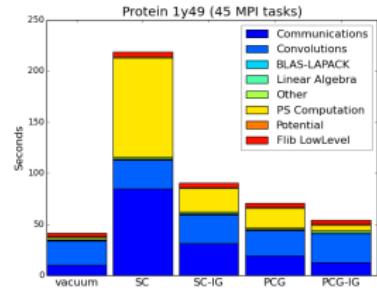
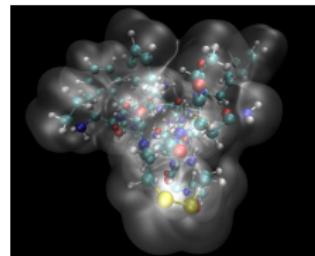
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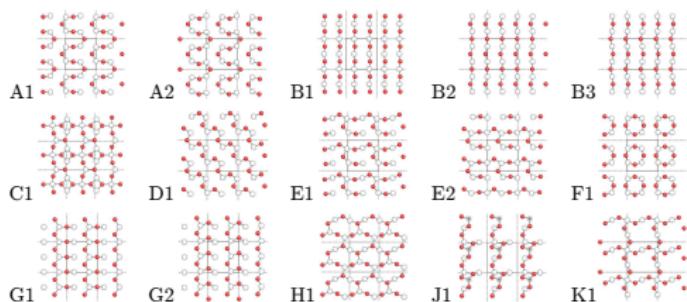
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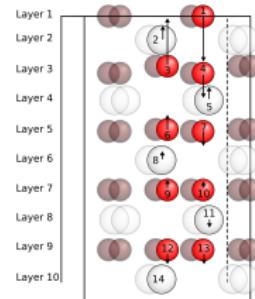
Structure predictions: surface reconstructions of CaF₂

Global structure predictions in vacuum show:

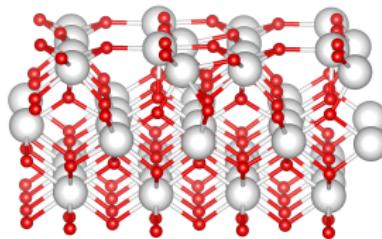
- CaF₂ terminations $\gamma_{111} < \gamma_{100}(111)$
- a plethora of reconstructions for (100) in a small energy range (168 meV per surface atom)



CaF₂ (100) reconstructions¹³



(100) cleaved slab



(100) C1 lowest energy reconstruction

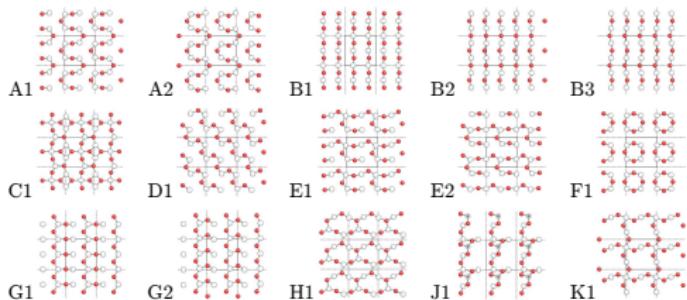
¹³G. Fisicaro et al. Phys. Rev. Materials 1, 033609 (2017)

Structure predictions: surface reconstructions of CaF₂

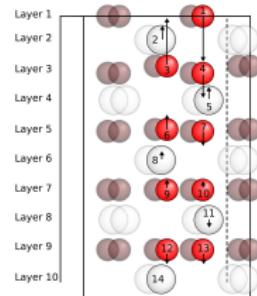
Structure predictions in water suggest that terminations with low-coordination surface atoms (A or B-type) are more stable



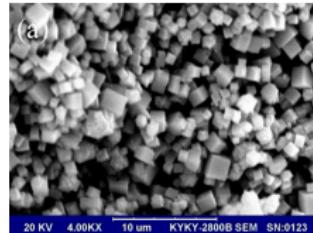
wet environment promote (100) growth instead of the (111)



CaF₂ (100) reconstructions¹⁴



(100) cleaved slab



SEM images of the as-prepared CaF₂ microparticles

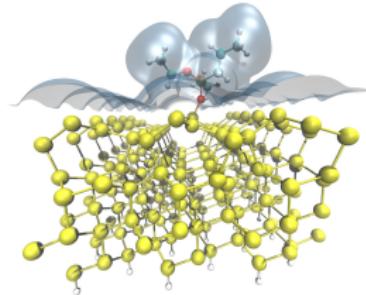
¹⁴G. Fisicaro *et al.* Phys. Rev. Materials 1, 033609 (2017)

Structure predictions: molecular doping of silicon

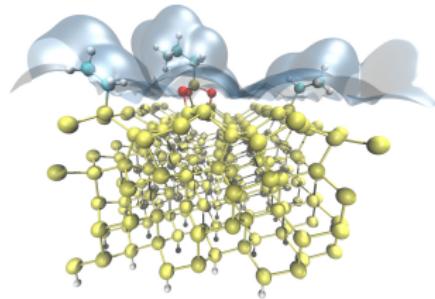
Diethyl-1-propyl phosphonate molecule on top of a silicon (111) surface (mesitylene)¹⁵.

Global structure predictions predicts:

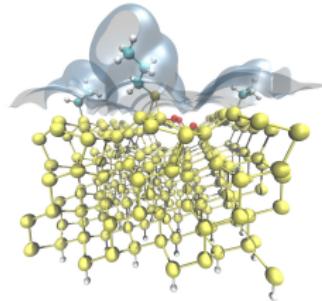
- dissociation of the organic molecule (~ 3.22 eV decrease in energy wrt the not broken configuration)
- chemical adsorption with O-Si bonds
- subsequent double bond between P-Si



Unbroken molecule on (111) silicon surface



Broken molecule with O-Si bonds

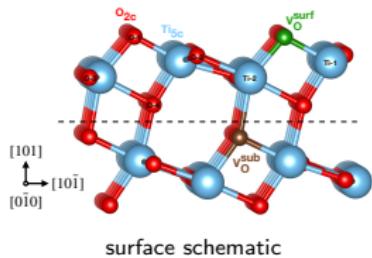
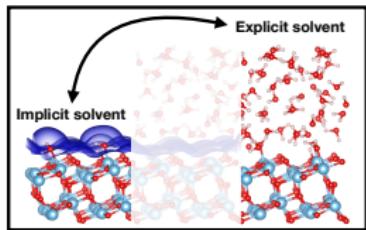


Broken molecule with P-Si bonds

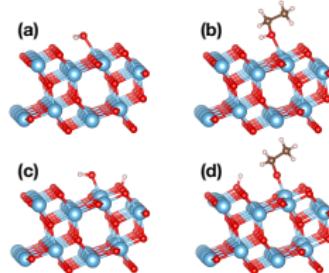
¹⁵R. Puglisi, G. Fisicaro, et al. Sci. Rep. 9, 5647 (2019)

Structure predictions: Anatase TiO₂ (101) surface

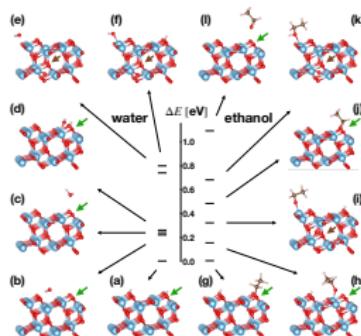
We investigated wet environment¹⁶ effects for ethanol and water adsorption on Anatase TiO₂ (101) surfaces. We performed structure predictions at a density functional theory level for molecules interacting with the perfect and defective anatase (101) surface under both vacuum and wet conditions.



surface schematic



Molecular and dissociative adsorption at perfect surface



Low-energy structures for adsorption at the defective surface (O vacancy)

¹⁶G. Fisicaro, et al. J. Phys. Chem. C 124, 2406-2419 (2020)

Conclusions

- Developed a solver for the Generalized Poisson and Poisson-Boltzmann equation
- Developed an implicit solvation model named “soft-sphere”
- Test and parametrization of the soft-sphere model on
 - dataset of solvation free energies (neutrals and ions) for aqueous and nonaqueous solvents
 - solid-liquid interfaces with contact angle
- Model molecular adsorption at various solid/liquid interfaces

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- Computer resources were provided by the Swiss National Supercomputing Centre (CSCS) under Project ID s707,s869,s963.
- Dr. L. Genovese (L_Sim - CEA Grenoble - France), Prof. S. Goedecker (Uni Basel, Switzerland), Prof. N. Marzari (EPFL and PSI, Switzerland), Prof. O. Andreussi (Boise State University, USA).

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Thank you
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