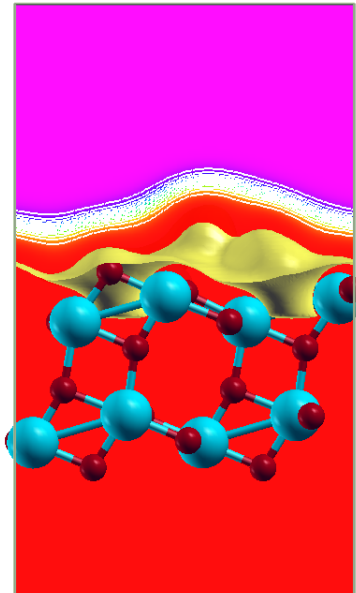


FIRST-PRINCIPLES MOLECULAR DYNAMICS SIMULATIONS AT SOLID-LIQUID INTERFACES WITH A CONTINUUM SOLVENT

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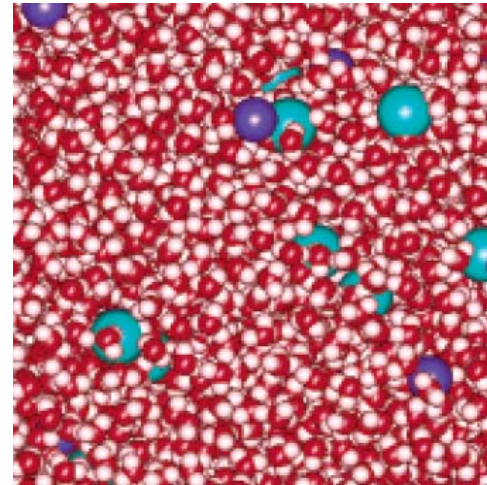
January 22, 2009

OVERVIEW

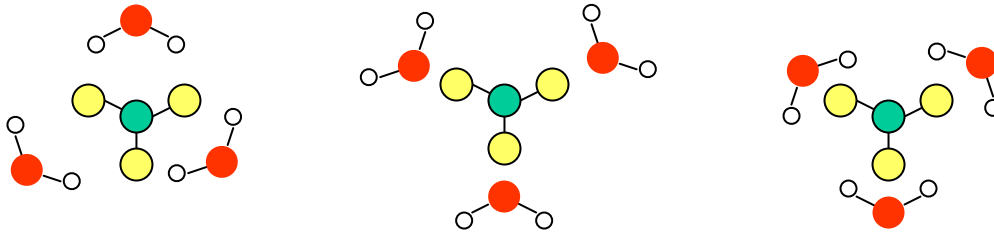
- **Molecular simulations in solution**
- **The continuum solvent model: what and why**
- **An approach to the electrostatic energy in the context of plane-waves and pseudopotentials**
- **The cavitation energy contribution**
- **Applications to π -dimers**
- **The treatment of solid-liquid interfaces**
- **Molecular dynamics at the TiO₂ anatase surface**

MOLECULAR SIMULATIONS IN SOLUTION

The explicit inclusion of the solvent molecules involves several methodological challenges



- Huge number of configurations associated with multiple local minima



- Solid or glassy phases not representing the solution
- Energetics of the solute is lost amidst the massive contribution of the solvent

⇒ **Lengthy molecular dynamics in large supercells**

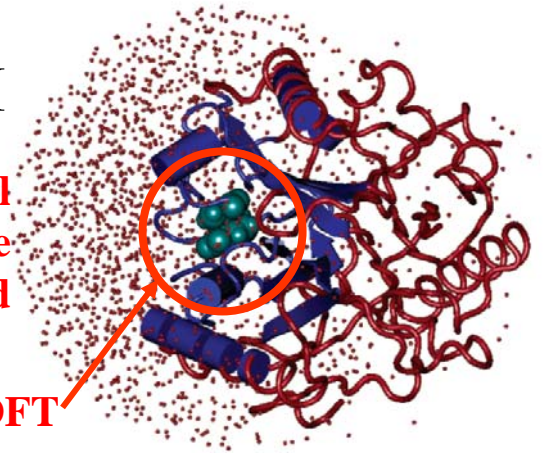
MOLECULAR SIMULATIONS IN SOLUTION

**Alternatives to the
use of explicit
solvents in quantum
simulations**

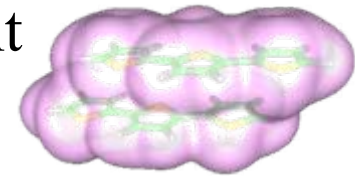
Hybrid QM-MM
methods

Classical
Force
Field

DFT

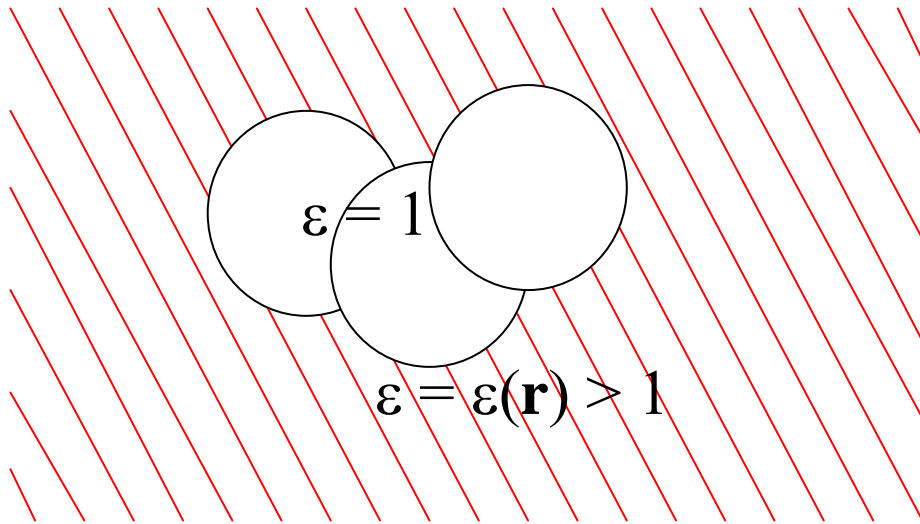


Continuum solvent
methods



Both are common in quantum-chemistry implementations for molecular systems. Little precedents in plane-waves basis frameworks and in materials applications

THE CONTINUUM SOLVENT MODEL



In a polarizable medium, the **solvation free energy** may be written:

$$\Delta G_{\text{sol}} = \Delta G_{\text{ele}} + \Delta G_{\text{cav}} + \dots$$

$$H_{\text{M}} = H_{\text{M}}^0 + V_{\text{int}}[\rho]$$

Describes in an averaged way the dielectric effect of the solvent.
Solute-solvent specific interactions are lost.

THE ELECTROSTATIC CONTRIBUTION, ΔG_{ele}

DFT total energy :

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

The term $\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ is labeled "ions-electrons".
The term $\frac{1}{2} \int \rho\phi[\rho]d\mathbf{r}$ is labeled "Hartree energy, E_H ".

Electrostatic potential:
is computed from ρ using
the Poisson equation

Poisson equation in vacuum $\nabla^2 \phi = -4\pi \rho$

Efficiently solved with FFT

Poisson equation in a dielectric $\epsilon(\mathbf{r})$ $\nabla(\epsilon\nabla\phi) = -4\pi\rho$

More expensive to solve, e.g., with a multigrid technique

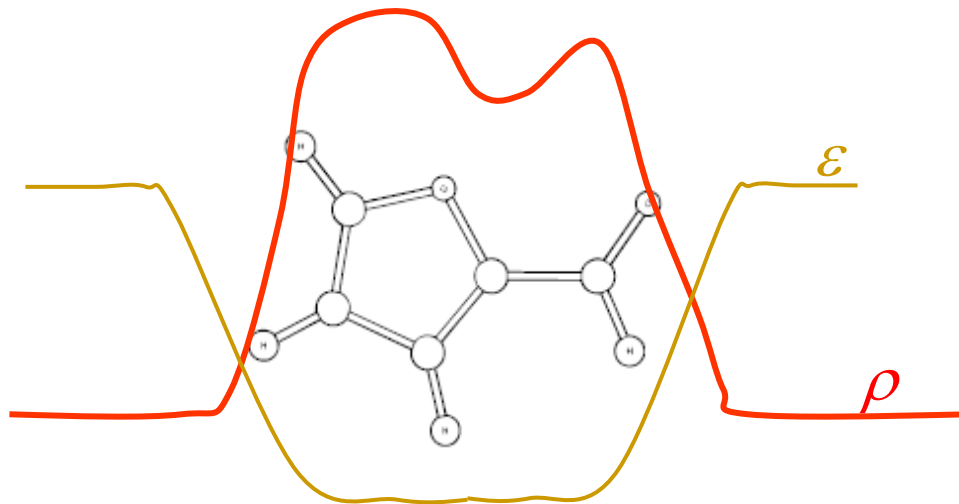
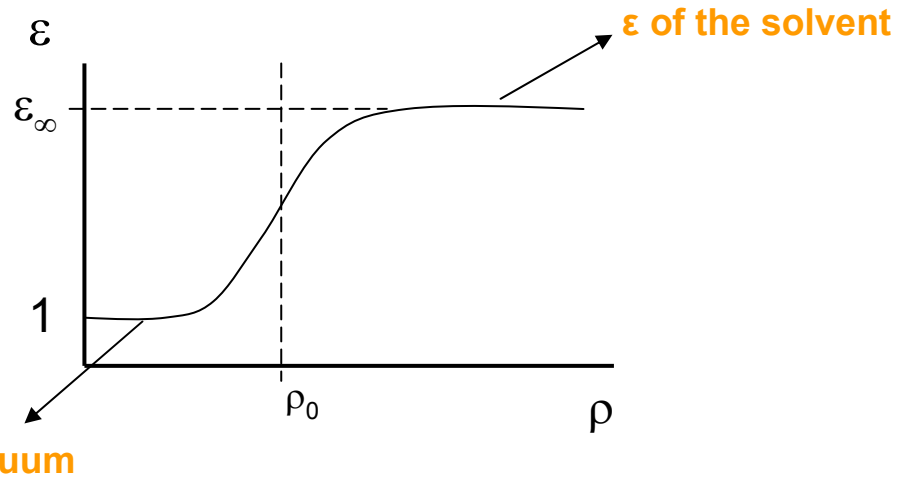
Fattebert, Gygi. *Int. J. Quantum Chem.* 93, 139 (2003)

THE ELECTROSTATIC CONTRIBUTION, ΔG_{ele}

A smooth dielectric model

$$\epsilon = \epsilon(\rho)$$

$$\epsilon[\rho] \begin{cases} \epsilon_{\infty} & \text{if } \rho \rightarrow 0 \\ 1 & \text{if } \rho > \rho_0 \end{cases}$$



THE ELECTROSTATIC CONTRIBUTION, ΔG_{ele}

$$\hat{h}_i^{ks} \psi_i = \epsilon_i \psi_i$$

$$\hat{h}_i^{ks} = -\frac{1}{2} \nabla_i^2 + v_H + v_{xc} + v_{ps}$$

\uparrow
 $\frac{\delta E_H}{\delta \rho}$

Vacuum, $\epsilon=1$

$$\frac{\delta E_H}{\delta \rho}(\mathbf{r}) = \phi(\mathbf{r})$$

Solvent, $\epsilon = \epsilon(\rho)$

$$\frac{\delta E_H}{\delta \rho}(\mathbf{r}) = \phi(\mathbf{r}) + V_\epsilon(\mathbf{r}),$$

$$V_\epsilon(\mathbf{r}) = -\frac{1}{8\pi} (\nabla \phi(\mathbf{r}))^2 \frac{\delta \epsilon}{\delta \rho}(\mathbf{r})$$

Fattebert, Gygi.
*Int. J. Quantum
Chem.* 93, 139
(2003)

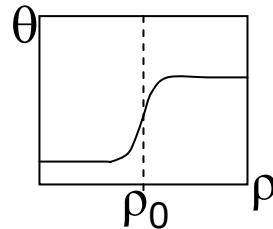
THE CAVITATION CONTRIBUTION, ΔG_{cav}

Cavitation energy from surface tension $\Delta G_{\text{cav}} = 4\pi R^2 \gamma$

Our approach $\longrightarrow \Delta G_{\text{cav}} = \gamma S$

How do we get S ?

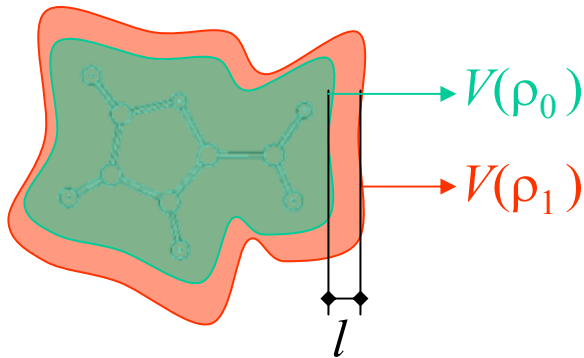
1) Definition of the volume



$\theta \begin{cases} 1 & \text{if } \rho > \rho_0 \\ 0 & \text{if } \rho < \rho_0 \end{cases}$

$$V(\rho_0) = \int \theta(\mathbf{r}) d\mathbf{r}$$

2) Get the volume at ρ_0 and at ρ_1



$$dS = \frac{dV(\rho_1) - dV(\rho_0)}{l}$$

$$S = \int [\theta_{\rho_1}(\mathbf{r}) - \theta_{\rho_0}(\mathbf{r})] \frac{\nabla \rho(\mathbf{r})}{\rho_0 - \rho_1} d\mathbf{r}$$

S is computed as a difference between two volumes corresponding to two values of ρ , divided by the width of the film resulting in between

SOLVATION AND CAVITATION ENERGIES FOR NEUTRAL SPECIES (kcal/mol)

	ΔG_{sol}			ΔG_{cav}	
	Expt. ⁵⁵⁻⁵⁷	This model	PCM	This model	PCM
H ₂ O	-6.3	-8.4	-5.4	5.7	5.7
NH ₃	-4.3	-3.2	-1.6	6.6	6.6
CH ₄	2.0	5.4	6.9	7.5	10.0
CH ₃ OH	-5.1	-3.6	-0.8	9.0	9.6
CH ₃ COCH ₃	-3.9	-1.7	3.5	13.7	14.3
HOCH ₂ CH ₂ OH	-9.3	-9.3	-6.7	13.0	12.3
CH ₃ CONH ₂	-9.7	-10.5	-4.6	12.7	12.8
CH ₃ CH ₂ CO ₂ H	-6.5	-6.0	-2.4	14.8	14.6
mean unsigned error		1.5	4.0		

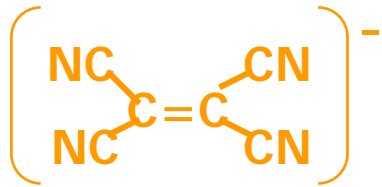
Scherlis, Fattebert, Gygi, Cococcioni, Marzari.
J. Chem. Phys., 124, 74103 (2006)

SOLVATION AND CAVITATION ENERGIES FOR IONIC SPECIES (kcal/mol)

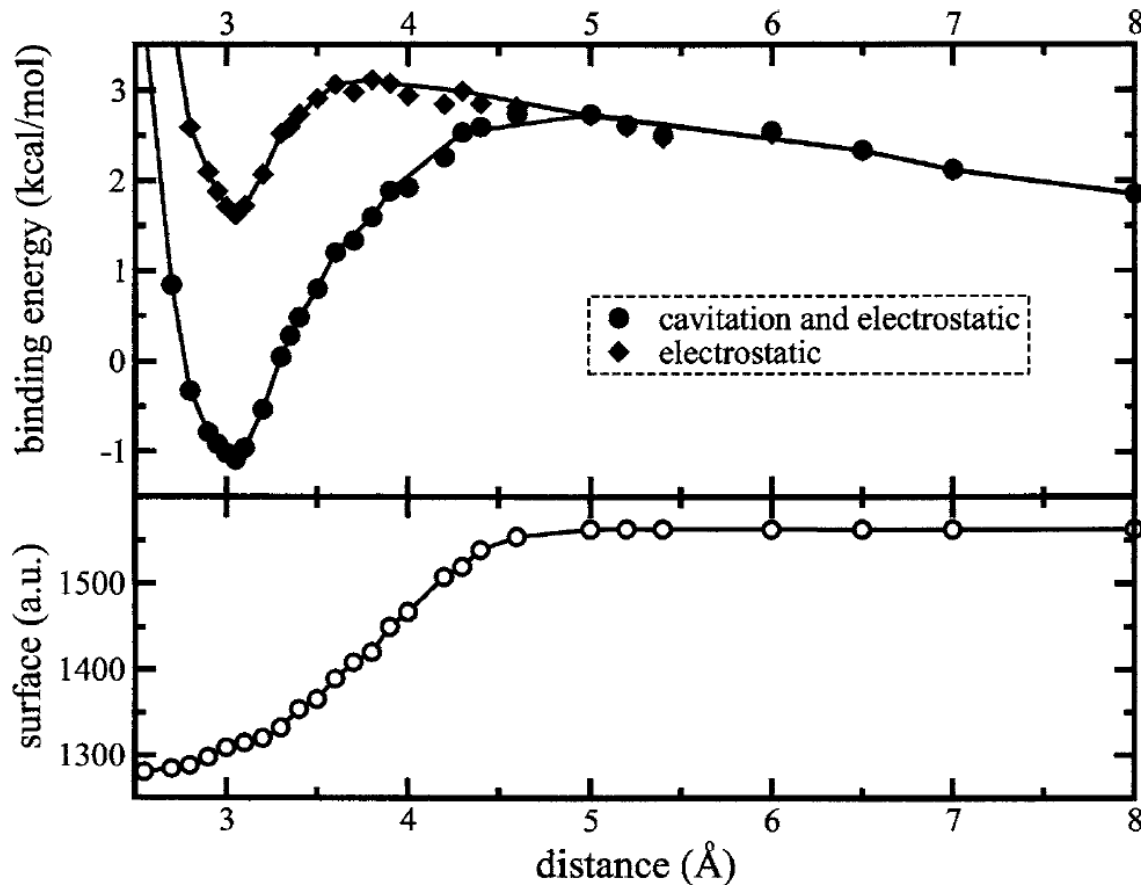
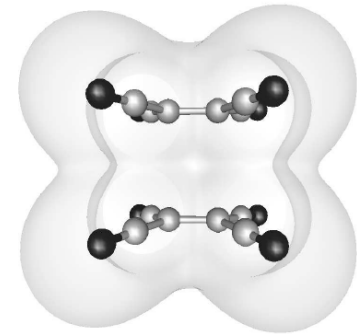
	ΔG_{sol}			ΔG_{cav}	
	Expt. ⁵⁵⁻⁵⁷	This model	PCM	This model	PCM
Cl ⁻	-75	-66.9	-72.6	7.9	5.8
NO ₃ ⁻	-65	-57.8	-62.6	10.5	9.7
CN ⁻	-75	-64.8	-70.2	8.4	7.0
CHCl ₂ CO ₂ ⁻	-66	-74.7	-53.5	16.3	15.7
Ag ⁺	-115	-110.0	-102.3	5.7	4.0
CH ₃ NH ₃ ⁺	-73	-81.0	-65.1	9.4	10.2
CH ₃ C(OH)CH ₃ ⁺	-64	-70.6	-55.2	13.5	14.4
C ₅ H ₅ NH ⁺ (pyridinium)	-58	-60.8	-59.0	15.0	13.9
mean unsigned error		7.1	6.6		

Scherlis, Fattebert, Gygi, Cococcioni, Marzari.
J. Chem. Phys., 124, 74103 (2006)

π -DIMERS IN SOLUTION: THE TCNE \cdot^- ANIONS

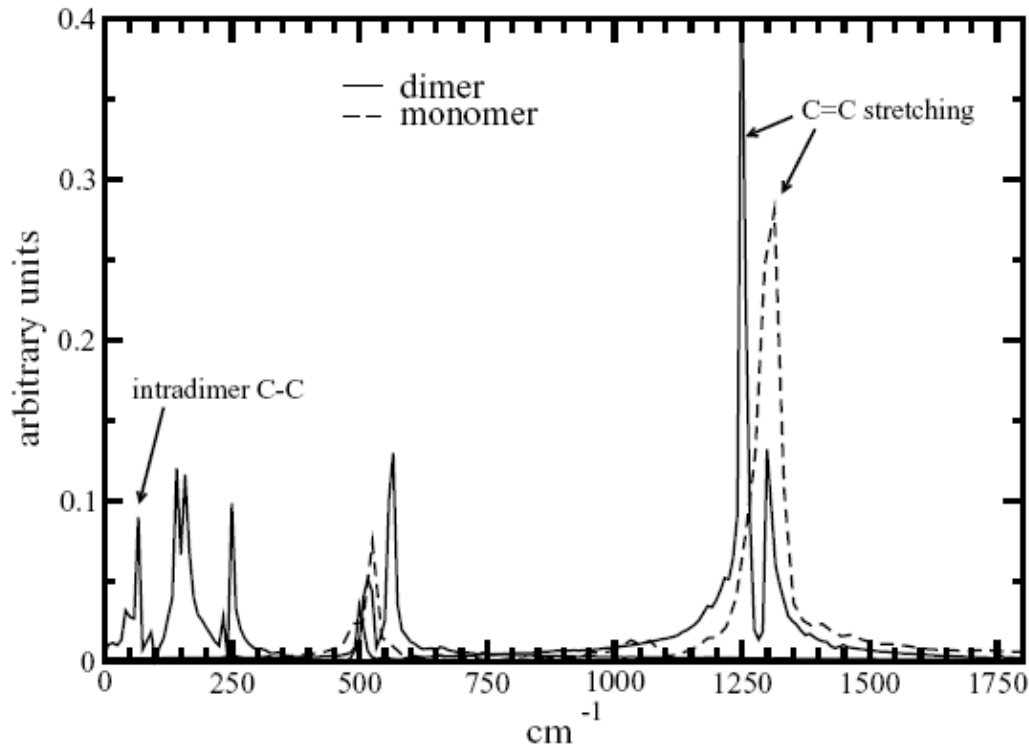


Tetracyanoethylen: dimerizes
in solution at low temperature



π -DIMERS IN SOLUTION: THE TCNE \cdot^- ANIONS

Vibrational frequencies from MD



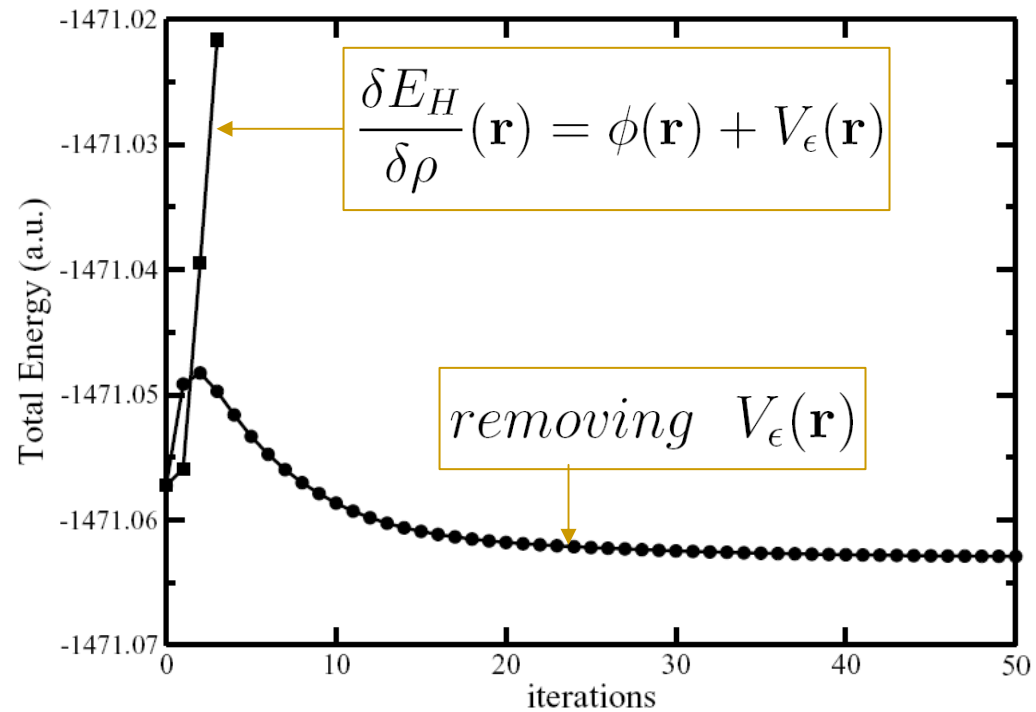
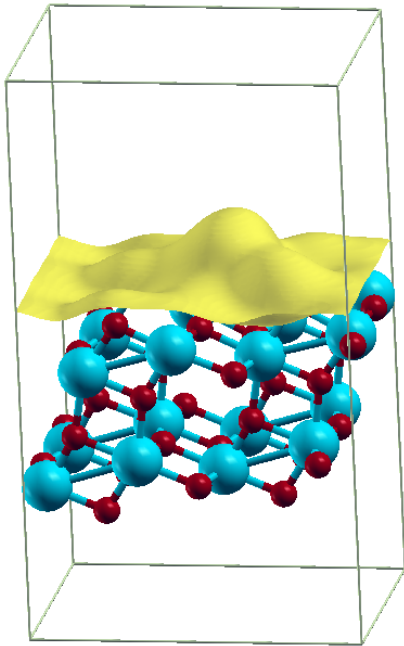
C=C (cm^{-1})

	Solid State (experimental)	Solution (simulation)
Monomer	1421	1310
Dimer	1364	1250

The shift in the C=C stretching upon dimerization is nicely reproduced by the model

SOLID-LIQUID INTERFACES: THE PROBLEM IN THE CONVERGENCE

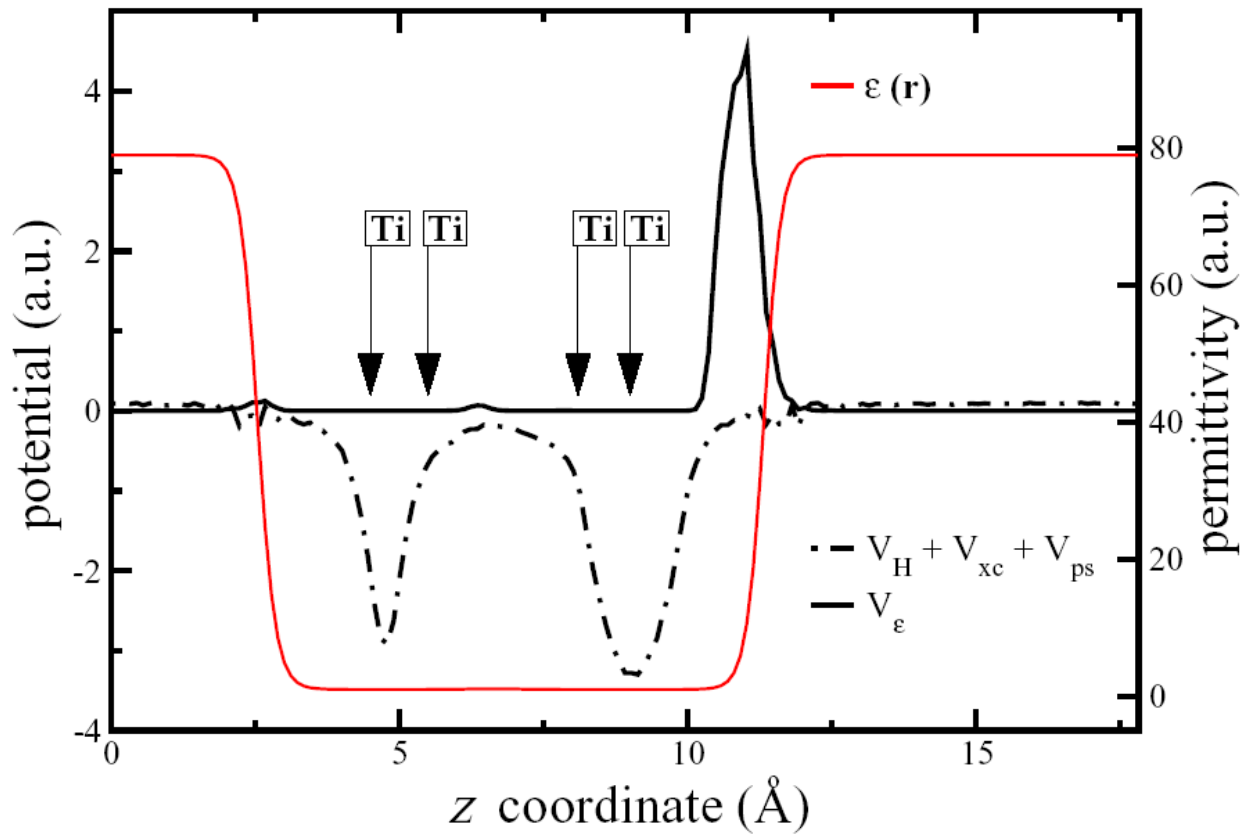
Car-Parrinello electronic relaxation



Inclusion of V_ϵ seems to affect the convergence of the self-consistent calculation of periodic surfaces.

SOLID-LIQUID INTERFACES: THE PROBLEM IN THE CONVERGENCE

Comparison of V_ϵ with the rest of the contributions to the potential

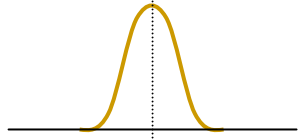


The choice of the self-consistent ρ to delimitate the region filled by the continuum induces a response of the potential opposing the discontinuity imposed by the same ρ

$$V_\epsilon(\mathbf{r}) = -\frac{1}{8\pi} (\nabla\phi(\mathbf{r}))^2 \left(\frac{\delta\epsilon}{\delta\rho}(\mathbf{r}) \right)$$

A POSITION DEPENDENT FORMULATION FOR THE DIELECTRIC

Definition of ϵ as a function of a non-self consistent, or “fake” density $\gamma(\mathbf{r})$

$$\gamma(\mathbf{r}) = \sum_I e^{-\left(|\mathbf{r}-\mathbf{R}_I| - R_{vdw}^I\right)}$$


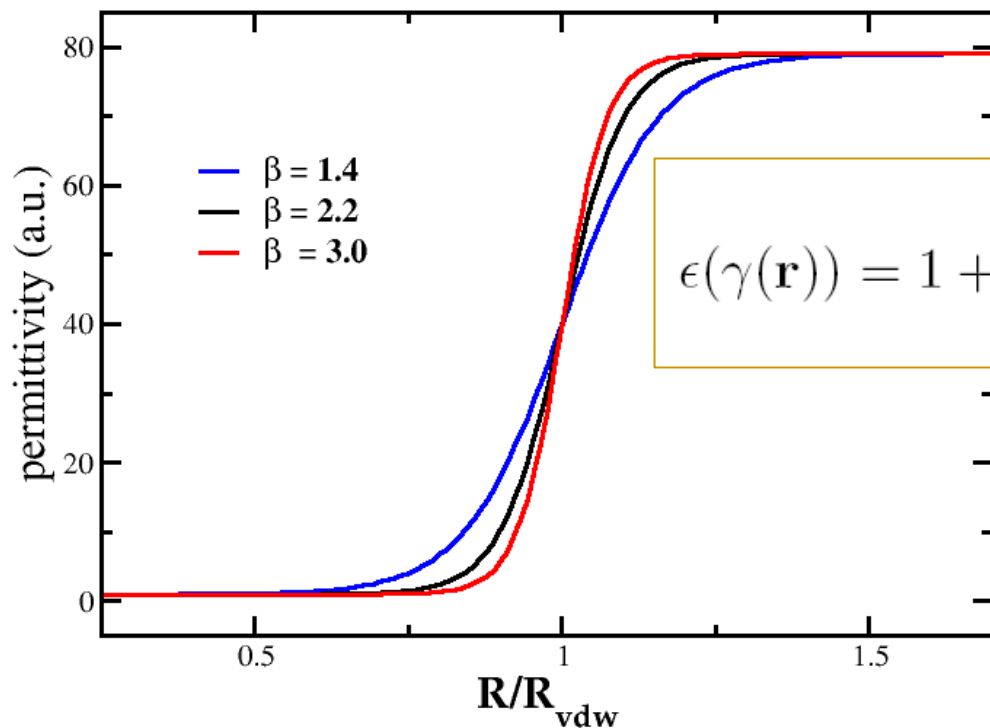
The dependence of ϵ on ρ is removed, and therefore $V_\epsilon = 0$

$$V_\epsilon = -\frac{1}{8\pi} (\nabla\phi)^2 \frac{\partial\epsilon}{\partial\rho} = 0, \quad \frac{\delta E_H}{\delta\rho} = \phi$$

Now E_H depends explicitly on $\mathbf{R}_I \Rightarrow$ new contribution to the forces

$$\frac{\partial E_H}{\partial \mathbf{R}_I} = -\frac{1}{8\pi} \int \frac{\partial\epsilon(\mathbf{R}_I)}{\partial \mathbf{R}_I} (\nabla\phi(\mathbf{r}))^2 d\mathbf{r} + \int \phi(\mathbf{r}) \frac{\partial\rho_{tot}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r}$$

A POSITION DEPENDENT FORMULATION FOR THE DIELECTRIC



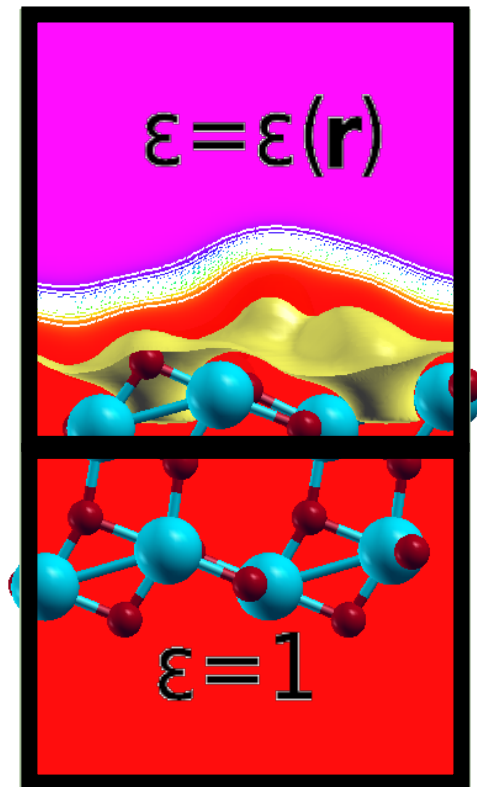
$$\epsilon(\gamma(\mathbf{r})) = 1 + \frac{\epsilon_{\infty} - 1}{2} \left(1 + \frac{1 - \gamma(\mathbf{r})^{2\beta}}{1 + \gamma(\mathbf{r})^{2\beta}} \right)$$

β can be tuned to reproduce the ρ -dependent solvation

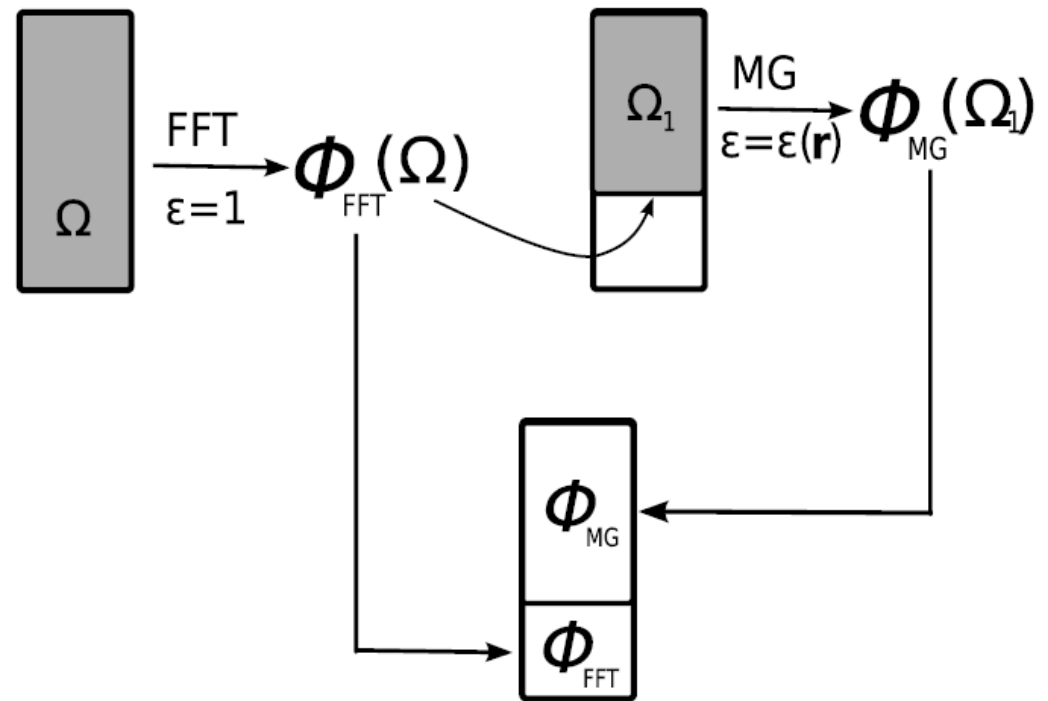
	$\epsilon(\rho)$	$\epsilon(R_I)$	Exp
ΔG_{sol} (kcal/mol)			
CH₃CONH₂	-10.5	-9.9	-9.7
NO₃⁻	-57.8	-62.5	-65
CH₃NH₃⁺	-81	-85.4	-73

IMPROVING THE EFFICIENCY: COMBINATION OF FFT AND MULTIGRID SOLVERS

The MG scheme is slower than FFT, but accepts any kind of boundary conditions. This property can be exploited to reduce the size of the grid submitted to the MG solver.



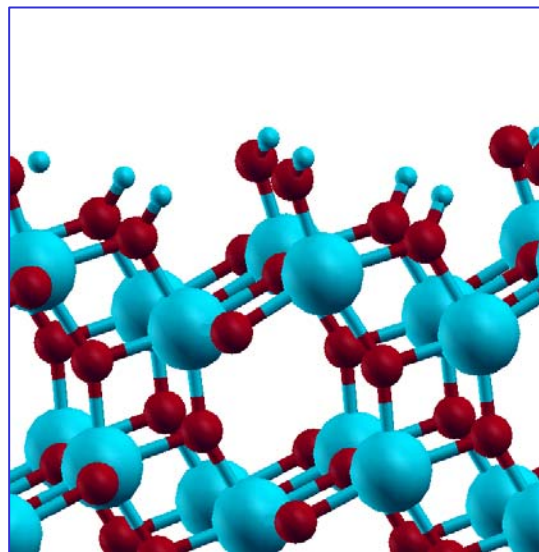
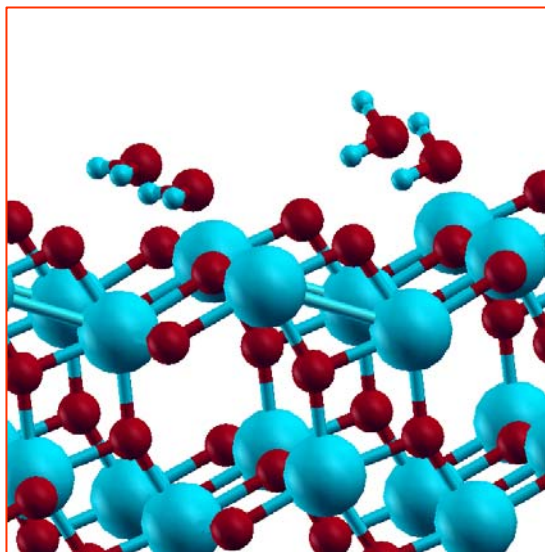
FFT → "dry" region MG → "wet" region



ADSORPTION OF H₂O ON THE TiO₂ SURFACE

Anatase (101)

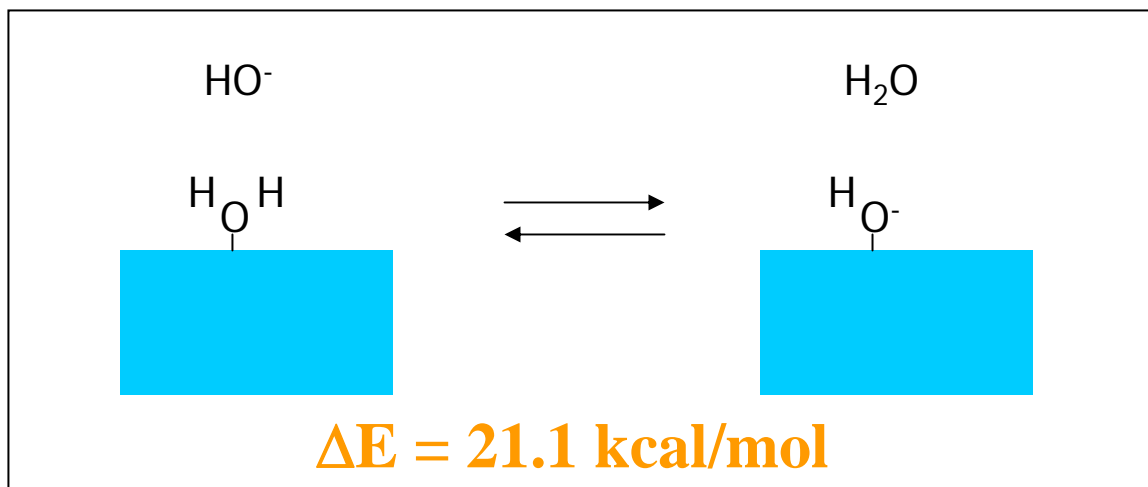
Molecular versus Dissociated



	$E_{\text{Dissociated}} - E_{\text{Molecular}}$
vacuum	11.9
solvent	0.2

Relative adsorption energies per water molecule (kcal/mol)

PROTON EXCHANGE ON THE TiO₂ SURFACE

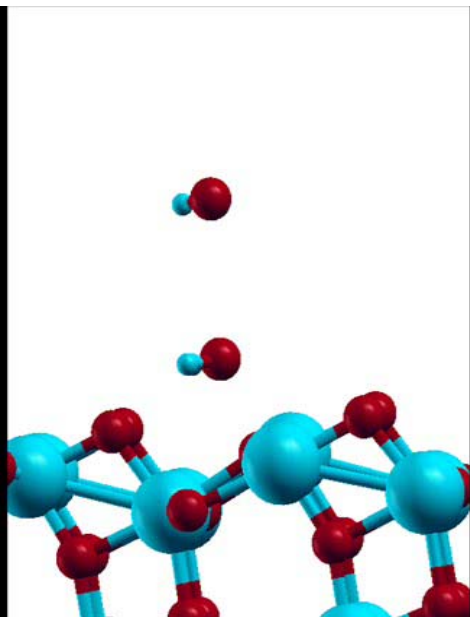


Charge localization

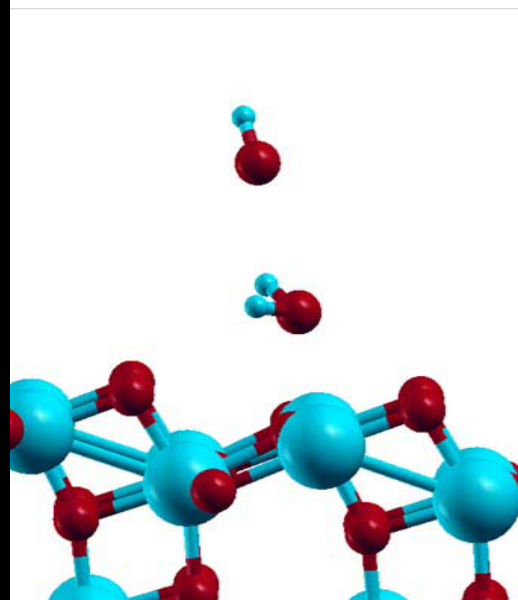
	gas phase	solvent
	-0.5	-1.0
	-0.5	0.0

PROTON EXCHANGE ON THE TiO₂ SURFACE

Gas phase, 0.5 ps



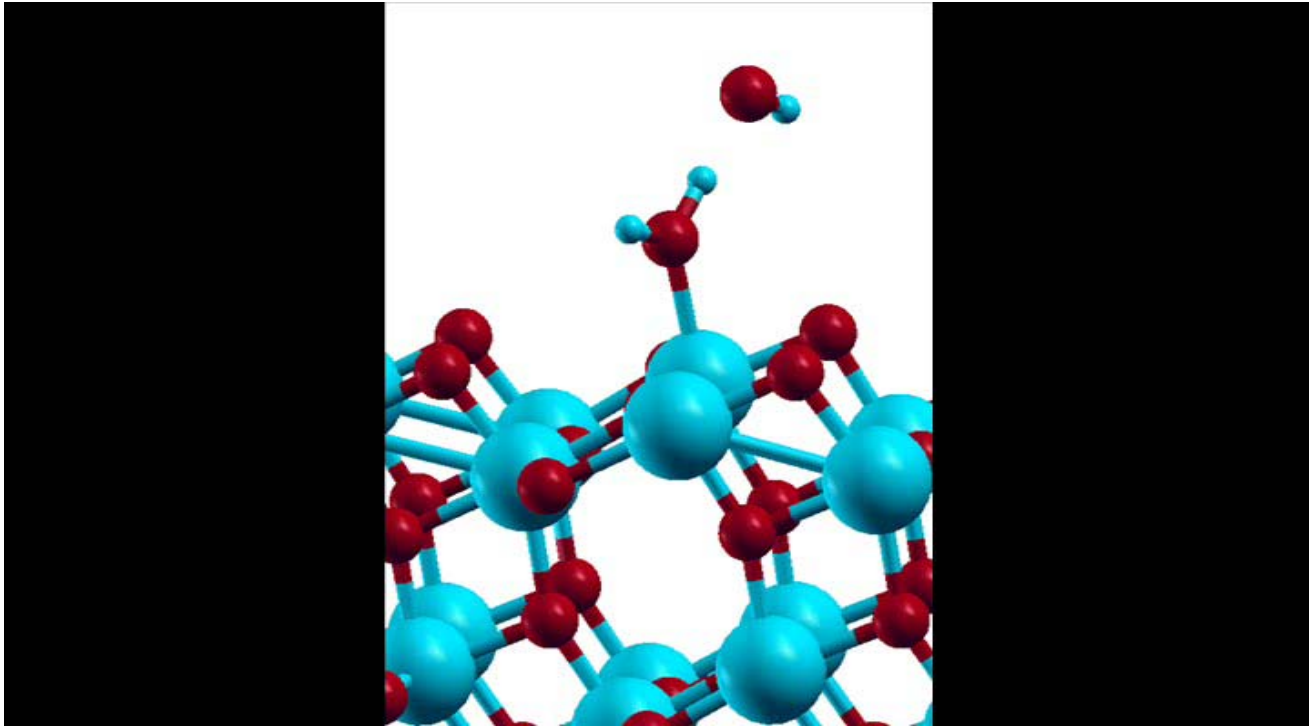
Solution, 1 ps



The proton transfer occurs immediately in the gas phase. In the solvent, the OH⁻ anion is stabilized.

PROTON EXCHANGE ON THE TiO₂ SURFACE

Solution



FINAL REMARKS

A dielectric medium defined as a function of the self-consistent charge density provokes a strong response in the effective potential, which in solid-liquid systems may spoil the convergence of the Car-Parrinello electronic dynamics.

Such a response can be avoided with a dielectric based on a non self-consistent charge, which can be equivalent to have a position-dependent permittivity. This involves a new term in the ionic forces.

The methodology presented here is a powerful instrument to explore the kind of equilibria $\text{Ti-OH}_2 + \text{OH}^- \Leftrightarrow \text{Ti-OH}^- + \text{H}_2\text{O}$. Besides, it can be useful to assess the role of the solvent in a great diversity of problems in surface chemistry, including the effects on structure, on vibrational frequencies, or on charge transfer phenomena, among others.

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