



# Soft-sphere continuum solvation in electronic-structure calculations

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## 1 Introduction

The computational study of chemical reactions in complex, wet environments is critical for applications in many fields. It is often essential to study chemical reactions in the presence of an applied electrochemical potential, taking into account the complex electrostatic screening coming from the solvent and the electrolytes [1-3].

The effects of a complex wet environment surrounding an atomic system can be included into a density functional

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

simply taking the electrostatic potential as the solution of the generalized Poisson and the Poisson-Boltzmann equation for neutral and ionic solutions, respectively. In the present work an implicit solvation approach is presented based on a continuous permittivity built up with atomic-centered "soft" spheres. Such an approach combines many of the advantages of the self-consistent continuum solvation model [3], but in addition it is able to describe accurately and simultaneously neutral and charged systems.

## 3 The soft-sphere model [7]

### Total free energy of solvation

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

Non-electrostatic terms  $G^{cav}$ ,  $G^{rep}$ ,  $G^{dis}$  can be expressed as linear functions of the "quantum surface"  $S$  and "quantum volume"  $V^{[2-3]}$ :

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

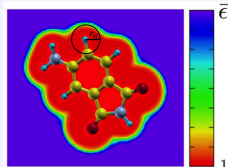
### Dielectric cavity

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

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

with  $r_i = f r_i^{vdW}$  proportional to Unified Force Field radii.

Smooth interface  $\rightarrow$  fast analytic calculation of derivatives and forces



## 2 Generalized Poisson solver: a minimization problem

The generalized Poisson equation (GPE):  $\mathcal{A}\phi(\mathbf{r}) = \nabla \cdot \epsilon(\mathbf{r})\nabla\phi(\mathbf{r}) = -4\pi\rho(\mathbf{r})$

$$\epsilon(\mathbf{r}) = \epsilon(\mathbf{R}_i^{atom}) \quad \text{or} \quad \epsilon(\mathbf{r}) = \epsilon(\rho^{elec}(\mathbf{r}))^{[2-3]} \quad \rho(\mathbf{r}) = \rho^{elec}(\mathbf{r}) + \rho^{ions}(\mathbf{r})$$

The Action integral:  $\mathcal{I} = \int \frac{1}{2} \nabla\phi(\mathbf{r})\epsilon(\mathbf{r})\nabla\phi(\mathbf{r}) - 4\pi\rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r}$

The GPE has been discretized on a cubic mesh. Then the system  $A\phi = b$  has been solved by means of a preconditioned conjugate gradient algorithm [4-6], where  $b = -4\pi\rho(\mathbf{r})$ .

### Preconditioned Conjugate Gradient algorithm:

1.  $r_0 = b$
2. for  $k = 0, 1, \dots$  do
3.  $s_k = P_k^{-1} r_k$
4. if  $k = 0$  then
5.  $p_0 = s_0$
6. else
7.  $p_k = s_k + \beta_k p_{k-1}$  (where  $\beta_k = \frac{(s_k, r_k)}{(s_{k-1}, r_{k-1})}$ )
8. end if
9.  $\alpha_k = \frac{(s_k, r_k)}{(p_k, A p_k)}$
10.  $\phi_{k+1} = \phi_k + \alpha_k p_k$
11.  $r_{k+1} = r_k - \alpha_k A p_k$
12. end for

$\beta_k = 0 \rightarrow$  Preconditioned Steepest Descent algorithm

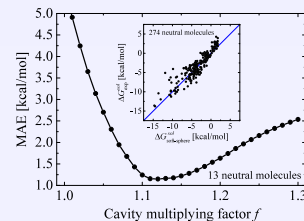
## 4 Parametrization

✓ Improved flexibility allows high simultaneous accuracy on neutrals, cations and anions

Table I. Mean Absolute Errors in aqueous solvation free energies (kcal/mol) extracted for several solvation models<sup>a</sup>. Dataset: 274 neutrals, 60 anions and 53 cations of the Minnesota Solvation Database, version 2012.

Method	neutrals	cations	anions
soft-sphere <sup>a</sup>	1.12	2.13	2.96
sccs	1.14	2.27	5.54
SMS	0.55	2.70	3.70
SM12	0.59	2.90	2.90
FR/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

<sup>a</sup> parametrization with UFF radii,  $\alpha + \gamma = 11.5$  dyne/cm and  $\beta = 0.0$  GPa.



✓ The limited number of parameters of the model allows fast tuning for different environments

Method	Mesitylene	Ethanol
soft-sphere	0.71	1.28
SMS	0.40	1.53

## 5 Solid-liquid interfaces and contact angle

The contact angle  $\theta_C$  quantifies the wettability of a surface and reflects the equilibrium between liquid, solid and vapor molecular interactions:

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

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

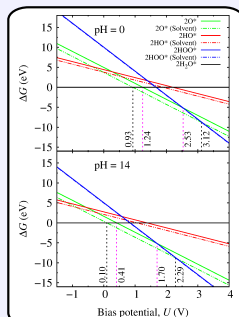
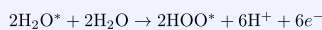
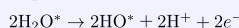
Table II. Simulated spreading coefficient  $S$  [mJ/m<sup>2</sup>] and contact angle [degree] for several surfaces in contact with water.

Surface	$S$	$\theta_C$
Silver (001)	33	-
SiO <sub>2</sub> (001) cleaved	35	-
SiO <sub>2</sub> (001) reconstructed	-69	87
Diamond (001)	-76	92
Graphene	-82	97

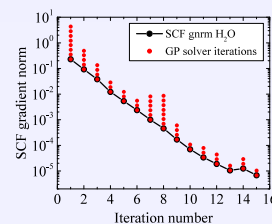
## 6 Electronic-structure calculations with implicit solvent [5]

### Structure of CdS (1120) surface in electrochemical media

Formation free energies of various surface terminations (O, OH, OOH) in water, varying pH and bias potentials. The following reactions were considered:

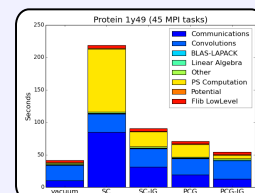


### Convergence for H<sub>2</sub>O in implicit water



### Run data for 1y49 protein (122 atoms)

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



## 7 Conclusion

A soft-sphere solvation model for *ab-initio* electronic-structure calculations has been developed, parametrized and tested. The continuous permittivity allowed for the analytical calculation of the additional terms to the forces as well as the cavity-dependent non-electrostatic contributions to the total energy — described in terms of the quantum surface. With fixed the atomic radii, only two fitting parameters are needed to define the model, independently of the cluster or slab geometry. The flexibility of the model to locally change atomic radii allows to simultaneously simulate neutral and charged systems. A new benchmark protocol for solid-liquid interfaces is proposed in terms of wettability and contact angles.

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