# Continuum solvation model for ab initio molecular dynamics simulations

J.-L. Fattebert* and F. Gygi

Center for Applied Scientific Computing (CASC)
Lawrence Livermore National Laboratory
P.O. Box 808, L-551, Livermore, CA 94551, USA
* fattebert1@llnl.gov

## ABSTRACT

In electronic structure calculations, a polarizable solvent can be represented as a continuous homogeneous dielectric. In most models, the value of the dielectric presents a discontinuity at the solute-solvent interface. For first principles pseudopotential DFT calculations based on plane waves or real-space discretization, such an approach is impractical. We present a continuum solvation model in which the electrostatic effects of the solvent are described by a Poisson equation with a smooth continuous dielectric function depending on the electronic density only. This equation is discretized on a grid by finite differences and is solved iteratively by multigrid. This model does not introduce any ionic forces depending explicitly on the molecular cavities and is thus appropriate for geometry optimizations and molecular dynamics simulations.

**Keywords**: Ab initio molecular dynamics, geometry optimization, continuum solvation model, Poisson equation.

## 1 INTRODUCTION

First principles numerical simulations of chemical or biological processes in solution are very expensive if the molecules of the solvent are explicitly introduced in the calculation [1]. On the other hand, calculations in vacuo can be very inaccurate to study properties of molecules in solution. As an alternative, continuum solvation models representing the electrostatic effect of the solvent lead to very realistic simulations [2]. The polarizable solvent is modeled by a continuous homogeneous and isotropic medium characterized by a dielectric permittivity. Such a model permits static calculations, as well as geometry optimizations, but its current implementations are inadequate for molecular dynamics simulations.

In models like the conductor-like screening model (COSMO) [3] or the polarizable continuum model (PCM) [4], the value of the dielectric constant presents a discontinuity at the solute-solvent interface. A common way to define the interface is to build a cavity around the solute from interlocking spheres centered on atoms or atomic groups [5]. Instead of solving a Poisson problem with a discontinuous dielectric, one often represents the polarization of the solvent by placing equivalent discrete charges on the molecular cavity. However this can lead to various problems when computing ionic forces [6]. For first principles pseudopotential density functional theory (DFT) calculations based on plane waves or real-space finite difference discretization, such an approach is impractical since discontinuous functions can be represented only very poorly in these numerical bases. Also in pseudopotential calculations, we want to avoid point charges like those defined on the cavity surfaces in PCM or COSMO. Both approaches would lead to inaccurate ionic forces and thus poor energy conservation during the molecular dynamics.

Note also that it is difficult to define properly universal molecular cavities. Barone et al. [5] for example propose rules to determine the radii of spheres used to build molecular cavities. This approach produces solvation free energies in very good agreement with experimental values. However, these rules are based on as many as 11 parameters to describe molecules containing 10 different atomic species. Moreover, these rules are based not only on the atoms composing a molecule in solvation, but also on how its constituents are linked together.

The solute-solvent interface being anyway much more complicated than a simple surface made of interlocking spheres, there is no reason to limit our model to a discontinuous dielectric function. Here we present a continuum solvation model where the electrostatic effects of the solvent are described by a Poisson equation with a smooth continuous dielectric function depending on the electronic density only. This model does not introduce any ionic forces depending explicitly on the shape of molecular cavities, a very convenient property for geometry optimizations and ab initio molecular dynamics simulations.

In this paper we report the preliminary results obtained with this model, including total energy calculations and geometry optimizations. The model is briefly described in Section 2 and some numerical results are presented in Section 3.

## 2  MODEL

In pseudopotentials DFT calculations, we define the electronic density as

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} 2|\psi_j(\mathbf{r})|^2 \tag{1}$$

where $\psi_j, j = 1, \ldots, N$ are the $N$ occupied electronic orbitals solution of the Kohn-Sham equations. Here we assume for simplicity that they are all occupied by 2 electrons. The electrostatic interaction between valence electrons in vacuo is represented by the Hartree potential $\phi$ solution of the Poisson equation

$$-\nabla^2\phi = 4\pi\rho \tag{2}$$

with periodic or Dirichlet boundary conditions.

To include the electrostatic effects of a solvent modeled by a continuous linear isotropic dielectric medium, we replace Eq.(2) by

$$-\nabla(\epsilon\nabla\phi) = 4\pi\rho \tag{3}$$

where $\epsilon = 1 + \chi$ is a dielectric function. For the polarizability $\chi$, we choose 0 in the solute cavity — polarizability included in the quantum treatment of the solute — and a positive value $\chi_\infty$ (77.36 for water for example) outside of this cavity to describe the solvent not treated explicitly.

Since the solvent is located in regions where the electronic density of the solute is small, one can use $\rho$ to define the molecular cavities, and therefore $\epsilon$. The possibility of defining a cavity based upon an electronic isosurface has already been proposed by Foresman et al. in their isodensity polarizable continuum model (IPCM) [7]. However, to be able to represent accurately $\epsilon$ on a grid, it is important here to have a smooth function. We propose to use the following

$$\epsilon(\mathbf{r}) = 1 + \frac{\chi_\infty}{2}\left(1 + \frac{1 - (\rho(\mathbf{r})/\rho_0)^2}{1 + (\rho(\mathbf{r})/\rho_0)^2}\right). \tag{4}$$

The isodensity surface $\rho = \rho_0$ defines a cavity surface where $\epsilon$ takes its medium value $1 + \chi_\infty/2$. In pseudopotentials calculations, the pseudo-electronic density $\rho$ can be very low in the core of the atoms. To avoid spurious effects on $\epsilon$, we "add" some density to the function $\rho$ used to define $\epsilon$ at the atoms centers. As a consequence, $\epsilon$ keeps a saturated value of 1 inside the solute, without explicit dependence on the atomic positions. More details will be published elsewhere.

## 3  NUMERICAL RESULTS

Since $\epsilon$ is a function of $\rho$ only, one can write a solver that requires $\rho$ as the only input and returns $\phi$. The Poisson equation is discretized on a regular grid using

|  | $\rho_0 = 0.0002$ | $\rho_0 = 0.0004$ | PCM[1] |
|---|---|---|---|
| $H_2O$ | -9.1 | -12.9 | -8.3 |
| $CH_4$ | -0.97 | -2.1 | -0.2 |
| $NH_3$ | -5.6 | -8.4 | -6.2 |
| $CH_3OH$ | -6.7 | -10.1 | -5.9 |
| $CH_3CH_3$ | -1.2 | -2.7 | -0.5 |
| $CH_3NH_2$ | -5.0 | -8.0 | -5.3 |

Table 1: Electrostatic solvation energies (in Kilocalories per mole)

a high-order finite difference scheme and is solved iteratively by multigrid [8]. This solver has been coupled to the real-space ab initio code developed by one of us (J.-L. F.) [9] for the numerical tests presented here, but can as well be coupled to a plane-wave code where the electronic density is also represented on a regular grid.

Figure 3 illustrates the behavior of the dielectric function $\epsilon$ defined by Eq.(4) for $\rho_0 = 0.0002$ obtained by a self-consistent calculation of the $CH_3OH$ molecule. Geometry optimizations are carried out using ionic forces calculated from the Hellmann-Feynman theorem [10] as in vacuo.

We present in Table 3 the numerical results obtained for some small molecules and various values of the parameter $\rho_0$. In our calculations, we use the Hamann pseudopotentials [11] and PBE exchange-correlation functional [12]. The energy difference between gas phase and continuum dielectric solvent calculations are compared to electrostatic solvation energies obtained by PCM for the Gaussian density functional method [13]. For the results presented in Table 3, we used a grid spacing of $0.2[Bohr]$. Note that the values obtained with $\rho_0 = 0.0002$ agree with the PCM results within $1[Kcal/mol]$.

Calculations of solvation free energies would require quantities like the cavitation, repulsion and dispersion energies [2]. These terms are not discussed here since we are only interested in reactions and dynamics for molecules staying in solution. We assume that their contributions can be neglected in this case.

Relaxation of the molecules showed that the optimal geometries obtained with our solvation model — for reasonable parameters — are very similar to the gas phase geometries for the examples presented here. Actually electrostatic solvation energies estimated from the gas phase geometries differ by less than $0.3[Kcal/mol]$.

## ACKNOWLEDGMENTS

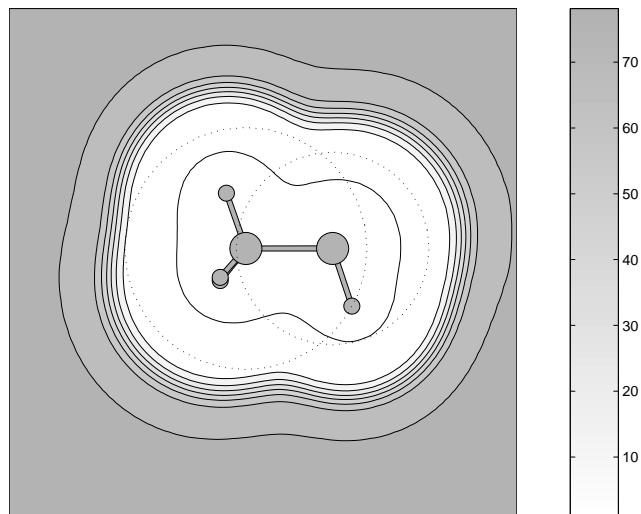[1]from Ref. [13] with a generalized gradient approximation exchange-correlation functional.

Figure 1: Contour plot of the dielectric function $\epsilon$ with $\rho_0 = 0.0002$ for $CH_3OH$ in a plane containing $C - O$. The contour the closest to the molecule corresponds to $\epsilon = 1.01$. Dotted circles denote the spheres composing a molecular cavity according to Ref. [5]

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