A generalized Poisson and Poisson-Boltzmann solver for electrostatic environments

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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 applied electrochemical potentials, taking into account the non-trivial electrostatic screening coming from the solvent and the electrolytes. As a consequence the electrostatic potential has to be found by solving the generalized Poisson and the Poisson-Boltzmann equation for neutral and ionic solutions, respectively. In the present work solvers for both problems have been developed. A preconditioned conjugate gradient method has been implemented to the generalized Poisson equation and the linear regime of the Poisson-Boltzmann, allowing to solve iteratively the minimization problem with some ten iterations of a ordinary Poisson equation solver. In addition, a self-consistent procedure enables us to solve the non-linear Poisson-Boltzmann problem. Both solvers exhibit very high accuracy and parallel efficiency, and allow for the treatment of different boundary conditions, as for example surface systems. The solver has been integrated into the BigDFT and Quantum-ESPRESSO electronic-structure packages and will be released as an independent program, suitable for integration in other codes.

I. INTRODUCTION

Many important chemical processes take place in solution both in the context of basic and industrial research. The computational study of such chemical reactions in wet environments is therefore of cross-disciplinary interest to physics, chemistry, materials science, chemical engineering, and biology. Computational studies can complement these investigations by giving insight into new processes and materials as well as reducing development times and production costs. Solar-energy harvesting in a dye-sensitized cell or electro-catalytic water splitting are two simple examples of relevance for applications in the energy and environment context.

Molecular properties in the presence of a solution are often very different compared to pure in vacuum conditions making vacuum-like ab initio calculations an inappropriate approach for such problems. An inclusion of the solute-solvent interaction in ab initio simulations is thus mandatory. On the atomistic scale, an explicit inclusion of all solvent molecules in the simulation should be in principle the natural way to account for solvent effects. Due to the very large number of water and possibly other molecules required, this approach enormously increases the computational cost and limits at the same time the size of the system contained in the explicit dielectric medium. The study of the solute-solvent interaction at length scales larger than the molecular sizes would become virtually impossible. Investigations like structure predictions or reaction path determination would become unaffordable in such a purely atomistic approach. Moreover, fully atomistic simulations of solvation effects would need to deal with the extensive sampling, required to characterize liquid configurations, and with the well-known limitations that current state-of-the-art ab initio methods present in describing liquid water, in particular regarding its structural and dielectric properties.

An implicit inclusion of the solute-solvent interactions could solve these issues. Starting from the earliest work of Onsager, the quantum chemistry community investigated implicit solvation models extensively. In these models the solvent is introduced as a continuous homogeneous and isotropic medium fully described by a dielectric function. Among them, the polarizable continuum model (PCM) developed by Tomasi and co-workers is one of the most popular. In this approach a dielectric cavity surrounding the atomistic system is introduced where the permittivity takes on the value of one in regions occupied by atoms and some different value characteristic for the dielectric solvent medium considered outside.

Density functional theory (DFT) is a widely used method to investigate material properties at the atomistic scale. In such ab initio calculations the electronic-structure problem is solved by minimizing the total energy of the system which is a functional of the electronic density

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

(1)

where the four terms on the right side of Eq. (1) are, respectively, the standard kinetic energy, the interaction energy with an external potential, the electrostatic and
the exchange-correlation energy. For gas-phase molecular simulations the potential $\phi(r)$ generated by a given charge density $\rho(r)$ is given by the solution of the standard Poisson (SPe) equation

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

An implicit inclusion of the solvent can be obtained by introducing a continuum dielectric cavity by means of a dielectric distribution $\epsilon(r)$. Then the potential is given by the solution of the generalized Poisson equation (GPe)

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

If the system is surrounded by an ionic solution, an extra-term has to be added on the right side of Eq. (3). It accounts for the ionic distribution in the liquid and depends on the local electrostatic potential $\phi(r)$. The resulting non-linear differential equation would therefore become

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

where $\rho^{ions}(r)$ is the local ionic concentration of the ions in the dielectric solvent, written as a sum of concentration contributions $c_i$ of ions of type $i \in \{1, 2, ..., m\}$ and valence $Z_i$, which in turn are $\phi$-dependent functionals:

$$\rho^{ions}(\phi(r)) = e N_A \sum_{i=1}^{m} Z_i c_i(\phi(r)), \tag{5}$$

where $e$ is the elementary charge and $N_A$ the Avogadro’s number. The most common expression for the $c_i(\phi)$ functional gives rise to the well-known Poisson-Boltzmann (PBe) equation

$$(\epsilon(r)) are generally discretized on a finite grid. In order to solve numerically Eq. (3), both the potential $\phi(r)$, the charge density $\rho(r)$ and the dielectric function $\epsilon(r)$ are generally discretized on a finite grid. In principle also the generalized Poisson operator

$$A = \nabla \cdot (\epsilon) \nabla \tag{6}$$

should be discretized on the same mesh. It will be shown that depending on the adopted strategy to solve numerically Eq. (3), the discretization of the differential operator $A$ can be avoided in exchange of a iterative procedure based on a SPe solver.

An alternative would be to solve the GPe iteratively as suggested in Ref. [15]. In this approach the polarization field introduced by the spatially varying dielectric function is added as a source term to the charge density of the ordinary Poisson equation and the Poisson equation is solved repeatedly until self-consistency between the potential and the polarization charge density induced by it is reached. Our approach completes and simplifies this treatment, reducing considerably the number of SPe iterations, thereby presenting a robust and powerful iterative solver.

Considering that reliable convergence can be an issue in mixing schemes, an alternative approach based on a minimization procedure is desirable. Such an approach can be based on an action integral whose Euler Lagrange equation is the GPe [Eq. (3)]:

$$I = \int \left[ \frac{1}{2} \nabla \phi(r) \epsilon(r) \nabla \phi(r) - 4\pi \rho(r) \phi(r) \right] \, dr. \tag{7}$$

Any numerical minimization scheme can then be applied to solve the electrostatic problem.

In Sec. II B our strategy to solve Eq. (3), based on a preconditioned conjugate gradient (PCG) algorithm, will be presented. The preconditioner exactly represents the operator in the limit of a slowly varying dielectric constant and is based on the standard Poisson solver of BigDFT.

The possibility of solving the generalized Poisson equation under various boundary conditions (BC) will be very
important. In our approach the boundary conditions enter in a straightforward way by means of the preconditioner, i.e., through the solution of the SPEs.

A. Self-consistent iterative procedure

A strategy to solve the GPe for a given charge density $\rho(\mathbf{r})$ is by means of a self-consistent (SC) iterative procedure. Applying simple algebraic manipulations, Eq. (3) can be rewritten as

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

where $\rho^\text{pol}(\mathbf{r})$ is the polarization charge density. In this approach an extra-term $\rho^\text{iter}(\mathbf{r})$

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

induced by the spatially-varying dielectric function $\epsilon(\mathbf{r})$ is added as a source to the charge density of the ordinary Poisson equation. Hence the GPe can be solved by a self-consistent loop on the potential $\phi(\mathbf{r})$, obtained by a SPE solver onto the second member of Eq. (8). The residual $r_k$, quantifying the convergence, is the difference between the extra terms of Eq. (9) between subsequent iterations. Algorithm 1 describes the procedure. In order to stabilize the iterative method, a linear mixing of the extra-term $\rho^\text{iter}(\mathbf{r})$ at steps $k$th and $(k+1)$th has been introduced by means of the mixing parameter $\eta$.

The polarization charge induced in the dielectric medium can be easily related to the extra-term of Eq. (9):

$$\rho^\text{pol}(\mathbf{r}) = \rho^\text{iter}(\mathbf{r}) + \frac{\epsilon(\mathbf{r}) - 1}{\epsilon(\mathbf{r})} \rho(\mathbf{r})$$

This charge represents the response of the surrounding implicit dielectric. It lies in the transition region between the inner and outside part of the cavity and stabilizes the solute density enveloped by the solvent.

B. Preconditioned conjugate gradient

Although a reasonably small number of iterations can be obtained in a self-consistent scheme, minimization techniques can produce more efficient methods to handle Eq. (3) if sophisticated schemes are utilized. In addition, the formulation as a minimization problem would allow to better control the convergence behavior.

Solving this equation with a preconditioned steepest descent (PSD) method is essentially identical to the self-consistency approach of Sec. II A, once a standard Poisson solver is taken as preconditioner. In particular, a good preconditioner for a PSD minimization, which inverse applied to a residual vector $r_k$ provides the preconditioned residual $v_k$, is as follows:

$$\mathcal{P}^{SD} v_k(\mathbf{r}) = \epsilon(\mathbf{r}) \nabla^2 v_k(\mathbf{r}) = -4\pi r_k(\mathbf{r}). \tag{11}$$

Being the Laplacian of $v_k(\mathbf{r})$ related to the residual vector $r_k$ by means of Eq. (11), the generalized Poisson operator becomes

$$\mathcal{A} v_k(\mathbf{r}) = \nabla \cdot \epsilon(\mathbf{r}) \nabla v_k(\mathbf{r}) = \nabla \epsilon(\mathbf{r}) \cdot \nabla v_k(\mathbf{r}) - 4\pi r_k(\mathbf{r}). \tag{12}$$

Such a PSD approach can be described by Algorithm 2 with $\beta_k = 0$. Fixing $\alpha_k = 1$ it corresponds to the previously described self-consistent approach.

In a PSD scheme the number of iterations $l$ needed for convergence is proportional to the condition number $\kappa$ (i.e. the ratio between the largest and the smallest eigenvalue of the product operator $\mathcal{P}^{-1} \mathcal{A}$). Minimization methods with a faster convergence rate than the preconditioned steepest descent algorithm can significantly improve the convergence speed.

We use a preconditioned conjugate gradient scheme, where $l \propto \sqrt{\kappa}$. In such minimization procedure a good preconditioner can lower $\kappa$ and, therefore, the overall number of iterations. Algorithm 2 describes the implemented PCG procedure to compute the electrostatic potential $\phi(\mathbf{r})$ starting from a given charge density $\rho(\mathbf{r})$. The minimization procedure starts from an initial gradient $r_0$ computed on an input guess $\phi_0$. $\mathcal{P}$ is the preconditioner which inverse has to be applied to the residual vector $r_k$ returning the preconditioned residual $v_k$, and, finally, $\phi_k$ is the solution of Eq. (3). The convergence criterion is imposed on the Euclidean norm of the residual vector $r_k$.

Both the performance and accuracy in a PCG scheme critically depend on the preconditioner chosen. We implemented a preconditioner based on the solution of the standard Poisson equation (namely on a standard Poisson solver). Once a residual vector $r_k$ is given at the step 3 of Algorithm 2, we define a preconditioned residual from the following equation:

$$\mathcal{P}^{CG} v_k(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} \nabla^2 v_k(\mathbf{r}) \sqrt{\epsilon(\mathbf{r})} = -4\pi r_k(\mathbf{r}). \tag{13}$$
Algorithm 2 Preconditioned conjugate gradient

1: \( r_0 = -4\pi \rho - A\phi_0 \), \( p_{-1} = 0 \)
2: for \( k = 0, 1, \ldots \) do
3: \( v_k = p^{-1}r_k \)
4: \( p_k = v_k + \beta_k p_{k-1} \) (where \( \beta_k = \frac{(v_k, r_k)}{(v_{k-1}, r_{k-1})}, k \neq 0 \))
5: \( \alpha_k = \frac{(v_k, r_k)}{(p_k, Ap_k)} \)
6: \( \phi_{k+1} = \phi_k + \alpha_k p_k \)
7: \( r_{k+1} = r_k - \alpha_k Ap_k \)
8: end for

This equation has to be solved with respect \( v_k(\mathbf{r}) \) once \( r_k(\mathbf{r}) \) is given.

In addition to speeding up the PCG procedure, the preconditioner defined by Eq. (13) retains a further feature which guarantees accuracy and fast performance for the whole electrostatic solver. In step 7 of Algorithm 2 we have to apply the generalized Poisson operator \( A \) to the preconditioned residue \( p_k \), which means, thanks to step 3, applying it to \( v_k \). Using a change of variable \( v_k'(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} v_k(\mathbf{r}) \), the GPe becomes

\[
\nabla \cdot \epsilon(\mathbf{r}) \nabla v_k(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} \nabla^2 v_k'(\mathbf{r}) - v_k'(\mathbf{r}) \nabla^2 \sqrt{\epsilon(\mathbf{r})}. \tag{14}
\]

Now simple algebraic manipulations and Eq. (13) allow to rewrite the generalized Poisson operator \( A \) as

\[
A v_k(\mathbf{r}) = \nabla \cdot \epsilon(\mathbf{r}) \nabla v_k(\mathbf{r}) \]
\[
= -v_k(\mathbf{r}) q(\mathbf{r}) - 4\pi r_k(\mathbf{r}), \tag{15}
\]

where \( q(\mathbf{r}) = \sqrt{\epsilon(\mathbf{r})} \nabla^2 \sqrt{\epsilon(\mathbf{r})} \) is calculated once at the beginning of the PCG procedure and kept fixed for the whole minimization loop. Therefore thanks to the chosen preconditioner, the action of the operator \( A \) can be simplified to a simple multiplication between the potential \( v_k(\mathbf{r}) \) and a constant vector \( q(\mathbf{r}) \) related to the spatially-varying dielectric function \( \epsilon(\mathbf{r}) \). This feature, which provides the exact operator output, makes our PCG procedure robust and fast, avoiding any finite difference differentiation. Furthermore, reducing the PCG algorithm to simple vector operations, makes its parallelization straightforward, delegating it to the chosen SPE solver. A similar discussion holds for the boundary conditions, which enter in a natural way by means of the preconditioner, i.e through the solution of the ordinary Poisson equation, both in the SC and PCG algorithm.

C. Numerical results

Both the self-consistent iterative procedure (Algorithm 1) and the preconditioned conjugate gradient minimization scheme (Algorithm 2) have been implemented and tested. As SPE solver (step 4 of Algorithms 1 and step 3 of Algorithm 2), we used the Interpolating Scaling Function (ISF) Poisson Solver, allowing to obtain highly accurate electrostatic potentials for free, wire, surface, and periodic boundary conditions at the cost of \( O(N \log(N)) \) operations, where \( N \) is the number of discretization points (see Ref. [14]).

To test both solvers analytic three dimensional functions have been used. An orthorhombic grid of uniform mesh spacing \( h_{\text{grid}} \) and \( (n_x, n_y, n_z) \) points in each directions has been used. Fig. 1 shows plots of these benchmark fields along a particular direction passing through the box center and parallel to the y axis. All functions depend on the radial distance \( r \) from the center of the simulation domain.

A normalized Gaussian function has been chosen for the electrostatic potential \( \phi(\mathbf{r}) \) (red dash line in Fig. 1) and the charge density \( \rho(\mathbf{r}) \) has been derived from the chosen potential and dielectric function, applying the generalized Poisson differential operator of Eq. (6) (red dot line). In order to reproduce the dielectric environment in electrostatic problems typically used for a solute system embedded in a solvent (i.e. a cavity where the majority of the atomic charge density is confined), the error function \( 1 + (\epsilon_0 - 1)h(d_0, \Delta; r) \) has been chosen to represent the spatially varying electric constant \( \epsilon(\mathbf{r}) \) (solid black line in Fig. 1), where

\[
h(d_0, \Delta; r) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{r - d_0}{\Delta} \right) \right]. \tag{17}
\]

Here \( \Delta \) is a parameter which controls the transition region (\( \approx 4\Delta \) wide) between the inner part within the cavity of radius \( d_0 \) and the external part, and \( \epsilon_0 \) is the dielectric constant of the surrounding medium. These bench-
mark functions have been used for both free, surface and periodic boundary conditions.

To implement the nabla differential operator needed for Algorithm 1, central, forward and backward finite difference filters of order 16 have been used, which match the accuracy of the underlying SPE solver. We remark that the use of these finite difference filters is not needed for Algorithm 2 as soon as the correction term of Eq. (16) is pre-calculated.

Fig. 2 shows solver performances. The top graphs report the residual norm as function of the iteration number. The residual norm is defined as the Euclidean norm of the residual vector \( r_k \). Graphs in lower panel present the output accuracy as a function of the iteration number. The accuracy in the whole paper is defined as the maximum value of the difference between the final numerical solution and the analytical potential. In this test case a cubic box of length 10 [arb. units] has been chosen with \( n_x = n_y = n_z = 300 \). The Gaussian variance for the potential \( \phi(r) \) was \( \sigma = 0.5 \), and the parameters of \( \epsilon(r) \) were \( d_0 = 1.7 \), \( \Delta = 0.3 \) and \( \epsilon_0 = 78.36 \) (all in [arb. units]). The mixing parameter in step 6 of Algorithm 1 has been fixed to be \( \eta = 0.6 \), resulting in a robust convergence for all cases. Lower values slow down the convergence for the chosen test functions.

The PCG solver (black squares) exhibits a faster convergence with respect to the SC one (blue circles), reaching an accuracy of \( \sim 10^{-10} \) with some ten iterations. Furthermore its behavior does not change with the boundary conditions as is the case with the SC algorithm. It is worth remembering that each PCG iteration involves only a single solution of the ordinary Poisson equation and as well as of fully parallelizable vector operations. If an accuracy of \( \sim 10^{-4} - 10^{-5} \) is enough, then some five iterations solve the electrostatic problem. These features make the developed PCG algorithm together with the chosen preconditioner of Eqs. (13) very efficient for atomistic calculations where the generalized Poisson equation needs to be solved repeatedly. Performances of the implemented PCG procedure are also higher than multigrid approaches to solve the GPe, where a number of iterations between 17 and 25 are needed to reach an accuracy of \( \sim 10^{-8.16} \).

For the sake of completeness, the preconditioned steep-
est descent scheme (Algorithm 2 with $\beta_k = 0$) has been tested with the preconditioner described by Eq. (11). Residual norm convergence as well as the accuracy of the solution (not reported) behaves like the self-consistent approach (Algorithm 1, blue circles of Fig. 2). An integration of DII$S$ in the PSD loop effectively lowered the iteration numbers, but didn’t show better performances with respect to the PCG approach.

III. POISSON-BOLTZMANN EQUATION

The generalized Poisson equation so far discussed holds for a solute plunged in a neutral solution where no mobile charges are present. In order to extend the library to ionic solutions, effects of mobile ions have to be taken into account which, being free to move inside the dielectric medium, modify the spatial distribution of charge and potential close to the interface and giving rise to the well known double layer.

In general, mobile charges can be included in the electrostatic problem by means of a continuum mean-field approach, assuming point-like ions in thermodynamic equilibrium. Once the equilibrium is reached, ionic concentrations explicitly depend on the local electrostatic potential $\phi(r)$. Following this idea, the potential $\phi(r)$ generated by a charge density $\rho(r)$ placed in contact with a ionic solution can be extracted solving the generalized Poisson equation (Eq. (4)). Several models have been proposed in the literature for the ionic bulk concentrations [see Eq. (5)]. Gouy$^{17}$ and Chapman$^{18}$ proposed a Boltzmann distribution

$$c_i[\phi](r) = c_i^\infty \exp \left( -\frac{Z_i e \phi(r)}{kT} \right),$$

where $k$ is the Boltzmann constant and $T$ the absolute temperature of the solvent. Combining Eqs. (4,5,18) the well-known Poisson-Boltzmann equation can be recovered. It arises from the equilibrium between thermal and electric forces, which depend, respectively, on the ionic concentration and electrostatic potential. At equilibrium the total average force must be zero and Eq. (18) holds. In the regions where the electrostatic energy is smaller then $kT$, i.e. $Z_i e \phi(r)/kT \ll 1$, the exponential of Eq. (18) can be approximated with a linear function of $\phi(r)$, switching the non-linear problem of Eq. (4) into a linear one.

The Poisson-Boltzmann equation correctly predicts ionic profiles close to the solid-liquid interface with ionic solutions. However it strongly overestimates ionic concentrations close to highly charged surfaces or multivalent ions. In order to overcome these drawbacks, several models have been proposed$^{19}$. Finite ion size effects can be included in the model by introducing an additional internal force. Using a Bikerman-type expression to model steric effects$^{20}$ and imposing that at equilibrium the total average force (thermal, electric and steric) must go to zero, a Langmuir-type equation for the ionic concentrations can be found

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

(19)

In Eq. (19) $c_i^{\max}$ are the maximum local concentration that a ionic species of effective radius $R_i$ can attain. This last is given by

$$c_i^{\max} = \frac{p}{4 \frac{\pi R_i^3 N_A}},$$

(20)

where $p$ is the packing coefficient. The combination of Eqs. (4,5,19) give rise to the so-called modified Poisson-Boltzmann (MPBe) equation$^{12-23}$. It accounts for finite ion size effects representing an extension of the PBe, preventing ion concentrations to exceed $c_i^{\max}$. Note that if $c_i^{\max} \to \infty \forall i \in \{1,2,3,\ldots,m\}$, Eq. (19) is reduced to Eq. (18) and the standard Poisson-Boltzmann equation holds.

Both PBe and MPBe equations consider ions in solution as pointlike. A further extension can account for finite size effects in an explicit way, describing ions by means of insulating spheres plunged in the dielectric solvent$^{24}$. This correction allows for a local modification of the solvent permittivity as well as the inclusion of two new forces: one related to a non-uniform dielectric which tend to move ions into high-permittivity regions; another due to the interaction of the ion dipole and the non-uniform local electric field (dielectrophoretic force).

The Poisson-Boltzmann equation is more difficult to solve than the generalized Poisson equation due to the fact that it leads to a non-linear problem. If $Z_i e \phi(r)/kT \ll 1$, Eq. (18) can be approximated by a linear function of $\phi(r)$, and the Poisson-Boltzmann problem of Eq. (4) becomes linear. In Sec. II B a particular preconditioner, i.e. Eq. (13), has been proposed for the solution of the GPe. Furthermore the generalized Poisson operator has a linear term with respect to $\phi(r)$ [Eq. (16)]. Therefore Algorithm 2 is expected to solve the linear regime of the PBe, where the $A$ operator is now given by Eq. (16) with an additional linear term:

$$Av_k(r) = \nabla \cdot (\epsilon(r) \nabla v_k(r)) + 4 \pi \rho^{\text{ions}}[\phi](r) = -v_k(r) \left[ q(r) + 4 \pi \epsilon^2 N_A \sum_{i=1}^m Z_i^2 c_i^{\infty} \right] - 4 \pi r_k(r),$$

(21)

where $q(r)$ has been defined in Sec. II B. In the general non-linear case, at variance to the generalized Poisson equation discussed in the previous sections, there
Algorithm 3  Self-Consistent iterative procedure for the Poisson-Boltzmann equation

1: set \( \rho_0^{\text{ions}} \)
2: for \( k = 0, 1, \ldots \) 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 1 or 2)
5: compute \( \rho_k^{\text{ions}}[\phi_k] \)
6: \( \rho_k^{\text{ions}} = \eta \rho_k^{\text{ions}}[\phi_k] + (1 - \eta) \rho_k^{\text{ions}} \)
7: \( r_{k+1} = \rho_k^{\text{ions}} - \rho_k^{\text{ions}} \)
8: end for

Algorithm 4  Improved Self-Consistent iterative procedure for the Poisson-Boltzmann equation

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

is no general consensus on what flavor of the Poisson-Boltzmann equation is most appropriate for various problems. Therefore a (M)PBe solver should allow to solve various formulations of this equation. Since it is unlikely that for all variants an action integral can be established (allowing for a minimization scheme), a self-consistent approach should be the most appropriate algorithm.

Such a procedure has been implemented and it is detailed in Algorithm 3. The ionic charge density \( \rho_k^{\text{ions}}[\phi] \) is included as source term to the charge density of the generalized Poisson equation which, in turn, is solved repeatedly until self-consistency between the potential and the ionic charge induced by it is reached. Starting with an initial input guess \( \rho_0^{\text{ions}} \) for the ionic charge density, on each self-consistent cycle a generalized Poisson solver (Algorithm 1 or 2) is applied to numerically compute the electrostatic potential \( \phi(r) \). Then the ionic charge is computed using the new potential and mixed with the old density by means of a linear scheme tuned by the parameter \( \eta \).

In order to speed up performances of the (M)PBe solver, an improved version is reported in Algorithm 4. On each iteration \( k \) the electrostatic problem at step 4 is solved only for the previous residual vector \( r_{k-1} \) once \( \rho_k^{\text{ions}} \) has been updated at step 3. Then the overall solution is given at step 5 as sum over all potential corrections \( \phi_k' \). This procedure substantially corresponds to the general self-consistent approach of Algorithm 3, now using on each step information of the previous as input guess. It is worth noting that the improved Algorithm 4 can be coupled only with the faster PCG solver (Algorithm 2) for the GPe.

A. Numerical performances

To show performances and accuracy of the Poisson-Boltzmann solver, both Algorithms 3 and 4 have been applied to analytical test cases. Following the strategy reported in Sec. II C, all the involved fields and functions, i.e. the potential, the charge density and the operator have been discretized on the orthorhombic three dimensional grid and same parameters have been used to set up all analytical functions. The electrostatic problem lies in a cavity where the great majority of the charge density is confined, described by means of a dielectric function \( \epsilon(r) \) (solid black line of Fig. 1). A normalized Gaussian function has been chosen for the electrostatic potential \( \phi(r) \) (red dash line of Fig. 1), whereas the charge density \( \rho(r) \) has been derived from the chosen potential and dielectric function, applying the Poisson-Boltzmann differential operator.

A monovalent \((Z_1 = -Z_2 = 1)\) binary aqueous electrolyte solution has been considered, with a close packing coefficient \( p = 0.74 \), effective ionic radius \( R_i = 3 \ [\text{Å}] \) and bulk ion concentrations \( c_i^\infty = 100 \ [\text{mol/m}^3] \) kept fixed for all ions. As discussed in Sec. III, the PCG algorithm has been applied to solve the linear Poisson-Boltzmann equation with the same GPe preconditioner of Eq. (13). In Fig. 3 the euclidean norm of the residual vector \( r_k \) (black squares) and the accuracy of the numerical solution (blue circles) have been reported. Similar performances have been found with respect to the generalized Poisson solver, reaching an accuracy of \( \sim 10^{-10} \) with some ten iterations and proving that the PCG procedure is a well suited and fast method also for the linear regime of the PBe.

In the general non-linear case, Algorithms 3 and 4 have been applied. An input guess \( \rho_0^{\text{ions}} = 0 \) has been chosen. We found that only a relatively small number of self-consistency iterations is needed in this approach to solve both the Poisson-Boltzmann and the modified Poisson-Boltzmann problem. Fig. 4 shows the euclidean norm of the residual vector \( r_k \) (black squares) and the accuracy of the numerical solution (blue circles) for the modified Poisson-Boltzmann solver with free boundary conditions. The solver exhibits a fast convergence, reaching an accuracy of \( \sim 10^{-10} \) with some five iterations. The inset shows \( \rho^{\text{ions}}[\phi] \) as given by Eqs. (5,19), revealing an ionic density saturation in the solvent for electrostatic poten-
FIG. 3. Euclidean norm of the residual vector \( r_k \) (black squares) and accuracy of the numerical solution (blue circles) for the linear Poisson-Boltzmann equation with free boundary conditions (Algorithm 2 has been applied with \( \mathcal{A} \) the linear Poisson-Boltzmann operator).

Effects of complex wet environments surrounding an atomistic system can be approximately included into density functional calculations by simply introducing a dielectric cavity surrounding the atomistic system and taking in Eq. (1) the electrostatic potential \( \phi(\rho(\mathbf{r})) \) as solution of the generalized Poisson or Poisson-Boltzmann equation. The PCG solver for the GPe (Algorithm 2) has been implemented in the electronic-structure package BigDFT, extending the capability of the code beyond vacuum-simulations. Two distinct approaches have been implemented and tested to build up a dielectric cavity enveloping the atomic system. In both approaches the cavity, mapped by the dielectric function \( \epsilon(\mathbf{r}) \), is fully differentiable and continuous in the whole simulation domain.

In the first approach a function \( \epsilon(\mathbf{r}) \) is defined starting from spherical-symmetric atom-centered cavities. Each sphere depends only on the radial distance with respect to a fixed atomic position. The whole rigid cavity is kept fixed during the whole SCF cycle in a DFT simulation. On the other hand, it could be argued that regions occupied by atoms and their associated electronic charge density are strictly related. In other words, the actual value of the charge density might determine how much “space” is occupied by the solute. Starting from this idea, a cavity can be build up directly from the electronic density, as it has been shown in various publications.

In this second approach the dielectric function is not explicitly space-dependent, but can be implicitly mapped by means of the electronic charge density.

### IV. ELECTRONIC STRUCTURE COMPUTATIONS

A. Rigid cavity

The most widespread continuum solvation model, which tries to include the effects of a surrounding dielectric medium in an implicit way, is the polarizable continuum model developed by J. Tomasi and co-workers. In the PCM formulation the cavity surrounding the solute is sharp and discontinuous, and a polarization charge density is exactly localized at the vacuum-dielectric interface. In this way the dielectric environment is represented by an effective surface polarization charge, reducing the electrostatic problem into a two-dimensional one. Furthermore the cavity can be considered rigid since it depends only on the atomic coordinates which does not vary during a SCF cycle in DFT simulations.

For a first test of the electrostatic solvers (Algorithm
1 and 2) integration in an electronic-structure code, a PCM-like cavity has been considered. The dielectric function \( \epsilon(r) \) is given by the product of spherical-symmetric atom-centered error functions. Differently from the early PCM model, we here define a cavity which is fully differentiable and continuous. In particular, for a system of \( N \) atoms of coordinates \( \mathbf{R}_i \) (for \( i = 1, ..., N \))

\[
\epsilon(r, \{\mathbf{R}_i\}) = (\epsilon_0 - 1) \left\{ \prod_i h(d_i, \Delta; d(r, \mathbf{R}_i)) \right\} + 1, \tag{22}
\]

where \( \epsilon_0 \) is the dielectric constant of the surrounding medium and the function \( h \) is defined by Eq. (17). In Eq. (22) \( d(r, \mathbf{R}_i) = ||r - \mathbf{R}_i|| \), \( d_i \) are the cavity radii which depend on the particular atom species, and \( \Delta \) a parameter (kept fix for all atoms) which controls the transition region (\( \approx 4 \Delta \) wide) from 0 to 1 where the polarization charge is located. Starting from Eq. (22), all vectors which explicitly depend on \( \epsilon(r) \) can be analytically computed. The cavity is uniquely defined once \( \mathbf{R}_i, d_i \) and \( \Delta \) are fixed. All environment-dependent fields are calculated once at the start of the solver and kept fixed throughout the procedure.

In must be noticed that this definition of the cavity relies on the explicit dependence of \( \epsilon(r, \{\mathbf{R}_i\}) \) from the atomic coordinates \( \mathbf{R}_i \) (and, consequently, of the system Hamiltonian). This dependence gives rise to additional terms when atomic forces are computed. The analytical rigid cavity above described should overcome this problem allowing a direct analytic calculation of such additional contributions. Moreover, the values of \( d_i \) and of \( \Delta \) have to be tuned by the user, usually by choosing a solvent-dependent scaling factor with respect to empirical Van der Waals radii\(^{20}\). A solution that would remove part of this arbitrariness should therefore avoid an explicit use of atomic coordinates in the cavity mapping. This will be the subject of the following section.

### B. Charge-dependent cavity

For this definition of the cavity, the dielectric function does not explicitly depend in the atomic positions, but implicitly via the charge density \( \rho^{\text{elec}} \)

\[
\epsilon(r) = \epsilon(\rho^{\text{elec}})(r). \tag{23}
\]

This approach allows the cavity to self-consistently change during the SCF loop, strictly following the modification of the electronic charge density. A cavity surrounding an atomic system can be generated by means of two threshold parameter, i.e. \( \rho_{\text{max}} \) and \( \rho_{\text{min}} \), fixing \( \epsilon(r) = 1 \) in regions when \( \rho^{\text{elec}}(r) > \rho_{\text{max}} \) and \( \epsilon(r) = \epsilon_0 \) when \( \rho^{\text{elec}}(r) < \rho_{\text{min}} \). Like \( d_i \) in the rigid case, \( \rho_{\text{max}} \) fix the width of the cavity, whilst the extension of the transition region, previously defined by \( \Delta \), is now tuned by \( \rho_{\text{min}} \).

Several features make the self-consistent cavity more advantageous with respect to the rigid one. First, once the electron charge density is given, only two parameters uniquely define both the cavity and the transition region for the whole atomic system. Furthermore, since the dielectric function does not explicitly depend on the atomic coordinates, the evaluation of ionic forces can be done without modifications with respect to a simulation in gas-phase.

Among several ways to define the functional dependence on the electronic charge density, the self-consistent continuum solvation (sccs) model developed in Ref. \([15]\) has been implemented. It allows to fit experimental solvation energies on a set of 240 neutral solutes with a mean absolute error of 1.2 kcal/mol:

\[
\epsilon(\rho^{\text{elec}}) = \begin{cases} 
1 & \rho^{\text{elec}} > \rho_{\text{max}} \\
\epsilon_0 e^{w(\rho^{\text{elec}})} & \rho_{\text{min}} < \rho^{\text{elec}} < \rho_{\text{max}}, \\
\epsilon_0 & \rho^{\text{elec}} < \rho_{\text{min}}
\end{cases}, \tag{24}
\]

where \( w(x) \) is a continuous smooth function describing the transition region between vacuum (where atoms are placed) and the full dielectric medium:

\[
w(x) = \frac{1}{2\pi} \left[ z(x) - \sin(z(x)) \right]; \tag{25}
\]

\[
z(x) = 2\pi \frac{\ln \left( \frac{\rho_{\text{max}}}{\rho_{\text{min}}} \right)}{\ln \left( \frac{\rho_{\text{max}}}{\rho_{\text{min}}} \right)} . \tag{26}
\]

A good description of this region by means of Eq. (24) is mandatory for the procedure convergence as well as for the mapping of the polarization charge there confined. Since \( \epsilon(r) \) explicitly depends on \( \rho^{\text{elec}}(r) \), its variation needs to be included in the Kohn-Sham (KS) potential. Starting from Eq. (3) and integrating by parts, the electrostatic energy can be rewritten as

\[
E_{\text{ex}}[\rho] = \frac{1}{2} \int \rho \phi[\rho] d\mathbf{r} = \frac{1}{8\pi} \int \epsilon[\rho](\nabla \phi[\rho])^2 d\mathbf{r}. \tag{27}
\]

Its functional derivative with respect to \( \rho \) gives the electrostatic potential \( \phi \) plus an additional term \( v_e(\mathbf{r}) \)

\[
v_e(\mathbf{r}) = -\frac{1}{8\pi} \frac{\partial \epsilon(\rho^{\text{elec}})}{\partial \rho^{\text{elec}}}|\nabla \phi(\mathbf{r})|^2, \tag{28}
\]

which has to be added to the KS potential.

### C. Solvation Free energies

In order to test the integration and performances of the generalized Poisson solver into \textit{ab initio} codes, the whole procedure previously described, i.e. Algorithm 1 and 2 of Sec. II A and II B, rigid and charge-dependent cavities of
Sec. IV A and IV B as well as the additional term of Eq. (28) have been integrated in the main BigDFT package. This extension allows to handle complex wet environments in electronic-structure calculations, including implicitly the effects of a solvent surrounding an atomic system.

The electrostatic solvation energy is defined as difference between the total energy of a given atomic system in the presence of the dielectric environment and the energy of the same system in vacuum

$$\Delta G^{el} = G^{el} - G^0. \quad (29)$$

A full comparison with experimental solvation energies needs the inclusion of non-electrostatic contributions. In this case the main terms in the solute Hamiltonian, as introduced by PCM, are

$$\Delta G^{sol} = \Delta G^{el} + G^{cav} + G^{rep} + G^{dis} + G^{tm} + P \Delta V, \quad (30)$$

where $\Delta G^{el}$ is the electrostatic contribution, $G^{cav}$ the cavitation energy, i.e. the energy necessary to build up the solute cavity inside the solvent medium. $G^{rep}$ is a repulsion term representing the continuum counterpart of the short-range interactions induced by the Pauli exclusion principle, whilst $G^{dis}$ reflects van der Waals interactions. The thermal term $G^{tm}$ accounts for the vibrational and rotational changes and, finally, $P \Delta V$ includes volume change in the solute Hamiltonian.

The inclusion of all non-electrostatic contributions goes beyond the aim of the present paper, where testing of the generalized Poisson solver and its integration into first principle atomistic calculations is the main goal. Therefore only electrostatic solvation energies have been computed for a set of small neutral organic molecules.

Water has been chosen as solvent for all cases, with a dielectric constant of $\varepsilon_0 = 78.36$ (experimental value at low frequency and ambient conditions). Final energies for all molecules have been extracted after a full geometry optimization both in vacuum and in aqueous solution. In all cases the surrounding dielectric medium lowers the total energy of the system with respect to vacuum, because the polarization of the dielectric stabilizes the solutes.

Table I reports electrostatic solvation energy $\Delta G^{el}$ obtained both with rigid and self-consistent cavities under free boundary conditions. As previously stated, a critical point of PCM approaches is the choice of shape and size of the cavity, which should mimic the solute incorporating the whole atomic charge density. From its first formulation, PCM atomic radii $R_i$ were fixed proportional to the van der Waals radii, $R_i = f \cdot R_i^{vdw}$. In our rigid model, a proportional factor of $f = 1.2$ has been fixed and the Pauling’s set of atomic radii has been considered (except for the hydrogen atoms bound to heteroatoms which have a radius value of 1 Å). Having a further degree of freedom with respect to sharp PCM cavities, a $\Delta = 0.5$ [a.u.] has been tuned and kept constant for all atoms.

| Molecule | $\Delta G^{el}_{\text{PCM}}$ | $\Delta G^{el}_{\text{rigid}}$ | $\Delta G^{el}_{\text{sccs}}$ | $\Delta G^{el}_{\text{sccs-bigDFT}}$ |
|----------|-----------------|-----------------|-----------------|-----------------|
| CH₃ | -6.65 | -6.28 | -5.39 | -5.33 |
| H₂O | -8.98 | -8.32 | -8.21 | -8.23 |
| CH₄ | -0.61 | -1.20 | -0.68 | -0.63 |
| CH₃OH | -6.78 | -6.57 | -5.89 | -5.83 |
| CH₃NH₂ | -4.51 | -5.71 | -4.53 | -4.45 |
| CH₃CONH₂ | -12.53 | -12.97 | -11.87 | -11.87 |

As reference, in Table I sccs calculations from Ref. [15] together with PCM calculations have been reported. The latter were performed with the Gaussian 09 code along with the version of PCM which was the default in Gaussian 03, as specified by the keyword g03defaults. Only electrostatic solvation effects were included in the calculation and, to simplify the comparison, the simple van der Waals surface was adopted with Pauling’s set of atomic radii (explicit hydrogens), but without the additional smoothing used to describe the solvent-excluded surface. The Perdew-Berke-Ernzerhof (PBE) functional functional and the extended triple-zeta 6-311+g(d,p) basis set were used for both geometry optimizations and energy calculations, in vacuum and in solution, consistently with the set up used for the parameterization of the electrostatic solvation energy in sccs.

In all calculations soft norm-conserving pseudopotentials including non-linear core correction and Pauling’s set of atomic radii along with PBE functional were used to describe the core electrons and exchange-correlation, respectively.

For the self-consistent cavity, values of $\rho_{max} = 5 \cdot 10^{-3}$ and $\rho_{min} = 1 \cdot 10^{-4}$ have been fixed which produces a mean absolute error of 1.20 kcal/mol for the solvation energies of a database of 240 molecules. A perfect agreement has been reached which confirms the performance and reliability of the integrated generalized Poisson solver.

In order to test and validate the whole library in BigDFT, the effects of grid resolution and boundary conditions on the electrostatic solvation energies for the same set of neutral molecules have been investigated. The global accuracy is strictly related to the size of the simulation box and the spatial grid resolution $h_{grid}$. However a decrease of the latter can affect the whole cost of the calculation both in time and memory usage. Consequently it is worth to investigate the effects of the dielectric medium’s inclusion in a DFT run with respect to the vacuum case.

In this respect Kohn-Sham total energies have been extracted both in vacuum and in the presence of the solvent (water) as function of the spatial grid $h_{grid}$. Its accuracy is reported in Fig. 5 as difference with the reference value at $h_{grid} = 0.20$ bohr. Results show that the accuracy is
not affected by the surrounding dielectric environment (filled symbols, solid lines) with respect to the vacuum case (empty symbols, dash lines). Following the same guidelines, the accuracy of the electrostatic solvation energy [Eq. (29)] with respect to the spatial grid $h_{\text{grid}}$ has been investigated and reported in Fig. 6. Results show that a $h_{\text{grid}} = 0.30$ bohr in BigDFT with free boundary condition provides electrostatic solvation energies with an accuracy lower than $\sim 10^{-2}$ kcal/mol.

Since isolated systems embedded in a wet environment are the subject of interest, spurious long range electrostatic interactions with periodic images due to artificially imposed periodicities along certain direction can be problematic. In the developed procedure the boundary conditions enter through the preconditioner, i.e. the SPe solver. Since in the BigDFT Poisson solver all the common boundary conditions such as free, wire and surface are exactly implemented, such spurious interactions do not exist at any stage of our approach. Fig. 7 reports the difference between the electrostatic solvation energies computed with periodic and free boundary conditions as function of the periodic cell length and keeping fixed the spatial grid $h_{\text{grid}} = 0.20$ bohr. Molecules have been ordered according to the strength of their electrostatic dipole, from largest to smallest. Dipole values for each molecule are reported on Table II both in vacuum and in the present of a water solvent. It can be noticed that the presence of the polar solvent increases the electrostatic dipoles of the molecules. As it might be expected, the free BC calculation represents the asymptotic results for periodic BC calculation of increasing box sizes. Interactions with image-molecules are less relevant for molecules with small dipole moment like CH$_4$, but are not negligible for molecules with larger dipoles such as CH$_3$CONH$_2$. In such cases unrealistic large periodic boxes are required for periodic BC to reproduce the free boundary condition results with high accuracy.

Numerous processes of practical interest involve surfaces in contact with neutral or ionic solvents, leading to an induced polarization charge of the dielectric medium or an electric double layer. The BigDFT package allows to use exact surface boundary conditions avoiding spuri-
TABLE II. Molecule dipole norm in vacuum and water solvent (in Debye).

| Molecule       | Dipole_{vacuum} | Dipole_{water} |
|----------------|-----------------|----------------|
| CH$_3$CONH$_2$ | 3.88            | 5.76           |
| H$_2$O         | 1.81            | 2.41           |
| CH$_3$OH       | 1.57            | 2.14           |
| NH$_3$         | 1.49            | 1.98           |
| CH$_3$NH$_2$   | 1.27            | 1.78           |
| CH$_4$         | 0.00            | 0.00           |

FIG. 8. TiO$_2$ surface in contact with water: isosurfaces of the polarization charge $\rho_{pol}$ in the implicit dielectric medium.

In the present work a library to handle complex wet-environments in electronic-structure calculations has been presented. It allows to include on the atomistic scale effects of an aqueous environment in an implicit way. The solver is able to handle both the generalized Poisson and several variants of the Poisson-Boltzmann equation. The core of the generalized Poisson solver is a preconditioned conjugate gradient algorithm which allows to numerically solve the minimization problem with some ten iterations. The same algorithm works for the linear case of the Poisson-Boltzmann equation, whilst for the general case a self-consistent procedure has been implemented. The chosen preconditioner is based on the ISF Poisson solver for the standard Poisson equation, which can handle all common boundary conditions exactly. The code requires a small amount of memory and is very fast and in addition also highly parallelized. We have shown that coupled with BigDFT, our method can correctly reproduce electrostatic solvation energies of a set of small neutral organic molecules. Effects of grid resolution and boundary conditions on the electrostatic solvation energies have been reported. The whole library, will be released as an independent program suitable for integration in other electronic structure codes. A GPU-accelerated version of this software package is also in preparation, following the guidelines indicated in Ref. [37].

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