Coupling Quantum Monte Carlo to a Nonlinear Polarizable Continuum Model for Spherical Solutes

Claudio Amovilli,*,† Claudia Filippi,‡ and Franca Maria Floris†

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy, and Instituut-Lorentz for Theoretical Physics, Universiteit Leiden, Niels Bohrweg 2, Leiden, NL-2333 CA, The Netherlands

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Starting from the nonlinear dielectric response model of Sandberg and Edholm, we derive an analytical expression of the polarization contribution to the solvation free energy in terms of the electronic density of the solute and the dielectric properties of the solvent. The solvent inhomogeneity is taken into account with the use of a smooth switching function whose spacial variation is established on the basis of how the solvent is arranged around the solute. An explicit form of a local potential representing the solvent effect on the solute is thus obtained by functional analysis. This effective potential can be combined with density functional or quantum chemical methods for the quantum mechanical treatment of the solute. Here, we use quantum Monte Carlo techniques for the solute and apply the method to the hydration of atomic ions finding very good agreement with experimental data.

1. Introduction

Significant theoretical effort has been devoted over the years to the development and improvement of continuum models of solvation.[1,2] Even though current computer capabilities often allow the inclusion of the first shells of solvation in the quantum mechanical part of the calculation, the continuum models are still the most widely used methods to simulate the effect of a solvent in theoretical studies of very large solutes,[3] of optical and spectroscopic properties of solutes, and of chemical reactivity in solution.[2]

In the basic polarization continuum model (PCM),[4] the solute is treated at a pure ab initio quantum mechanical level and is embedded in a linear, homogeneous, and isotropic dielectric medium characterized by a constant relative permittivity. This medium represents the solvent and, in the basic PCM, interacts with the solute only electrostatically. The solution of this electrostatic problem requires the definition of a cavity, i.e., a region of space from which the solvent is excluded and in which the solute is placed. Typically, the shape of the cavity is modeled on the solute and is often constructed to contain the largest possible amount of solute electronic distribution. The problem is then solved by coupling the Poisson's equation of the solute−solvent system with an effective Schrödinger equation for the solute. The Hamiltonian operator for the solute contains two terms: the Hamiltonian of the solute in vacuo and the so-called solvent reaction potential, i.e., the potential due to the solvent polarization, which is derived from the solution of the coupled Poisson's equation.

The effective Scrödinger equation of the PCM can be used to obtain the molecular properties of a solute in a given solvent. For an exhaustive description of possible applications, we refer the reader to the recent review of ref 2. Here, we only mention some of the most important ones such as geometrical deriva-

tives,[5,6] spectroscopic properties,[7−9] and linear and nonlinear response properties to external electric and magnetic fields.[10,11] If the solute is a reaction complex, one can study chemical reactions,[12,13] effective intermolecular interaction potentials mediated by the solvent,[14,15] and various other aspects of supermolecular chemistry in solution.[16,17]

The basic PCM cannot, however, be used when the dielectric permittivity depends on the electric field. This occurs when the medium is exposed to a strong electric field. In this case, orientational polarization due to the molecular dipoles of the medium reaches an upper limit, leading to the so-called dielectric saturation. Electric fields of such strength can be encountered in proximity of ionic solutes.

Recently, the problem of the extension of PCM to a nonlinear framework has been re-examined by Sandberg and Edholm.[18] The nonlinear dielectric response is based on the Langevin−Debye statistical theory,[19] which works very well in the gas phase but is inadequate for condensed matter. This inadequacy has been resolved by Sandberg and Edholm by introducing an appropriate Onsager correction factor in the basic Langevin−Debye equation.

In this work, we present an approach that combines the nonlinear dielectric response theory of Sandberg and Edholm with density functional or quantum chemical methods for the treatment of spherical solutes. In particular, we choose quantum Monte Carlo (QMC) methods for the quantum mechanical treatment of the solute. Starting from the results of Sandberg and Edholm, we rewrite the relative dielectric permittivity of the solvent in terms of the displacement field. We derive then an expression for the polarization free energy that contains explicitly the solute wave function and the dielectric properties of the solvent. Finally, from the polarization free energy, a local potential representing the effect of the solvent on spherical solutes can be obtained and used in the Schrödinger equation for the solute.

The outline of the paper is as follows. In Section 2, we discuss the superposition between the charge cloud of solute and solvent

* Address correspondence to this author. E-mail: amovilli@dcci.unipi.it.
† Università di Pisa.
‡ Universiteit Leiden.

molecules. In Section 3, we illustrate the theory in detail. In Section 4, we present the results for some selected atomic isoelectronic systems in water solution, and in Section 5, we draw the conclusions and discuss future directions.

2. Charge Overlap in Water: Atomic Ions Solvated Clusters

The dielectric properties of a medium are commonly measured at the macroscopic scale and, consequently, the continuum models[2] developed to study the solute electronic response to solvation need some ad hoc parametrization in passing to the microscopic scale. Typically, in such models, the solute is placed in an empty cavity in the dielectric medium, with the size of the cavity properly adjusted to reproduce some experimental property as for example the free energy of solvation.[20] A further common assumption is that the boundary of the cavity separates the domain of solute electrons from the domain of the continuum medium. Under these conditions, linear dielectric response theory and standard quantum chemistry methods can be combined[4,21,22] and a variety of efficient computer programes[23,24] are available for many practical purposes.

Severe complications may arise at the microscopic scale if there is superposition between the electronic clouds of solute and solvent molecules. In the overlap region, there is still a solvent response of electronic type and the electron−electron interaction is modified by effects of quantum origin[25] like exchange and correlation.

To illustrate the degree of charge overlap, we consider the prototypical examples of the isoelectronic series (10 electrons) of atomic solutes F^-, Ne, Na^+, and Mg^{2+} in water solution. These systems have been extensively studied at various levels of calculation[18,26−33] and, from the data available in the literature, it is possible to establish reliable geometries for the first hydration shell. Using these geometries, we can then estimate the charge overlap by counting the electrons of solvent and of solute which fall in a sphere of a given radius centered on the atomic solute. This was made possible by using electron configurations generated by accurate quantum Monte Carlo wave functions obtained for isolated water and atomic systems. It is important to remark that the present analysis is only qualitative because we consider the electron distribution of the isolated species.

In Figure 1, for each atomic system, we plot the number of solvent electrons in the sphere and the number of solute electrons outside the sphere as a function of the sphere radius. The two functions easily permit us to visualize charge overlap since they are zero where there are no electrons of the solvent and of the solute, respectively. For the ions, the vertical line corresponds to the Born radius,[34] which reproduces a polarization free energy of −106 kcal/mol for F^-, −93 kcal/mol for Na^+, and −442 kcal/mol for Mg^{2+}. These numbers are reliable polarization contributions to the total free energies of solvation (see Section 4 and ref 35).

From Figure 1, it is evident that the electronic distributions of water and ions may overlap at the intermolecular distances stabilized by the electrostatic interactions. While charge overlap is negligible for Ne, it is quite pronounced for F^- in the region where H bonds with water are formed. For the two cations, Na^+ and Mg^{2+}, there is charge overlap but it is less than that for F^-. In all cases, polarization effects are not accounted for in Figure 1 and should enhance charge overlap.

If we look at the Born radii, it is in general difficult to relate them to a contact radius between solute and solvent molecules. For F^-, the Born radius falls in the region of the overlap and
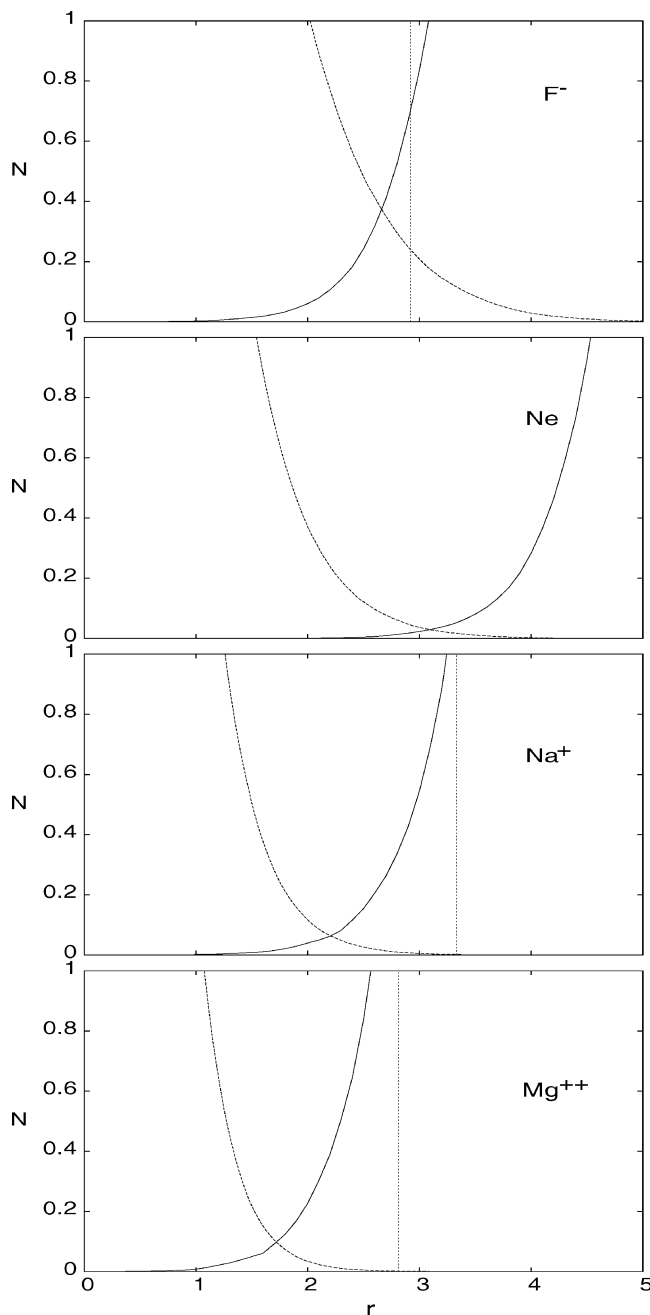

Figure 1. Number of solvent (water) electrons contained in the sphere centered on the solute (the atomic ions F^-, Ne, Na^+, and Mg^{2+}) and number of solute electrons which are outside the same sphere, as a function of the sphere radius. For the ions, the vertical line corresponds to the Born radius (see text). The distance is in au.

can be viewed as a (soft) contact radius. However, for the cations, the Born radius represents a good value for a sphere that contains all solute electrons but, in this sphere, there is still a significant fraction of one solvent electron. Other atomic radii commonly used in continuum models (see, for example, ref 20) are not significantly different from the Born radii and therefore show the same behavior.

The phenomenon of charge penetration of solute in the domain of the dielectric solvent has several implications for the validity of continuum models. First, it is quite difficult to reproduce the different behavior of anions and cations in water with a model of dielectric response. Then, a description in terms of a sharp cavity separating the solvent and solute domains is clearly inadequate and, since it is not realistic to resort to the anisotropy of dielectric permittivity for water, it is necessary

to introduce some type of inhomogeneity to mimic the effect of hydrogen bonds. Finally, when too pronounced, charge overlap also leads to severe computational problems.[36]

To overcome some of the above difficulties, the exact solution of Poisson's equation has previously been performed within the linear dielectric response[21,37−39] and an additional apparent volume polarization charge density lying outside the cavity has been included in the calculation of the reaction potential. More recently, the electrostatic problem of solvation has been generalized to include the dependence of solvent dielectric permittivity on electric field and, for some systems, numerical solutions have been found in a nonlinear response framework.[18,40] In the next section, starting from these recent results, we make analytical progress for spherical solutes and show how to combine this nonlinear response of the solvent with the quantum mechanical treatment of such solutes.

3. Theory

In the present work, we start from the results of Sandberg and Edholm.[18] These authors developed a nonlinear response theory for the hydration of atomic ions based on a modified Langevin−Debye equation for the relative permittivity of water. Including the Onsager correction, through a scaling factor C_F, Sandberg and Edholm modified the basic Langevin−Debye equation[19] into the form

$$\frac{\epsilon(E) - 1}{\epsilon(E) + 2} = \frac{\eta^2 - 1}{\eta^2 + 2} + 3\left(\frac{\epsilon_r - 1}{\epsilon_r + 2} - \frac{\eta^2 - 1}{\eta^2 + 2}\right)L'(\mu\beta C_F F) \quad (1)$$

where $\epsilon(E)$ is the relative permittivity depending on the electric field E, and η^2 and ϵ_r are the square of the refractive index and the dielectric constant, respectively, namely the infinite and zero field limits of $\epsilon(E)$. The constant β is $1/k_B T$, μ is the dipole moment of solvent molecules, and F is the radial component of the Lorentz field defined as

$$F - \frac{3(\epsilon_r - \eta^2)}{(\epsilon_r + 2)\mu\beta C_F}L(\mu\beta C_F F) = \frac{(\eta^2 + 2)}{3}E \quad (2)$$

Here, $L(x)$ is the Langevin function $\coth(x) - 1/x$. The relative permittivity function $\epsilon(E)$, which solves the two equations above, is related to the dielectric permittivity ϵ as

$$\epsilon(E) = \epsilon + E\frac{\partial\epsilon}{\partial E} \quad (3)$$

The relative and dielectric permittivities coincide only in the limit of linear dielectric response. Sandberg and Edholm[18] solved the problem of a point charge Z placed in their model dielectric medium and computed $\epsilon(E)$ for all possible values of the radial component of the electric field. In particular, they obtained the dielectric permittivity for water as a function $\epsilon(Z/r^2)$, where r is the distance from the external charge. Even though, different from the reaction field methods, the Langevin−Debye model is not related to the definition of a sharp cavity, Sandberg and Edholm introduced a radius r_0 where the liquid solvent starts, to reproduce the polarization contribution to the solvation free energy for solutes which are atomic ions. In this case, Z was the charge of the ions and r_0 a well-adapted radius that defines the spherical surface which ideally separates the solute electron's domain by the solvent. r_0 was found to be solute dependent. A better modeling of solvent inhomogeneity will be discussed below.
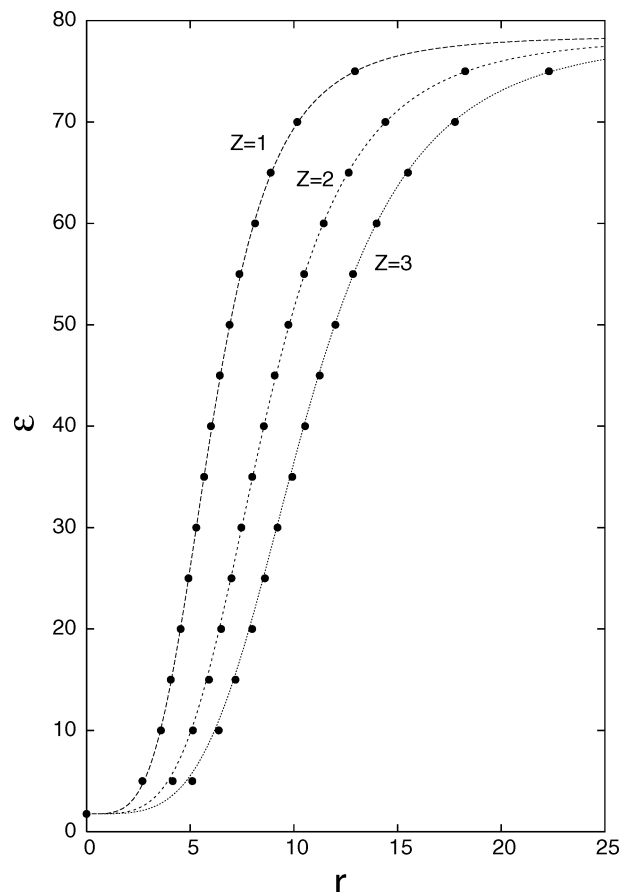

Figure 2. Radial relative dielectric permittivity of water (ϵ), at ambient conditions, in a point charge (Z) field from eq 4 (lines) and from Sandberg and Edholm work (circles).[18] The distance (r) is in au.

As described in the previous section, hydration leads to a superposition of the electron clouds of water and solutes that is more pronounced in the presence of hydrogen bonds. Thus, it is more realistic to abandon the idea of using artificial solvent hard cavities and the aforementioned modified Langevin−Debye approach offers an interesting new route for this purpose. To define a method that can be used in practical applications, we first need to make contact between the classical derivation above and the quantum theory methodologies used to calculate the solute electron distribution in the presence of an external perturbation. Our starting point is the following analytical expression for $\epsilon(Z/r^2)$, which we obtain by fitting the numerical results by Sandberg and Edholm:

$$\epsilon = \eta^2 + \frac{\epsilon_r - \eta^2}{1 + aZ^2/r^4} \quad (4)$$

where, for water at ambient conditions, the only fitting parameter a is fixed at the value 1350 au with a standard error of 35 au. This uncertainty on a translates into an uncertainty smaller than 0.05 kcal/mol on the polarization contribution to the free energy. In Figure 2, we demonstrate the good quality of the fit by comparing our function $\epsilon(Z/r^2)$ with the numerical results by Sandberg and Edholm for various values of the charge Z. It is now important to recognize that, for a point charge in a dielectric medium, Z/r^2 is the radial component of the electric displacement field apart for a constant $1/4\pi$ (ϵ_0 in atomic units). With the displacement field $\vec{D}$ defined by

$$\vec{D} = \epsilon_0\epsilon\vec{E} \quad (5)$$

we can rewrite the dielectric permittivity in eq 4 as ($\epsilon_0 = 1/4\pi$)

$$\epsilon(D) = \eta^2 + \frac{\epsilon_r - \eta^2}{1 + 16\pi^2 a D^2} \tag{6}$$

where $\vec{D}$ solves the Maxwell equations

$$\vec{\nabla} \cdot \vec{D} = \rho \text{ and } \vec{\nabla} \times \vec{E} = 0 \tag{7}$$

with ρ being the charge density of the solute and $\vec{E}$ the electrostatic field. For a spherical solute such as the atomic ions considered in this paper, the radial component of $\vec{D}$ has the form

$$D(r) = \frac{Q(r)}{4\pi r^2}$$

$$Q(r) = Z - \int_0^r \rho_e(s) 4\pi s^2 \, ds \tag{8}$$

where Z is now the nuclear charge and ρ_e is the electron density coming from the quantum mechanical calculation performed on the solute in the presence of the solvent.

Having established a contact between the modified Langevin–Debye approach and the quantum theory of solutes, we need now to define a suitable solvent effective potential acting on the solute electrons. The answer to this problem comes from the energy density of the electrostatic field, $W(r)$, which can be conveniently expressed in terms of $D(r)$ as

$$W(r) = \int_0^{D(r)} \vec{E} \cdot d\vec{D} = 4\pi \int_0^{D(r)} \frac{D}{\epsilon(D)} \, dD \tag{9}$$

With the use of eq 6, we obtain

$$W(r) = \frac{2\pi}{\eta^2}\left[D^2(r) - \frac{\epsilon_r - \eta^2}{16\pi^2 a\eta^2}\log\left(1 + \frac{16\pi^2 a\eta^2 D^2(r)}{\epsilon_r}\right)\right] \tag{10}$$

This expression of the energy density is valid only in the domain of the solvent. Otherwise, we have $E^2/8\pi = 2\pi D^2$ ($\epsilon = 1$). To avoid a drastic change from the solute to the solvent domain, we introduce a smooth switching function $g(r)$ defined as

$$g(r) = \begin{cases} 0 & r \leq r_0 \\ 3x^2 - 2x^3 & r_0 < r \leq r_1 \\ 1 & r_1 < r \end{cases} \text{ with } x = (r - r_0)/(r_1 - r_0) \tag{11}$$

where the two radii r_0 and r_1 define a region of superposition between the electron clouds of solute and solvent. We choose this functional form because its derivative is continuous and zero at r_0 and r_1. With this switching function, the energy density becomes

$$W(r) = 2\pi(1 - g)D^2(r) +$$
$$\frac{2\pi g}{\eta^2}\left[D^2(r) - \frac{\epsilon_r - \eta^2}{16\pi^2 a\eta^2}\log\left(1 + \frac{16\pi^2 a\eta^2 D^2(r)}{\epsilon_r}\right)\right] \tag{12}$$

and is valid over the whole range of radii. The use of this energy density is formally equivalent to the use of an effective dielectric permittivity given by

$$\epsilon^* = \frac{\epsilon(D)}{(1 - g)\epsilon(D) + g} \tag{13}$$

which varies monotonically from 1 to ϵ_r, from the ion to the bulk of the solvent. The use of a radial dependent effective dielectric permittivity has been considered in the past[41–43] and, more recently, permittivity profiles have been derived from simulations[44] but always limited to a linear response framework.

Finally, the polarization contribution to the solvation free energy with the energy density (eq 12) takes the simple expression

$$\Delta G_{pol} = 8\pi^2 \int_0^\infty g(s)\left[\left(\frac{1}{\eta^2} - 1\right)D^2(s) - \frac{\epsilon_r - \eta^2}{16\pi^2 a\eta^4}\log\left(1 + \frac{16\pi^2 a\eta^2 D^2(s)}{\epsilon_r}\right)\right]s^2 \, ds \tag{14}$$

The basic PCM can be recovered by setting $a = 0$ and using a step function instead of $g(r)$. A suitable effective potential representing the solvent effect can now be obtained as the functional derivative of polarization free energy with respect to the charge density of the solute:

$$v_{eff}[\rho](r) = \frac{\delta\Delta G_{pol}[\rho]}{\delta\rho(r)} \tag{15}$$

where $\rho(r) = Z\delta(r) - \rho_e(r)$. If we recognize that

$$D(r) = \frac{1}{r^2}\int_0^\infty H(r - s)\rho(s)s^2 \, ds \tag{16}$$

where $H(x)$ is the Heaviside step function, we obtain

$$v_{eff}[\rho](r) =$$
$$\frac{1}{4\pi\eta^2}\int_r^\infty g(s)D(s)\left[1 - \eta^2 - \frac{\epsilon_r - \eta^2}{\epsilon_r + 16\pi^2 a\eta^2 D^2(s)}\right]ds \tag{17}$$

This effective potential acting on the nucleus and on the electrons is a function of the density through the radial component of the displacement field $D(r)$ and can be used in a self-consistent procedure for the calculation of Kohn–Sham or molecular orbitals of density functional theory (DFT) or Hartree–Fock methods. For an application where a wave function-based method is used for the solute, it is possible to define a density-dependent local potential to be added to the electron Hamiltonian. If we reconstruct the polarization free energy from the functional derivative with respect to the charge density,[45] we can write

$$\Delta G_{pol} = \int_0^1 d\lambda \int_0^\infty 4\pi r^2 \, dr \, v_{eff}[\lambda\rho](r)\rho(r) \tag{18}$$

which leads to the following definition of $u_{loc}(r)$:

$$u_{loc}(r) = \int_0^1 d\lambda \, v_{eff}[\lambda\rho](r) \tag{19}$$

Using eq 17, we obtain

$$u_{loc}(r) = \frac{1}{8\pi\eta^2}\int_r^\infty g(s)D(s)\left[1 - \eta^2 - \frac{\epsilon_r - \eta^2}{16\pi^2 a\eta^2 D^2(s)}\log\left(1 + \frac{16\pi^2 a\eta^2 D^2(s)}{\epsilon_r}\right)\right]ds \tag{20}$$

In terms of the solute wave function ψ, we can finally write

Polarization Contribution to Solvation Free Energy

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$$\Delta G_{pol} = \int_0^\infty u_{loc}(r)\rho(r)4\pi r^2 \, dr = Zu_{loc}(0) - \langle\psi|\sum_{i=1}^{N_e} u_{loc}(\mathbf{r}_i)|\psi\rangle \quad (21)$$

Since u_{loc} depends on the wave function, self-consistency must be reached to obtain the optimal ψ in the presence of the solvent. It is important to remark that, at any step of the self-consistent cycle, the knowledge of u_{loc} allows the use of any quantum-mechanical method for the calculation of the updated wave function. In this work, we use the variational quantum Monte Carlo method (VMC) which, for the systems treated here, yields higher accuracy than standard quantum chemistry techniques. As the VMC wave function for the solutes, we employ a spin-free Slater–Jastrow form of the type

$$\psi(\mathbf{r}_1, \mathbf{r}_2, ...) = \Phi(\mathbf{r}_1, \mathbf{r}_2, ...)J(r_1, r_2, ..., r_{12}, ...) \quad (22)$$

The determinantal component is given by

$$\Phi = \sum_K D_K^\uparrow D_K^\downarrow d_K \quad (23)$$

where $D_K^\uparrow$ and $D_K^\downarrow$ are the Slater determinants written in terms of occupied orbitals of spin-up and spin-down electrons, respectively, and d_K are the mixing coefficients. The Jastrow correlation factor is the exponential of the sum of three contributions which are functions of electron–nuclear (e–n), electron–electron (e–e), and pure 3-body mixed e–e and e–n distances, respectively, and are expressed as systematic polynomial or Padé expansions.[46] In VMC, the distribution $|\psi|^2$ is sampled by using the Metropolis method and the energy is computed as a statistical average of the local energy E_L over a sufficiently large number M of electronic configurations $(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N_e})$ sampled from $|\psi|,^2$ namely

$$E = \frac{1}{M}\sum_{k=1}^M E_L(k) \quad (24)$$

where

$$E_L = -\frac{1}{2\psi}\sum_{i=1}^{N_e}\nabla_i^2\psi - \sum_{i=1}^{N_e}\frac{Z}{r_i} + \sum_{i<j}\frac{1}{r_{ij}} - \sum_{i=1}^{N_e}u_{loc}(r_i) + Zu_{loc}(0) \quad (25)$$

4. Calculations

Following the theory presented in the previous section, we compute the polarization contribution (ΔG_{pol}) to the experimental free energy of solvation in water (ΔG_{sol}) of the atomic ions F^-, Na^+, and Mg^{2+}.

As reference solvation free energies, we take the experimental values corresponding to the transfer from the gas to the liquid phase at 298 K at constant density/concentration of the solutes: $\Delta G_{sol} = -89.9, -439.3$, and 2.7 kcal/mol for Na^+,[35] Mg^{2+},[35] and Ne,[48] respectively. For F^-, we use the experimental value of $\Delta G_{sol} = -103.2 \pm 0.6$ kcal/mol,[47] which is compatible with the more recent result of -105 ± 2 kcal/mol found by the same authors[49] but has a smaller uncertainty. The solvation free energy of Ne can be used to establish a relationship between these experimental values and the calculated polarization contributions (eq 21). For Ne in water solution, since the electronic clouds of solute and solvent do not overlap (see Figure 1), ΔG_{sol} does not contain a solvent polarization contribution ($\Delta G_{pol} = 0$) and results from the so-called cavitation free energy and the contributions arising from long-range intermolecular forces. To

TABLE 1: VMC Electronic Energies (E_{VMC}) and Root-Mean-Square Fluctuations of the Local Energy (σ_{VMC}) for the Solutes Studied in This Work[a]

system	E_{VMC}	σ_{VMC}	E_{HF}
F^-	−99.8079(2)	0.903	−99.45940
Ne	−128.8964(3)	1.144	−128.54710
Na^+	−162.0248(3)	1.311	−161.67696
Mg^{2+}	−199.1808(4)	1.425	−198.83081

[a] The Hartree−Fock energies (E_{HF}) are shown for comparison. All data are in hartrees.

estimate a reference value of ΔG_{pol} for the three ions, we exploit their similarity with the Ne atom (spherical systems with the same number of electrons) and use the free energy of solvation of Ne to remove cavitation and other contributions from the corresponding values of the ions. We therefore obtain the "experimental" polarization term as $\Delta G_{pol}^{exp} = \Delta G_{sol} - \Delta G_{sol}$(Ne) = −105.9, −92.6, and −442.0 kcal/mol for F^-, Na^+, and Mg^{2+}, respectively.

This procedure is of course not rigorous for several reasons: for ions, the cavitation free energy is smaller than for Ne (see ref 50 for an estimate of variation of cavitation energy with the size of the cavity); the dispersion energy contribution is stronger for F^-; the Pauli repulsion for ions is significantly modified by charge-transfer terms;[51] finally, especially for F^-, electron correlation should give additional contributions to the one related to the dispersion energy. Given these considerations, we estimate the degree of charge overlap between solute and solvent through the following integral:

$$q_{co} = 4\pi\int_0^\infty g(r)\rho_e(r) \, dr \quad (26)$$

for our choice of $g(r)$. The parameter q_{co} will be relevant in discussing the discrepancies between calculated polarization free energy contributions and the experimental estimates defined above.

As the quantum mechanical method for the electronic structure calculation, we use the VMC method implemented in the CHAMP package[52] modified for the present solvation model. The solute wave function is optimized in variance minimization.[53] For all the solutes, we use a one-determinant Slater–Jastrow form with a double-ζ Slater basis set and fifth-order polynomials in the Jastrow factors. In Table 1, we show the VMC energies (E_{VMC}) and the root-mean-square fluctuation of the local energy (σ_{VMC}) for the atomic ions in vacuo as well as the corresponding Hartree−Fock results for comparison.[54−56] Our results for Ne are very close to the best VMC values available in the literature ($E_{VMC} = -128.9008(1)$ hartrees and $\sigma = 0.9$ hartree), obtained by Huang et al.[57] using a Jastrow factor that also includes terms motivated by the Fock expansion. For all systems, we recover 89% of the full correlation energy.

To study the solvation of the atomic ions in water, we need a simple rule to define the switching function $g(r)$ (eq 11), which establishes where the solvent starts and where the dielectric medium can be represented by its bulk properties. We choose the parameter r_0 using Figure 1 as the radius of the sphere centered on the solute that contains no more than 0.1 solvent electrons. As r_1, we take a characteristic atom−atom contact distance computed as the radius of the maximum of the oxygen-ion and of the hydrogen-ion radial distribution function for cations and anions, respectively.[32,58−60] Other choices of r_0 and r_1 may of course lead to the correct value of polarization energy but they do not possess a well-defined physical basis as the choice we propose. We remark that the sensitivity of the method to variations in r_0 and r_1 is smaller than the sensitivity of the

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TABLE 2: Computed Polarization Free Energies (ΔG_{pol}) and the Corresponding Experimental Estimates (ΔG_{pol}^{exp}) in kcal/mol for the Atomic Ions F$^-$, Na$^+$, and Mg^{2+} in Water[a]

system	E_{VMC}	σ_{VMC}	r_0	r_1	q_{co}	ΔG_{pol}	ΔG_{pol}^{exp}
F$^-$	$-99.9730(2)$	0.907	2.1	3.2	0.356	-103.9	-105.9
Na$^+$	$-162.1716(3)$	1.311	2.2	4.6	0.005	-92.1	-92.6
Mg^{2+}	$-199.8857(4)$	1.425	1.4	3.9	0.017	-442.0	-442.0

[a] The VMC solute electronic energies in water (E_{VMC}) and the root-mean-square fluctuations of the local energy (σ_{VMC}) in hartrees are shown. The radii r_0 and r_1 (au) define the switching function $g(r)$ (eq 11) and q_{co} (au) is the charge overlap (eq 26).

TABLE 3: Polarization Contribution to the Free Energy of Solvation in Water (ΔG_{pol}) Computed by Using the Basic PCM Model within DFT/B3LYP with a 6-311G++ Basis Set[a]

system	ΔG_{pol}	R	method for R	$\Delta G_{pol}(r_0)$	$\Delta G_{pol}(r_1)$
F$^-$	-105.6	2.29	fitted	-103.9	-91.5
Ne	0.0	3.10	estimated	N/A	N/A
Na$^+$	-92.6	3.35	fitted	-143.6	-67.4
Mg^{2+}	-442.0	2.80	fitted	-940.0	-317.9

[a] In the fourth column, we indicate whether the cavity radius R was set by fitting the experimental estimate of ΔG_{pol} (see text). In the last two columns, we list the values of ΔG_{pol} at the radii r_0 and r_1 of Table 2. The free energies are in kcal/mol and the radii are in au.

standard PCM to the choice of the cavity radius R: a variation of 5% in r_0 yields a variation of 1% in ΔG_{pol} while, in PCM, the same variation in R would result in a variation in ΔG_{pol} at least three times larger.

In Table 2, we summarize the results from the calculations in the presence of water solvent. Our results for ΔG_{pol} (eq 21) are in a substantial degree of agreement with the expected estimates obtained from the experimental solvation free energies of ions by subtracting the solvation free energy of Ne. The agreement is very good for cations while there is a difference of about -2 kcal/mol for F$^-$. Although this relatively small difference can be eliminated by reducing r_0, we do not follow this procedure since we want to maintain consistency in the choice of radii for all cases. Moreover, as explained above, the reference polarization free energy obtained from experiments as $\Delta G_{pol}^{exp} = \Delta G_{sol} - \Delta G_{sol}(Ne)$ cannot be considered a rigorous estimate for F$^-$ since it includes also contributions from nonclassical electrostatic interactions.

To quantify the effect of the use of a nonlinear model on the data of Table 2, we set the nonlinear parameter a to zero (eq 6) while retaining the switching function $g(r)$. We then compute ΔG_{pol} using the VMC densities previously obtained in combination with the nonlinear model, and find more negative values of ΔG_{pol}. The lowering is only -2 kcal/mol for F$^-$ and Na$^+$ but is as large as -50 kcal/mol for Mg^{2+}. We note that recomputing the VMC density consistently with the new conditions of solvation would lead to a more pronounced effect of polarization and a further deviation of ΔG_{pol} from the experimental values.

To test the effect of solvent penetration, we compute the polarization energies in the presence of a point charge instead of the ionic solute, without changing the switching function. For $Z = -1$, 1, and 2, we obtain -114.2, -91.9, and -441.0 kcal/mol, respectively. When compared with the VMC polarization energies of the solvated ions in Table 2, these results are consistent with the expected behavior: in anions, solvent penetration leads to a destabilization with respect to a point charge model while in cations it leads to a stabilization. The magnitude of the effect is proportional to the charge overlap.

In Table 3, we show the polarization contributions to the free energy of solvation calculated with Gaussian03[24] within the linear dielectric response basic PCM using the DFT/B3LYP method and a standard 6-311G++ basis set. The values of ΔG_{pol} depend on the choice of the cavity radius R. For Ne, if we choose R as the contact radius in Figure 1, we obtain $\Delta G_{pol} = 0$ as expected. For F$^-$, we obtain R as the radius, which minimizes the difference between the calculated ΔG_{pol} and the expected value -105.9 kcal/mol. For the cations Na$^+$ and Mg^{2+}, ΔG_{pol} varies monotonically with R spanning a range of hundreds of kilocalories per mole in the interval of solute−solvent charge overlap (see the last two columns in the table) and the chosen values of R are those which reproduce the experimental estimates of ΔG_{pol}. Therefore, apart from Ne, for which there

is not a solvent dielectric polarization, the cavity radius of the other solutes must be fixed to reproduce the expected ΔG_{pol}. On the other hand, the switching function $g(r)$ introduced in this work is defined a priori by considering a region accessible to the solvent electrons and distinguished from the bulk solvent. The use of this switching function in combination with a nonlinear dielectric response approach yields very good agreement with experiments without the need for any fitting parameter.

Finally, we show how, in principle, it is possible to account for the contributions to ΔG_{pol} which are dominated by nonclassical effects due to the electron−electron interaction in the region of solvent and solute overlap. To first approximation, we can relate these terms to the charge overlap q_{co} (eq 26) and set

$$\Delta\Delta G = \Delta G_{sol} - \Delta G_{sol}(Ne) - \Delta G_{pol} = \kappa q_{co} \qquad (27)$$

with the parameter κ fitted to solvation data such as those obtained in Table 2. This correction can be simply included in the calculation of the solute wave function by perturbing the local potential (eq 20) with the additional term derived from the definition of q_{co}, namely

$$u_{loc}(r) \rightarrow u_{loc}(r) - \kappa g(r) \qquad (28)$$

Since q_{co} is negligible for Na$^+$ and Mg^{2+}, the only available data from the present work are relative to F$^-$ and, due to experimental uncertainties on solvation free energies, yield a value of κ in the range -0.015 to -0.005 au. While additional solvation data are needed for a more reliable estimate of κ, we expect a value of κ of this order of magnitude.

5. Conclusion and Future Directions

In this work, we have studied the hydration of selected atomic ions to test a theoretical method for the calculation of polarization contribution to the solvation free energy within the continuum model in a nonlinear response framework. Our main achievement is embodied in eq 21 where the polarization free energy is explicitly written in terms of the solute density and of the solvent properties such as the refractive index, the zero-field dielectric constant, and a nonlinear response parameter fitted to the theory developed by Sandberg and Edholm.[18] The inhomogeneity of the solvent is taken into account with the use of a smooth switching function, which indicates where the solvent starts around the solute and where the bulk solvent is reached. This function is defined a priori on the basis of how the solvent is arranged around the solute. A local potential representing the solvent perturbation can then be obtained by functional analysis and used within density functional or quantum chemical methods for the quantum mechanical treatment of the solute. Here, we have employed the variational

Monte Carlo method for a series of atomic ions solvated in water and obtained polarization free energies in very good agreement with estimates derived from experimental data.

Even though the present approach has been developed for spherical solutes, it is possible to overcome this limitation if we can solve the two Maxwell equations (eq 7) in the general case and explicitly rewrite the displacement field $\vec{D}$ in terms of the solute charge density. To this end, we suggest employing the expression of the dielectric permittivity (eq 6), which only depends on the modulus of the displacement field, for non-spherical solutes as well. It then follows that the expression for the energy density W (eq 12) remains valid in the general case once an appropriate switching function g has been defined. Note that both functions W and g will depend on the vector position $\vec{r}$ and not just on its modulus. In practice, the crucial step for the extension of the present approach to general solutes is the calculation of the solenoidal part (null divergence) of $\vec{D}$, which is coupled to the effective dielectric permittivity ϵ^* (eq 13) through Maxwell's equation $\vec{\nabla} \times (\vec{D}/\epsilon^*) = 0$ and is zero for spherical solutes.

The generalization to nonspherical solutes as well as the study of effects of exchange and correlation on the solvation free energy are currently in progress. It appears that, given the possibility to easily introduce new terms into the local energy (eq 25), QMC is a particularly interesting tool to make further advances in the theory of continuum models of solvation and mimic the effect of a complex environment.

References and Notes

(1) Cramer, C. J.; Truhlar, D. G. *Chem. Rev.* **1999**, *99*, 2161.
(2) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.
(3) Orozco, M.; Luque, F. *Chem. Rev.* **2000**, *100*, 4187.
(4) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.
(5) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669.
(6) Li, H.; Jensen, J. H. *J. Comput. Chem.* **2004**, *25*, 1449.
(7) Olivares Del Valle, F. J.; Aguilar, M.; Tolosa, S.; Contador, J. C.; Tomasi, J. *Chem. Phys.* **1990**, *143*, 371.
(8) Cappelli, C.; Corni, S.; Tomasi, J. *J. Chem. Phys.* **2001**, *115*, 5531.
(9) Rivail, J. L.; Rinaldi, D.; Dillet, V. *Mol. Phys.* **1996**, *89*, 1521.
(10) Jaszunski, M.; Mikkelsen, K. V.; Rizzo, A.; Witanowski, M. J. *J. Phys. Chem. A* **2000**, *104*, 1466.
(11) Cammi, R.; Mennucci, B. *J. Chem. Phys.* **1999**, *110*, 9877.
(12) Amovilli, C. VB analysis of wave functions calculated for chemical reactions in solution. In *Valence Bond Theory*; Cooper, D. L., Ed.; Elsevier: Amsterdam, The Netherlands, 2002.
(13) Amovilli, C.; Floris, F. M.; Solà, M.; Tomasi, J. *Organometallics* **2001**, *20*, 1310.
(14) Floris, F.; Persico, M.; Tani, A.; Tomasi, J. *Chem. Phys. Lett.* **1992**, *199*, 518.
(15) Floris, F. M.; Tani, A. *J. Chem. Phys.* **2001**, *115*, 4750.
(16) Sanchez, M. L.; Martin, M. E.; Aguilar, M. A.; Olivares del Valle, F. J. *J. Comput. Chem.* **2000**, *21*, 705.
(17) Galvan, I. F.; Martin, M. E.; Aguilar, M. A. *J. Comput. Chem.* **2004**, *25*, 1227.
(18) Sandberg, L.; Edholm, O. *J. Chem. Phys.* **2002**, *116*, 2936.
(19) Debye, P. *Phys. Z.* **1912**, *13*, 97.
(20) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.
(21) Cances, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032.
(22) Amovilli, C.; Mennucci, B.; Floris, F. M. *J. Phys. Chem. B* **1998**, *102*, 3023.
(23) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(24) Frisch, M. J.; et al *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(25) Amovilli, C.; Mennucci, B. *J. Phys. Chem. B* **1997**, *101*, 1051.
(26) Markham, G. D.; Gluster, J. P.; Bock, C. L.; Trachtman, M.; Bock, C. W. *J. Phys. Chem.* **1996**, *100*, 3488.
(27) Peng, Z.; Ewig, C. E.; Hwang, M. J.; Waldman, M.; Hagler, A. T. *J. Phys. Chem. A* **1997**, *101*, 7243.
(28) Kovalenko, A.; Hirata, F. *J. Chem. Phys.* **2000**, *113*, 2793.
(29) Laidig, K. E.; Speers, P.; Streitwieser, A. *Coord. Chem. Rev.* **2000**, *197*, 125.
(30) Chipman, D. M. *J. Chem. Phys.* **2002**, *116*, 10129.
(31) Hori, A.; Hondoh, T. *Can. J. Phys.* **2003**, *81*, 33.
(32) Öhrn, A.; Karlström, G. *J. Phys. Chem. B* **2004**, *108*, 8452.
(33) Heuft, J. M.; Meijer, E. J. *J. Chem. Phys.* **2005**, *122*, 094501.
(34) Born, M. *Z. Phys.* **1920**, *1*, 45.
(35) Marcus, Y. *Ions Properties;* Dekker: New York, 1997.
(36) Cances, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **2001**, *115*, 6130.
(37) Chipman, D. M. *J. Chem. Phys.* **1996**, *104*, 3276.
(38) Chipman, D. M. *J. Chem. Phys.* **2004**, *120*, 5566.
(39) Chipman, D. M. *J. Chem. Phys.* **2006**, *124*, 224111.
(40) Sandberg, L.; Casemyr, R.; Edholm, O. *J. Phys. Chem. B* **2002**, *106*, 7889.
(41) Ehrenson, S. *J. Comput. Chem.* **1989**, *10*, 77.
(42) Cossi, M.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1994**, *228*, 165.
(43) Hyun, J. K.; Satheesan Babu, C.; Ichiye, T. *J. Phys. Chem.* **1995**, *99*, 5187.
(44) Blaak, R.; Hansen, J. P. *J. Chem. Phys.* **2006**, *124*, 144714.
(45) van Leeuwen, R.; Baerends, E. J. *Phys. Rev. A* **1995**, *51*, 170.
(46) Filippi, C.; Umrigar, C. J. *J. Chem. Phys.* **1996**, *105*, 213. The electron−electron−nucleus term is modified to contain only pure 3-body contributions.
(47) Pliego, J. R.; Riveros, J. M. *Chem. Phys. Lett.* **2000**, *332*, 597.
(48) Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016.
(49) Pliego, J. R.; Riveros, J. M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1622.
(50) Floris, F. M. *J. Phys. Chem. B* **2005**, *109*, 24061.
(51) Amovilli, C.; McWeeny, R. *Chem. Phys* **1995**, *198*, 71.
(52) CHAMP is a quantum Monte Carlo program package written by C. J. Umrigar and C. Filippi, and collaborators; http://www.ilorentz.org/~filippi/champ.html.
(53) Umrigar, C. J.; Wilson, K. G.; Wilkins, J. W. *Phys. Rev. Lett.* **1988**, *60*, 1719.
(54) Feller, D.; Boyle, C. M.; Davidson, E. R. *J. Chem. Phys.* **1987**, *86*, 3424.
(55) Fraga, S.; Karwowski, J.; Saxena, M. S. *Handbook of Atomic Data*; Elsevier: Amsterdam, The Netherlands, 1976.
(56) Davidson, E. R.; Hagstrom, S. A.; Chakravorty, S.; Umar, V.; Fischer, C. *Phys. Rev. A* **1991**, *44*, 7071.
(57) Huang, C. J.; Umrigar, C. J.; Nightingale, M. P. *J. Chem. Phys.* **1997**, *107*, 3007.
(58) Dang, L. X.; Rice, J. E.; Caldwell, J.; Kollman, P. A. *J. Am. Chem. Soc.* **1991**, *113*, 2481.
(59) Peng, Z.; Ewig, C. S.; Hwang, M. J.; Waldman, M.; Hagler, A. T. *J. Phys. Chem. A* **1997**, *101*, 7243.
(60) Floris, F. M.; Tani, A. Interaction potentials for small molecules. In *Molecular Dynamics. From classical to quantum methods*; Balbuena, P. B., Seminario, J. M., Eds.; Elsevier: Amsterdam, The Netherlands, 1999.