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Daniel M. Chipman

Citation: [The Journal of Chemical Physics](#) **112**, 5558 (2000); doi: 10.1063/1.481133

View online: <http://dx.doi.org/10.1063/1.481133>

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Reaction field treatment of charge penetration

Daniel M. Chipman

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

(Received 21 September 1999; accepted 5 January 2000)

Treatment of the important electrostatic effects of solvation by means of reaction field theory is becoming common in electronic structure calculations on molecules. Most extant reaction field methods neglect or crudely approximate the often important influence of volume polarization arising from solute charge that quantum mechanically penetrates outside the cavity that nominally encloses it. This work proposes and examines a new formulation that provides an accurate simulation of volume polarization effects while being much simpler to implement and use than an exact treatment. Detailed comparisons with other related methods are also given. © 2000 American Institute of Physics. [S0021-9606(00)30513-X]

INTRODUCTION

Solvation effects can dramatically alter the observed properties of molecules. While short range attractive van der Waals and repulsive cavitation and exchange interactions generally make significant contributions, in polar solvation the long range electrostatic interactions between solute and solvent are often dominant. Reaction field theory¹⁻⁴ provides a very convenient approximate treatment of the electrostatic interactions. For quantum mechanical calculation on the properties of a solute in the presence of solvent, the reaction field can be incorporated into the solute Hamiltonian operator as an effective potential energy term. This describes the equilibrium classical interaction of the solute charge density nominally enclosed inside a cavity with a polarizable dielectric continuum model of isotropic solvent lying everywhere outside the cavity. Recent reviews^{5,6} attest to the popularity of this approach and discuss its advantages and limitations in modern electronic structure theory. Within this model, the basic theoretical problem to be addressed is solution of Poisson's equation to obtain the electrostatic reaction potential that represents the solvent response.

We have recently pointed out^{7,8} that most extant solutions of Poisson's equation in this context are flawed by an inconsistency. Poisson's equation is usually solved under the assumption that all solute charge density resides inside the cavity, which leads to a solution in terms of an effective surface polarization charge density spread over the cavity boundary. However, in practice unconstrained quantum mechanical calculation of the solute charge density inevitably leads to a small tail penetrating outside the cavity into the dielectric continuum region. The long range electrostatic interaction of this tail with solvent makes additional rarely recognized contributions⁷⁻⁹ to the solution of Poisson's equation. Charge penetration not only modifies the commonly treated surface polarization, it also leads to an effective volume polarization charge density distributed in the region outside the cavity surface.

Several studies on representative small molecular solutes have been carried out to ascertain the importance of this charge penetration effect. For free energies of solvation the

effects were found¹⁰ to be modest but not negligible in neutral solutes, and quite significant in both cations and anions. Volume polarization was shown¹¹ to have little effect on the optimum cavity size. Large effects were found¹² on NMR chemical shielding constants, and it was speculated that large effects would also be found for other second- and higher-order properties such as spin-spin coupling constants, polarizabilities, magnetizabilities, etc., as well. These studies establish that it would be desirable to routinely include proper treatment of the effect of charge penetration in reaction field studies.

In the present work we present the formal analysis for a proposed new formulation of reaction field theory that provides an accurate treatment of the influence of penetrating charge through incorporation into the surface polarization of a certain previously discussed^{8,10} simulation of the volume polarization. Compared to exact treatment of the volume polarization, this method is much easier to implement and utilize in practical calculations. It will also have considerable advantages in determination of analytic gradients for geometry optimization.

Comparisons are also made to other related methods. Further insight is given into our recent demonstration¹³ that for high dielectric solvents the conductor-like screening models¹⁴⁻²⁹ provide a surface polarization that accurately includes the simulation of volume polarization due to charge penetration, although the representation is not accurate in low dielectric constant solvents. We further show here that for high dielectric solvents the surface polarization obtained in the recently proposed integral equation formulation³⁰⁻³⁶ of reaction field theory also accurately includes the simulation of volume polarization due to charge penetration, but again not for low dielectric solvents.

In the next section on background we establish some necessary notation and also give a brief review of the exact treatment of volume polarization. Then the new formulation proposed in this work is introduced and discussed. The section after that gives detailed comparisons with other related methods. Finally comes a summary and concluding discussion. Key equations will be numbered to make them stand out.

BACKGROUND

Notation for potentials and fields

The electrostatic potential produced by a well-behaved generic function $\rho(\mathbf{r})$ which is defined throughout all of space \mathbf{V} is given by

$$\Phi^{\rho}(\mathbf{r}) = \int_{\mathbf{V}} d^3\mathbf{r}' \rho(\mathbf{r}') \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right\}.$$

Similarly, the electrostatic potential produced by a well-behaved generic function $\sigma(\mathbf{s})$ which is defined on a closed surface Γ is given by

$$\Phi^{\sigma}(\mathbf{r}) = \int_{\Gamma} d^2\mathbf{s}' \sigma(\mathbf{s}') \left\{ \frac{1}{|\mathbf{r} - \mathbf{s}'|} \right\}.$$

Associated with a generic potential $\Phi^{\rho}(\mathbf{r})$ is an electric field given by $-\nabla\Phi^{\rho}(\mathbf{r})$. The negative of the normal component of this field at any point \mathbf{s} on the surface Γ is given by

$$\partial\Phi^{\rho}(\mathbf{s}) = \int_{\mathbf{V}} d^3\mathbf{r}' \rho(\mathbf{r}') \left\{ \frac{\partial}{\partial\mathbf{n}_{\mathbf{s}}} \frac{1}{|\mathbf{s} - \mathbf{r}'|} \right\},$$

where $\mathbf{n}_{\mathbf{s}}$ is a unit vector parallel to the outward-directed normal at point \mathbf{s} on Γ . Thus, the indicated normal derivative is given by

$$\frac{\partial}{\partial\mathbf{n}_{\mathbf{s}}} \frac{1}{|\mathbf{s} - \mathbf{r}'|} = - \frac{\mathbf{n}_{\mathbf{s}} \cdot (\mathbf{s} - \mathbf{r}')}{|\mathbf{s} - \mathbf{r}'|^3}.$$

It is convenient to further define certain operators that act only over the surface Γ , using notation similar to that invoked in discussions of the integral equation formulation.^{30–36} The operator \mathcal{S} acting on a given surface function $\sigma(\mathbf{s})$ produces the corresponding surface charge potential at the point \mathbf{s} on Γ , i.e.,

$$\mathcal{S}\sigma(\mathbf{s}) = \int_{\Gamma} d^2\mathbf{s}' \sigma(\mathbf{s}') \left\{ \frac{1}{|\mathbf{s} - \mathbf{s}'|} \right\}.$$

Thus, operator notation such as $\mathcal{S}\sigma(\mathbf{s})$ is to be interpreted as $[\mathcal{S}\sigma](\mathbf{s})$. The operator \mathcal{D}^* acting on a given surface function $\sigma(\mathbf{s})$ produces the negative of the outward-directed normal component of the electric field at the surface from $\Phi^{\sigma}(\mathbf{s})$, i.e.,

$$\mathcal{D}^*\sigma(\mathbf{s}) = \int_{\Gamma} d^2\mathbf{s}' \sigma(\mathbf{s}') \left\{ \frac{\partial}{\partial\mathbf{n}_{\mathbf{s}}} \frac{1}{|\mathbf{s} - \mathbf{s}'|} \right\}.$$

Note that this field is discontinuous across Γ . Thus, the corresponding negative of the outward-directed normal component of the electric field at a point \mathbf{s}^{int} on the interior face of Γ is $\mathcal{D}^*\sigma(\mathbf{s}) + 2\pi\sigma(\mathbf{s})$ while at a point \mathbf{s}^{ext} on the exterior face of Γ it is $\mathcal{D}^*\sigma(\mathbf{s}) - 2\pi\sigma(\mathbf{s})$. The closely related operator \mathcal{D} acting on a given surface function $\sigma(\mathbf{s})$ produces the corresponding surface dipole or double layer potential on Γ , i.e.,

$$\mathcal{D}\sigma(\mathbf{s}) = \int_{\Gamma} d^2\mathbf{s}' \sigma(\mathbf{s}') \left\{ \frac{\partial}{\partial\mathbf{n}_{\mathbf{s}'}} \frac{1}{|\mathbf{s} - \mathbf{s}'|} \right\}.$$

This potential is also discontinuous across Γ , and at a point \mathbf{s}^{int} is $\mathcal{D}\sigma(\mathbf{s}) - 2\pi\sigma(\mathbf{s})$ while at a point \mathbf{s}^{ext} is $\mathcal{D}\sigma(\mathbf{s}) + 2\pi\sigma(\mathbf{s})$. For the special case of a spherical surface $\mathcal{D}^*\sigma(\mathbf{s}) = \mathcal{D}\sigma(\mathbf{s})$, but the two operators will produce different results on a more general surface Γ . Also note that in general $\mathcal{D}\mathcal{S}\sigma(\mathbf{s}) = \mathcal{S}\mathcal{D}^*\sigma(\mathbf{s})$.

Reaction field theory

In the context of electronic structure calculations, the goal of reaction field theory is to represent the electrostatic influence of solvent polarization through an effective potential energy term included in the solute Hamiltonian operator. This potential energy is to be obtained from the equilibrium interaction of the real solute charge density with a certain electrostatic reaction potential $\Phi^{\text{rxn}}(\mathbf{r})$. With a classical dielectric continuum model of isotropic solvent, this reaction potential is determined as the solution of Poisson's equation.

The surface Γ is generally chosen to be the boundary of a cavity that nominally encloses the solute. The size and shape of this cavity is not uniquely determined by theoretical considerations, and a recent discussion¹¹ attests to the many prescriptions that have been put forth in practice. Inside Γ the dielectric constant is taken to be unity, since the polarizability there is to be accounted for by an electronic structure calculation on the solute, while outside Γ it is taken to be the experimental bulk value ϵ of the solvent under consideration. The solute is characterized by its charge density $\rho(\mathbf{r})$. For the present analysis we assume both Γ and $\rho(\mathbf{r})$ to be fixed and known. In practice this may represent only one step in an iterative process by which either or both are allowed to relax to become self-consistent with the reaction field.

To obtain the full solution of Poisson's equation, it must be recognized that unconstrained quantum mechanical calculation will inevitably lead to some tail of the solute charge density penetrating outside Γ . Thus, the solute charge density can be partitioned into the contributions $\rho(\mathbf{r}) = \rho^{\text{int}}(\mathbf{r}) + \rho^{\text{ext}}(\mathbf{r})$ where $\rho^{\text{int}}(\mathbf{r})$ represents the major portion lying inside the volume \mathbf{V}^{int} enclosed by Γ , and $\rho^{\text{ext}}(\mathbf{r})$ the small portion lying in the volume \mathbf{V}^{ext} outside of Γ .

This partitioning leads to two distinct terms in the exact reaction potential,⁸ representing the contributions from surface and volume polarization for electrostatics [SVPE]. Thus, the exact $\Phi^{\text{rxn}}(\mathbf{r})$ takes the form $\Phi^{\text{SVPE}}(\mathbf{r}) = \Phi^{\sigma}(\mathbf{r}) + \Phi^{\beta}(\mathbf{r})$. The first term represented by $\Phi^{\sigma}(\mathbf{r})$ accounts for the boundary condition due to the sudden change in dielectric constant across Γ . It is the potential arising from a surface polarization charge density $\sigma(\mathbf{s})$ which can be obtained by solving the equation

$$\mathcal{F}\sigma(\mathbf{s}) = \left(\frac{\epsilon - 1}{\epsilon + 1} \right) \left[\frac{1}{2\pi} \partial\Phi^{\rho}(\mathbf{s}) + \frac{1}{2\pi} \partial\Phi^{\beta}(\mathbf{s}) \right] \quad (1)$$

for all points \mathbf{s} on Γ , where the operator \mathcal{F} is defined as

$$\mathcal{F} = \mathcal{I} - \left(\frac{\epsilon - 1}{\epsilon + 1} \right) \frac{1}{2\pi} \mathcal{D}^*.$$

The second term represented by $\Phi^{\beta}(\mathbf{r})$ accounts for the penetration of solute charge outside Γ . It is the potential arising from a volume polarization charge density $\beta(\mathbf{r})$ given by

$$\beta(\mathbf{r}) = -\left(\frac{\epsilon-1}{\epsilon}\right)\rho^{\text{ext}}(\mathbf{r}), \quad (2)$$

and can be immediately written explicitly as

$$\Phi^\beta(\mathbf{r}) = -\left(\frac{\epsilon-1}{\epsilon}\right)\Phi^{\rho^{\text{ext}}}(\mathbf{r}).$$

We have previously pointed out^{8,10} that the effect of this volume polarization term can be closely simulated by a certain additional surface polarization charge density $\alpha(\mathbf{s})$. Thus, if $\alpha(\mathbf{s})$ is determined such that

$$S\alpha(\mathbf{s}) = \Phi^\beta(\mathbf{s}), \quad (3)$$

for all points \mathbf{s} on Γ , then it is easily shown that $\Phi^\alpha(\mathbf{r}) = \Phi^\beta(\mathbf{r})$ for all \mathbf{r} inside as well as on Γ . Simulating $\Phi^\beta(\mathbf{r})$ by $\Phi^\alpha(\mathbf{r})$ then gives the correct volume polarization potential in the most important region \mathbf{V}^{int} , at the expense of introducing some error in the less important region \mathbf{V}^{ext} . Explicit tests have shown¹⁰ that this simulation leads to very little loss in numerical accuracy, as compared to exact treatment of the volume polarization.

It is further worthwhile noting here that we have previously demonstrated^{10,12} through explicit numerical calculations on a variety of representative solutes that the actual amount of charge penetration is very insensitive to whether or not volume polarization is included and is also nearly independent of the dielectric constant value. Thus, for a given specification of the cavity surface Γ the amount of charge penetration will be found to be very nearly the same in virtually all of the extant reaction field methods, and will also be very nearly the same as that produced by evaluation with the gas phase wave function as well.

SS(V)PE METHOD

Combining the exact surface polarization and the additional simulation of volume polarization for electrostatics [SS(V)PE] leads to the single effective surface charge density denoted here by

$$\sigma^{\text{SS(V)PE}}(\mathbf{s}) = \sigma(\mathbf{s}) + \alpha(\mathbf{s}). \quad (4)$$

For most practical purposes the exact $\Phi^{\text{rxn}}(\mathbf{r})$ will be closely approximated¹⁰ by the potential $\Phi^{\sigma^{\text{SS(V)PE}}}(\mathbf{r})$. Therefore we propose and investigate here a new approximate method for treatment of solvation electrostatics based on direct determination of $\sigma^{\text{SS(V)PE}}(\mathbf{s})$.

From the fact noted above that the potentials $\Phi^\alpha(\mathbf{r})$ and $\Phi^\beta(\mathbf{r})$ are equal to each other for all \mathbf{r} inside Γ it follows that the corresponding electric fields $-\nabla\Phi^\alpha(\mathbf{r})$ and $-\nabla\Phi^\beta(\mathbf{r})$ must be equal to each other for all \mathbf{r} inside Γ , and more specifically at any point \mathbf{s}^{int} on the interior face of Γ . Taking into account the discontinuity across Γ of the field $-\nabla\Phi^\alpha(\mathbf{r})$ we then obtain the relation

$$\alpha(\mathbf{s}) + \frac{1}{2\pi}D^*\alpha(\mathbf{s}) = \frac{1}{2\pi}\partial\Phi^\beta(\mathbf{s}).$$

After simple algebraic manipulations this can be written as

$$\mathcal{F}\alpha(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right)\left[\left(\frac{\epsilon}{\epsilon-1}\right)2\alpha(\mathbf{s}) - \frac{1}{2\pi}\partial\Phi^\beta(\mathbf{s})\right].$$

Operating on both sides with S then gives

$$\mathcal{T}\alpha(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right)\left[\left(\frac{\epsilon}{\epsilon-1}\right)2\Phi^\beta(\mathbf{s}) - \frac{1}{2\pi}S\partial\Phi^\beta(\mathbf{s})\right],$$

where $\mathcal{T} = S\mathcal{F}$.

This operator \mathcal{T} , which recurs often throughout the present work, can be written in many formally equivalent ways by making use of the general relation $\mathcal{D}S = S\mathcal{D}^*$. However, these various forms may not be exactly equivalent in practice, where discretization over a grid of points on Γ leads to an approximate finite matrix representation of each operator. In the integral equation formulation³⁰⁻³⁶ the particular form

$$\mathcal{T} = S - \left(\frac{\epsilon}{\epsilon+1}\right)\frac{1}{2\pi}\mathcal{D}S + \left(\frac{1}{\epsilon+1}\right)\frac{1}{2\pi}S\mathcal{D}^*$$

is used. We prefer instead the form

$$\mathcal{T} = S - \left(\frac{\epsilon-1}{\epsilon+1}\right)\frac{1}{4\pi}(\mathcal{D}S + S\mathcal{D}^*),$$

which has the advantage of allowing its discrete approximate finite representation as a symmetric matrix.

A standard result from potential theory,³⁷ easily proven through judicious application of Green's theorem, shows that at any point \mathbf{r} inside Γ the contribution to the potential $\Phi^\rho(\mathbf{r})$ arising from charge density $\rho^{\text{ext}}(\mathbf{r})$ lying outside Γ can be represented from knowledge of just $\Phi^\rho(\mathbf{s})$ and $\partial\Phi^\rho(\mathbf{s})$ on Γ through

$$\begin{aligned} \Phi^{\rho^{\text{ext}}}(\mathbf{r}) = & \frac{1}{4\pi} \int_{\Gamma} d^2\mathbf{s}' \left[\partial\Phi^\rho(\mathbf{s}') \left\{ \frac{1}{|\mathbf{r}-\mathbf{s}'|} \right\} \right. \\ & \left. - \Phi^\rho(\mathbf{s}') \left\{ \frac{\partial}{\partial n_{\mathbf{s}'}} \frac{1}{|\mathbf{r}-\mathbf{s}'|} \right\} \right]. \end{aligned}$$

Evaluating this at a point $\mathbf{r} = \mathbf{s}^{\text{int}}$ and then extending to the corresponding point \mathbf{s} on Γ by taking into account the discontinuity of the last term, we obtain

$$\Phi^{\rho^{\text{ext}}}(\mathbf{s}) = \frac{1}{2}\Phi^\rho(\mathbf{s}) - \frac{1}{4\pi}\mathcal{D}\Phi^\rho(\mathbf{s}) + \frac{1}{4\pi}S\partial\Phi^\rho(\mathbf{s}). \quad (5)$$

This can be used to replace $\Phi^\beta(\mathbf{s})$ in the above expression for $\mathcal{T}\alpha(\mathbf{s})$, leading to

$$\begin{aligned} \mathcal{T}\alpha(\mathbf{s}) = & \left(\frac{\epsilon-1}{\epsilon+1}\right)\left[-\Phi^\rho(\mathbf{s}) + \frac{1}{2\pi}\mathcal{D}\Phi^\rho(\mathbf{s}) - \frac{1}{2\pi}S\partial\Phi^\rho(\mathbf{s}) \right. \\ & \left. - \frac{1}{2\pi}S\partial\Phi^\beta(\mathbf{s})\right]. \end{aligned}$$

Application of the operator S to Eq. (1) puts it into the analogous form

$$\mathcal{T}\sigma(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right)\left[\frac{1}{2\pi}S\partial\Phi^\rho(\mathbf{s}) + \frac{1}{2\pi}S\partial\Phi^\beta(\mathbf{s})\right].$$

From the last two equations above we see immediately that $\sigma^{\text{SS(V)PE}}(\mathbf{s})$ as specified in Eq. (4) satisfies the equation

$$\mathcal{T}\sigma^{\text{SS(V)PE}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right)\left[-\Phi^\rho(\mathbf{s}) + \frac{1}{2\pi}\mathcal{D}\Phi^\rho(\mathbf{s})\right]. \quad (6)$$

This is the most important result of the present work. There are two major practical advantages of this formulation. First, the right-hand side (RHS) of the equation involves the entire solute potential as conveniently calculated through integrals over all of space \mathbf{V} , whereas previous treatments^{10,13} of volume polarization have required difficult integrations over that part of space represented by \mathbf{V}^{ext} . Second, the solution $\sigma^{\text{SS(V)PE}}(\mathbf{s})$ directly collects both exact surface polarization and simulation of volume polarization without the need to piece together separate individual determinations of $\sigma(\mathbf{s})$ and $\alpha(\mathbf{s})$. This should greatly facilitate formulation and calculation of the analytic gradients with respect to nuclear displacements that are useful for geometry optimization purposes. Note also that no explicit evaluation of the solute electric field is required in this formulation.

While less useful for computation, it is convenient for formal comparison with other methods to use Eq. (5) to recast Eq. (6) as

$$\mathcal{T}\sigma^{\text{SS(V)PE}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \left[\frac{1}{2\pi} \mathcal{S}\partial\Phi^{\rho}(\mathbf{s}) + \left(\frac{\epsilon}{\epsilon-1}\right) 2\Phi^{\beta}(\mathbf{s}) \right].$$

COMPARISON TO OTHER APPROXIMATE METHODS

Neglect of volume polarization

In the most common approach, volume polarization is neglected during the solution of Poisson's equation, and the reaction potential $\Phi^{\text{rxn}}(\mathbf{r})$ is approximated as a surface polarization for electrostatics [SPE] with potential $\Phi^{\text{SPE}}(\mathbf{r})$, which is the electrostatic potential due to a surface charge density σ^{SPE} determined by

$$\mathcal{F}\sigma^{\text{SPE}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \frac{1}{2\pi} \partial\Phi^{\rho}(\mathbf{s}). \quad (7)$$

Note that solute charge density outside the cavity will contribute to the field on the RHS here, but not in the correct manner as given in Eq. (1) for the exact $\sigma(\mathbf{s})$. Operating with \mathcal{S} brings this to the form

$$\mathcal{T}\sigma^{\text{SPE}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \frac{1}{2\pi} \mathcal{S}\partial\Phi^{\rho}(\mathbf{s})$$

that is convenient for formal comparison with other methods described in this work.

Conductor-like screening models

In the conductor-like screening model^{14–20} [COSMO] the reaction potential $\Phi^{\text{rxn}}(\mathbf{r})$ is approximated as $\Phi^{\sigma^{\text{COSMO}}}(\mathbf{r})$, which is the electrostatic potential due to a surface charge density σ^{COSMO} determined by

$$\mathcal{S}\sigma^{\text{COSMO}}(\mathbf{s}) = -\left(\frac{\epsilon-1}{\epsilon+0.5}\right) \Phi^{\rho}(\mathbf{s}). \quad (8)$$

The closely related “generalized” version^{21–29} [GCOSMO] utilizes instead a slightly different dielectric screening factor to give a surface charge density σ^{GCOSMO} determined by

$$\mathcal{S}\sigma^{\text{GCOSMO}}(\mathbf{s}) = -\left(\frac{\epsilon-1}{\epsilon}\right) \Phi^{\rho}(\mathbf{s}). \quad (9)$$

Through a series of manipulations similar to those described above in connection with $\alpha(\mathbf{s})$, the equations defining these conductor-like models can be written in the form

$$\mathcal{T}\sigma^{\text{COSMO}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \left[-\left(\frac{1}{\epsilon+0.5}\right) 2\Phi^{\rho}(\mathbf{s}) + \left(\frac{\epsilon-1}{\epsilon+0.5}\right) \frac{1}{2\pi} \mathcal{S}\partial\Phi^{\rho}(\mathbf{s}) + \left(\frac{\epsilon}{\epsilon+0.5}\right) 2\Phi^{\beta}(\mathbf{s}) \right],$$

and

$$\mathcal{T}\sigma^{\text{GCOSMO}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \left[-\left(\frac{1}{\epsilon}\right) 2\Phi^{\rho}(\mathbf{s}) + \left(\frac{\epsilon-1}{\epsilon}\right) \frac{1}{2\pi} \mathcal{S}\partial\Phi^{\rho}(\mathbf{s}) + 2\Phi^{\beta}(\mathbf{s}) \right],$$

which allows for convenient formal comparison with other methods.

Integral equation formulation

A recently proposed method described as being based on an integral equation formulation [IEF]^{30–36} brings together the situations of isotropic solvents, liquid crystals, and ionic solutions into a single general formalism. However, in the present work we are concerned only with the special case of an isotropic solvent, and the IEF equations then simplify somewhat. The reaction potential $\Phi^{\text{rxn}}(\mathbf{r})$ is approximated as $\Phi^{\sigma^{\text{IEF}}}(\mathbf{r})$, which is the electrostatic potential due to a surface charge density σ^{IEF} determined in our notation by

$$\mathcal{T}\sigma^{\text{IEF}}(\mathbf{s}) = \left(\frac{\epsilon}{\epsilon+1}\right) \left[-\Phi^{\rho}(\mathbf{s}) + \frac{1}{2\pi} \mathcal{D}\Phi^{\rho}(\mathbf{s}) - \left(\frac{1}{\epsilon}\right) \frac{1}{2\pi} \mathcal{S}\partial\Phi^{\rho}(\mathbf{s}) \right]. \quad (10)$$

Note that this equation for the IEF method is very similar to Eq. (6) defining the SS(V)PE method, but it will be seen that the differences are important.

Although apparently not explicitly used, it is claimed^{31,32} in connection with the IEF method that

$$\frac{1}{2} \Phi^{\rho}(\mathbf{s}) - \frac{1}{4\pi} \mathcal{D}\Phi^{\rho}(\mathbf{s}) + \frac{1}{4\pi} \mathcal{S}\partial\Phi^{\rho}(\mathbf{s}) = 0,$$

whereupon one would obtain $\sigma^{\text{IEF}}(\mathbf{s}) = \sigma^{\text{SPE}}(\mathbf{s})$, the result corresponding to neglect of volume polarization. This claim would be correct if no solute charge density penetrated outside the cavity, which must therefore be an implicit assumption underlying the IEF derivation. However, we have shown in Eq. (5) that the quantity on the left-hand side (LHS) of the last equation above does not vanish in general, but instead is given by $\Phi^{\rho^{\text{ext}}}(\mathbf{s})$. In preparation for formal comparison with other methods, we use this to recast the IEF equation as

$$\mathcal{T}\sigma^{\text{IEF}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \left[\frac{1}{2\pi} \mathcal{S}\partial\Phi^{\rho}(\mathbf{s}) + \left(\frac{\epsilon}{\epsilon-1}\right)^2 2\Phi^{\beta}(\mathbf{s}) \right].$$

Contributions from solute charge inside and outside the cavity

All the polarization charge densities of the various methods considered here depend linearly on the solute charge density $\rho(\mathbf{r})$. Therefore, it is possible to easily separate each polarization charge density into the sum of two terms, one depending only on $\rho^{\text{int}}(\mathbf{r})$ and the other only on $\rho^{\text{ext}}(\mathbf{r})$, and we will now consider this instructive exercise. The final equation listed above for each method has been obtained with this goal in mind.

Strictly for purposes of formal comparison in this subsection, we temporarily define two surface charge densities that depend on contributions to the solute normal electric field at Γ through the equations

$$\mathcal{F}\tau^{\text{int}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \frac{1}{2\pi} \partial\Phi^{\rho^{\text{int}}}(\mathbf{s}),$$

and

$$\mathcal{F}\mu^{\text{ext}}(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon+1}\right) \frac{1}{2\pi} \partial\Phi^{\rho^{\text{ext}}}(\mathbf{s}),$$

and two surface charge densities that depend on contributions to the solute potential at Γ through the equations

$$\mathcal{T}\omega^{\text{int}}(\mathbf{s}) = -\left(\frac{\epsilon-1}{\epsilon+1}\right) 2\Phi^{\rho^{\text{int}}}(\mathbf{s}),$$

and

$$\mathcal{T}\nu^{\text{ext}}(\mathbf{s}) = -\left(\frac{\epsilon-1}{\epsilon+1}\right) 2\Phi^{\rho^{\text{ext}}}(\mathbf{s}).$$

The respective superscripts on these new quantities are meant to emphasize that $\tau^{\text{int}}(\mathbf{s})$ and $\omega^{\text{int}}(\mathbf{s})$ depend only on $\rho^{\text{int}}(\mathbf{r})$ and that $\mu^{\text{ext}}(\mathbf{s})$ and $\nu^{\text{ext}}(\mathbf{s})$ depend only on $\rho^{\text{ext}}(\mathbf{r})$.

We see that the exact SVPE reaction potential arises from a surface polarization charge density determined by

$$\sigma(\mathbf{s}) = \tau^{\text{int}}(\mathbf{s}) + \frac{1}{\epsilon} \mu^{\text{ext}}(\mathbf{s})$$

together with a volume polarization charge density given by

$$\beta(\mathbf{r}) = -\left(\frac{\epsilon-1}{\epsilon}\right) \rho^{\text{ext}}(\mathbf{r}).$$

In the SS(V)PE formulation proposed here, the exact surface polarization charge density is augmented by an additional surface polarization charge density that simulates the volume polarization and is given by

$$\alpha(\mathbf{s}) = \left(\frac{\epsilon-1}{\epsilon}\right) \mu^{\text{ext}}(\mathbf{s}) + \nu^{\text{ext}}(\mathbf{s}).$$

This produces an effective combined surface polarization charge density given by

$$\sigma^{\text{SS(V)PE}}(\mathbf{s}) = \tau^{\text{int}}(\mathbf{s}) + \mu^{\text{ext}}(\mathbf{s}) + \nu^{\text{ext}}(\mathbf{s}),$$

and it is verified that Eq. (4) is satisfied. If volume polarization is neglected during the derivations, the surface polarization charge density is given by

$$\sigma^{\text{SPE}}(\mathbf{s}) = \tau^{\text{int}}(\mathbf{s}) + \mu^{\text{ext}}(\mathbf{s}),$$

which has the same dependence on $\rho^{\text{int}}(\mathbf{r})$ as found in $\sigma(\mathbf{s})$ and $\sigma^{\text{SS(V)PE}}(\mathbf{s})$, but differs from them in its dependence on $\rho^{\text{ext}}(\mathbf{r})$.

The conductor-like screening models have surface polarization charge densities determined by

$$\begin{aligned} \sigma^{\text{COSMO}}(\mathbf{s}) = & \left(\frac{\epsilon-1}{\epsilon+0.5}\right) \tau^{\text{int}}(\mathbf{s}) + \left(\frac{1}{\epsilon+0.5}\right) \omega^{\text{int}}(\mathbf{s}) \\ & + \left(\frac{\epsilon-1}{\epsilon+0.5}\right) \mu^{\text{ext}}(\mathbf{s}) + \left(\frac{\epsilon}{\epsilon+0.5}\right) \nu^{\text{ext}}(\mathbf{s}), \end{aligned}$$

and

$$\begin{aligned} \sigma^{\text{GCOSMO}}(\mathbf{s}) = & \left(\frac{\epsilon-1}{\epsilon}\right) \tau^{\text{int}}(\mathbf{s}) + \frac{1}{\epsilon} \omega^{\text{int}}(\mathbf{s}) \\ & + \left(\frac{\epsilon-1}{\epsilon}\right) \mu^{\text{ext}}(\mathbf{s}) + \nu^{\text{ext}}(\mathbf{s}). \end{aligned}$$

The parts depending on $\rho^{\text{int}}(\mathbf{r})$ differ significantly from any of the other methods discussed here, having nonunity coefficients of $\tau^{\text{int}}(\mathbf{s})$ and also depending on the quantity $\omega^{\text{int}}(\mathbf{s})$, although in a way that becomes small at high dielectric constant. The parts depending on $\rho^{\text{ext}}(\mathbf{r})$ can be rewritten as $(\epsilon/(\epsilon+0.5))\alpha(\mathbf{s})$ in COSMO and as simply $\alpha(\mathbf{s})$ in GCOSMO, the latter agreeing with the way in which $\sigma^{\text{SS(V)PE}}(\mathbf{s})$ depends on $\rho^{\text{ext}}(\mathbf{r})$.

The integral equation formulation leads to a surface polarization charge density determined by

$$\sigma^{\text{IEF}}(\mathbf{s}) = \tau^{\text{int}}(\mathbf{s}) + \mu^{\text{ext}}(\mathbf{s}) + \left(\frac{\epsilon}{\epsilon-1}\right) \nu^{\text{ext}}(\mathbf{s}),$$

which agrees with $\sigma(\mathbf{s})$, $\sigma^{\text{SS(V)PE}}(\mathbf{s})$, and $\sigma^{\text{SPE}}(\mathbf{s})$ in its dependence on $\rho^{\text{int}}(\mathbf{r})$, but differs from each of them in its dependence on $\rho^{\text{ext}}(\mathbf{r})$. This result can also be written as $\sigma^{\text{IEF}}(\mathbf{s}) = \tau^{\text{int}}(\mathbf{s}) + (\epsilon/(\epsilon-1))\alpha(\mathbf{s})$. But examination of Eq. (3) which defines $\alpha(\mathbf{s})$ shows that the quantity $(\epsilon/(\epsilon-1))\alpha(\mathbf{s})$ is actually independent of ϵ . Thus, the IEF method has the remarkable property of depending on the solute charge density penetrating outside the cavity in a manner that is independent of solvent dielectric constant.

From these expressions, we see that if no solute charge penetrates outside the cavity then the SVPE, SS(V)PE, SPE, and IEF methods will each provide the full correct solution of Poisson's equation, although the COSMO and GCOSMO methods will not. But in the general case that some solute charge does penetrate outside the cavity, then each of these methods becomes distinct from the others.

Limit of infinite dielectric constant

In the limit of the dielectric constant becoming infinitely large, additional connections can be found among the various approximate methods considered in this work. The present analysis shows that in this limit the method denoted here as SS(V)PE becomes equivalent to COSMO and GCOSMO; actually this result was also implicit¹³ in our earlier analysis. Under the restrictive assumption that no solute charge penetrates outside the cavity, it was proved previously³¹ that the IEF method also becomes equivalent to COSMO and

GCOSMO in this limit. The present analysis shows that this relation still holds true even with charge penetration, and so IEF is also equivalent to SS(V)PE in this limit. Note, however, that the SPE method still differs from the others in this limit if some solute charge penetrates outside the cavity.

It may also be mentioned here that if some solute charge penetrates outside the cavity, then only the exact SVPE reaction potential gives in this limit the true conductor solution for which $\Phi^p(\mathbf{r}) + \Phi^{\text{rxn}}(\mathbf{r}) = 0$ at all points \mathbf{r} outside Γ . The SS(V)PE, COSMO, GCOSMO, and IEF methods give in this limit the true conductor solution for points \mathbf{s} on Γ , but not at points \mathbf{r} outside Γ unless there is no charge penetration.

Charge Rule

The known total solute charge given by

$$\bar{\rho} = \int_{\mathbf{V}} d^3\mathbf{r} \rho(\mathbf{r}) = \sum_{\text{nuclei}} Z_{\nu} - N_{\text{elec}}$$

can be partitioned into contributions from solute charge inside and outside the cavity, viz. $\bar{\rho} = \bar{\rho}^{\text{int}} + \bar{\rho}^{\text{ext}}$. The total charge associated with a generic function $\sigma(\mathbf{s})$ defined on Γ is given by

$$\bar{\sigma} = \int_{\Gamma} d^2\mathbf{s} \sigma(\mathbf{s}).$$

This can be evaluated for the exact surface polarization charge density $\sigma(\mathbf{s})$ of reaction field theory by integrating the defining equation over Γ and applying Gauss's Law, which leads to

$$\bar{\sigma} = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{int}}.$$

The total volume polarization charge is easily evaluated to obtain

$$\bar{\beta} = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{ext}}.$$

Thus, the total polarization charge associated with the exact SVPE reaction field satisfies the simple Charge Rule

$$\bar{\sigma} + \bar{\beta} = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}, \quad (11)$$

relating it to the known total solute charge.

We have previously shown⁸ that the total polarization charge associated with simulation of volume polarization is given by

$$\bar{\alpha} = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{ext}}$$

where

$$\bar{\rho}^{\text{ext}} = \int_{\mathbf{V}_{\text{ext}}} d^3\mathbf{r} g(\mathbf{r}) \rho(\mathbf{r}).$$

Here the weighting function $g(\mathbf{r})$ is unity on Γ and falls off slowly with distance outside of Γ . Thus, if most of the solute charge is contained within the cavity so that $\rho(\mathbf{r})$ drops off rapidly with distance outside Γ , then we will have $\bar{\rho}^{\text{ext}}$

$\approx \bar{\rho}^{\text{ext}}$. This has been confirmed in practice, where it has been found¹⁰ that $\bar{\rho}^{\text{ext}}$ typically gives about 90% of the magnitude of $\bar{\rho}^{\text{ext}}$. Thus, $\bar{\alpha} \approx \bar{\beta}$ and the new method proposed in this work produces total polarization charge given by

$$\bar{\sigma}^{\text{SS(V)PE}} = - \left(\frac{\epsilon - 1}{\epsilon} \right) (\bar{\rho}^{\text{int}} + \bar{\rho}^{\text{ext}}), \quad (12)$$

which approximately satisfies the Charge Rule.

If volume polarization is neglected, analogous analysis of the equation for the SPE surface polarization charge leads to

$$\bar{\sigma}^{\text{SPE}} = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{int}}, \quad (13)$$

which does not satisfy the Charge Rule unless all the solute charge is contained within the cavity.

We have previously shown¹³ that the total COSMO charge is given by

$$\bar{\sigma}^{\text{COSMO}} = - \left(\frac{\epsilon - 1}{\epsilon + 0.5} \right) (\bar{\rho}^{\text{int}} + \bar{\rho}^{\text{ext}}), \quad (14)$$

which does not satisfy the Charge Rule, and that the total GCOSMO charge is given by

$$\bar{\sigma}^{\text{GCOSMO}} = - \left(\frac{\epsilon - 1}{\epsilon} \right) (\bar{\rho}^{\text{int}} + \bar{\rho}^{\text{ext}}), \quad (15)$$

which agrees with $\bar{\sigma}^{\text{SS(V)PE}}$ and does approximately satisfy the Charge Rule.

After straightforward manipulation of the equation for the IEF surface polarization charge density, Gauss's Law can be applied to determine that

$$\bar{\sigma}^{\text{IEF}} = - \left[\left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{int}} + \bar{\rho}^{\text{ext}} \right]. \quad (16)$$

Thus, as previously remarked, with this method the solute charge density penetrating outside the cavity contributes in a manner that is independent of ϵ . Note that in high dielectric solvents where $(\epsilon - 1)/\epsilon \approx 1$, the numerical value of $\bar{\sigma}^{\text{IEF}}$ will approximately satisfy the Charge Rule. In fact, with the IEF method a particular value of dielectric constant can always be found for which the Charge Rule will accidentally be exactly satisfied numerically. For example, in a typical case where $\bar{\rho}^{\text{ext}} = 0.90\bar{\rho}^{\text{ext}}$, the factor of 0.90 that is actually related to the distribution of solute charge penetrating outside the cavity happens to be numerically equivalent to $(\epsilon - 1)/\epsilon$ for a dielectric constant of $\epsilon = 10$. This example illustrates that exact or near numerical satisfaction of the Charge Rule is not necessarily evidence that the influence on the reaction potential of solute charge penetrating outside the cavity is being treated correctly.

Much has been written on use of the Charge Rule in conjunction with various approximate methods. It is often advocated the calculated surface charge density be renormalized by some *ad hoc* procedure to enforce its exact satisfaction. In certain instances there is some merit in this for the SPE method that completely neglects volume polarization. Thus, there is evidence¹⁰ renormalization helps somewhat to

correct the very large errors associated with SPE free energies of solvation for ionic solutes, and it is conceivable although not yet established that it may ameliorate large errors found¹² in SPE for second- and higher-order properties even of neutral solutes.

However, it is our view that there is yet no firm evidence that charge renormalization is desirable in any of the methods such as SS(V)PE, COSMO, GCOSMO, and IEF that already approximate in some manner the effects of volume polarization. Rather it is likely that any renormalization would make things worse in the SS(V)PE method which produces, by construction, the same electrostatic potential everywhere inside the cavity that would be produced by an SVPE treatment of the exact volume polarization together with the exact surface polarization. Any further modification of the total SS(V)PE surface polarization in the guise of a renormalization would therefore compromise this exact solution inside the cavity. The only error in the SS(V)PE approximate solution of Poisson's equation lies in incorrect representation of the volume polarization contribution to the electrostatic potential in the less important region outside the cavity, and this error cannot be rectified by such a simple procedure as modification of the surface charge density. This argument also applies to the COSMO, GCOSMO, and IEF methods in the limit of infinite dielectric constant, since they are then each equivalent to SS(V)PE, and presumably also applies to them in the case of high dielectric constant solvents where they do not deviate very far from the infinite dielectric constant limit.

CONCLUSION

We have proposed a new formulation of reaction field theory denoted SS(V)PE that is expected to provide an accurate solution of Poisson's equation for use in conjunction with treating equilibrium electrostatic solvation effects in electronic structure calculations. In the SS(V)PE method the classical reaction potential is approximated as the electrostatic potential due to the surface charge density specified by Eq. (6). This supplies the exact surface polarization charge density arising from the boundary condition due to the sudden change in dielectric constant at the cavity surface and furthermore also an accurate simulation of the exact volume polarization arising from quantum mechanical penetration of solute charge density outside the cavity. This approach avoids the major difficulties associated with exact evaluation of the volume polarization, and should also facilitate the inclusion of volume polarization effects in determination of analytic gradients in reaction field theory. Formal comparison to exact SVPE treatment has shown the advantages of this new method over other approximate methods such as SPE, COSMO, GCOSMO, and IEF.

If no solute charge penetrates outside the cavity, then the SS(V)PE, SPE, and IEF methods all supply the exact solution of Poisson's equation, although COSMO and GCOSMO still differ. If some solute charge does penetrate outside the cavity, then all of these approaches become approximate and different from one another, with no simple relations among them in general.

It should be mentioned that care should be taken to accurately evaluate the solute electrostatic potential $\Phi^p(\mathbf{r})$ that is needed in conjunction with the SS(V)PE, COSMO, GCOSMO, and IEF methods that incorporate in some manner an approximation to the volume polarization. In particular, a multipole expansion is convergent and usually accurate only in regions strictly outside the charge density it represents. Thus, if solute charge penetration is a significant issue then a multipole expansion should not be expected to give an accurate representation of $\Phi^p(\mathbf{s})$ on Γ .

In the limit of infinite dielectric constant, the SS(V)PE, COSMO, GCOSMO, and IEF methods all become equivalent, while SPE still differs. For high dielectric solvents it can be expected that these will be close to their infinite dielectric constant limits, and so the SS(V)PE, COSMO, GCOSMO, and IEF methods will remain similar to one another and should each provide satisfactory results. The differences among these methods will be more pronounced in lower dielectric constant solvents, where the unique advantages of the SS(V)PE formulation should become manifest.

The exact SVPE solution of Poisson's equation satisfies a simple Charge Rule relating the total polarization charge to the known solute net charge. The SS(V)PE and GCOSMO methods will approximately satisfy this Charge Rule under a wide variety of conditions of dielectric constant and, up to a point, of the amount of solute charge penetrating outside the cavity. The SPE and COSMO methods will not consistently satisfy the Charge Rule very well over a wide variety of such conditions, although SPE will approach it if the amount of solute charge penetrating outside the cavity is very small, and COSMO will approach it if the dielectric constant is large. The IEF method also will not consistently satisfy the Charge Rule very well over a wide variety of such conditions, but will approach it if the amount of solute charge penetrating outside the cavity is very small or the dielectric constant is large, and may even appear to exactly satisfy it if certain numerical factors involving the dielectric constant and the distribution of solute charge penetrating outside the cavity accidentally cancel one another. It is therefore pointed out that apparent numerical satisfaction of the Charge Rule in particular cases should not necessarily be taken as evidence of correct treatment of the influence of solute charge penetrating outside the cavity. Furthermore, *ad hoc* charge renormalization to enforce exact satisfaction of the Charge Rule is not recommended for any of the SS(V)PE, COSMO, GCOSMO, or IEF methods.

Volume polarization effects are particularly large¹⁰ for ionic solutes. Thus, the SS(V)PE method should be especially advantageous for characterization of ions and zwitterions and also for evaluation of properties involving a change of charge, such as pK_a and redox potential. The appropriate generalization of the SS(V)PE method should also be very useful for describing electron transfer and vertical electronic excitation, which are both governed in part by a low optical dielectric constant, and where, furthermore, the amount of charge penetration may be somewhat different between the initial and final states.

In conclusion, the SS(V)PE formulation proposed here has the advantages of being easy to implement and of being

more robust than other approximate methods in providing accurate solutions of Poisson's equation over a wide range of conditions. A computer program is currently being developed for electronic structure calculation with SS(V)PE treatment of solvation, and numerical results will be reported in due course.

ACKNOWLEDGMENTS

The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is contribution No. NDRL-4160 from the Notre Dame Radiation Laboratory.

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