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Simulation of volume polarization in reaction field theory

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In the reaction field theory of solvation, penetration of charge density outside the cavity nominally enclosing the solute leads to a volume polarization that contributes in addition to the commonly recognized surface polarization. In principle the exact volume polarization charge density is spread everywhere outside the cavity, but its effect can be closely and concisely simulated by a certain additional surface polarization charge density. Formal comparison is made to conductorlike screening models, and it is found that these improve on common approaches that neglect volume polarization by automatically including the simulation of volume polarization. A revised method to numerically determine this simulation is also described. © 1999 American Institute of Physics. [S0021-9606(99)51716-9]

INTRODUCTION

Recent reviews^{1,2} attest to the increasing popularity of reaction field theory used in conjunction with a dielectric continuum model³⁻⁶ of solvent to estimate the electrostatic effects of solvation on the properties of a solute molecule. The solute can be treated quantum mechanically by appropriately including in its Hamiltonian operator an effective potential energy term⁷⁻¹⁰ describing the solvent influence. Although the relevant equations can be solved analytically for spherical and certain other regular cavity shapes, this potential must be determined numerically in the case of a general cavity that is closely adapted to the actual shape of the solute. In that event, the effect is usually explicitly or implicitly represented in terms of an apparent surface polarization charge density spread over the boundary of the cavity that nominally encloses the solute. However, quantum mechanical calculation of the solute usually produces a tail of the wave function that penetrates outside the cavity, leading to an additional but rarely recognized apparent volume polarization charge density spread throughout the dielectric continuum outside the cavity.^{11,12} In the past this effect has been treated in a few atomic and molecular calculations with spherical cavities,¹³⁻¹⁵ but only recently has a general implementation for more general irregular shaped cavities been reported.¹⁶ Volume polarization effects have been shown to have a significant influence on free energies of solvation^{16,17} and to have a large effect on nuclear magnetic resonance (NMR) shielding constants.¹⁸ It has been speculated that the influence will also be large on other second and higher-order properties.¹⁸

In principle, the volume polarization charge extends as far out into the dielectric continuum as the tail of the solute charge density remains non-negligible. However, in practice its effects can be closely simulated through a certain additional surface polarization charge density.¹² This simulation exactly represents the volume polarization effect everywhere inside the cavity. The price of the simplification is a small

error in the representation outside the cavity, but that is not very significant in practice.¹⁶ Highly accurate numerical representation of the volume polarization effect requires it to be evaluated on a three dimensional grid of nodes distributed on and outside the cavity.¹⁶ The simulation, therefore, allows a much more concise approximate representation, since it only requires a two dimensional grid of nodes located on the cavity surface.

In this work we further explore this simulation of the volume polarization. The formal relation to conductorlike screening models¹⁹⁻³⁶ is considered, and it is found that these implicitly include the simulation of volume polarization. This clarifies various findings in the literature that were previously poorly understood. Also, the procedure originally suggested¹⁶ for numerical determination of the simulation is revised to obtain a more accurate and more efficient method.

BACKGROUND

Solute charge density

Let $\rho(\mathbf{r})$ represent the solute charge density determined from some kind of quantum mechanical calculation. For simplicity of analysis we assume it is fixed and known, although it may actually represent just one step in an iterative process in which $\rho(\mathbf{r})$ is allowed to relax to become self-consistent with its own reaction field. The entire space \mathbf{V} is partitioned by some given closed boundary surface Γ into an interior part \mathbf{V}^{int} nominally accommodating the solute and an exterior part \mathbf{V}^{ext} occupied by the surrounding solvent. The solute charge enclosed by the cavity

$$\bar{\rho}^{\text{int}} \equiv \int_{\mathbf{V}^{\text{int}}} d^3\mathbf{r}' \rho(\mathbf{r}'),$$

together with the solute charge penetrating outside the cavity

$$\bar{\rho}^{\text{ext}} \equiv \int_{\mathbf{V}^{\text{ext}}} d^3\mathbf{r}' \rho(\mathbf{r}'),$$

combine to give the known total solute charge

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$$\bar{\rho} \equiv \int_{\mathbf{v}} d^3\mathbf{r}' \rho(\mathbf{r}') = \bar{\rho}^{\text{int}} + \bar{\rho}^{\text{ext}}.$$

If this charge density were in a vacuum, it would produce an electrostatic potential $\Phi^{\rho}(\mathbf{r})$ given by

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

Exact polarization potential

The solvent is represented as a homogeneous structureless dielectric continuum extending to infinity in all directions that is characterized by an isotropic macroscopic dielectric constant ϵ . It is convenient to represent the effect of the reaction field arising from polarization of the solvent in terms of an electrostatic potential $\Phi^{\text{pol}}(\mathbf{r})$ which is determined by certain apparent charge distributions. From this, the potential energy of interaction \mathcal{V}^{pol} between the solvent and the electrons and nuclei of the solute can easily be obtained from

$$\mathcal{V}^{\text{pol}} = \sum_{\nu}^{\text{nuclei}} Z_{\nu} \Phi^{\text{pol}}(\mathbf{R}_{\nu}) - \sum_i^{\text{electrons}} \Phi^{\text{pol}}(\mathbf{r}_i).$$

Incorporating this potential energy in an appropriate manner into the solute Hamiltonian operator⁷⁻¹⁰ then accounts for the reaction field influence of solvent on properties of the solute.

The total electrostatic potential due to solvent polarization is given by the sum of two contributions

$$\Phi^{\text{pol}}(\mathbf{r}) = \Phi^{\sigma}(\mathbf{r}) + \Phi^{\beta}(\mathbf{r}),$$

which are obtained by solving Poisson's equation. The first term in Φ^{pol} represents the commonly treated surface polarization given by

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

The surface polarization charge density involved here is obtained by solving the integral equation

$$\sigma(\mathbf{s}) = \frac{(\epsilon - 1)}{4\pi} \left[\frac{\partial \Phi^{\rho}}{\partial n_s}(\mathbf{s}) + \frac{\partial \Phi^{\beta}}{\partial n_s}(\mathbf{s}) + \frac{\partial \Phi^{\sigma}}{\partial n_s}(\mathbf{s}^{\text{ext}}) \right],$$

which utilizes the outward-directed continuous normal derivatives of Φ^{ρ} and Φ^{β} evaluated at the surface and the discontinuous normal derivative of Φ^{σ} evaluated just outside the surface. The second term in Φ^{pol} represents the rarely considered volume polarization given by

$$\Phi^{\beta}(\mathbf{r}) = \int_{\mathbf{v}} d^3\mathbf{r}' \frac{\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = - \left(\frac{\epsilon - 1}{\epsilon} \right) \int_{\mathbf{v}^{\text{ext}}} d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

The volume polarization charge density involved here is obtained from

$$\beta(\mathbf{r}) = \begin{cases} 0 & \text{for } \mathbf{r} \in \mathbf{V}^{\text{int}} \\ - \left(\frac{\epsilon - 1}{\epsilon} \right) \rho(\mathbf{r}) & \text{for } \mathbf{r} \in \mathbf{V}^{\text{ext}}, \end{cases}$$

and is evidently caused by penetration of solute charge outside the cavity.

The total volume polarization charge is obviously given by

$$\bar{\beta} \equiv \int_{\mathbf{v}} d^3\mathbf{r}' \beta(\mathbf{r}') = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{ext}}$$

and application of Gauss's Law³⁷ shows that total surface polarization charge is given by

$$\bar{\sigma} \equiv \int_{\Gamma} d^2\mathbf{s}' \sigma(\mathbf{s}') = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{int}}.$$

Combining these leads to the Charge Rule¹²

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

that relates the total polarization charge $\bar{\sigma} + \bar{\beta}$ to the known solute charge $\bar{\rho}$, e.g., zero for a neutral molecule.

Simulation of volume polarization

It has also been pointed out¹² that the effect of volume polarization can be closely simulated by a certain additional surface charge distribution that produces an electrostatic potential of

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

The additional surface polarization charge density $\alpha(\mathbf{s})$ involved here is obtained by solving the integral equation

$$\Phi^{\alpha}(\mathbf{s}) = \Phi^{\beta}(\mathbf{s})$$

that is to hold for all surface points \mathbf{s} . Then it also follows¹² that $\Phi^{\alpha}(\mathbf{r}) = \Phi^{\beta}(\mathbf{r})$ for all \mathbf{r} inside Γ as well. Thus, Φ^{α} errs only in representing Φ^{β} outside the cavity, and so it should provide a good approximation to the direct effect of volume polarization. Furthermore, the indirect effect of volume polarization in determining the surface polarization $\sigma(\mathbf{s})$ can be obtained exactly¹² from Φ^{α} .

This simulation carries a total polarization charge of

$$\bar{\alpha} \equiv \int_{\Gamma} d^2\mathbf{s}' \alpha(\mathbf{s}') = - \left(\frac{\epsilon - 1}{\epsilon} \right) \int_{\mathbf{v}^{\text{ext}}} d^3\mathbf{r}' g(\mathbf{r}') \rho(\mathbf{r}').$$

Here $g(\mathbf{r}')$ is a weighting function that can be shown¹² to be unity on Γ and to fall off slowly outside the surface to become zero at infinity. If the cavity is large enough to hold most of the solute charge density so that outside the penetrating charge falls off rapidly to zero, we will then have

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

This expectation has been confirmed in actual calculations¹⁶ that found $\bar{\alpha}$ to be about 90% of $\bar{\beta}$ for several small neutral and singly charged solutes. Thus, simulating the volume polarization by this additional surface polarization leads to an additional surface charge that is almost enough to make up the Charge Rule, i.e.,

$$\bar{\sigma} + \bar{\alpha} \approx - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}.$$

Taking Φ^{pol} to be $\Phi^{\sigma} + \Phi^{\alpha}$ should, therefore, provide a very good approximation to the exact polarization.

Neglect of volume polarization

For completeness, the common approximation of neglecting volume polarization (nvp) should also be mentioned. This corresponds to dropping both the direct contribution of Φ^{β} to Φ^{pol} and the indirect contribution that comes from its influence on the surface polarization potential. The resulting surface polarization charge density is then denoted as $\sigma^{\text{nvp}}(\mathbf{s})$. In that situation the entire polarization potential is given just by $\Phi^{\sigma^{\text{nvp}}}$, so the total polarization charge given by

$$\bar{\sigma}^{\text{nvp}} \equiv \int_{\Gamma} d^2s' \sigma^{\text{nvp}}(\mathbf{s}') = - \left(\frac{\epsilon - 1}{\epsilon} \right) \bar{\rho}^{\text{int}}$$

is not sufficient to make up the anticipated Charge Rule. Various *ad hoc* suggestions have been made^{9,11,12,23,38} to ‘renormalize’ $\sigma^{\text{nvp}}(\mathbf{s})$ to produce a modified distribution $\sigma^{\text{ren}}(\mathbf{s})$ that exactly satisfies the Charge Rule

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

However, calculations¹⁶ have shown that these methods are usually incapable of accurately reproducing the actual effects of volume polarization on free energies of solvation.

RELATION TO CONDUCTORLIKE SCREENING MODELS

COSMO and GCOSMO

In the conductorlike screening model (COSMO^{19–25}) the polarization potential Φ^{pol} is taken to be that of a certain surface charge distribution $\sigma^{\text{COSMO}}(\mathbf{s})$ that is defined by a two-step procedure. In the first step the conductorlike solution appropriate to the limit of an infinite dielectric constant is determined by setting to zero the total electrostatic potential at the cavity surface. In the second step this solution is made applicable to a finite dielectric through scaling by a certain function of the dielectric constant. These logically distinct steps can be operationally combined into a single step to obtain the relation

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

that is to hold for all surface points \mathbf{s} . Similarly, a slight modification^{26–36} dubbed the generalized GCOSMO can be operationally defined through

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

Here we investigate how these models are related to the exact solution of Poisson’s equation which includes both surface and volume polarization as described above.

Limit of large dielectric constant

The formal relations are easiest to see in the limit $\epsilon \rightarrow \infty$ where the equilibrium response of the solvent becomes equivalent to that of a pure conductor. For the exact surface polarization a brief derivation leads to

$$\Phi^{\sigma_{\infty}}(\mathbf{r}) = - \int_{\text{Vint}} d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

for all \mathbf{r} on and outside Γ , and for the exact volume polarization we immediately obtain

$$\Phi^{\beta_{\infty}}(\mathbf{r}) = - \int_{\text{Vext}} d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

for all \mathbf{r} . Combining these shows that the total polarization potential satisfies

$$\Phi^{\sigma_{\infty}}(\mathbf{r}) + \Phi^{\beta_{\infty}}(\mathbf{r}) = - \Phi^{\rho}(\mathbf{r}),$$

for all \mathbf{r} on and outside Γ . This is exactly the expected result, since the total potential $\Phi^{\rho} + \Phi^{\text{pol}}$, with $\Phi^{\text{pol}} = \Phi^{\sigma_{\infty}} + \Phi^{\beta_{\infty}}$, should vanish both on and everywhere outside the cavity surface for a conducting medium.

Simulation of the volume polarization is determined by finding the additional surface charge density α_{∞} that satisfies

$$\Phi^{\alpha_{\infty}}(\mathbf{s}) = \Phi^{\beta_{\infty}}(\mathbf{s}),$$

for all \mathbf{s} on Γ . Since neither distribution $\beta_{\infty}(\mathbf{r})$ nor $\alpha_{\infty}(\mathbf{s})$ has any source terms inside the cavity, there follows the generalization $\Phi^{\alpha_{\infty}}(\mathbf{r}) = \Phi^{\beta_{\infty}}(\mathbf{r})$ for all \mathbf{r} on and inside Γ .

For use below we also note the relations $\bar{\sigma}_{\infty} = -\bar{\rho}^{\text{int}}$ and $\bar{\alpha}_{\infty} \approx \bar{\beta}_{\infty} = -\bar{\rho}^{\text{ext}}$ for the total polarization charges.

Now we can examine how the previously proposed conductorlike models compare with these exact results. For $\epsilon \rightarrow \infty$ the COSMO and GCOSMO models become identical and are determined by

$$\Phi^{\sigma_{\infty}^{\text{COSMO}}}(\mathbf{s}) = - \Phi^{\rho}(\mathbf{s}).$$

Thus, the COSMO solution is not just the exact surface charge density, but rather the sum of that plus the additional surface charge density that simulates volume polarization, viz.,

$$\sigma_{\infty}^{\text{COSMO}}(\mathbf{s}) = \sigma_{\infty}(\mathbf{s}) + \alpha_{\infty}(\mathbf{s}).$$

It, therefore, provides a more complete representation of the full polarization potential than would be given by just taking the infinite dielectric constant limit of the exact surface polarization charge density $\sigma(\mathbf{s})$ [or of $\sigma^{\text{nvp}}(\mathbf{s})$] alone.

Note that despite its name, the COSMO polarization potential $\Phi^{\sigma_{\infty}^{\text{COSMO}}}(\mathbf{r})$ differs from the exact conductor solution obtained just above when there is any solute charge penetration outside the cavity. The reason for this apparent discrepancy is that in the COSMO derivation the solution has been assumed to take the form of only a surface charge density and the conductor criterion has been applied only at the cavity surface. Thus, the total potential is correctly zero at the cavity surface, but with solute charge penetration it is incorrectly nonzero outside the cavity. These features have the

fortunate consequence that the COSMO solution automatically includes the simulation of volume polarization.

These results clarify certain points remarked on previously in the literature. It has been estimated²³ that COSMO models reduce the error in satisfaction of the Charge Rule by an order of magnitude over previous surface charge models. It has also been noted in practical calculations³⁶ that GCOSMO very nearly satisfies the Charge Rule for neutral solutes. These findings are now seen from the present analysis to result from the fact that the total COSMO surface charge

$$\bar{\sigma}_{\infty}^{\text{COSMO}} = \bar{\sigma}_{\infty} + \bar{\alpha}_{\infty},$$

includes a contribution from the simulation of volume polarization that has been shown previously both from theoretical arguments¹² and from numerical calculations¹⁶ to closely approximate the total exact volume polarization charge. Therefore, the Charge Rule is nearly satisfied and the whole question of charge renormalization is much less important in COSMO than in previous nvp surface charge models.

Note that COSMO and GCOSMO models do not necessarily have any less solute charge penetration outside the cavity than other models, as has sometimes been implied in the literature. The improvement in satisfaction of the Charge Rule by the total apparent surface charge in such conductorlike screening models arises instead from including the simulation of volume polarization, thereby placing additional apparent polarization charge on the cavity surface.

Comments on surface charge renormalization within COSMO

Even though inclusion of the simulation of volume polarization in the total COSMO surface charge leads to near satisfaction of the Charge Rule, it is of interest to inquire about how or whether the remaining small discrepancy could be corrected. This matter is considered in the present subsection, still assuming infinite dielectric constant for simplicity.

With the usual model of surface polarization that neglects volume polarization, surface charge renormalization can be justified as an attempt to represent the effects of volume polarization, although previously proposed procedures generally fall far short of this mark in practice.

In contrast, the role of any correction procedure within conductorlike models must be somewhat different. The present work clearly shows that in conductorlike models correction of the remaining error corresponds not to treating the potential due to the volume polarization itself, but rather to treating the difference between the potentials arising from the true volume polarization and from its simulation. In COSMO this difference is already zero everywhere inside and on the cavity, so any proper correction should only affect the potential outside the cavity where all the remaining error actually exists. But this goal cannot be accomplished by any modification of the COSMO surface charge distribution, since this would necessarily have the consequence of compromising the potential inside the cavity. Saying it another way, the additional surface charge distribution given by the simulation described here is already optimal for representa-

tion of the volume polarization. Any further modification of the surface charge distribution to improve satisfaction of the Charge Rule must therefore be harmful to the representation of the potential inside the cavity. Consequently, we do not recommend any surface charge renormalization when using conductorlike models.

This is not to say, however, that other simplified procedures cannot be constructed that simultaneously improve the description of volume polarization and also lead to satisfaction of the Charge Rule. In this regard, a proposed double-cavity correction procedure²³ within COSMO is of interest. This has an initial step of placing an additional surface charge distribution on an outer cavity surface placed about 1 Å outside the original surface. If the two surface charge distributions were to be determined in a mutually self-consistent manner to make the total potential vanish on both surfaces, this would indeed further improve the representation of volume polarization. The actual proposed procedure²³ of holding the inner surface distribution fixed while adjusting the outer surface distribution to make the total potential vanish on the outer surface can be rationalized as a first approximation to this mutually self-consistent solution, since the outer distribution will be significantly smaller in overall magnitude than the inner one. Furthermore, if the outer surface is large enough to enclose essentially all the solute charge density, it can be shown that the additional charge on the outer surface will be just that required to satisfy the Charge Rule. However, in a final step this proposal²³ collapses the charge obtained on the temporary outer surface back onto the original inner surface, at which stage it effectively becomes a surface charge renormalization method. It will therefore ultimately lead to a significant disturbance of the conductorlike solution in the important region inside the cavity.

Another proposed modification²⁴ of COSMO is concerned with the separate matter of the difference between using the potential generated by the actual solute charge density and using the approximate potential generated by a distributed multipole representation. The latter can be viewed as the potential of a surrogate solute charge density which is entirely enclosed by the cavity. However, the present analysis shows that when some solute charge penetrates outside the cavity the optimal choice uses the potential from the actual solute density, since this exactly introduces the desirable simulation of volume polarization. Any other choice, such as the potential obtained from a distributed multipole analysis, must therefore, be regarded as leading to an approximation to the true conductorlike solution.

Finite dielectric constant

The relations obtained above also allow some comment to be made on the scaling used to specify the finite dielectric constant dependence of conductorlike screening models. The exact volume polarization has a simple known scaling given by

$$\beta(\mathbf{r}) = \left(\frac{\epsilon - 1}{\epsilon} \right) \beta_{\infty}(\mathbf{r}),$$

so that $\bar{\beta}=[(\epsilon-1)/\epsilon]\bar{\beta}_\infty=-[(\epsilon-1)/\epsilon]\bar{\rho}^{\text{ext}}$, and similarly the simulation of volume polarization also scales as

$$\alpha(\mathbf{s})=\left(\frac{\epsilon-1}{\epsilon}\right)\alpha_\infty(\mathbf{s}),$$

so that $\bar{\alpha}=[(\epsilon-1)/\epsilon]\bar{\alpha}_\infty\approx-[(\epsilon-1)/\epsilon]\bar{\rho}^{\text{ext}}$. The dielectric constant dependence of the exact surface polarization charge density $\sigma(\mathbf{s})$, on the other hand, is very complicated in general and can not be written as a simple multiplicative scaling factor times $\sigma_\infty(\mathbf{s})$, except in certain very special cases. But even so, the scaling dependence of the total exact surface polarization charge $\bar{\sigma}$ is known, and is simply given by $\bar{\sigma}=[(\epsilon-1)/\epsilon]\bar{\sigma}_\infty=-[(\epsilon-1)/\epsilon]\bar{\rho}^{\text{int}}$. Therefore, an assumption of scaling according to

$$\sigma(\mathbf{s})=\left(\frac{\epsilon-1}{\epsilon}\right)\sigma_\infty(\mathbf{s}),$$

would at least lead to the theoretically correct value of $\bar{\sigma}$, even if not of the exact detailed distribution of $\sigma(\mathbf{s})$.

Thus, neither the COSMO scaling

$$\sigma^{\text{COSMO}}(\mathbf{s})=\left(\frac{\epsilon-1}{\epsilon+0.5}\right)\sigma_\infty^{\text{COSMO}}(\mathbf{s}),$$

that is valid only for a fixed point dipole in a spherical cavity nor the GCOSMO scaling

$$\sigma^{\text{GCOSMO}}(\mathbf{s})=\left(\frac{\epsilon-1}{\epsilon}\right)\sigma_\infty^{\text{GCOSMO}}(\mathbf{s}),$$

that is valid only for a fixed point charge in a spherical cavity is correct in general. However, the GCOSMO scaling may be slightly preferred on the grounds that it produces a total polarization charge $\bar{\sigma}^{\text{GCOSMO}}$ that does have the theoretically correct scaling with dielectric constant. In any event, it should be kept in mind that conductorlike screening models are expected to be most applicable for high dielectric solvents, where there is only a small numerical difference between the factors $(\epsilon-1)/(\epsilon+0.5)$ and $(\epsilon-1)/\epsilon$, and consequently the particular choice of scaling is then really not very important.

NUMERICAL DETERMINATION OF THE SIMULATION OF VOLUME POLARIZATION

Preliminaries

We have previously outlined a method¹⁶ to numerically approximate the additional surface charge distribution $\alpha(\mathbf{s})$ that simulates the effects of volume polarization through equating $\Phi^\alpha(\mathbf{r})$ to $\Phi^\beta(\mathbf{r})$ at a finite number of points \mathbf{r} situated well inside the cavity. However, an alternative method, originally developed to implement COSMO¹⁹ and later applied in another related context,³³ suggests a better solution through relating $\Phi^\alpha(\mathbf{s})$ to $\Phi^\beta(\mathbf{s})$ at a finite number of points \mathbf{s} situated on the cavity surface. Here we show how that method can be applied in the present context to determine the additional surface charge density that represents the simulation of volume polarization.

The exact continuous surface charge distribution $\alpha(\mathbf{s})$ can be approximated in terms of its values $\{\alpha_j\}$ at a finite

number N of nodes $\{\mathbf{s}_i\}$ on Γ . Many reasonable ways have been proposed in the literature to obtain effective distributions of such nodes for description of effective molecular surfaces, not only in connection with specification of solute cavities but also often in other contexts such as visualization of the molecular electrostatic potential. For the present purposes, we need only assume that the location of each node \mathbf{s}_i and the surface area w_i associated with it have been specified by some appropriate procedure. The total surface area of the cavity is then

$$S_\Gamma\equiv\int_\Gamma d^2\mathbf{s}'=\sum_{i=1}^N\int_{\Gamma_i} d^2\mathbf{s}'_i=\sum_{i=1}^N w_i.$$

In principle, Γ_i denotes the region of the surface having area w_i that is associated with the node \mathbf{s}_i , and \mathbf{s}'_i is a dummy integration variable ranging over this region. These quantities are used here for clarity of the presentation, but it turns out that in the present context the regions Γ_i never actually need to be specifically defined or constructed (unless that is required by the particular algorithm used to determine the segment surface areas w_i).

System matrix

Integrating the equation defining α

$$\int_\Gamma d^2\mathbf{s}'\frac{\alpha(\mathbf{s}')}{|\mathbf{s}-\mathbf{s}'|}=\Phi^\beta(\mathbf{s}),$$

over one particular surface element Γ_i , and breaking up the remaining integral that ranges over the entire surface into contributions from each separate surface element, leads to

$$\int_{\Gamma_i} d^2\mathbf{s}'_i\sum_{j=1}^N\int_{\Gamma_j} d^2\mathbf{s}'_j\frac{\alpha(\mathbf{s}'_j)}{|\mathbf{s}'_i-\mathbf{s}'_j|}=\int_{\Gamma_i} d^2\mathbf{s}'_i\Phi^\beta(\mathbf{s}'_i),$$

for all $i=1\cdots N$. Now we assume that $\alpha(\mathbf{s}'_j)$ varies slowly over the region Γ_j and so can be approximated by the constant value α_j , and similarly that $\Phi^\beta(\mathbf{s}'_i)$ varies slowly over the region Γ_i and so can be approximated by the constant value $\Phi^\beta(\mathbf{s}_i)$. Determination of the latter values of the exact volume polarization potential at all of the surface nodes is described in detail in the next subsection.

These manipulations cast the problem into a finite matrix equation of the form

$$\underline{A}\underline{\alpha}=\underline{B}$$

where $\underline{\alpha}$ is a column vector of the α_j values, \underline{B} is a column vector of the $B_i\equiv w_i\Phi^\beta(\mathbf{s}_i)$ values, and \underline{A} is the symmetric system matrix having elements

$$A_{ij}\equiv\int_{\Gamma_i} d^2\mathbf{s}'_i\int_{\Gamma_j} d^2\mathbf{s}'_j\frac{1}{|\mathbf{s}'_i-\mathbf{s}'_j|}.$$

Once the system matrix is constructed, it is straightforward to solve these linear simultaneous equations to find the desired N values of α_j .

For $j\neq i$ it is reasonable to assume that the integrand is constant to obtain the approximation

$$A_{ij} \approx \frac{w_i w_j}{|s_i - s_j|}.$$

But this approximation cannot be adopted for the diagonal element A_{ii} due to the singularity in the integrand. For this case we have verified that the expression

$$A_{ii} \approx w_i \sqrt{4\pi w_i},$$

is exact for Γ_i a small circular cap section of a sphere, is also exact for a flat circular element of any size, and is accurate to better than one part in a thousand for a flat regular polygon of any size having six or more sides. As an aside, we note that with these approximations there is a common factor of w_i that could be cancelled out from the elements A_{ij} and B_i in the system equations (or, equivalently, the initial integration described above over the surface element Γ_i could be omitted), but at the cost of then producing a modified system matrix that is nonsymmetric.

A slightly improved approximation has been previously proposed¹⁹ for the diagonal elements, which in the present context becomes

$$A_{ii} \approx C w_i \sqrt{4\pi w_i}.$$

The constant C was determined¹⁹ to have the value 1.07 based on numerical evaluation for a sphere divided into various numbers of equivalent finite segments. However, it should be pointed out that for more general division of a sphere into nonequivalent finite segments or for segmentation of a nonspherical cavity a different value C_i would be appropriate for each different segment Γ_i .

This basic idea of scaling the diagonal elements of the system matrix to improve the accuracy of finite approximations can be adapted to the surface integration scheme we and others have used^{16,39} that invokes nodes and weights optimized for Gaussian integration over a sphere of all spherical harmonics up to some maximum order. For this purpose we have considered a set having 50 nodes,⁴⁰ sets having 110, 194, 302, 434, 590, 770, 974, and 1202 nodes,⁴¹ and alternative sets also containing 590 and 770 nodes.⁴² For each node s_i in each set, we have determined the value of C_i which leads to exact satisfaction of the equation $\sum_{j=1}^N A_{ij} = 4\pi w_i$ that can be analytically derived for a spherical cavity of unit radius. The values of C_i thereby found ranged from a low of 0.799 to a high of 1.829. The average value of C_i for each set ranged from 1.093 to 1.111, and the overall average value of C_i from all sets was 1.104.

To see how the situation may change with a more challenging cavity having both convex and concave regions, we also considered a dumbbell shaped cavity. Highly accurate approximations to the exact results for $\sum_{j=1}^N A_{ij}$ with this particular cavity were obtained for each node s_i using the facility in the Mathematica program⁴³ to numerically integrate over a singular function to a user-specified precision. The same distributions just noted above, after appropriately projecting the unit sphere nodes and weights onto the actual surface as described previously,^{16,39} were used to determine finite approximations to this quantity. The values of C_i that led to satisfaction of the essentially exact results in this case ranged from a low of 0.556 to a high of 1.862, and the

average value of C_i for each set ranged from 0.893 to 1.199. Thus, the values of C_i are somewhat more variable in this more difficult case of a nonspherical cavity. Remarkably, however, the overall average value of C_i from all sets for this situation was 1.104, essentially the same as found for spherical cavities.

We conclude from these studies that incorporation of a constant factor of $C = 1.104$ into the formula for the diagonal elements should be useful to modestly improve the overall accuracy when the system matrix is determined from nodes and weights determined for Gaussian integration of a sphere. Actually, of course, the inclusion or omission of this factor becomes more and more inconsequential as the number of nodes becomes large.

Volume polarization potential on the surface

The procedure described here to determine the surface charge distribution that simulates volume polarization requires the values $\Phi^\beta(s_i)$ of the exact volume polarization potential at various nodes s_i on the surface. These values could be obtained by the method we have described previously¹⁶ that carries out angular integrations first and radial integrations last. That strategy is optimal for evaluation of the true volume polarization energy, which requires the volume polarization potential to be evaluated at many points both on and off the cavity surface. However, if the primary interest is just in the approximation corresponding to simulation of volume polarization, then the true volume polarization potential is only required at a much smaller number of points lying on the cavity surface and more efficient alternative methods that carry out radial integrations first and angular integrations last can be used instead.

We assume that an origin can be found inside the cavity such that each node s_i can be uniquely specified by the solid angular coordinate Ω_i of the ray from the origin through the node. As discussed previously¹⁶ this places some mild restrictions on the cavity shapes that can be treated. Then we may write

$$\begin{aligned} \Phi^\beta(s_i) &= - \left(\frac{\epsilon - 1}{\epsilon} \right) \int d^2\Omega_{\mathbf{r}'} J(s_i; \Omega_{\mathbf{r}'}), \\ &\approx - \left(\frac{\epsilon - 1}{\epsilon} \right) \sum_{j=1}^N w_j J_{ij}, \end{aligned}$$

where in principle

$$J(s_i; \Omega_{\mathbf{r}'}) \equiv \int_{r_{\min}(\Omega_{\mathbf{r}'})}^{\infty} r'^2 dr' \frac{\rho(\mathbf{r}')}{|\mathbf{s}_i - \mathbf{r}'|},$$

but in practice it can be assumed that at a particular radial distance r' the integrand varies slowly over the solid angle $\Omega_{\mathbf{r}'}$, so all that is required is

$$J_{ij} \equiv \int_{s_j}^{\infty} r_j'^2 dr_j' \frac{\rho(\mathbf{r}_j')}{|\mathbf{s}_i - \mathbf{r}_j'|},$$

where in the last integral $s_j \equiv |\mathbf{s}_j| = r_{\min}(\Omega_j)$ and the integrand is evaluated only for \mathbf{r}_j' lying on the ray corresponding to Ω_j , i.e., $\mathbf{r}_j' = (r_j', \Omega_j)$.

The quantities J_{ij} can be obtained directly through numerical integration over the radial variable. This is most efficiently accomplished by taking advantage of the fact that in the regions of interest⁴⁴ the radial dependence of $\rho(\mathbf{r}'_j)$ can be approximated as a single exponential $p_j \exp(-\zeta_j r'_j)$. The parameters p_j and ζ_j are easily determined by fitting to the value of $\rho(\mathbf{s}_j)$ and its radial derivative at the cavity surface. Then a simple linear transformation of variable can be made to throw the primary exponential variation of the integrand into the weighting function of a Gauss–Laguerre numerical integration. Then only a small number of radial integration points should be necessary to achieve high accuracy for J_{ij} . If efficiency is of more concern than high accuracy, then $\rho(\mathbf{r}'_j)$ may be completely replaced by its single exponential approximation to further facilitate the numerical integration.

CONCLUSION

This work has considered some aspects of the simulation of volume polarization in the reaction field model of solvation with a dielectric continuum treatment of the solvent. The relation of the exact solution of Poisson's equation to so-called conductorlike screening models has been examined in some detail. It is found that, despite the name, even with infinite dielectric constant they do not correspond to the full conductor solution when some solute charge penetrates outside the cavity. This is fortunate, since the simulation of volume polarization is thereby automatically included, and a surface polarization is obtained that actually improves on the usual one that neglects volume polarization. Also, improved methods are described for numerical evaluation of the simulation in practice.

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