Quantum Monte Carlo formulation of volume polarization in dielectric continuum theory

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When the nuclei and the electrons of a solute are placed within a cavity in a dielectric continuum medium, the Poisson's equation takes the form

$$\mathrm{div}\mathbf{E} = 4\pi\rho^{(\mathrm{tot})}\,, \tag{1}$$

where $\mathbf{E}$ is the total electric field and $\rho^{(\mathrm{tot})}$ is the total charge density given by the nuclear and electronic distribution of the solute, and the polarization charge distribution due to the response of the medium to the presence of the solute.

Volume polarization charge density

The so-called volume polarization charge density is given by

$$\rho^{(\mathrm{pol})}_{\mathrm{vol}}(\mathbf{r}) = \left(\frac{1}{\epsilon} - 1\right)\rho_e(\mathbf{r})\,, \tag{2}$$

where $\rho_e(\mathbf{r})$ is the electronic density.

$\rho^{(\mathrm{pol})}_{\mathrm{vol}}(\mathbf{r})$ is non zero only outside the cavity where the dielectric constant of the solvent is different from one. The contribution to the electrostatic potential due to the volume polarization charge density is given by the following integral over the domain outside the cavity $\mathcal{C}$

$$\phi^{(\mathrm{pol})}_{\mathrm{vol}}(\mathbf{r}) = \int_{\mathbf{r}'\notin\mathcal{C}} \frac{\rho^{(\mathrm{pol})}_{\mathrm{vol}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' = \left(1-\frac{1}{\epsilon}\right)\langle\Psi|\sum_{i=1}^{N}\frac{\theta(\mathbf{r}_i)}{|\mathbf{r}-\mathbf{r}_i|}|\Psi\rangle\,, \tag{3}$$

where $\theta(\mathbf{r})$ is equal to 1 outside and to 0 inside the cavity and N is the number of solute electrons. We adopt the commonly used definition of a cavity in terms of interlocking spheres. Consequently, a given point is considered outside the cavity if the distance of the point from the centre of each sphere is greater than the corresponding radius.

In the variational Monte Carlo (VMC) approach, the integral [Eq. (3)] can be easily estimated by sampling a set of configurations $(\mathbf{r}_1^{(k)},\ldots,\mathbf{r}_N^{(k)})$ from the square of the wave function Ψ^2 using the Metropolis Monte Carlo method. The values of the integrand computed with these configurations are averaged to give

$$\phi^{(\mathrm{pol})}_{\mathrm{vol}}(\mathbf{r}) \approx \frac{1}{M}\sum_{k=1}^{M}\left[\left(1-\frac{1}{\epsilon}\right)\sum_{i=1}^{N}\frac{\theta(\mathbf{r}_i^{(k)})}{|\mathbf{r}-\mathbf{r}_i^{(k)}|}\right]\,, \tag{4}$$

where the estimate tends to the exact result as $M \to \infty$. If we compare this expression with the analogous equation for a discretized set of n_c volume polarization charges:

$$\phi_{\rm vol}^{\rm (pol)}(\mathbf{r}) \approx \sum_{l=1}^{n_c} \frac{q_l}{|\mathbf{r}-\mathbf{r}_l|}\,, \tag{5}$$

we see that our expression corresponds to $n_c \leq N \times M$ point charges with charge $q_l = (1-1/\epsilon)/M$ and positions $\mathbf{r}_l = \mathbf{r}_i^{(k)}$ if $\theta(\mathbf{r}_i^{(k)}) = 1$, corresponding to the sampled one-electron coordinates outside the cavity.

Surface polarization charge

For the computation of the polarization charge at the cavity surface, we slightly modify the traditional scheme. Once the electric field has been obtained after some self-consistent procedure, the surface polarization charge density σ at the position $\mathbf{r}$ of the cavity border, is given by the relation

$$\sigma(\mathbf{r}) = \frac{(1-\epsilon)}{4\pi\epsilon}\,\mathbf{n}_+ \cdot \mathbf{E}_-(\mathbf{r})\,, \tag{6}$$

where $\mathbf{n}_+$ is the unity vector pointing from $\mathbf{r}$ outside the cavity, and $\mathbf{E}_-$ is the total electric field evaluated at the surface immediately inside the cavity. The electric field results from the superposition of the fields generated by polarization and free charges, and can be written as

$$\mathbf{E} = \mathbf{E}_{\rm solute} + \mathbf{E}_{\rm surf} + \mathbf{E}_{\rm vol};\,. \tag{7}$$

From above we have

$$\begin{aligned}\mathbf{E}_{\rm solute}(\mathbf{r}) + \mathbf{E}_{\rm vol}(\mathbf{r}) \approx & \sum_{\alpha}^{\rm nuclei} Z_\alpha \frac{(\mathbf{r}-\mathbf{R}_\alpha)}{|\mathbf{r}-\mathbf{R}_\alpha|^3} + \\ & + \frac{1}{M}\sum_{k=1}^{M}\sum_{i=1}^{N}\left[-1+\theta(\mathbf{r}_i^{(k)})\left(1-\frac{1}{\epsilon}\right)\right]\frac{(\mathbf{r}-\mathbf{r}_i^{(k)})}{|\mathbf{r}-\mathbf{r}_i^{(k)}|^3}\,,\end{aligned} \tag{8}$$

where $\mathbf{R}_\alpha$ is the vector position of the solute nucleus α. This equation is formally exact only in the limit of $M \to \infty$ but, for the variational Monte Carlo calculations like those performed in this work, the length of the run can be easily made sufficiently long to ensure a small statistical error.

For the surface charge contribution, we have instead

$$\begin{aligned}\mathbf{n}_+ \cdot \mathbf{E}_{\rm surf-}(\mathbf{r}) &= -2\pi\sigma(\mathbf{r}) \\ &+ \int_\Sigma \frac{\mathbf{n}_+ \cdot (\mathbf{r}-\mathbf{r}_a)}{|\mathbf{r}-\mathbf{r}_a|^3}\sigma(\mathbf{r}_a)\,da\,,\end{aligned} \tag{9}$$

where the integral is defined over the cavity surface Σ. As in standard PCM, the cavity is here defined as the outermost surface obtained by centering spheres of different radii on the solute nuclei. The surface charge distribution σ is discretized by dividing the surface in small area elements and placing point charges at the centre of each of them.

While, in standard PCM, such elements have well defined shapes, we adopt here a different approach. We fix the number of point charges per unit surface, p say, which is chosen to be the same on all the spheres of the cavity. When not too close to a seam between two spheres, a point charge is assigned to a portion of surface with area a given by the inverse of the number density p. The surface charge density σ at the position $\mathbf{r}_k$ of the point charge q_k is thus approximated as

$$\sigma(\mathbf{r}_k) \approx \frac{q_k}{a} \ . \tag{10}$$

After a straightforward procedure the point charges are given as

$$q_k = \sum_j G_{kj}(\Sigma, \epsilon)\ \mathbf{n}_+ \cdot [\mathbf{E}_{\rm vol}(\mathbf{r}_j) + \mathbf{E}_{\rm solute}(\mathbf{r}_j)] \ , \tag{11}$$

where G_{kj} depends only on the shape of the cavity and on the solvent dielectric constant. Eq. (11) establishes a relation between the Poisson's equation and the solute Schrödinger equation from which the electron density (and subsequently the volume polarization charges) is derived, and is the basis for a self-consistent procedure which leads to a simultaneous solution of both equations.

Quantum mechanical treatment of the solute

As many-body wave function to describe the solute, we employ a spin-free Slater-Jastrow form of the type

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ...) = \Phi(\mathbf{r}_1, \mathbf{r}_2, ...)\mathcal{J}(r_1, r_2, ..., r_{12}, ...) \ . \tag{12}$$

The determinantal component is given by

$$\Phi = \sum_K D_K^{\uparrow} D_K^{\downarrow}\ d_K \ , \tag{13}$$

where $D_K^{\uparrow}$ and $D_K^{\downarrow}$ are the Slater determinants constructed from the occupied orbitals of spin-up and spin-down electrons, respectively, and d_K are the mixing coefficients. The Jastrow correlation factor $\mathcal{J}$ is the exponential of the sum of three fifth-order polynomials of the electron-nuclear (e-n), the electron-electron (e-e), and of pure 3-body mixed e-e and e-n distances, respectively [2]. In this work, we use a single-determinantal wave function for all saturated solutes, and a multi-determinantal reference for the unsaturated systems.

All determinantal and Jastrow parameters of the solute wave function Ψ are simultaneously optimized within variational Monte Carlo by energy minimization [3]. In particular, the optimization of the wave function parameters is achieved using Eq. (11) together with the minimization of the energy functional

$$\begin{aligned} F[\Psi] = \langle \Psi | \mathcal{H}_{\rm elec} | \Psi \rangle + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \\ + \frac{1}{2} \int \left[\sum_\alpha Z_\alpha \delta(\mathbf{r} - \mathbf{R}_\alpha) + \rho_e(\mathbf{r}) \right] \sum_k^{\rm surf,vol} \frac{q_k}{|\mathbf{r} - \mathbf{r}_k|}\ d\mathbf{r} \, . \end{aligned} \tag{14}$$

where $\mathcal{H}_{\rm elec}$ is the Hamiltonian of the solute electrons in the field of the solute nucleus α. The last term in the right hand side of Eq. (14) is a sum over all surface and volume charges and corresponds to the so-called polarization contribution to the free energy of solvation.

The basic loop of self consistency we adopt is the following: (i) At the j-th iteration, a VMC run is performed to generate a new set of volume polarization charges $\mathbf{q}^{(j+1)}$ [Eq. (4)] given a previous set $\mathbf{q}^{(j)}$ and the solute wave function $\Psi^{(j)}$; (ii) with the solvent reaction field described by the new set of charges $\mathbf{q}^{(j+1)}$, the optimal wave function $\Psi^{(j+1)}$ is obtained by energy minimization. At convergence, a diffusion Monte Carlo (DMC) calculation can also be performed using the converged polarization charges determined in VMC and the corresponding optimal wave function. The algorithm has been implemented in the CHAMP package [4].

Illustrative examples

Several numerical results and plots showing the performance of the present approach in practical applications can be found in the source paper[5]. Here we show some pictorial examples to illustrate how surface and volume polarization charges are displayed from a three-dimensional view for three selected small solutes. In these examples, the radii of the cavity spheres are not corresponding to those commonly used in standard PCM calculations. In our paper[5], we analyzed the behavior of volume and surface contributions to the polarization free energy of solvation in many different situations, including the case of small unrealistic cavities. In the figure below we have the following situations: (a) methyl fluoride (CH_3F), escaped charge (fraction of electrons in the solvent domain) 1.26, 204 surface charges, 75696 volume charges, (b) methylamine (CH_3NH_2), escaped charge 0.52, 352 surface charges, 31549 volume charges, (c) acetone (CH_3COCH_3), escaped charge 0.228, 676 surface charges, 13477 volume charges.

References

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[4] 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`.

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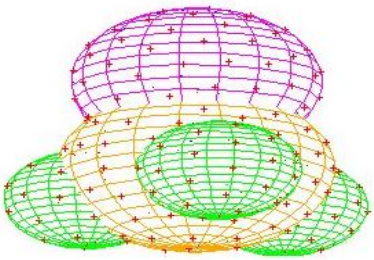
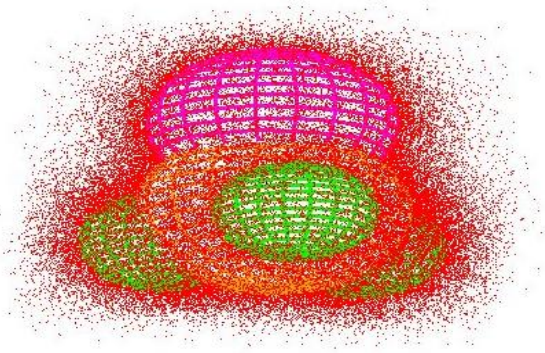
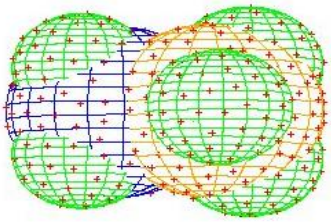
Methyl fluoride surface charges



Methyl fluoride volume charges



Methylamine surface charges



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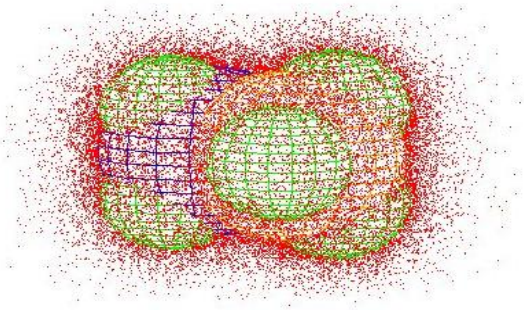
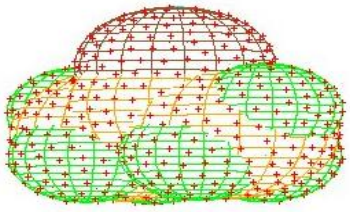


Acetone surface charges



Acetone volume charges