A framework to generalize Polarizable Continuum Models to capture the non-local response of solvents

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Solvent methods for Electronic structure calculations

Explicit solvent
Joint density functional
Non-local Polarizable continuum

Joint Density Functional Theory (JDFT)
An exact variational principle for an electronic system described by its density $n$ in contact with a fluid described by a set of molecular densities $N_i$; there exists an exact free energy functional:

\[ A[n, \{ N_i \}] = A_{0}[n] + \Omega[n] \{ N_i \} + \Delta A[n, \{ N_i \}] \]

which is minimized by the equilibrium set of densities.


Polarizable Continuum Models (PCM)

- Place the electronic system in a dielectric cavity:
  - Determined from spheres centered on atoms / groups
  - Determined by thresholding the electron density $\rho$

- Replace effect of fluid by dielectric response ($\epsilon$) and optionally Debye screening ($\kappa$; $\rho(n)$)

where $n$ fit to solution energies.


Locality Assumptions

Polarizable Continuum Models assume:
- Cavity formed from atom-centered spheres account for solvent molecule size
- Cavity determined from local electron density
  - describes a physical effect spanning solvent molecule size, and hence
  - must be different for each solvent (separate threshold $n$)
- Solvent response reduced to point dipoles (dielectric) and point charges (Debye screening)

Goal: use explicit fluid JDFT to construct a more physical PCM which
- constructs cavities based on a model electron density for the solvent molecule
- includes finite molecule size effects in the solvent response
- with all finite-size parameters derived from ab initio calculations of the solvent.

Constant density-product cavity determination

- Postulate cavity based on a convolution of explicit and solvent electron densities

\[ s(n)(\mathbf{r}) = \frac{1}{2} \text{erf} \log \left( \frac{\mathbf{r} - \mathbf{r}'}{\mathbf{r}} \right) \]

assuming a spherically averaged model for the solvent electron density.

- Correlate $R_\text{fc} = \left( \sum r_s^2 \right)^{1/2}$ (exclusion radius) to sum of Van der Waals radii $R_i$ for all pairs of atoms to determine a solvent independent threshold

$\quad \n = 1.2 \times 10^{-3}$

Non-local Linear Response

- Consider a solvent molecule with charge density $n_{\text{sol}}(\mathbf{r})$ and susceptibility

\[ \chi_{\text{sol}}(\mathbf{r}, \mathbf{r}') = -\frac{4\pi}{c^2} \rho_{\text{sol}}(\mathbf{r}) \rho_{\text{sol}}(\mathbf{r}') \]

- Exact susceptibility of a fluid of molecules with density $n_{\text{sol}}(\mathbf{r})$ free to rotate and polarize:

\[ \chi_{\text{sol}}(\mathbf{r}, \mathbf{r}') = \chi_{\text{sol}}(0) - n_{\text{sol}}(\mathbf{r}) \sum_i \rho_i(\mathbf{r}) \rho_i(\mathbf{r}') \]

Fluid effect on electronic system with charge density $n = n_{\text{sol}}$ is

\[ A_{\text{sol}}[n] = \frac{1}{2} \log \left( \frac{1}{n} \right) \int \frac{d\mathbf{r}}{4\pi} \left( \frac{1}{\sqrt{n}} - 1 \right)^{-1} \frac{1}{4\pi} \left( \frac{1}{\sqrt{n}} - 1 \right)^{-1} \]


Typical cavities and bound charge (in liquid water)

Excited State Methods

Water HOMO shift from gas to liquid:

- Experiment: 4.6 eV
  - PCM: 3.6 eV
  - Nonlocal PCM: 3.9 eV
  - Ice Embedding: 3.8 eV

computed using $G^0W^0$ (COHSEX) with orbital-free DFT embedding.


Electrostatic Solvation Energies in liquid water

Solvent energies including cavitation

- Cavitation energy in terms of curvature invariants of $s(\mathbf{r})$ functions (constrained to constant surface energy $\epsilon$):

\[ E_{\text{cav}} = \int d^3 \mathbf{r} \sqrt{s(n_{\text{sol}}(\mathbf{r}))} \]


Solvation Energies: Dispersion corrections and higher methods

- Interatomic dispersion corrections (to be replaced electronic functionals)
- Correlated method estimates using first-order-correct embedding