Electronic structure calculations go for a swim

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Overview

• Why does solvation matter?

• Implicit solvent model for density functional theory calculations

• Real space method for solving the Poisson equation in a dielectric medium
So you want to study solvated systems?

Ubiquitin
Just add water...

Ubiquitin with water
DNA packaging in nature

Hernan G. Garcia, Paul Grayson, Lin Han et al., Biopolymers 85 (2), 115 (2007).
Defining the free energy of solvation

• Free energy cost of building up a molecule inside a solvent

$$\Delta G_{\text{sol}} = \Delta G_{\text{el}} + \Delta G_{\text{cav}}$$

• The ideal solvent model
  • Provides accurate solvation energies without a ridiculous number of parameters
  • Uses a natural and straightforward definition of the solvent cavity

The standard DFT approach

\[ E[\rho] = T[\rho] + E_{xc}[\rho] + \int \rho(r)v_{\text{ion}}(r)dr + \frac{1}{2} \int \rho(r)\phi[\rho]dr \]

Electrostatic term

- Given the electron density we compute the corresponding electrostatic potential via the Poisson equation:

\[ \nabla^2 \phi = -4\pi \rho \]

- Under periodic boundary conditions we compute the solution in reciprocal space as:

\[ \phi(G) = \sum_G \frac{-4\pi}{G^2} \rho(G)e^{iG \cdot r} \]
DFT with implicit solvent

- Replace the *explicit* solvent molecules with a dielectric continuum that *implicitly* replicates the electrostatic interaction between solvent and solute

\[ \epsilon[\rho(r)] \]
**Dielectric functional**

\[ \nabla \cdot (\epsilon[\rho] \nabla \phi) = -4\pi \rho \]
**Poisson equation in the presence of a dielectric**

- From this generalized Poisson equation the electrostatic energy can then be computed as:

\[ E_{es}[\rho] = \frac{1}{8\pi} \int_{\Omega} \epsilon[\rho]|\nabla \phi|^2 \, d\mathbf{r} \]
DFT with implicit solvent

• The electrostatic contribution to the Kohn-Sham potential is found from the functional derivative:

\[ \frac{\delta E_{es}[\rho]}{\delta \rho} = \phi(r) + V_\epsilon(r) \]

• The additional term arises from the dependence of the dielectric functional on the charge density

\[ V_\epsilon(r) \equiv -\frac{1}{8\pi} |\nabla \phi(r)|^2 \frac{\delta \epsilon}{\delta \rho} \]

• This results in a tunable solvent cavity as self-consistency is achieved
Properties of the dielectric functional

• Uses the electron density to define the solvent cavity

• The dielectric functional is expressed as:

\[
\epsilon[\rho(\mathbf{r})] = 1 + \frac{\epsilon_\infty - 1}{2} \left( 1 + \frac{1 - (\rho/\rho_0)^{2\beta}}{1 + (\rho/\rho_0)^{2\beta}} \right)
\]

• This results in an implicit solvent model which only depends on two parameters

\[\rho_0\] Density threshold which modulates the size of the solvation cavity

\[\beta\] Smoothes the transition in the function from vacuum to the bulk permittivity
Dielectric functional for self-consistent solvent cavity

\[ \epsilon[\rho(r)] = 1 + \frac{\epsilon_{\infty} - 1}{2} \left( 1 + \frac{1 - (\rho/\rho_0)^{2\beta}}{1 + (\rho/\rho_0)^{2\beta}} \right) \]
Solvent cavity

- Smooth surface of solvation cavity results from natural definition through the charge density
- Dielectric parameters chosen such that the solvation effect on the total energy matches the cohesion energy of liquid water

\[ \beta = 1.3 \]
\[ \rho_0 = 0.0004 \]

\[ \epsilon[\rho(r)] = 1.01 \]

Solving the generalized Poisson equation

\[ \nabla \cdot (\epsilon[\rho] \nabla \phi) = -4\pi \rho \]

\[ \phi(r) = 0 \text{ on cell boundary} \]

- Solved in real space by multigrid method
- Multigrid properties
  - Finite difference method but makes use of multiple meshes to gain accuracy and speed convergence
  - Scales linearly with the number of grid points
Cavitation energy

• Simply the amount of work necessary to create the solvent cavity and can be estimated as

\[ \Delta G_{\text{cav}} = \gamma S(\rho_0) \]

• The cavity surface area for a given density threshold \( \rho_0 \) and surface thickness \( \Delta \)

\[ S(\rho_0) = \int \frac{|\nabla \rho(r)|}{\Delta} \left( \psi_{\rho_0-\Delta/2}[\rho(r)] - \psi_{\rho_0+\Delta/2}[\rho(r)] \right) dr \]

• The functional derivative gives an additional potential to include in the Kohn-Sham potential
Surface area of a Gaussian charge density

\[ A_C(r_\alpha) = 4\pi r_\alpha^2 = -4\pi \ln(\rho_\alpha) \]
Summary and a look ahead

• Introduced a general solvation model which effectively relies on only two parameters

• Implementation in CASTEP and eventually ONETEP
  • Interfaced with multigrid solver from ‘The Finite Element ToolKit’ (http://www.fetk.org/) for calculating electrostatic contribution to solvation energy
  • Implementing cavitation contribution to solvation energy

• Eventually using this model to study the bending and packaging of DNA
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• Founding papers

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