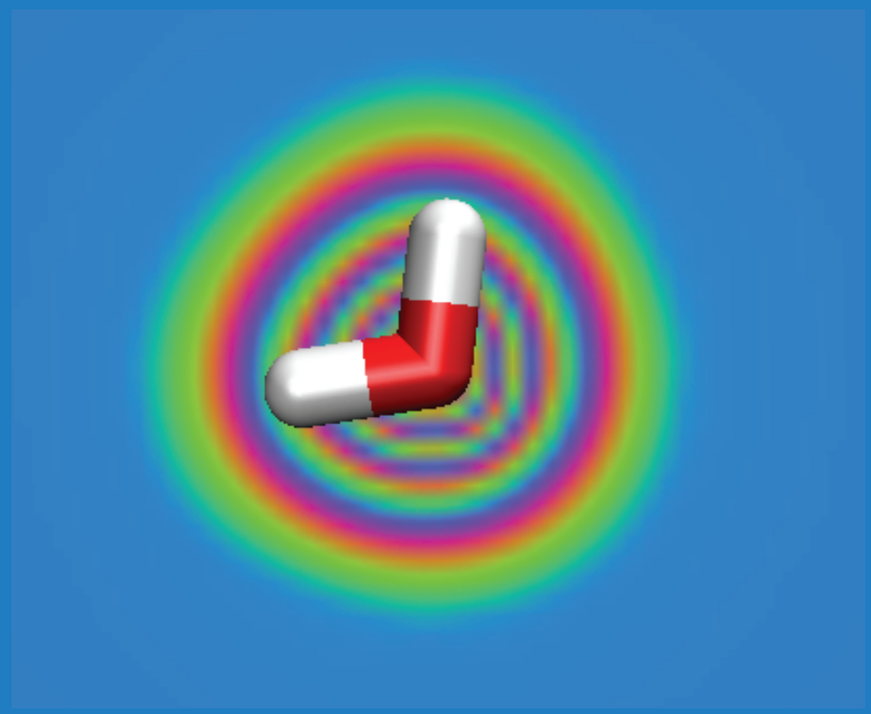
Electronic structure calculations go for a swim

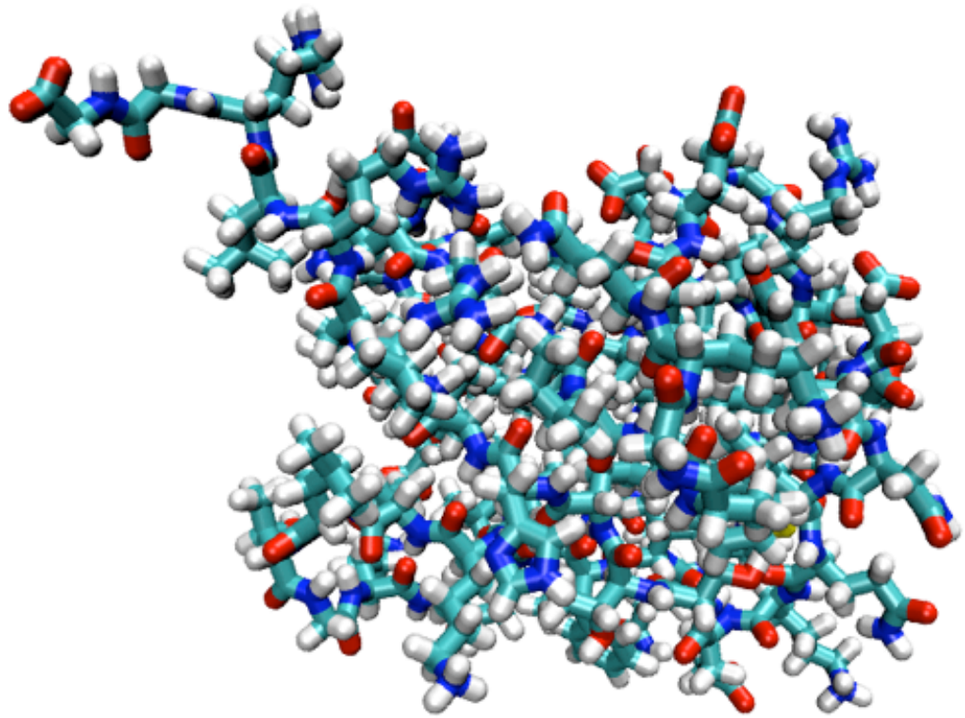


Hatem H. Helal
Electronic structure discussion group
October 31, 2007

Overview

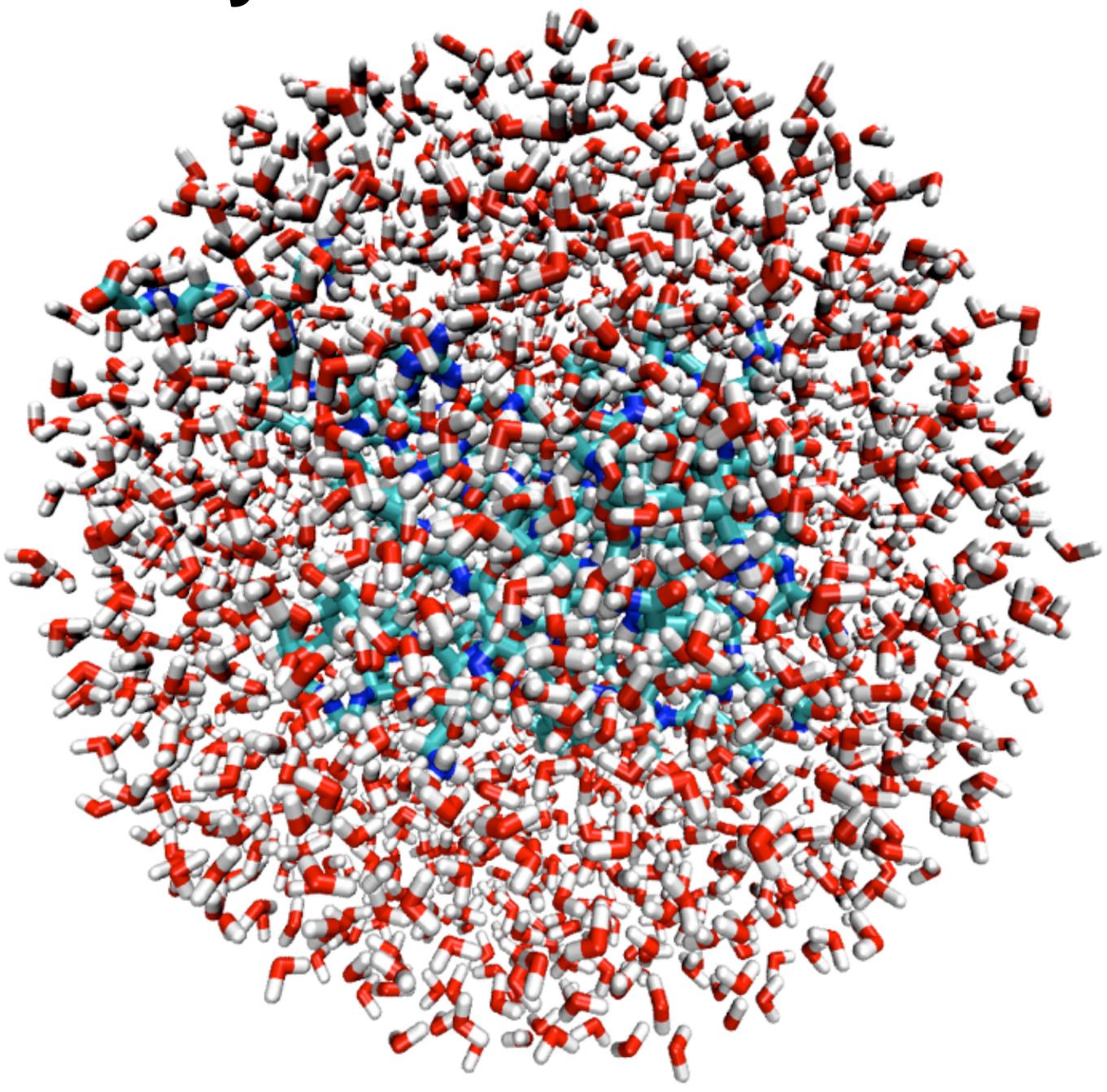
- Why does solvation matter?
- Implicit solvent model for density functional theory calculations
- Real space method for solving the Poisson equation in a dielectric medium

So you want to study solvated systems?



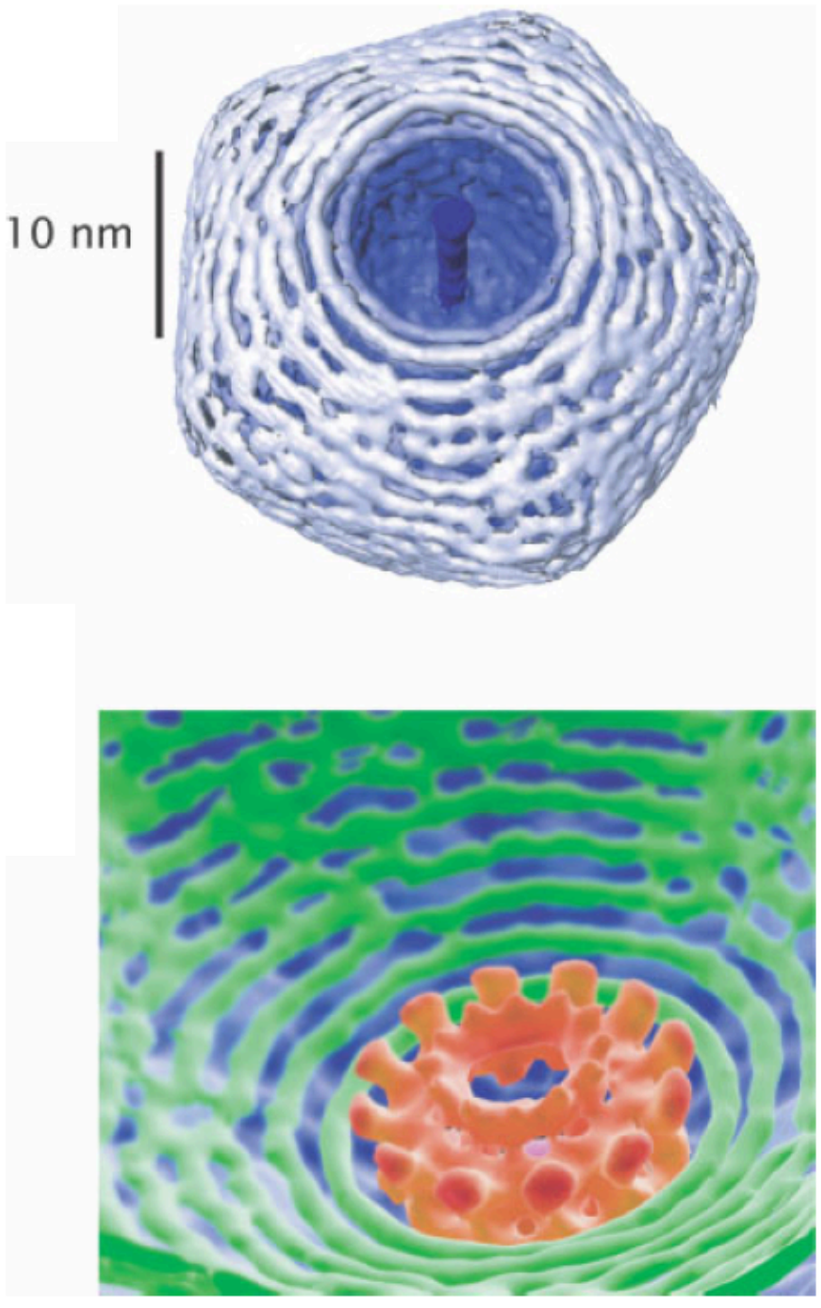
Ubiquitin

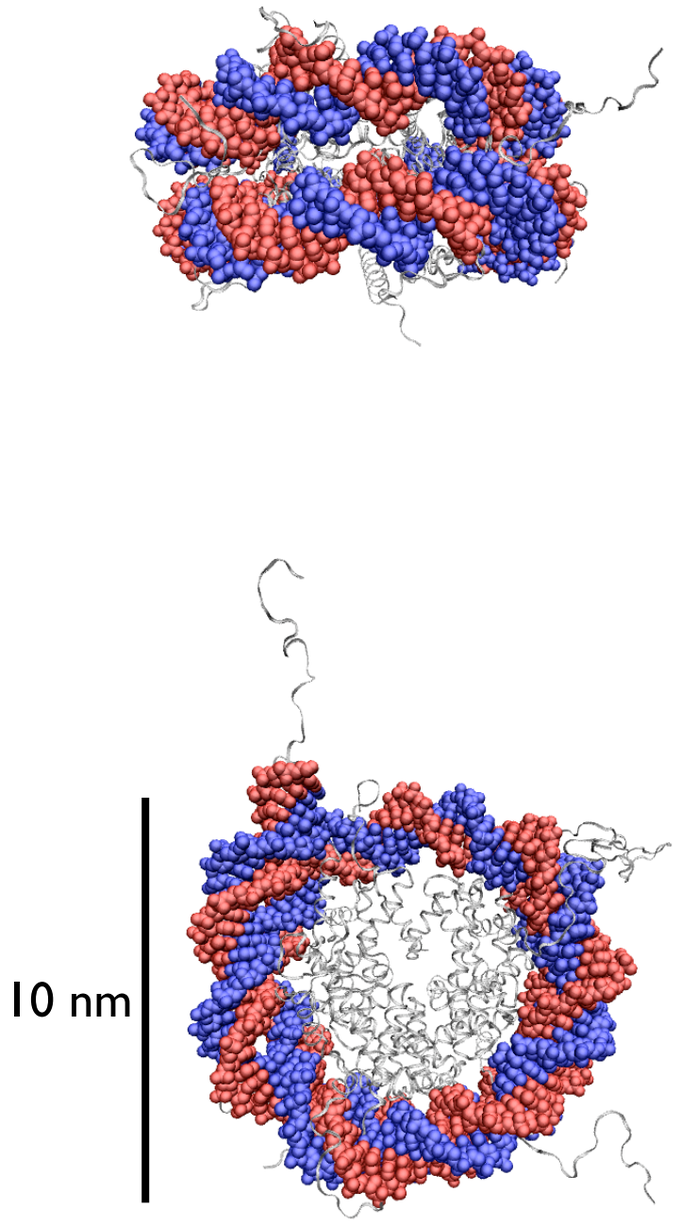
Just add water...



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

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

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

- D. A. Scherlis, J. L. Fattebert, F. Gygi et al., J. Chem. Phys. **124** (7), 074103 (2006).
- J. L. Fattebert and F. Gygi, Int. J. Quantum Chem **93** (2), 139 (2003).
- J. L. Fattebert and F. Gygi, J. Comput. Chem. **23** (6), 662 (2002).

The standard DFT approach

$$E[\rho] = T[\rho] + E_{\text{xc}}[\rho] + \int \rho(\mathbf{r}) v_{\text{ion}}(\mathbf{r}) d\mathbf{r} + \underbrace{\frac{1}{2} \int \rho(\mathbf{r}) \phi[\rho] d\mathbf{r}}_{\text{Electrostatic term}}$$

- 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:

$$\phi(\mathbf{G}) = \sum_{\mathbf{G}} \frac{-4\pi}{\mathbf{G}^2} \rho(\mathbf{G}) e^{\imath \mathbf{G} \cdot \mathbf{r}}$$

DFT with implicit solvent

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

$\epsilon[\rho(\mathbf{r})]$

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:

$$E_{\text{es}}[\rho] = \frac{1}{8\pi}\int_{\Omega} \epsilon[\rho]|\nabla\phi|^2 d\mathbf{r}$$

DFT with implicit solvent

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

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

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

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

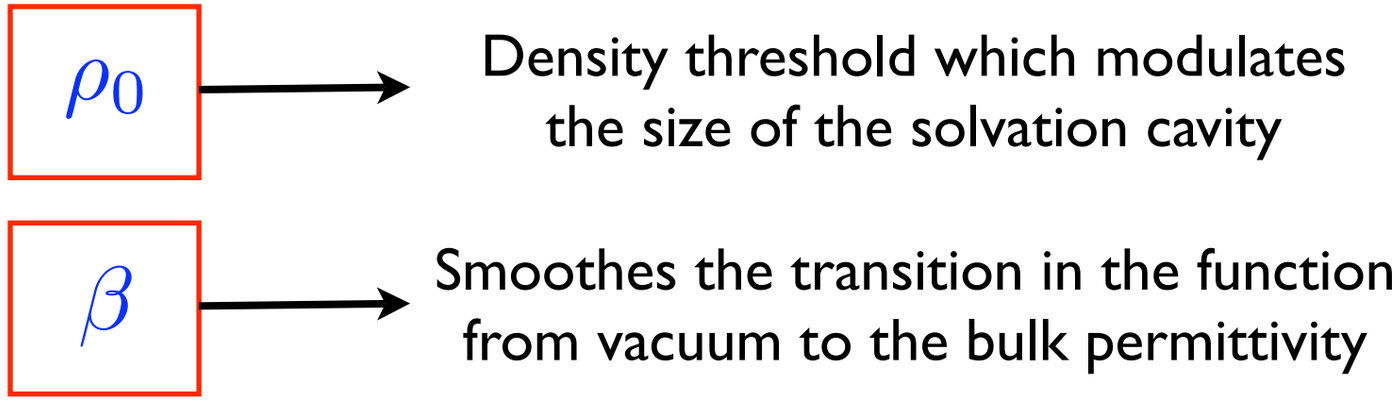
- This results in a tunable solvent cavity as self-consistency is achieved

Properties of the dielectric functional

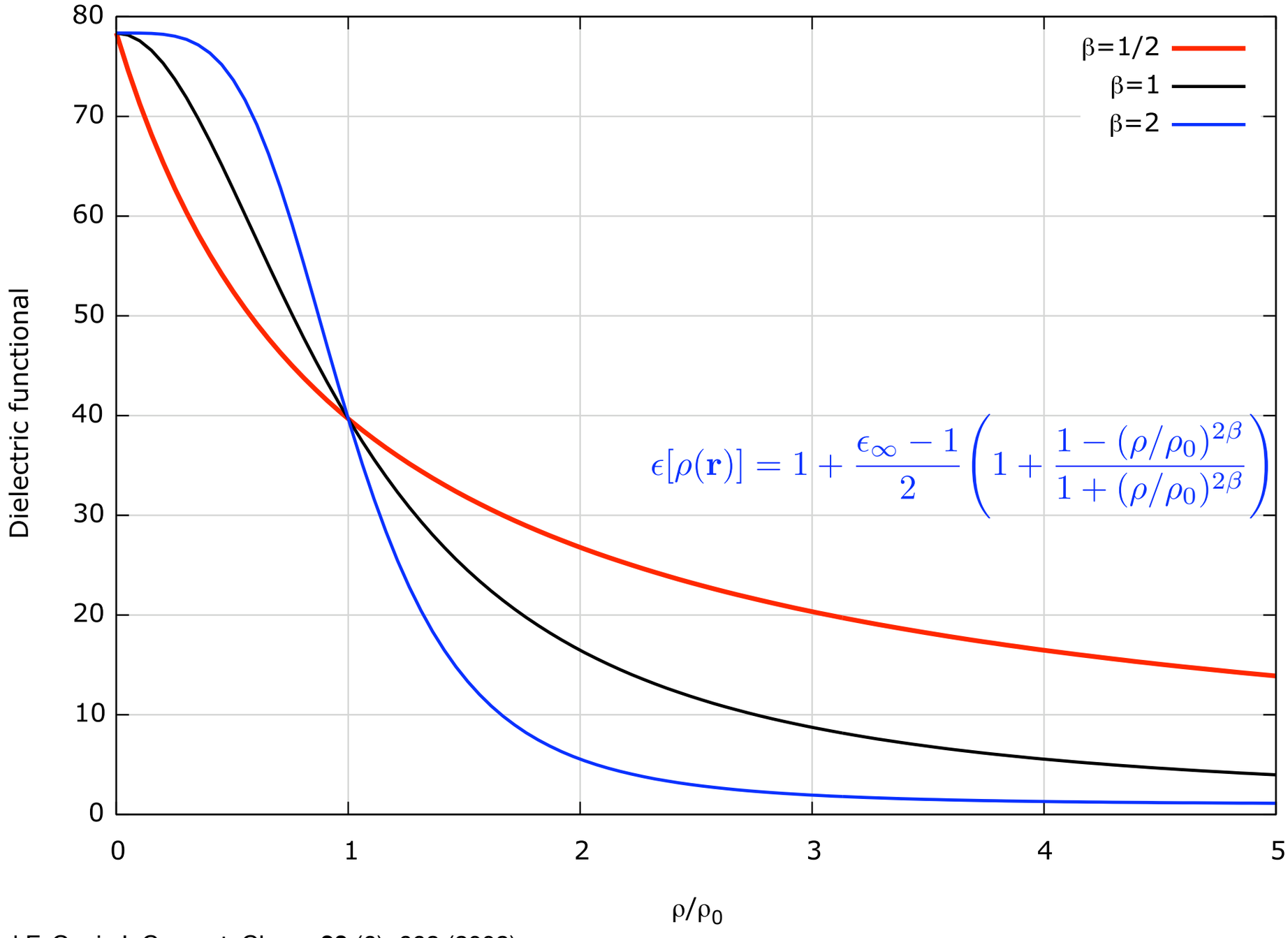
- Uses the electron density to define the solvent cavity
- The dielectric functional is expressed as:

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

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

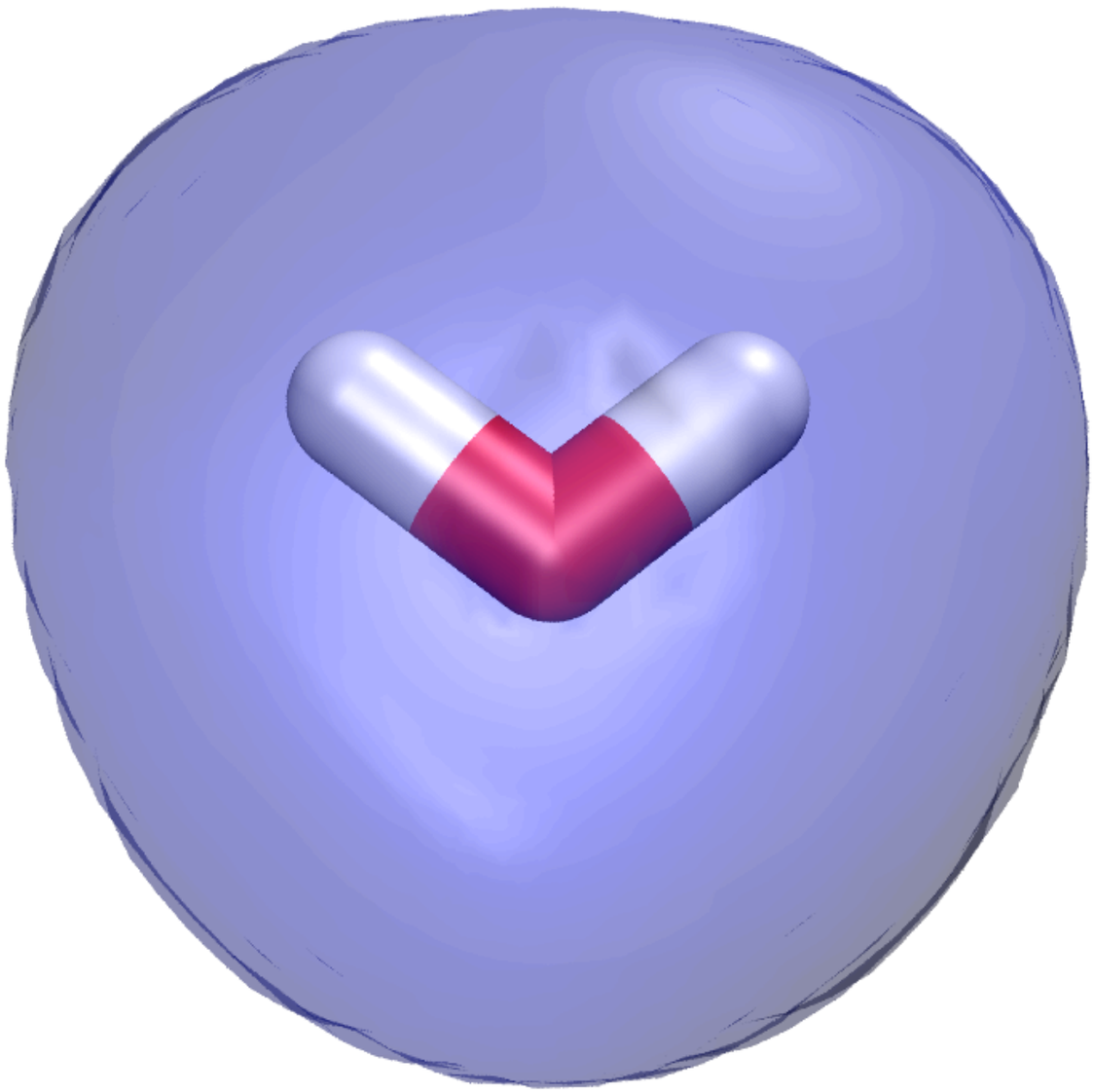


Dielectric functional for self-consistent solvent cavity



J. L. Fattebert and F. Gygi, J. Comput. Chem. **23** (6), 662 (2002).

Solvent cavity



$\epsilon[\rho(\mathbf{r})] = 1.01$

- 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

$$\beta = 1.3 \quad \rho_0 = 0.0004$$

J. L. Fattebert and F. Gygi, J. Comput. Chem. **23** (6), 662 (2002).

Solving the generalized Poisson equation

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

$$\phi(\mathbf{r}) = 0 \text{ on cell boundary}$$

- 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
  - Interfaced multigrid solver from 'The Finite Element ToolKit' (http://www.fetk.org/) with CASTEP

Cavitation energy

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

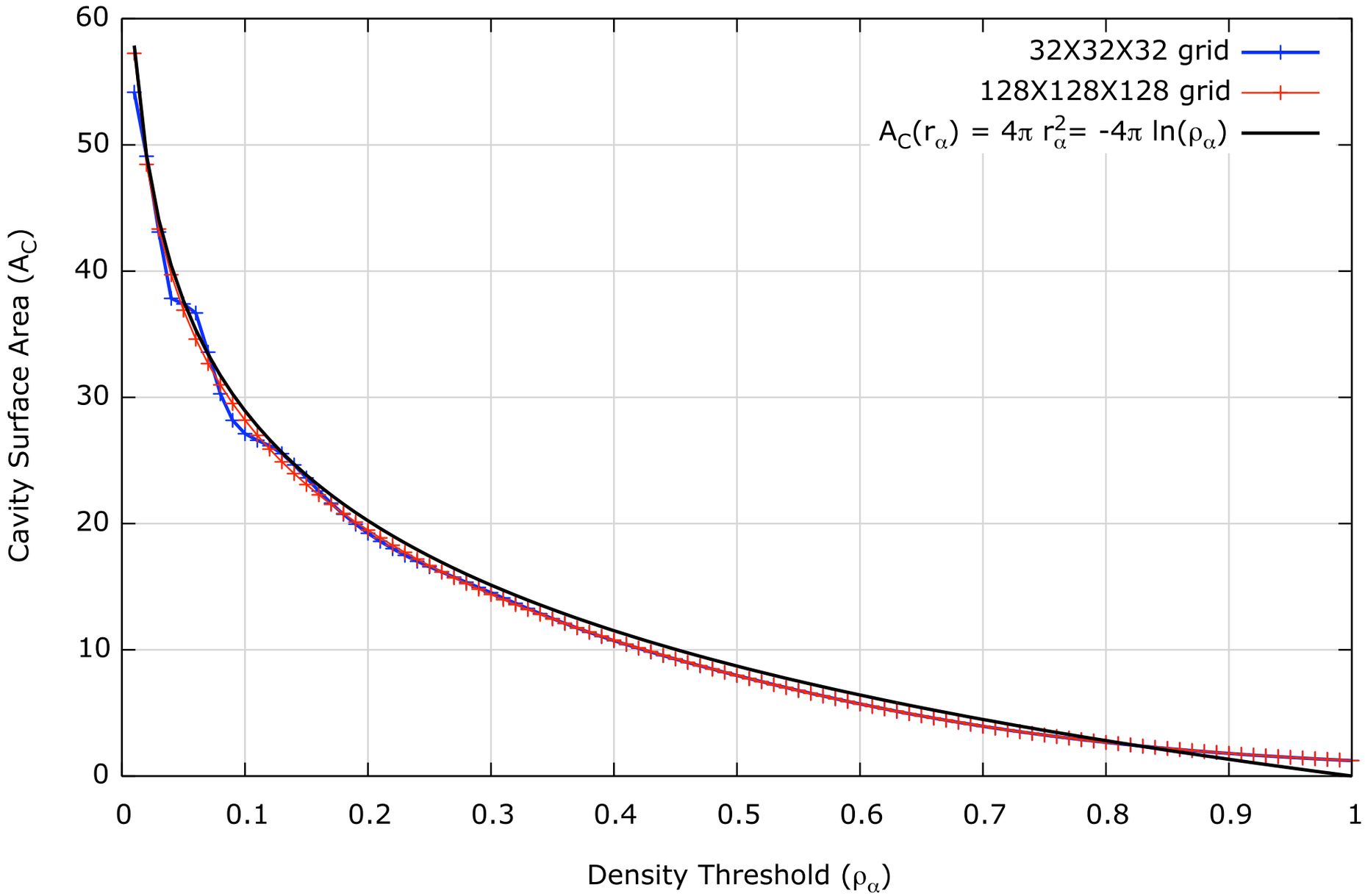
$$\Delta G_{\mathrm{cav}} = \gamma S(\rho_0)$$

- The cavity surface area for a given density threshold (ρ_0) and surface thickness (Δ)

$$S(\rho_0) = \int \frac{|\nabla \rho(\mathbf{r})|}{\Delta} \Big(\vartheta_{\rho_0 - \Delta/2}[\rho(\mathbf{r})] - \vartheta_{\rho_0 + \Delta/2}[\rho(\mathbf{r})] \Big) d\mathbf{r}$$

- The functional derivative gives an additional potential to include in the Kohn-Sham potential

Surface area of a Gaussian charge density



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

References and acknowledgments

- Founding papers
  - D. A. Scherlis, J. L. Fattebert, F. Gygi et al., J. Chem. Phys. **124** (7), 074103 (2006).
  - J. L. Fattebert and F. Gygi, Int. J. Quantum Chem **93** (2), 139 (2003)
  - J. L. Fattebert and F. Gygi, J. Comput. Chem. **23** (6), 662 (2002).
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  - Mike Payne and Jonathan Yates