Implicit Solvent and Multipole Corrections with Coulomb Cut-off

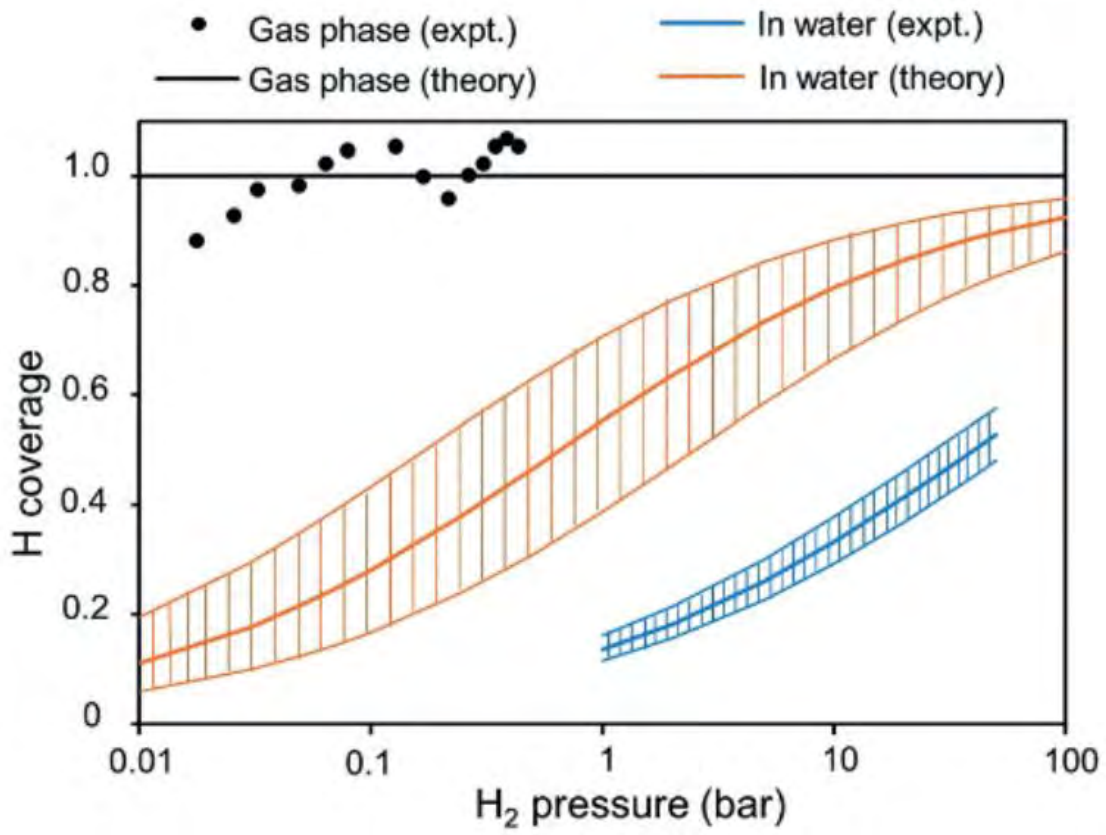
ONETEP Masterclass 2019

Gabriel Bramley

Why Model Water?

- The presence of water has a strong impact on reactivity.
- Many frontier areas of research require the consideration of water:
  - The hydrogen fuel cells[1].
  - The conversion of waste feedstock into fuel[2].
  - Simulation of electrochemical interfaces for electrocatalysis[3].
- The effect of water is complex – requires inclusion in computational simulations to fully model chemical systems.

Solvent Effect: Dissociation of H_2 on Pt



- Dissociative adsorption of H_2 slowed dramatically.[4]

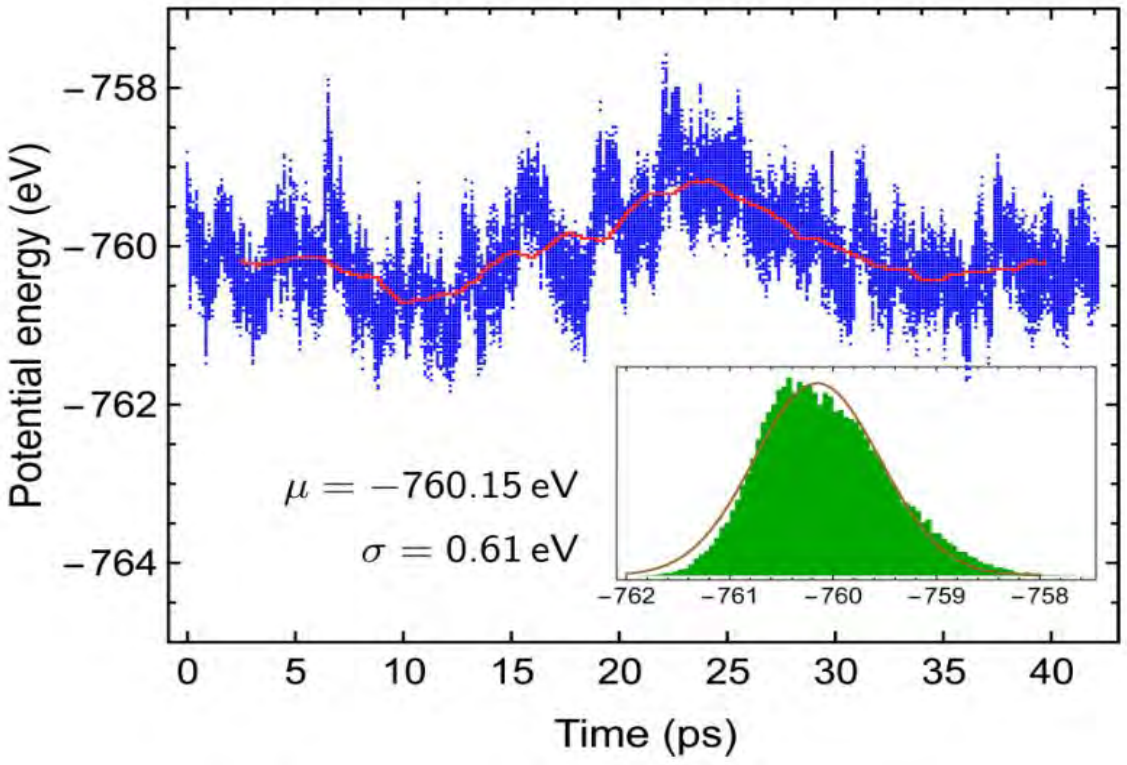
$$H_2(g) + H_2O^*(Pt) \longrightarrow 2\ H^*(Pt) + H_2O(l)$$

	ΔH_a^o / kJ mol^{-1}	ΔS_a^o / J mol^{-1} K^{-1}
Gas Phase	-59	-40
Aqueous Phase	-40	-113
Difference	19	-73

- Increased structuring of the water around Pt-H decreases entropy.
- Achieving 0.9 ML coverage in the aqueous phase would require **100 bar** H_2 pressure.

Y. Liu, M. Lee, J. Lercher, X. Chen, G. Yang, V. Glezakou, R. Rousseau, *Angew. Chem. Int. Ed.*, **2019**, 58, 3527–3532

Cost of *Ab initio* Molecular Dynamics

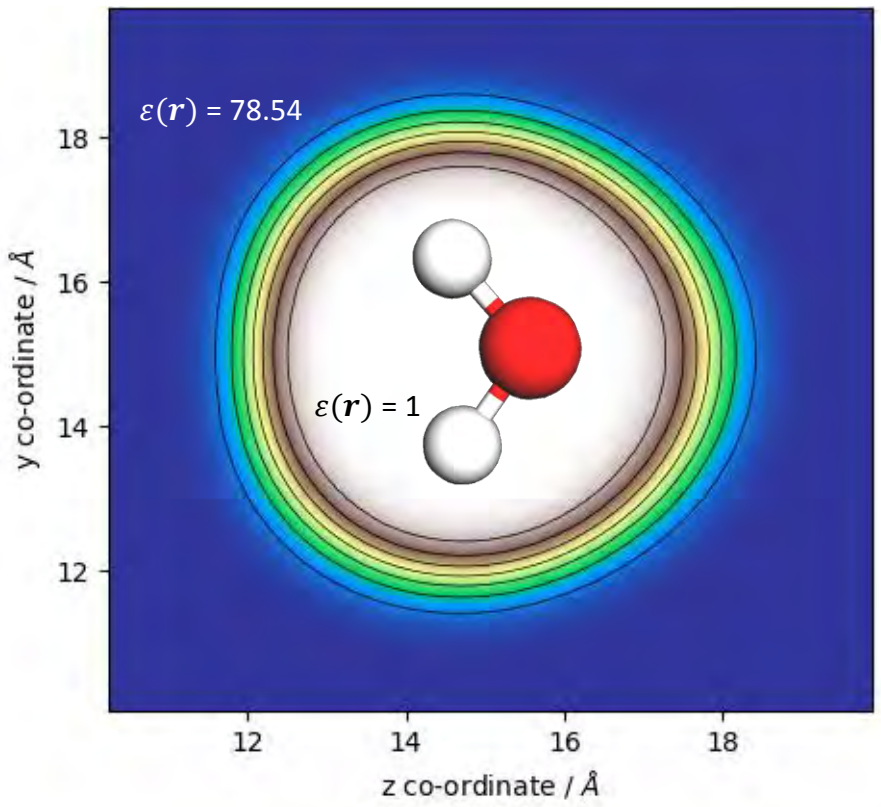


S. Sakong, K. Forster-Tonigold and A. Groß, *J. Chem. Phys.*, 2016, **144**, 194701.

- Equilibrium properties obtained as mean of configurations derived from Molecular Dynamics.
- For *ab initio* calculations, this becomes incredibly expensive.
- Achieving equilibration for a Pt(111) surface with 36 water molecules needs **40,000 DFT energy calculations**[5]!

Implicit Solvation

- Embeds the solute in a dielectric cavity, which emulates the equilibrium properties of water at room temperature.
- Removes the need to sample a wide configuration of water configurations.
- Provides a computationally efficient scheme to simulate solvent effects.



Implicit and Explicit Solvent Models

Implicit Solvent

+ Computationally inexpensive – allows high throughput methods and large system sizes.
+ Configurationally averaged (in principle).

- Discounts site-wise effects of hydrogen bonding.
- Ignores side reactions involving H_2O.

Explicit Solvent

+ In principle, exactly describes the solvation systems (with sufficient configurational sampling).
+ Fully accounts for site-wise effects of solvent.

- Computationally expensive to sample configuration space under thermodynamic positions.
- Water structure sensitive to the choice of functional.

Isodensity definition of the dielectric cavity.

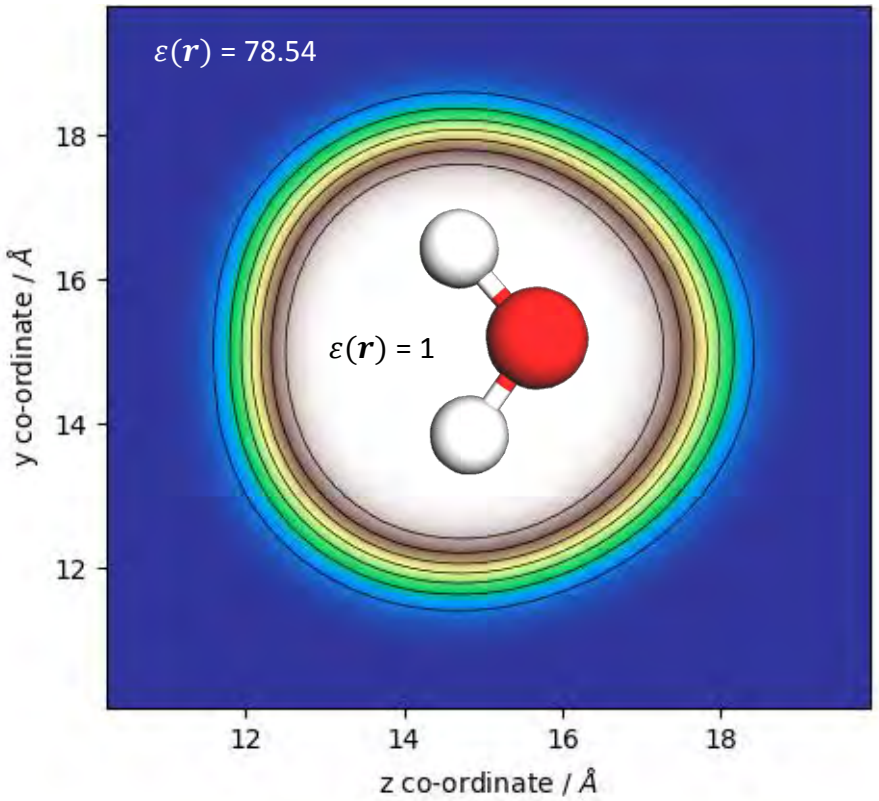
*Implemented into ONETEP by Jacek Dziedzic[9]

Fattebert-Gygi[6,7] and Scherlis[8] Solvation Scheme*

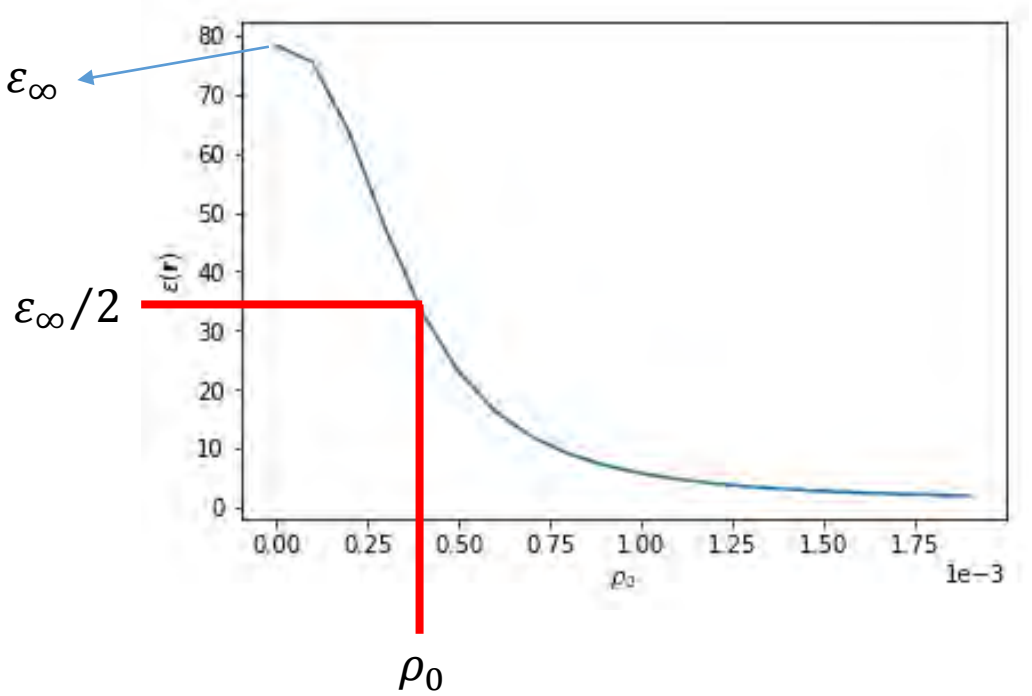
Real space, numerical solver for the Poisson-Boltzmann equation

Representation of non-electrostation/non-polar terms.

Isodensity Cavity (Fattebert-Gygi)



$$\varepsilon(\rho(\boldsymbol{r})) = 1 + \frac{\varepsilon_\infty - 1}{2}\left[1 + \frac{1 - (\rho(r)/\rho_0)^{2\beta}}{1 + (\rho(r)/\rho_0)^{2\beta}}\right]$$



D. A. Scherlis, J.-L. Fattebert, F. Gygi, M. Cococcioni and N. Marzari, *J. Chem. Phys.*, 2006, **124**, 074103.

Energetic Terms of the ISM

$$\Delta G_{solv} = \Delta G_{pol} + \Delta G_{non-polar}$$

- Polarisation term describes the **electronic response** to the dielectric.
- Corresponds to the electronic response of the
- Solvation contribution obtained through solving the Poisson-Boltzmann equation,

$$\nabla \cdot (\varepsilon[\rho]\nabla\phi) = -4\pi\rho_{tot}$$

- Represents the entropic penalty (cavitation energy) of forming an ordered solvation shell and the dispersion-repulsion interaction.
- A simple approximation commonly used is the linear relationship between the solvent surface area and its surface tension, $\Delta G_{non-polar} = \gamma S(\rho_0)$.

Electrostatic Term of ISM

Electrostatic Potential

Vacuum	SOLVATE	Solvent
$\nabla^2\phi = -4\pi\rho_{tot}$	→	$\nabla\cdot(\varepsilon[\rho]\nabla\phi) = -4\pi\rho_{tot}$
ϕ_0	→	$\phi_0 + \phi_r$

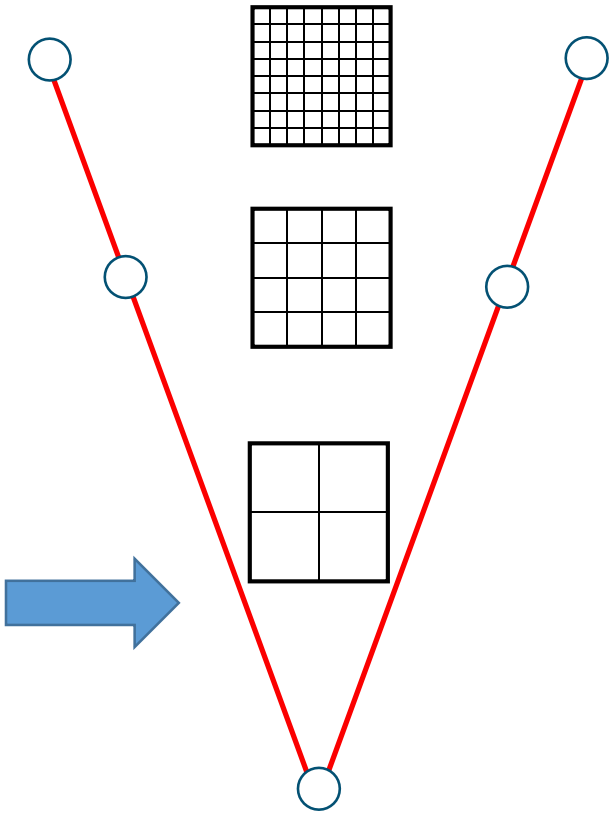
ϕ_r → Polarisation induced by dielectric

- Differences the changes in energy due to the polarisation field, ϕ_r corresponds to:

$$\Delta E_{ES} = \frac{1}{2}\int \rho_{tot}(\boldsymbol{r})\phi_r[\rho]d\boldsymbol{r}$$

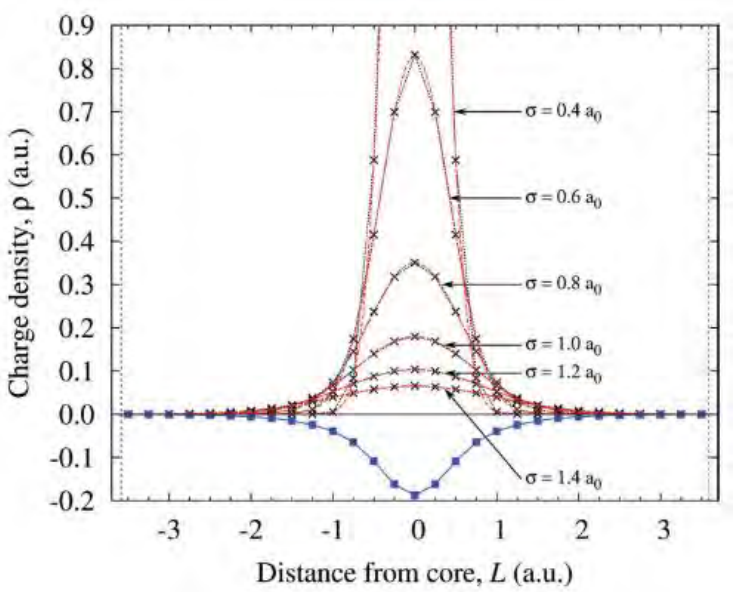
Multigrid and Defect Correction

- PB problem represented (discretised) on grid used for ρ.
- Slow convergence due to low frequency components.
- Multigrid (DL_MG library)[10] applies a hierarchy of coarse grids to smooth error of both low and high frequency components.



- Errors arise due to representing continuous property with discrete grid.
- The Defect correction is an iterative scheme which calculates higher order discretisations of the potential without requiring high-order finite difference solutions.

Smeared Ions and Charge Representation



Dziedzic, J., Fox, S. J., Fox, T., Tautermann, C. S. & Skylaris, C. K. Large-scale DFT calculations in implicit solvent - A case study on the T4 lysozyme L99A/M102Q protein. *Int. J. Quantum Chem.* **113,** 771–785 (2013).

- The electrostatic potential is calculated with the total charge density as opposed to the electron density[11]:

$$\rho_{tot} = \rho_{el} + \rho_{nuclei}$$

- Ionic core charge, ρ_{nuclei} represented by Gaussian smeared ions.
- Real-space methods numerical methods can more easily handle smeared ions as opposed to point charges.

Apolar Cavitation Term of ISM

$$\Delta G_{non-polar} = \gamma S(\rho_0)$$

- Common strategy to replace complex term with simple linear relationship of the Solvent Accessible Surface Area (SASA) with surface tension, γ.
- Encompasses contributions due to:
  - Entropic penalty of forming the cavity (ΔG_{cav}).
  - Further re-scaled γ by 0.281 to include dispersion and repulsion ($\Delta G_{dis-rep}$).

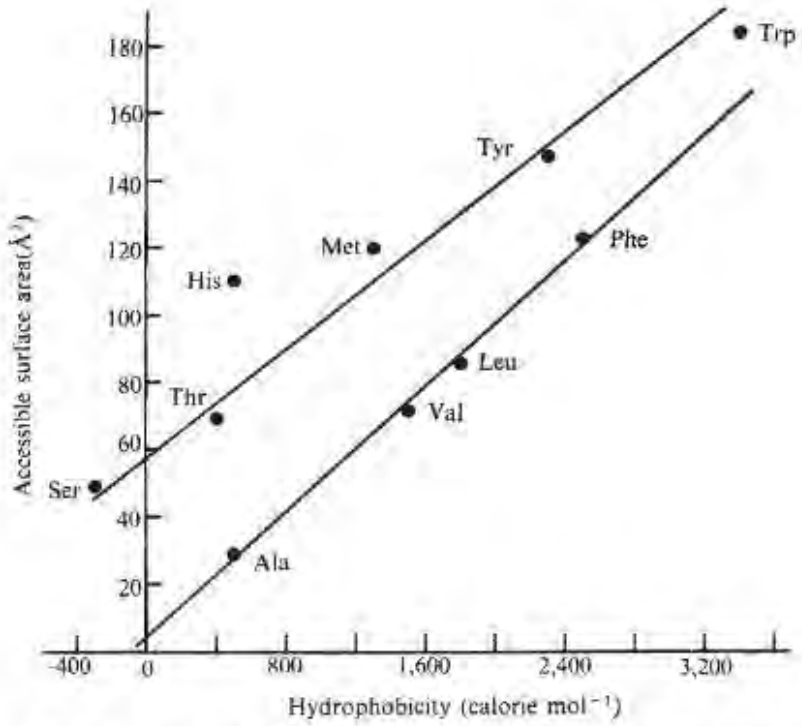
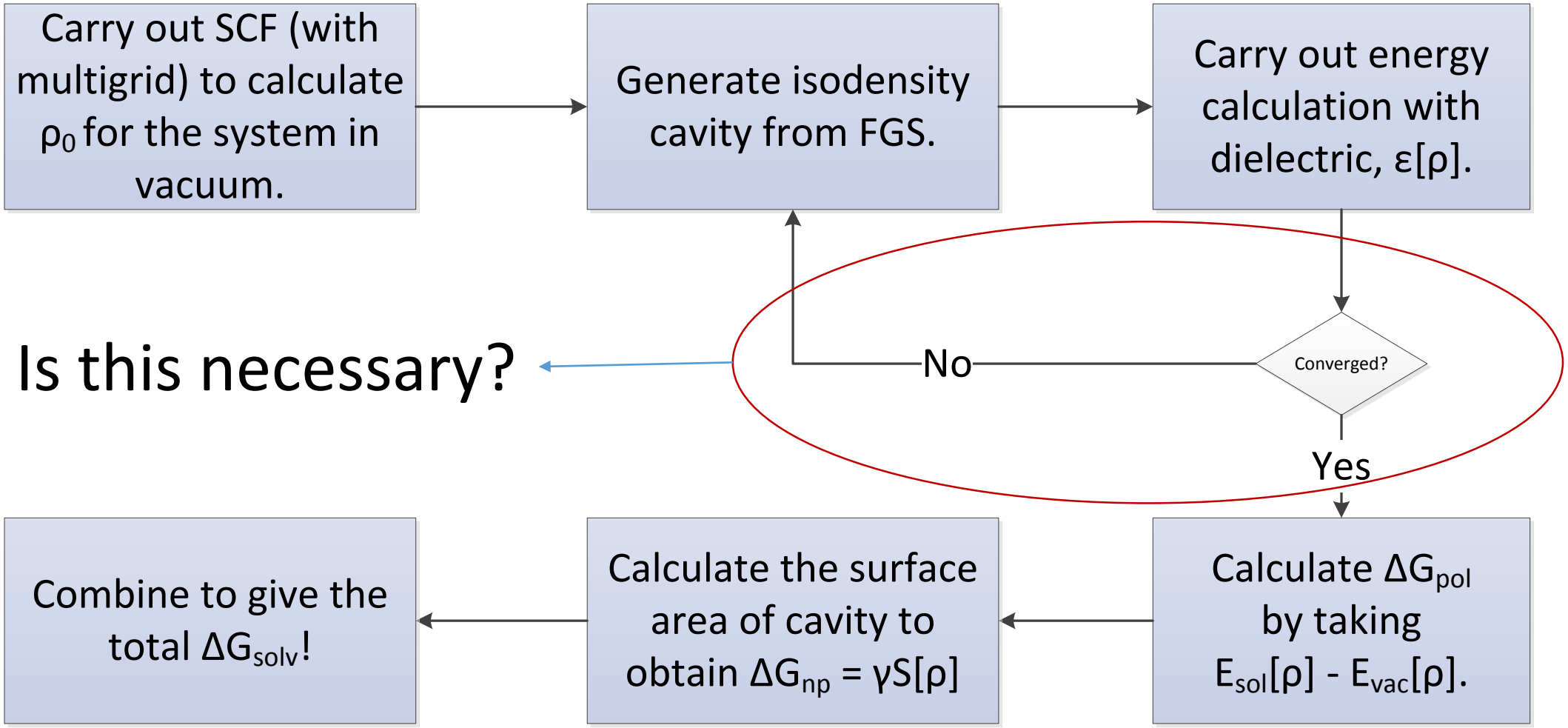


FIG. 1 Accessible surface areas of residue side chains (see text) plotted against hydrophobicity (free energy change for the transfer from 100% organic solvent to water[3]).

Chothia, C. , Hydrophobic bonding and accessible surface area in proteins *Nature,* **248**, 338–339 (1974).

Implicit Solvent Calculation Procedure



Is this necessary?

Why Fix the Cavity?

- If the cavity is allowed to vary with ρ, an extra term must be calculated[9].

$$\frac{\delta E_{ES}}{\delta \rho}(\boldsymbol{r}) = \phi(\boldsymbol{r}) - \frac{1}{8\pi}(\nabla\phi(\boldsymbol{r}))^2 \frac{\delta \varepsilon}{\delta \rho}(\boldsymbol{r})$$

- Leads to some numerical instability.
- $\frac{\delta \varepsilon}{\delta \rho} \approx 0$ except at the cavity boundary, where $\nabla\phi(\boldsymbol{r})^2 \approx 0$.

Calculation carried out with self-consistent cavity

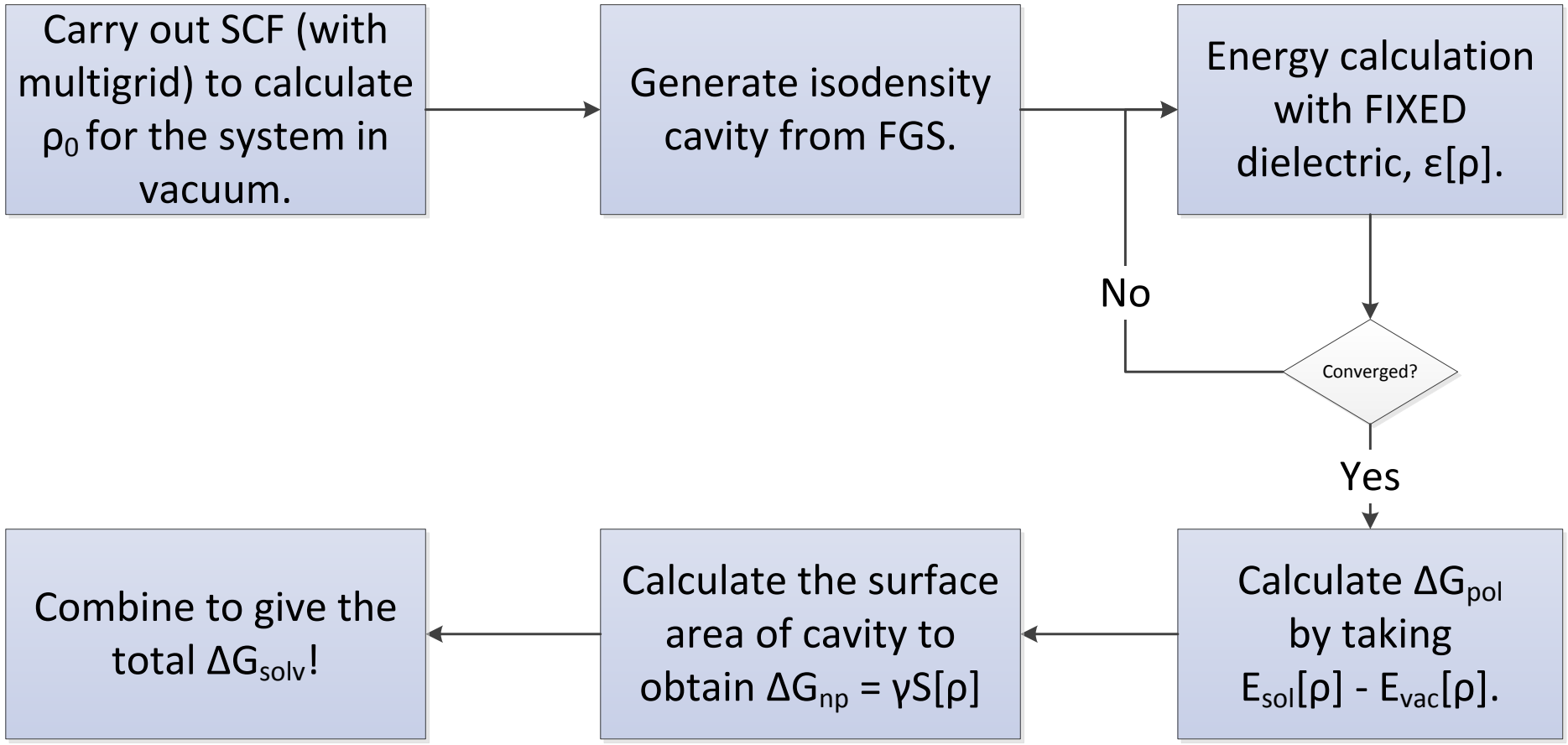
Approach	XC functional	Neutral species rms err.	max err.	r
FGS	PBE	5.0	8.8	0.87
This work[a]	PBE	1.6	2.8	0.93
This work[b]	PBE	5.0	8.9	0.87
This work[c]	PBE	1.8	3.1	0.93

Calculations carried out for a selection of 20 neutral molecules compared to the Minnessota Solvation Database. All in eVs.

Dziedzic, J., Helal, H. H., Skylaris, C.-K., Mostofi, A. A. & Payne, M. C. Minimal parameter implicit solvent model for ab initio electronic-structure calculations. *EPL (Europhysics Lett.* **95,** 43001 (2011).

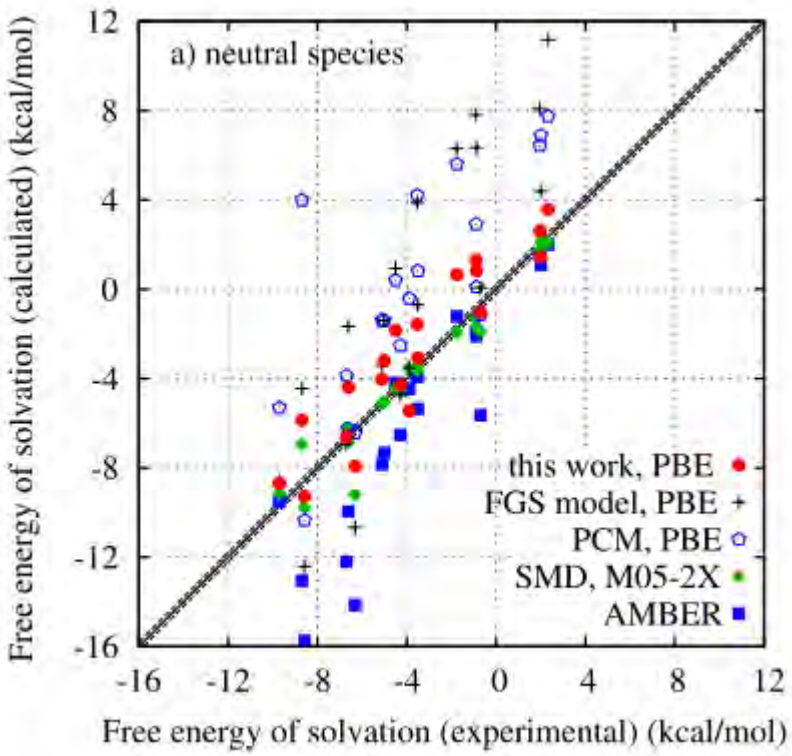
Calculation carried out with fixed cavity (ie. $\frac{\delta E_{ES}}{\delta \rho}(\boldsymbol{r}) = \phi(\boldsymbol{r})$)

Implicit Solvent Calculation Procedure

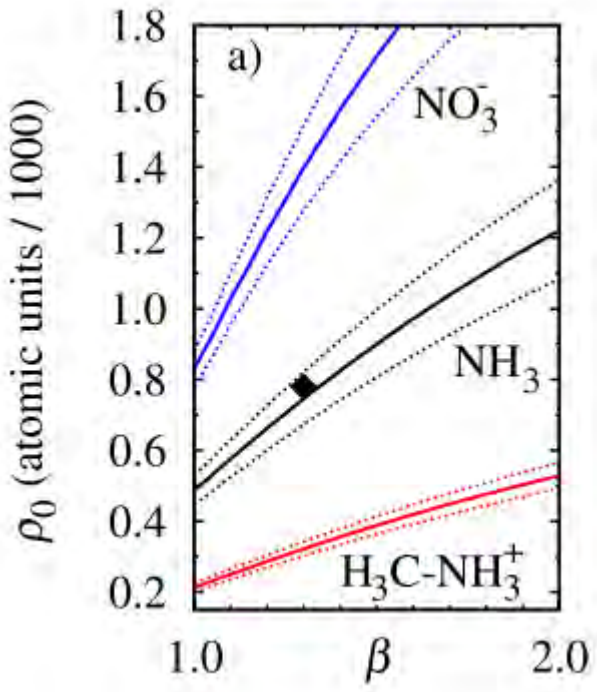


Confirmation for Neutral Molecules

Approach	XC functional	Neutral species rms err.	max err.	r
FGS	PBE	5.0	8.8	0.87
This work[a]	PBE	1.6	2.8	0.93
This work[b]	PBE	5.0	8.9	0.87
This work[c]	PBE	1.8	3.1	0.93
PCM	PBE	4.9	12.7	0.75
PCM	B3LYP	4.7	12.0	0.78
PCM	M05-2X	4.4	11.1	0.79
SMD	M05-2X	0.9	2.9	0.97
AMBER [9]	(classical)	3.3	7.84	0.64

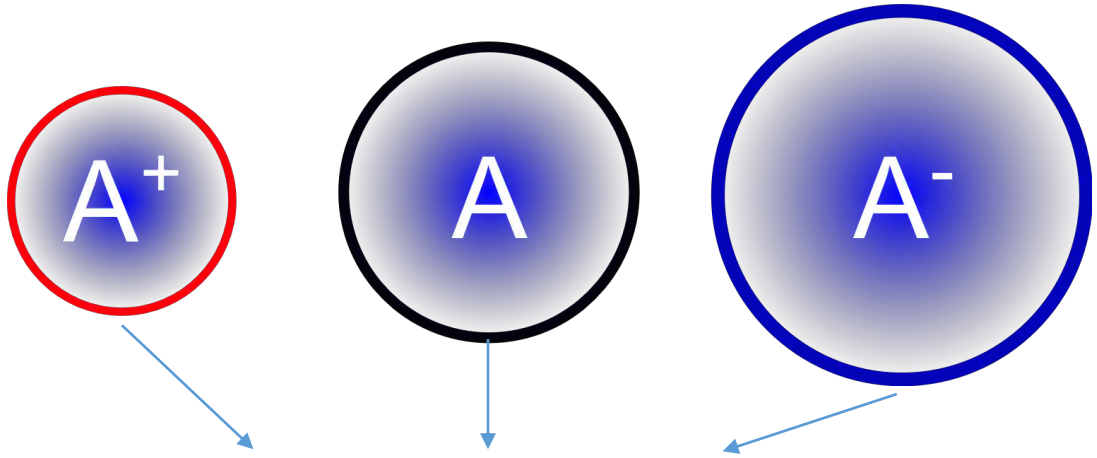


Errors with Cations and Anions



(Solid line shows the parameters of ρ_0 and β required to obtain experimental ΔG_{solv}).

- Caution! Default parameters for cavity lead to large errors for anions.



More negatively charged = Larger cavity

This does not necessarily represent the behaviour of molecular water.

Suggested Input for Solvation Calculation

```
is_implicit_solvent:    T
mg_defco_fd_order:     8
is_autosolvation:       T
is_include_apolar:      T
is_dielectric_model:    FIX_INITIAL
is_bulk_permittivity:     78.54
is_solvent_surf_tension: 0.0000133859 ha/bohr**
is_density_threshold:     0.00035
is_solvation_beta:        1.3
multigrid_bc    O O O     (OR P P P)
pspot_bc        O O O     (OR P P P)
ion_ion_bc      O O O     (OR P P P)
smeared_ion_bc  O O O     (OR P P P)
```

Turns on IS!

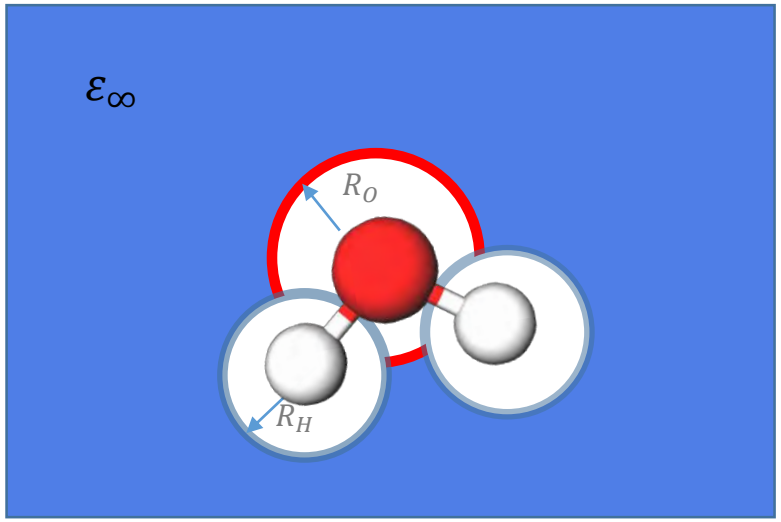
Runs vacuum calculation to generate cavity

Suggested parameters for aqueous water.

Sets boundary conditions to either fully open (O) or fully Periodic (P)

Functionalities Coming Soon…

Soft Sphere Cavitation

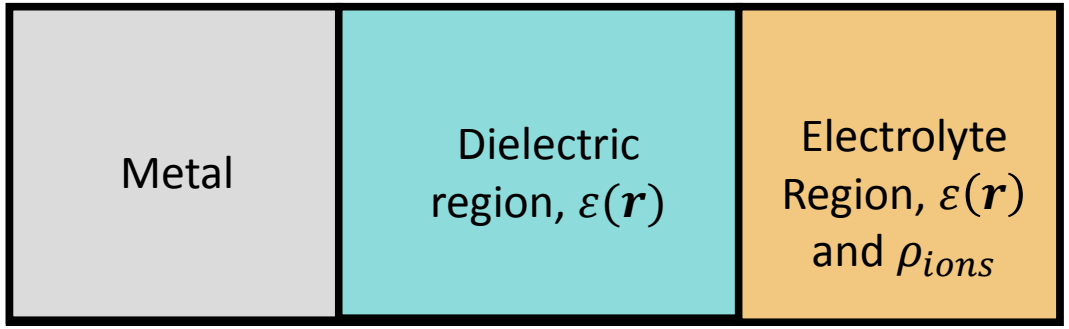


- Creates cavities as a set of atom centred distance function[12].
- Greater flexibility to parametrise individual species.

Poisson Boltzmann Ions

- Extend the solvation model beyond pure water by including solvated ions.

$$\nabla \cdot \left(\varepsilon(\boldsymbol{r})\nabla\phi(\boldsymbol{r})\right) = -4\pi(\rho_{tot}(\boldsymbol{r}) + \rho_{ions}[\phi](\boldsymbol{r}))$$



Coulomb Cut-off

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Electrostatic Potentials in PBC

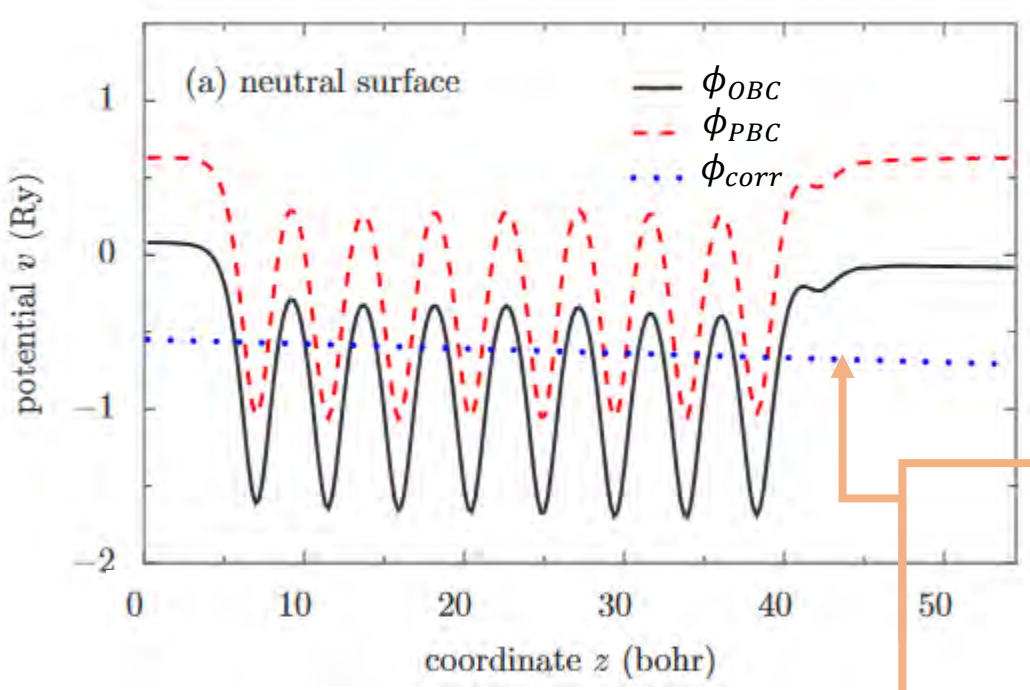
- Calculations in ONETEP are carried out using **Periodic Boundary Conditions** (PBC) by default.
- To obtain non-divergent electrostatic potentials, the simulation cell **must** be **neutral**.

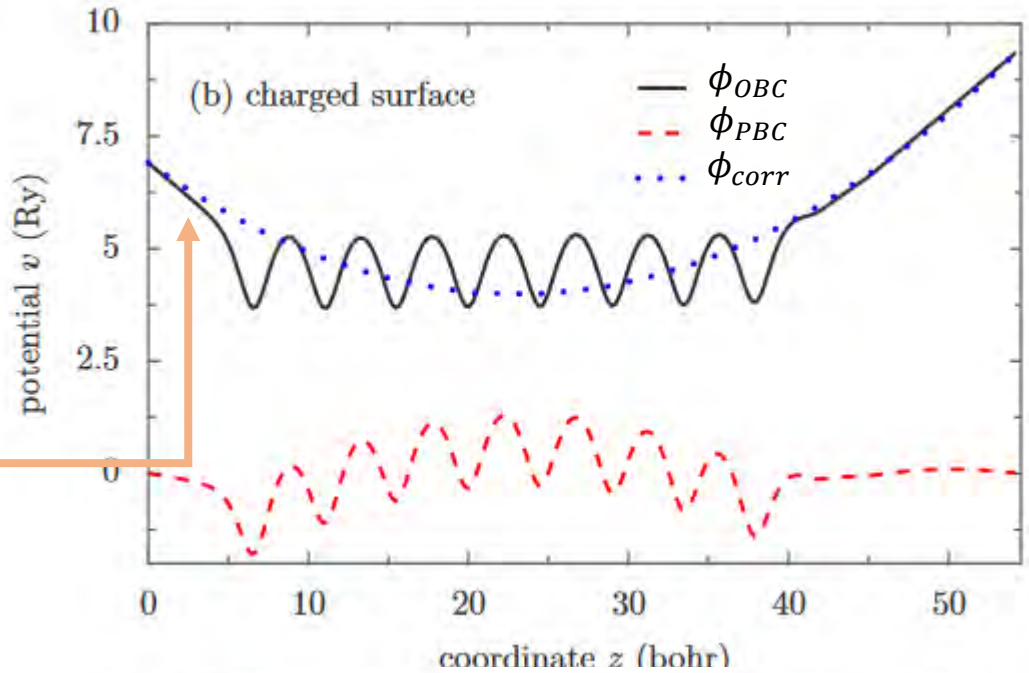
$$\nabla^2 \phi_{PBC}(\boldsymbol{r}) = -4\pi(\rho(\boldsymbol{r}) - \langle\rho\rangle)$$

- This is achieved by inserting a **uniform background charge** equivalent to the total charge across the cell[13].

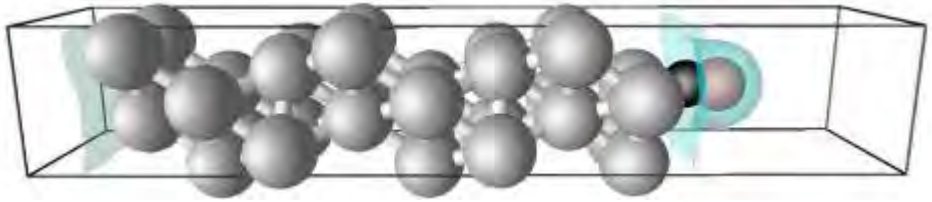
$$\langle\rho\rangle = q/\boldsymbol{\Omega} \qquad q = \int_{\boldsymbol{\Omega}} \rho(\boldsymbol{r})d\boldsymbol{r}$$

Electrostatic Potential in PBC





Dramatic errors introduced for charged/dipolar systems by ϕ_{corr}[14]!



Dabo, I., Kozinsky, B., Singh-Miller, N. E. & Marzari, N. Electrostatics in periodic boundary conditions and real-space corrections. *Phys. Rev. B - Condens. Matter Mater. Phys.* **77,** 115139 (2008).

How do we Correct This?

- The uniform background charge for systems with either a net dipole or net charge introduces unphysical, long-range interactions between the home cell and its periodic images.
- Several schemes exist to correct this issue:

1. Place a corrective potential in the cell (Gaussian Countercharge)[14.]
2. Switch to open boundary conditions (implemented in ONETEP through multigrid solver).
3. Truncate the electrostatic interactions of the simulation cell. (Coulomb cut-off)[15.]

Couloumb Cut-off Derivation

Coulomb Potential Under PBCs

$$\phi(\boldsymbol{r}) = \iiint_{-\infty}^{+\infty} \rho(\boldsymbol{r}')v(|\boldsymbol{r}-\boldsymbol{r}'|)\, d\boldsymbol{r}^3$$

Fourier Transform

$$\phi(\boldsymbol{G}) = n(\boldsymbol{G})v(\boldsymbol{G})$$

Coulomb Interaction:

$$v(|\boldsymbol{r}-\boldsymbol{r}'|) = \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \xrightarrow{\text{FT}} v(\mathbf{G}) = \frac{4\pi}{\mathbf{G}^2}$$

Coulomb Potential & Coulomb Cut-off

Truncate the Coulomb Interaction: beyond range, R_c:

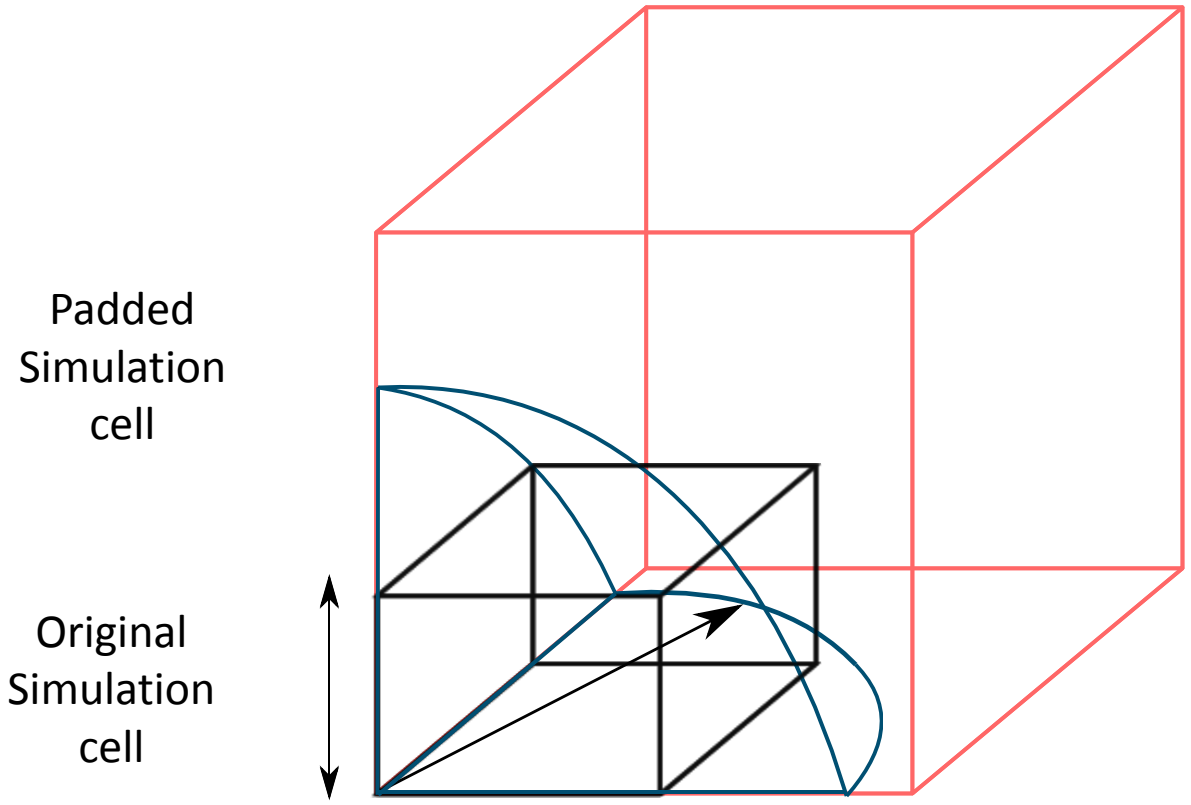
$$\tilde{v}(\boldsymbol{r}) = \begin{cases} (|\boldsymbol{r}-\boldsymbol{r}'|)^{-1} & R_c > \boldsymbol{r} \\ 0 & R_C < \boldsymbol{r} \end{cases}$$

$$\phi(\boldsymbol{r}) = \iiint_{0}^{R_C} \rho(\boldsymbol{r}')v(|\boldsymbol{r}-\boldsymbol{r}'|)\, d\boldsymbol{r}^3$$

Fourier Transform

$$\phi(\boldsymbol{G}) = \frac{4\pi}{\boldsymbol{G}^2}[1-\cos(GR_c)]$$

Conditions of Coulomb Cut-off in 3D



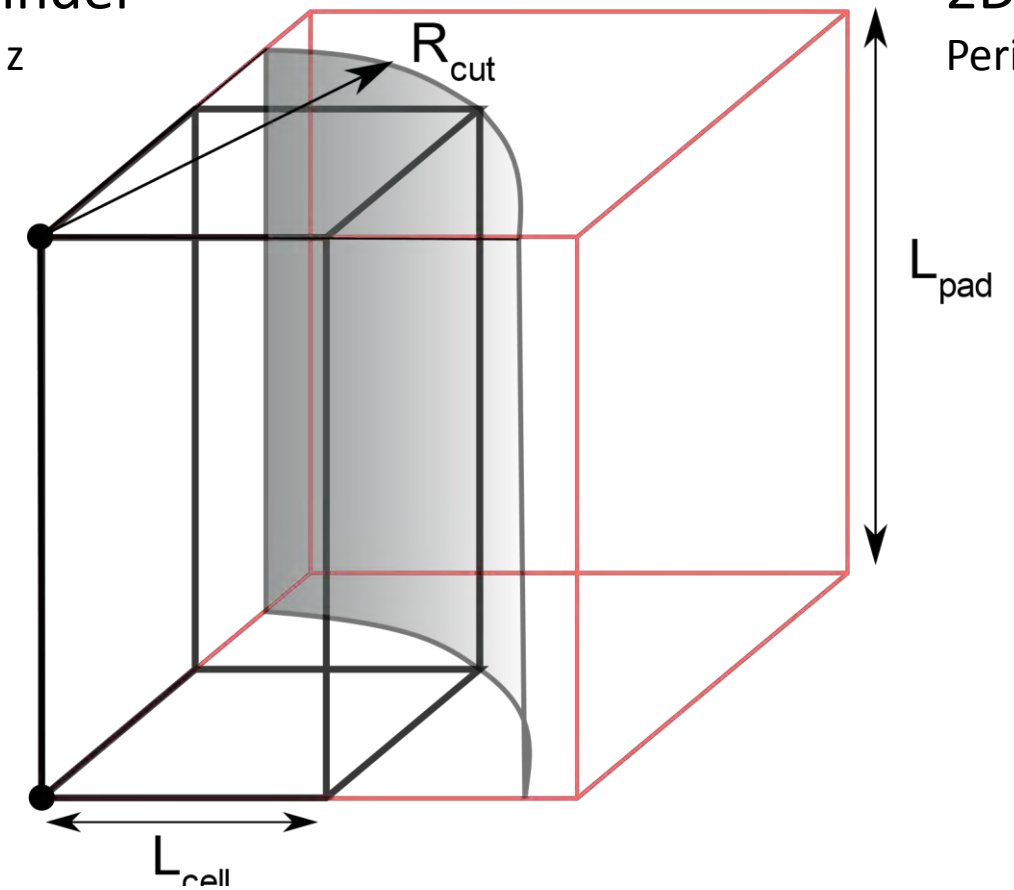
- Any area of non-zero density must be able to interact with all other non-zero density regions in the home cell. (ie. setting $R_c = \sqrt{3}L_{cell}$).
- Any area of non-zero density **<u>must not</u>** interact with an adjacent periodic image. (Use of a padded cell*).

- Padded cell: A simulation cell larger than the home cell in which the electron density is set to 0. (Automatically specified by the code – so don't worry about it!)

Reduced Dimensionality

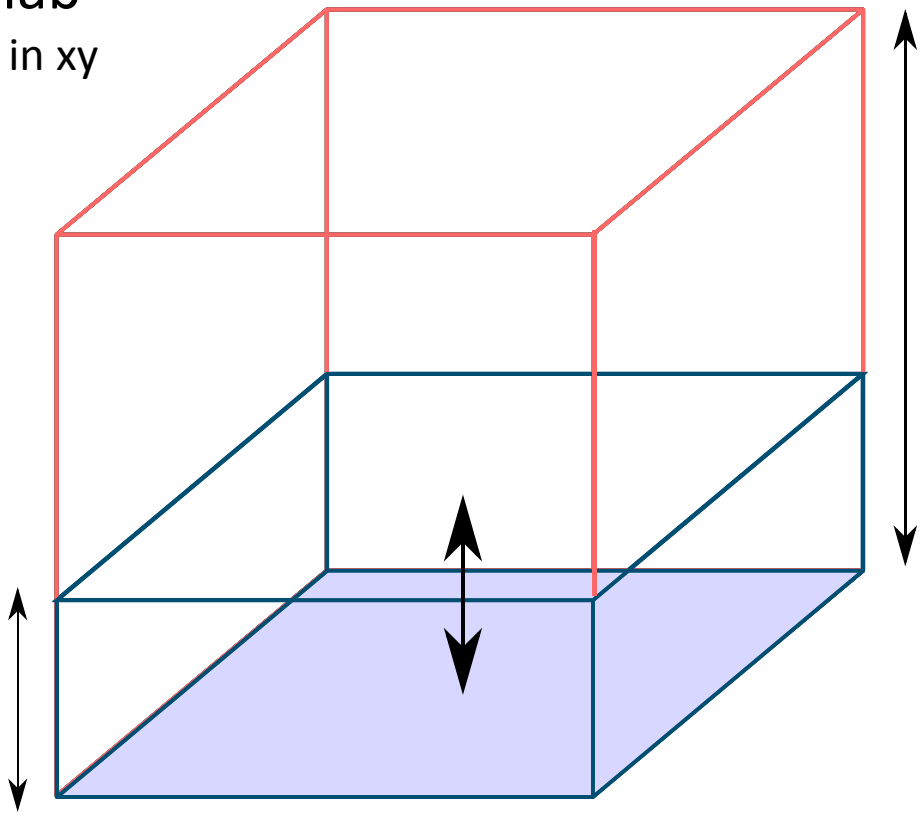
1D – Cylinder[16]

Periodic in z



2D – Slab[17]

Periodic in xy



How To Use Coulomb Cut-off

<u>Keywords</u>

- **COULOMB_CUTOFF_TYPE:**
  - Options: Sphere (3D), Slab (2D), Wire (1D).
- **COULOMB_CUTOFF_RADIUS:**
  - Controls R_c for Sphere type.
- **COULOMB_CUTOFF_LENGTH:**
  - Controls R_c for Slab and Wire types.

Activates Coulomb Cut-off!

Recommended value: $(1+\sqrt{3})L_{cell}$

Recommended value: $(1+\sqrt{2})L_{cell}$

R_C MUST BE EQUAL to THE CELL LENGTH IN Z (L_{cell}).

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