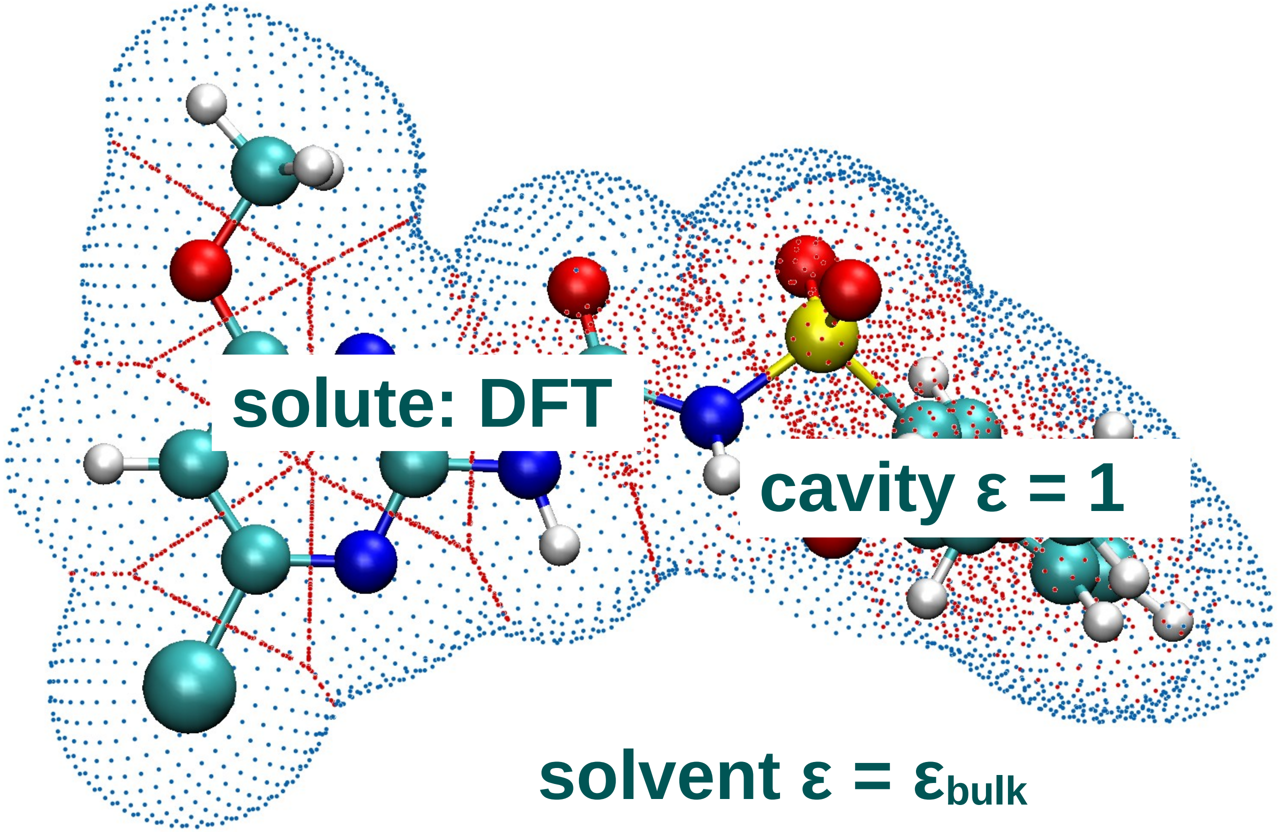
FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

IMPLICIT SOLVATION IN FHI-AIMS

Jakob Filser

Implicit solvation



J. Filser *et al.*, J. Chem. Theory Comput. **18**, 461 (2022).

Implicit solvation

Free energy of solvation

$$\Delta G_{\text{solv}} = \Delta G_{\text{solv}}^{\text{elstat}} + \Delta G_{\text{solv}}^{\text{non-elstat}}$$

Electrostatic interaction with dielectric continuum
Self-consistent with DFT

"Everything else"
Post-SCF correction or self-consistent

M. Sinstein *et al.*, J. Chem. Theory Comput. **13**, 5582-5603 (2017).

Implicit solvation in FHI-aims

Smooth cavity

SMPB

Stern layer modified Poisson-Boltzmann

Equivalent model to self-consistent continuum solvation (SCCS)

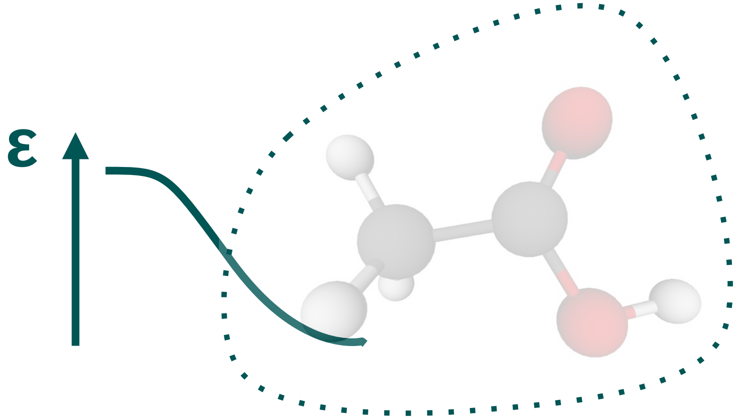
Electrolytes, (PBC)

Environ (WIP)

Originally implicit solvation module of QuantumEspresso now independent library

Different methods, including SCCS

Electrolytes, PBC



Sharp cavity

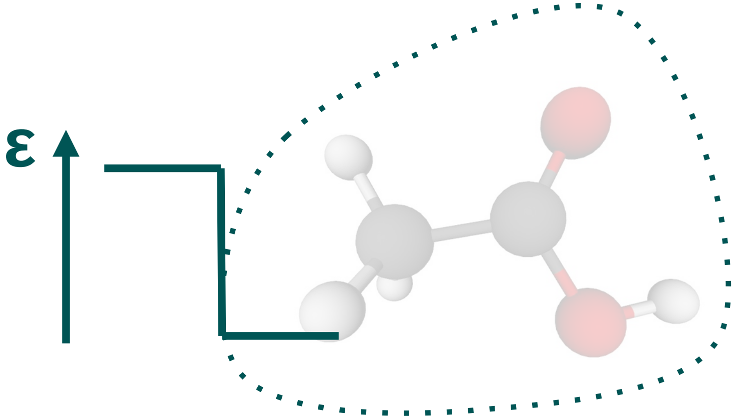
COSMO

Conductor-like screening model

MPE

Multipole expansion model

PBC (WIP)



MPE implicit solvation

Ansatz

$$\Phi(\mathbf{r}) = \varepsilon^{-1}(\mathbf{r}) \, \Phi_{\mathrm{H}}(\mathbf{r}) + \Phi_{\mathrm{MPE}}(\mathbf{r})$$

$\varepsilon^{-1}(\mathbf{r})$: Inverse dielectric permittivity

$\Phi_{\mathrm{H}}(\mathbf{r})$: Classical electrostatic potential in vacuum

$\Phi_{\mathrm{MPE}}(\mathbf{r})$: ?

Harmonicity in regions of constant permittivity

$$\varepsilon(\mathbf{r} \in X) = \mathrm{const.} \;\Rightarrow\; \nabla^2 \Phi_{\mathrm{MPE}}(\mathbf{r} \in X) = 0$$

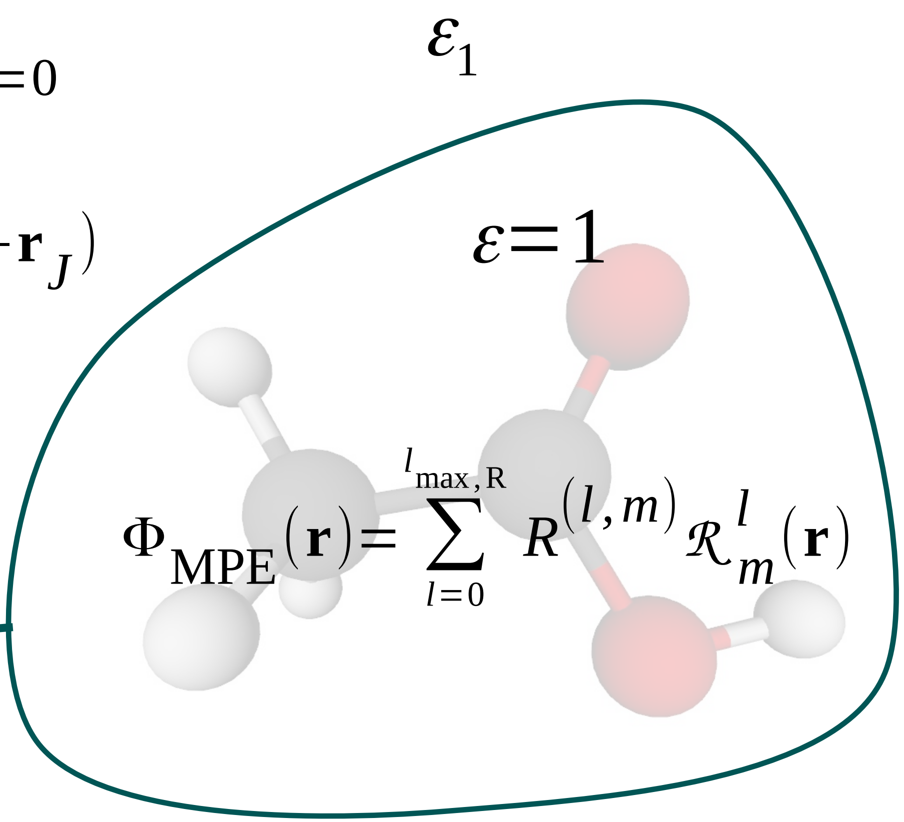
Series expansion in solid harmonic functions (multipoles)

$$\mathcal{R}_m^l(r, \theta, \varphi) = r^l Y_m^l(\theta, \varphi)$$
$$I_m^l(r, \theta, \varphi) = r^{-(l+1)} Y_m^l(\theta, \varphi)$$

MPE implicit solvation

$$\varepsilon(\mathbf{r}\in X)=\text{const.} \quad \Rightarrow \quad \nabla^2\Phi_{\text{MPE}}(\mathbf{r}\in X)=0$$

$$\Phi_{\text{MPE}}(\mathbf{r})=\sum_{J}\sum_{l=0}^{l_{\max,\text{Q}}} Q_J^{(l,m)}\, I_m^l(\mathbf{r}-\mathbf{r}_J)$$



$$\Phi_{\text{MPE}}(\mathbf{r})=\sum_{l=0}^{l_{\max,\text{R}}} R^{(l,m)}\, \mathcal{R}_m^l(\mathbf{r})$$

Enforce continuity of potential and flux density on boundary

M. Sinstein *et al.*, J. Chem. Theory Comput. **13**, 5582-5603 (2017).

MPE-*nc*

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MPE implicit solvation

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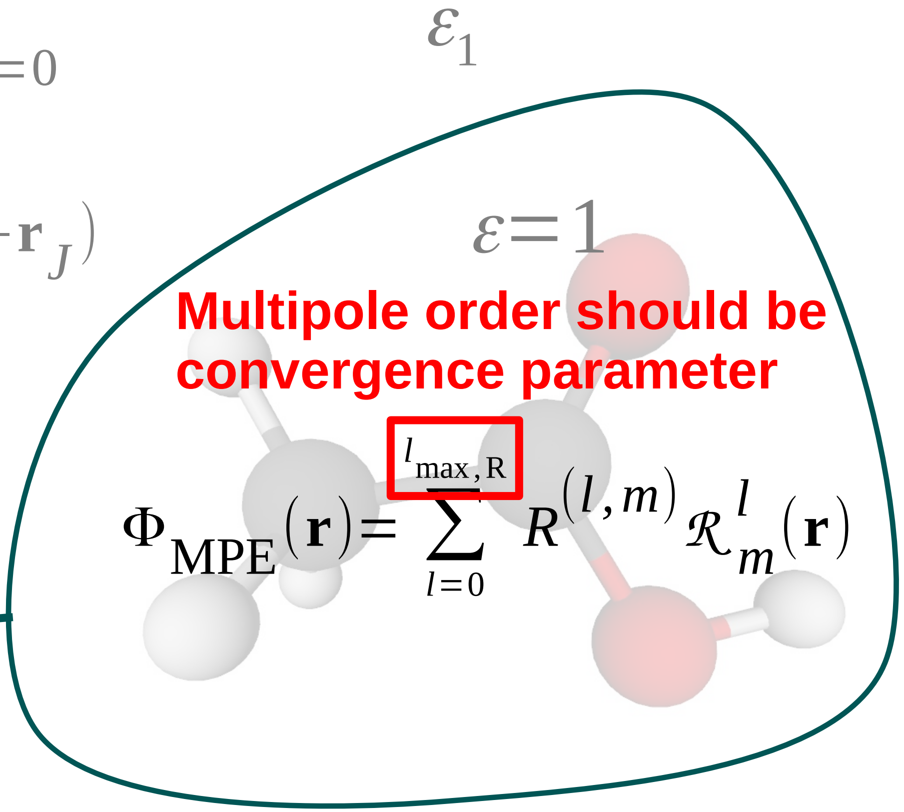
Enforce continuity of potential and flux density on boundary



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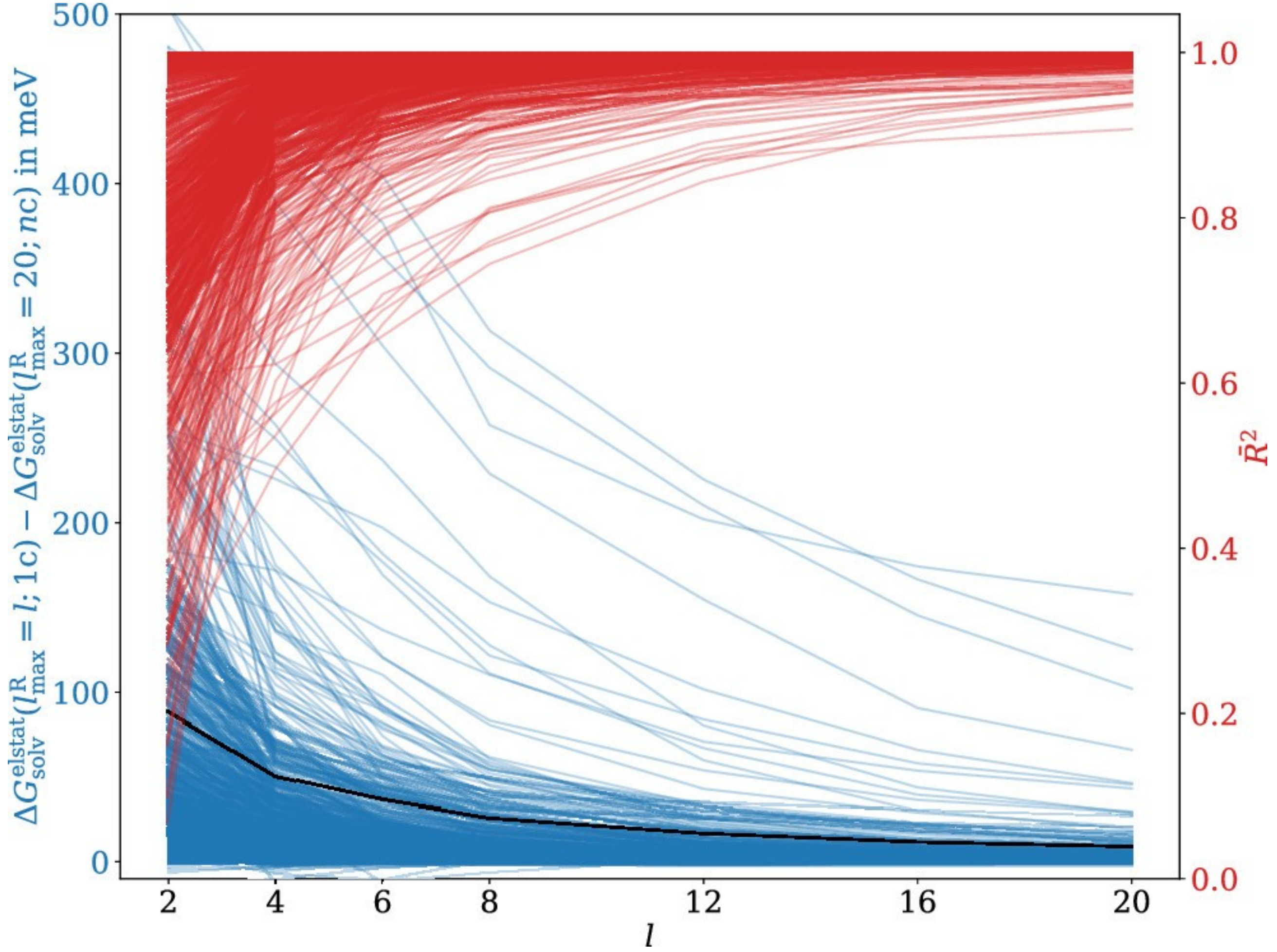
MPE convergence



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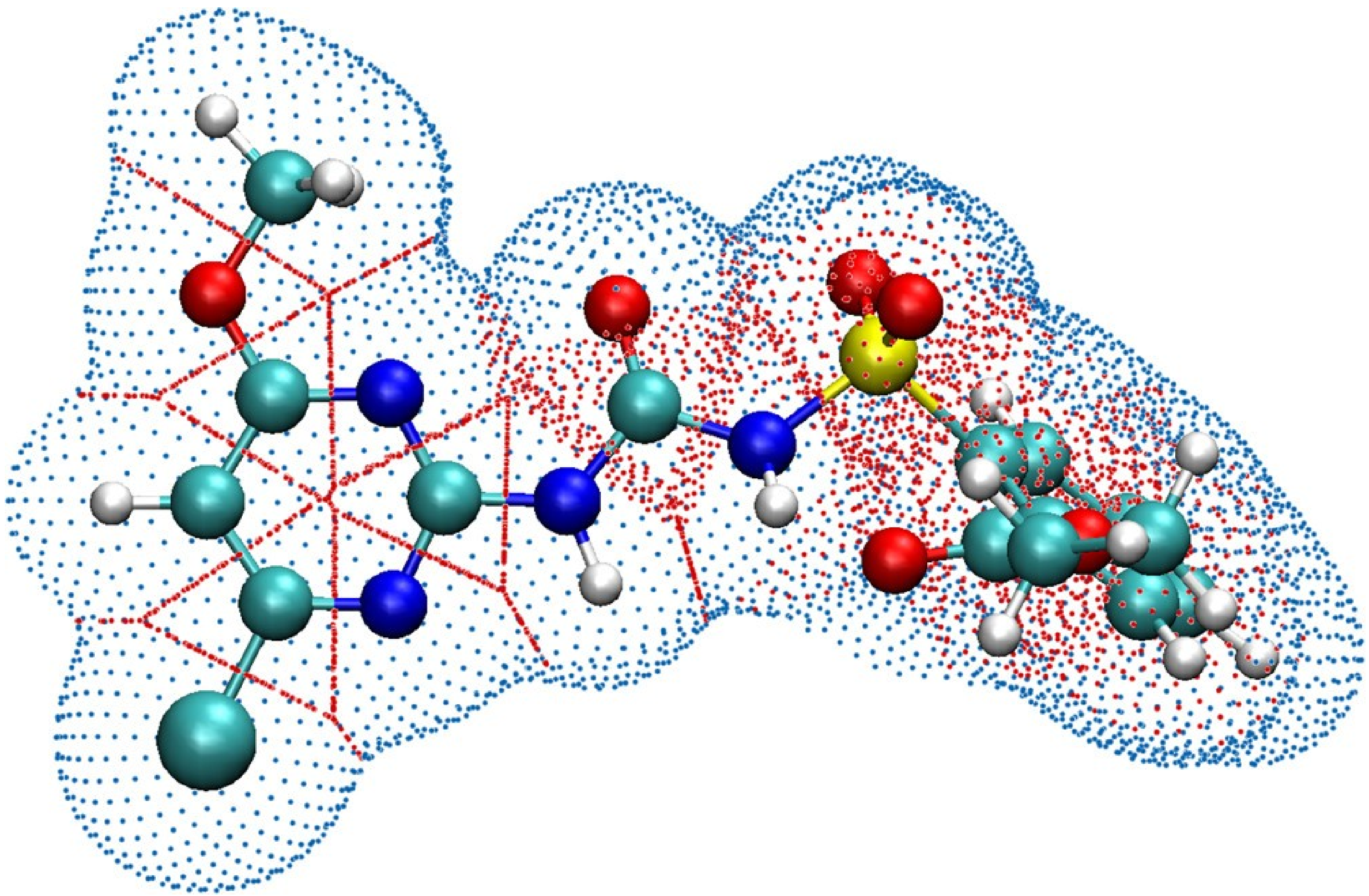
Subcavities



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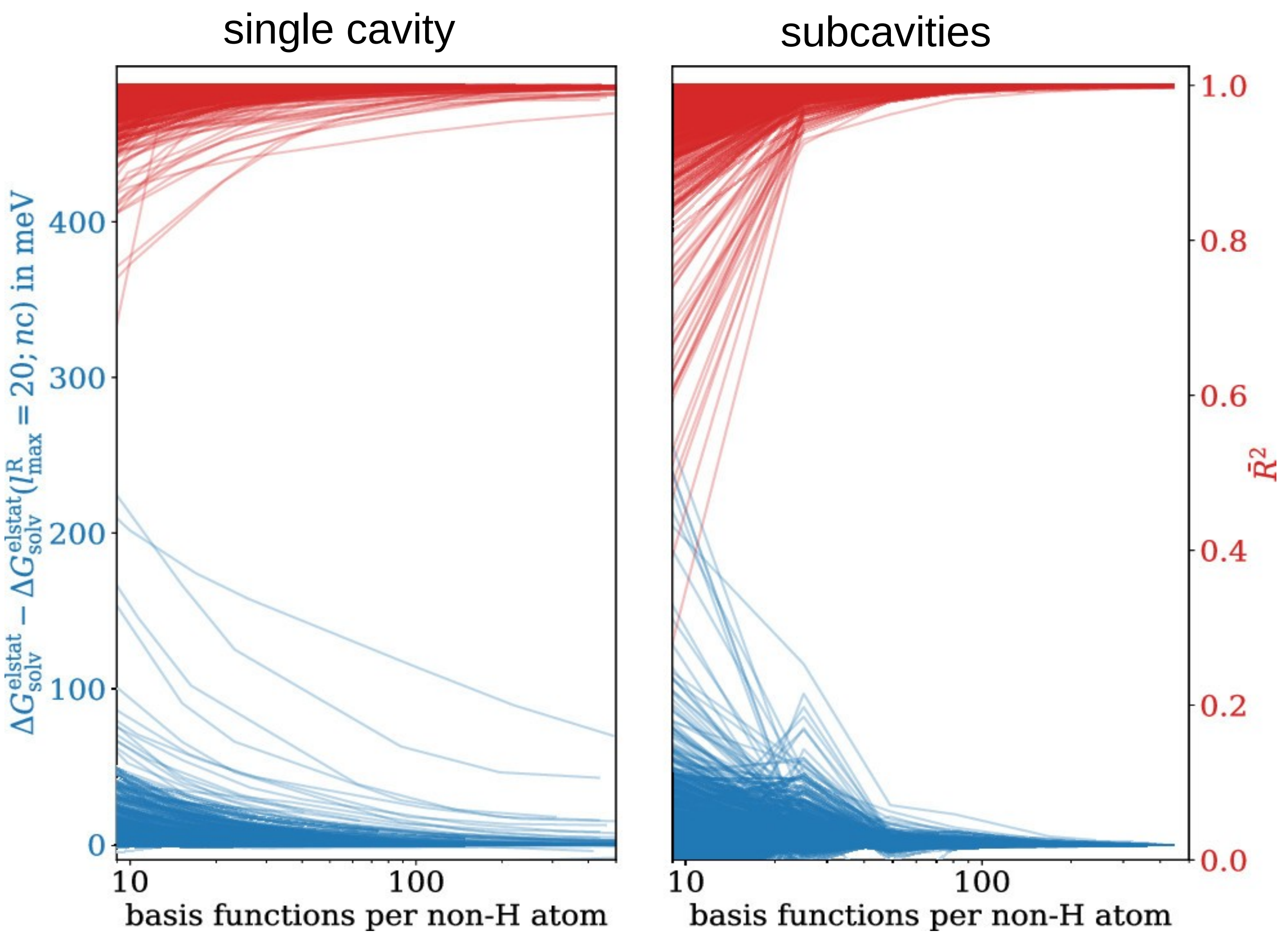
Subcavities



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MPE implicit solvation

Free energy of solvation

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$\Delta G_{\mathrm{solv}}^{\mathrm{elstat}}$:
Electrostatic interaction
with dielectric continuum
Self-consistent with DFT

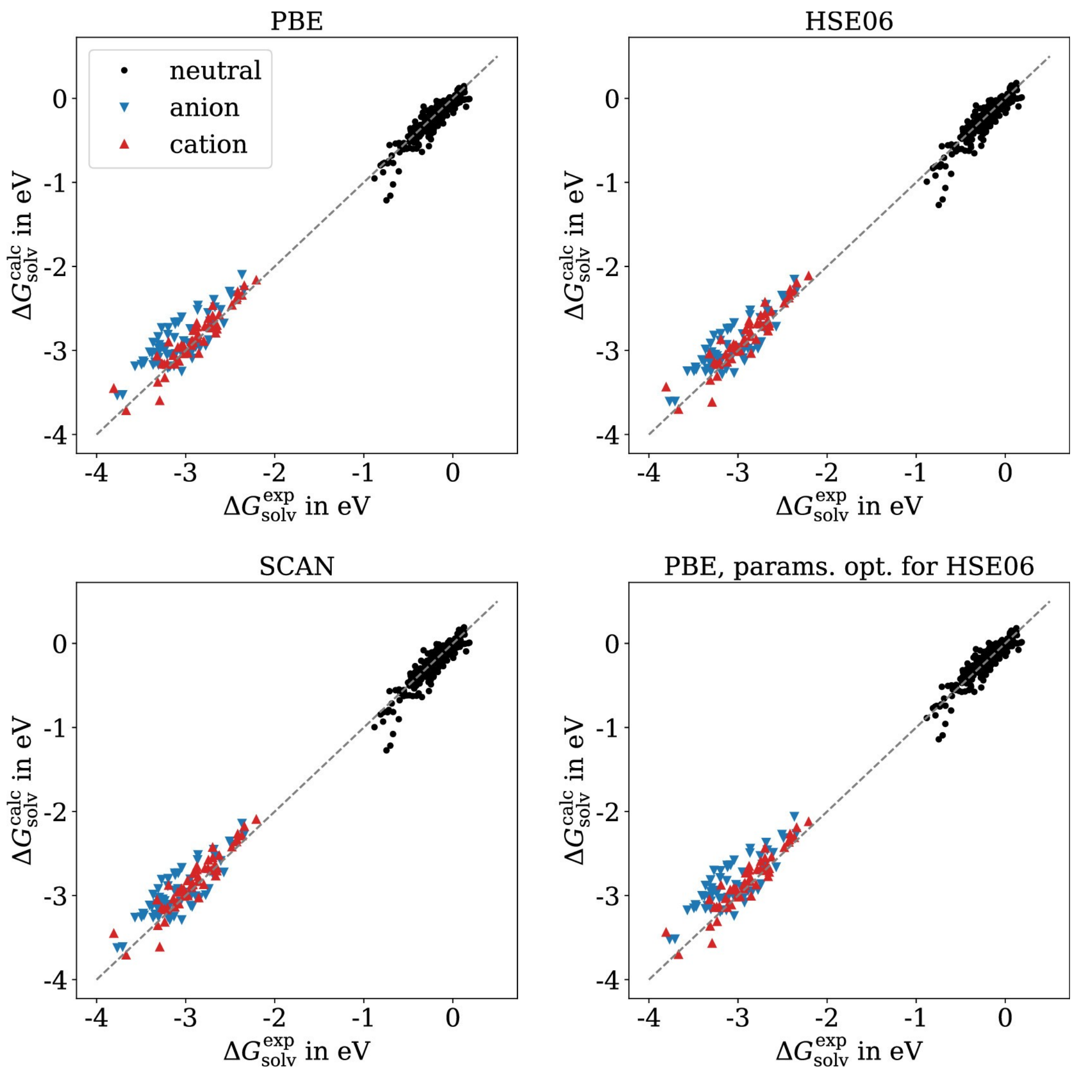
$\Delta G_{\mathrm{solv}}^{\mathrm{non-elstat}}$:
“Everything else“
Post-SCF
correction

$$\Delta G_{\mathrm{solv}}^{\mathrm{non-elstat}} = \alpha A$$

α:
Effective surface tension
Fitting parameter
Depends only on solvent

A:
Cavity surface area

MPE implicit solvation



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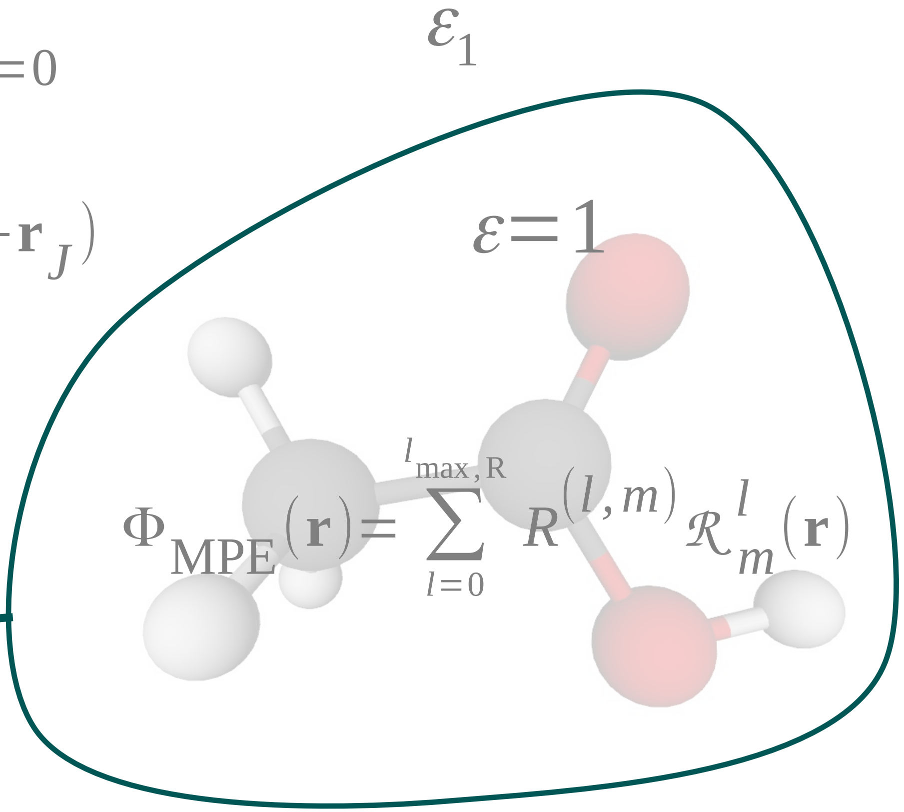
A few words on scaling

$$\varepsilon(\mathbf{r}\in X)=\text{const.} \;\Rightarrow\; \nabla^2\Phi_{\text{MPE}}(\mathbf{r}\in X)=0$$

$$\Phi_{\text{MPE}}(\mathbf{r})=\sum_J \sum_{l=0}^{l_{\max,Q}} Q_J^{(l,m)} I_m^l(\mathbf{r}-\mathbf{r}_J)$$



$$\Phi_{\text{MPE}}(\mathbf{r})=\sum_{l=0}^{l_{\max,R}} R^{(l,m)} \mathcal{R}_m^l(\mathbf{r})$$

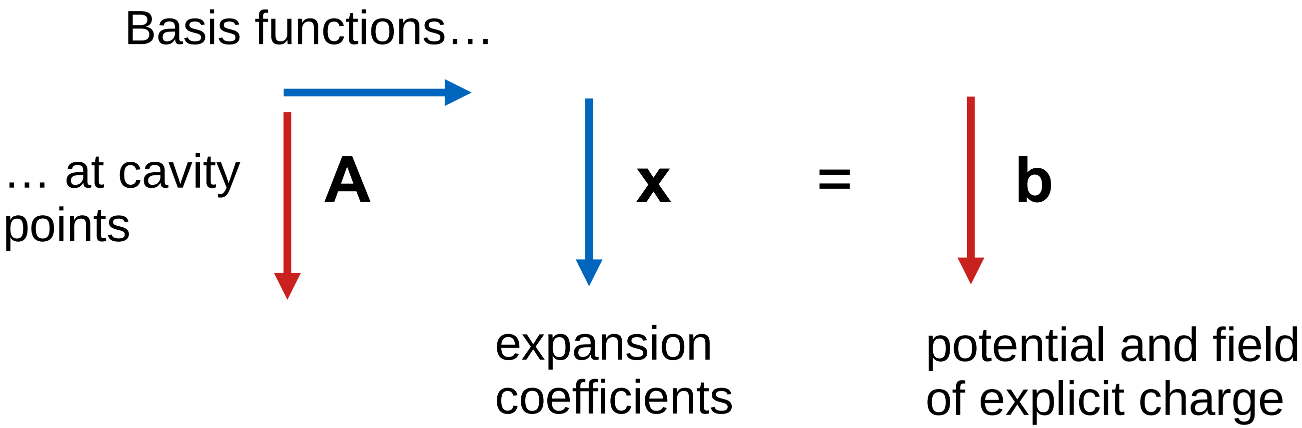
Enforce continuity of potential and flux density on boundary

Sampled on discrete boundary points

M. Sinstein *et al.*, J. Chem. Theory Comput. **13**, 5582-5603 (2017).

A few words on scaling

Boundary conditions cast into linear system

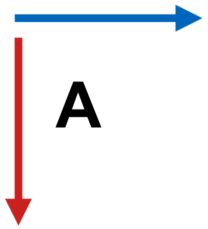


A few words on scaling

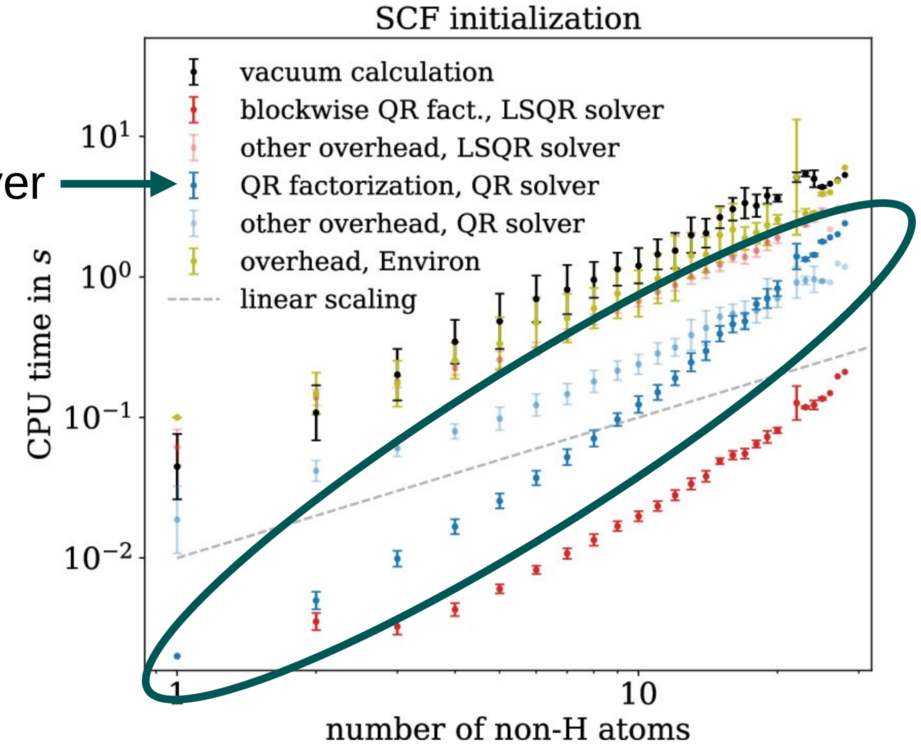
Boundary conditions cast into linear system

Basis functions (O(N))

At cavity
points (≈ O(N))



Dense solver



≈ O(N^2)

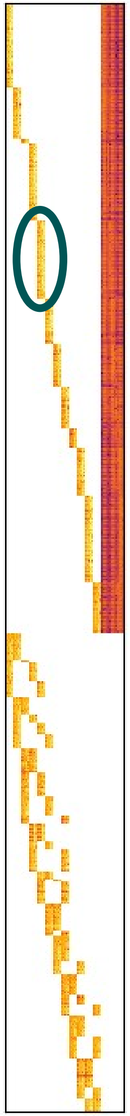
A few words on scaling

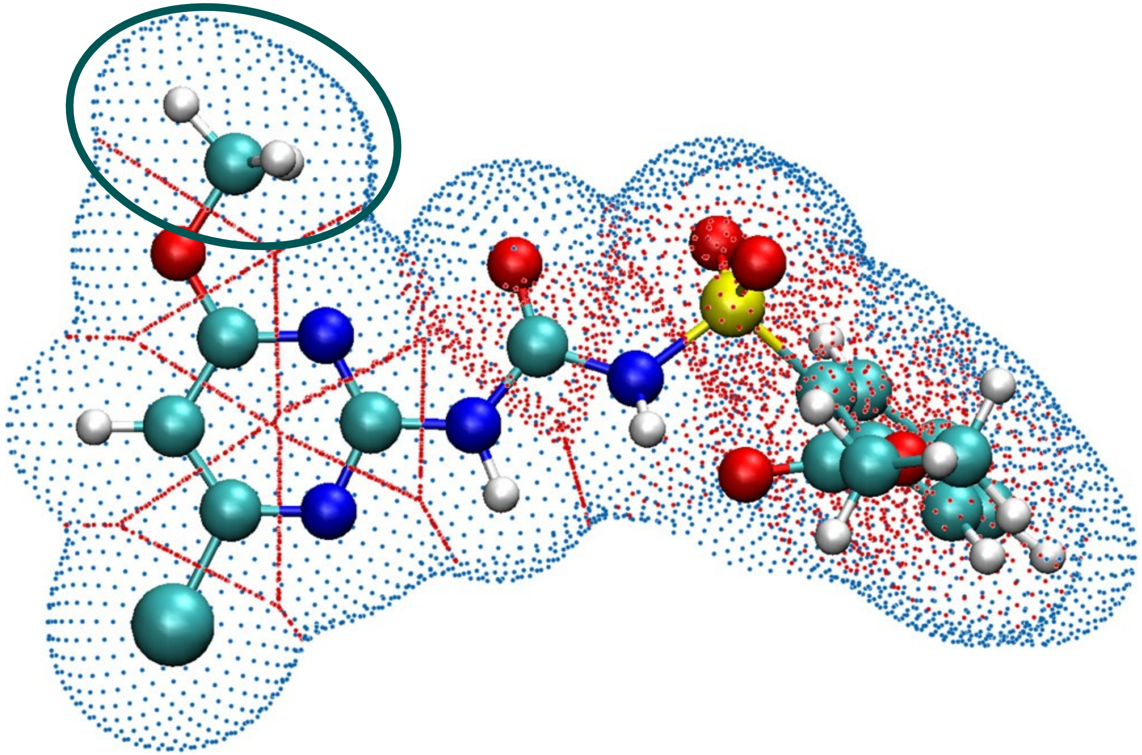
Matrix subblock:

Basis functions inside one subcavity (const.)

X

Surface points of one subcavity (≈ const.)





A few words on scaling

Matrix subblocks:

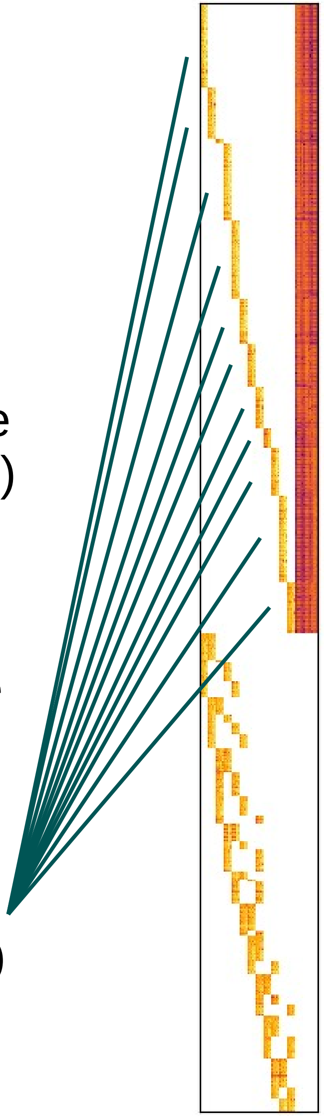
Basis functions inside one subcavity (const.)

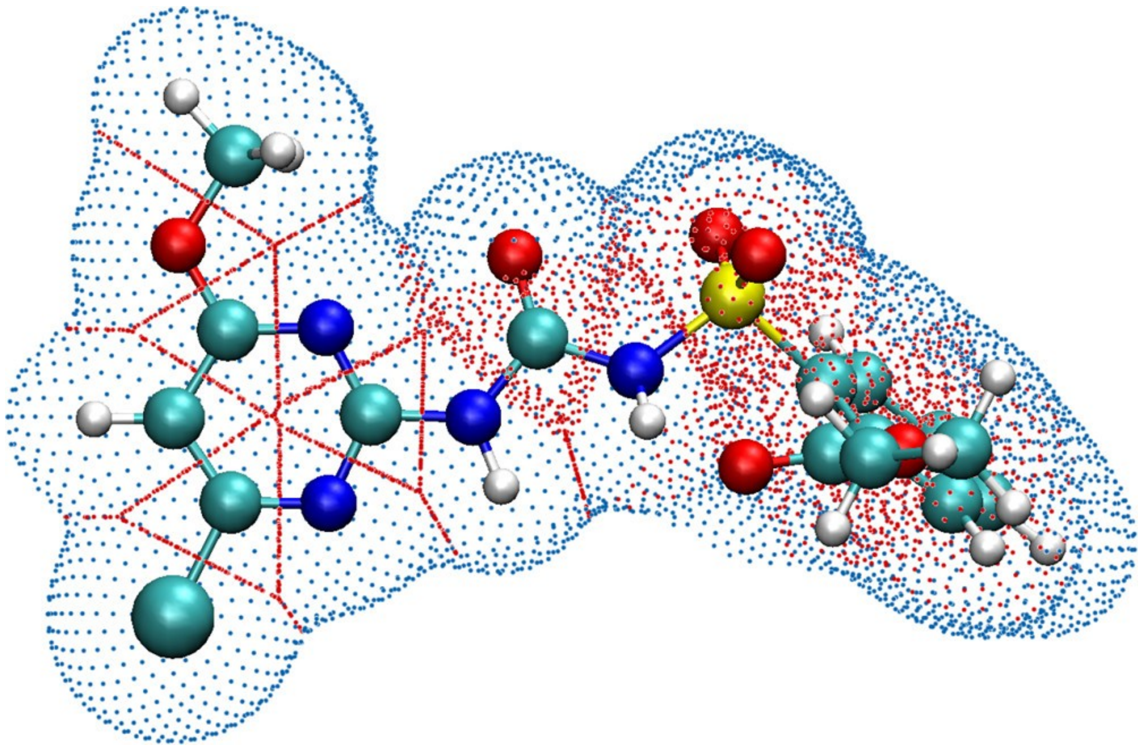
X

Surface points of one subcavity (≈ const.)

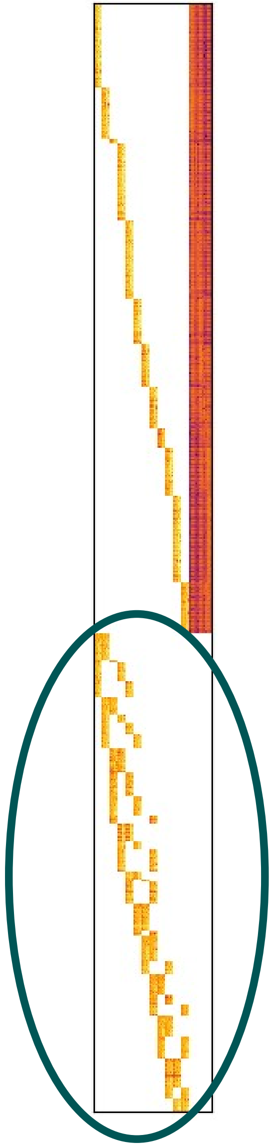
X

Heavy atoms (O(*N*))





A few words on scaling



Matrix subblocks:

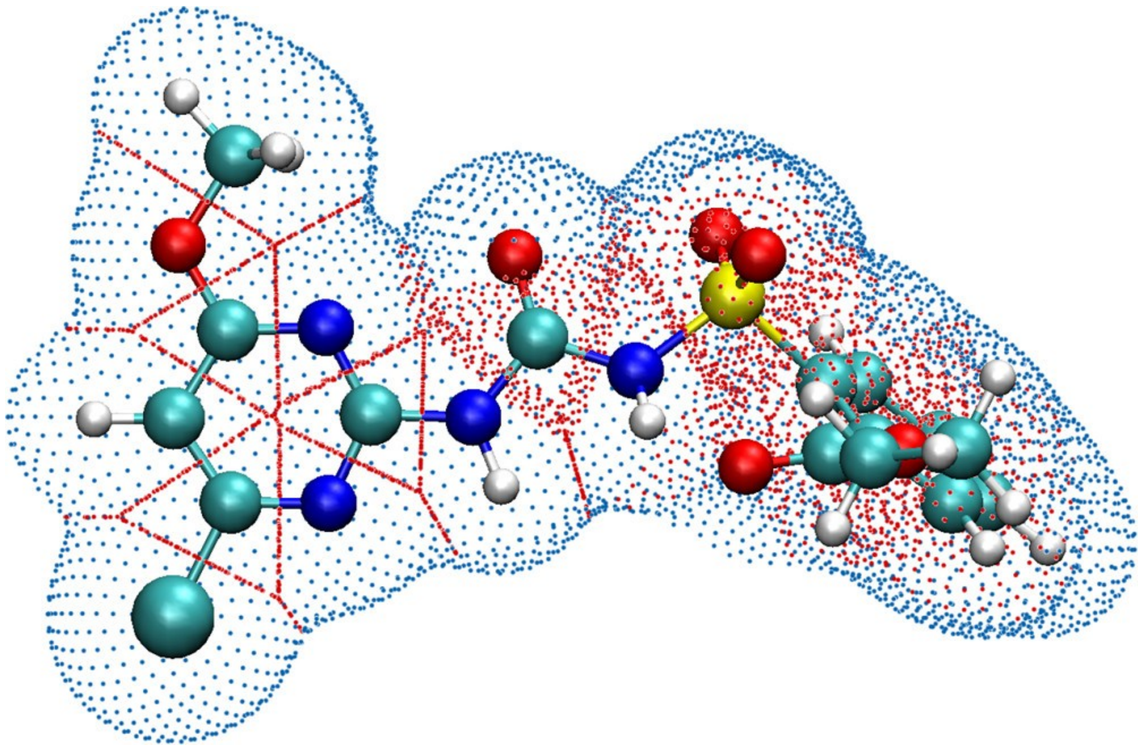
Basis functions inside one subcavity (const.)

X

Interface points between two subcavities (≈ const.)

X

Touching pairs of heavy atoms (≈ O(N))



A few words on scaling

Matrix subblocks:

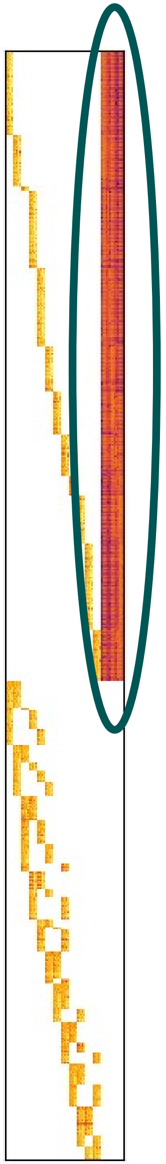
Basis functions outside cavity per heavy atom (const.)…

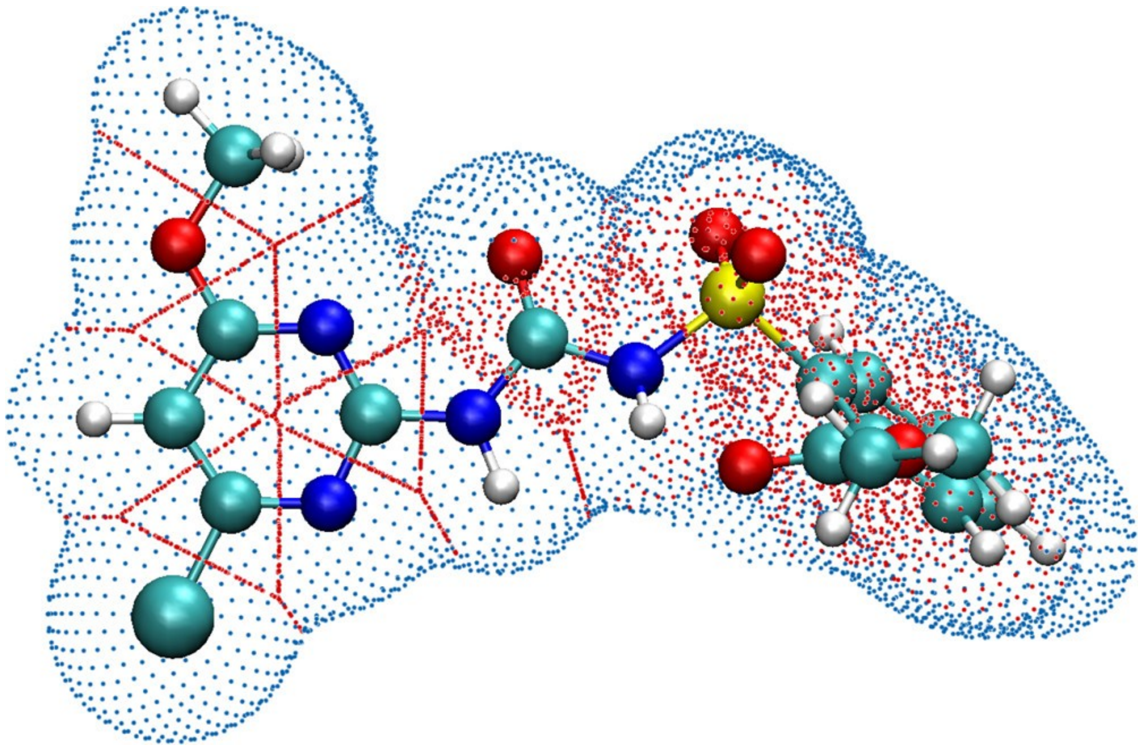
X

… for each heavy atom (O(N))

X

Total cavity surface points (≈ O(N))





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Matrix subblocks:

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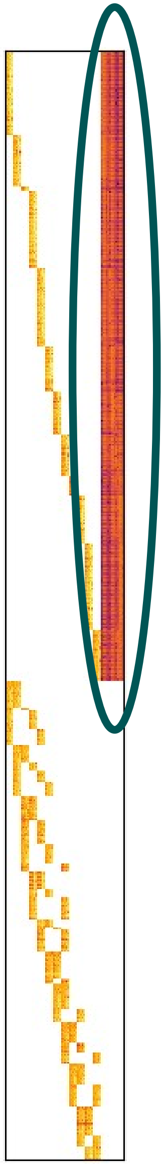
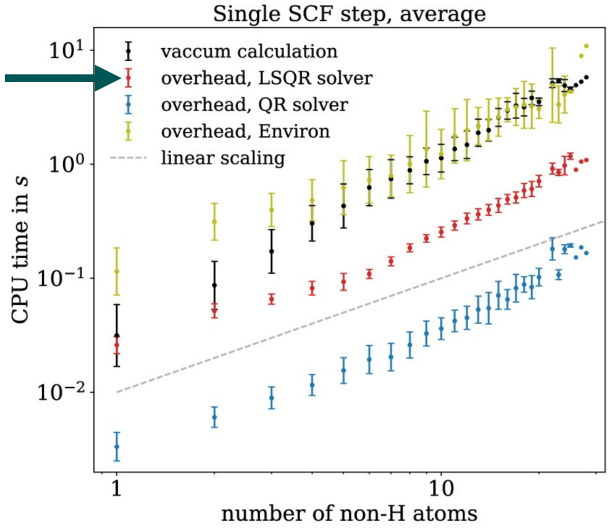
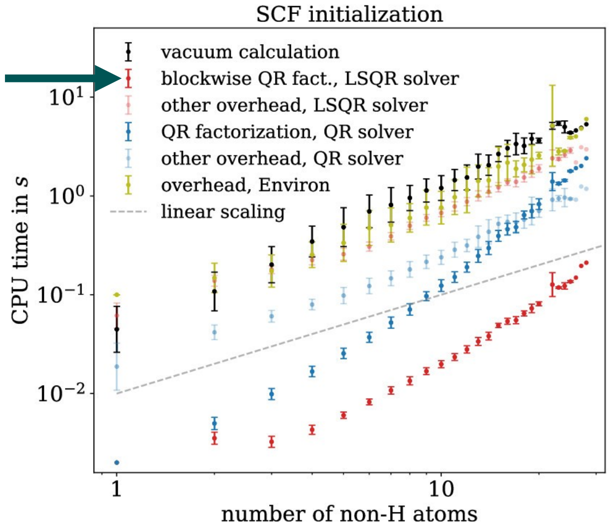


Sparse solver



Sparse solver



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Basis functions outside cavity per heavy atom (const.)…

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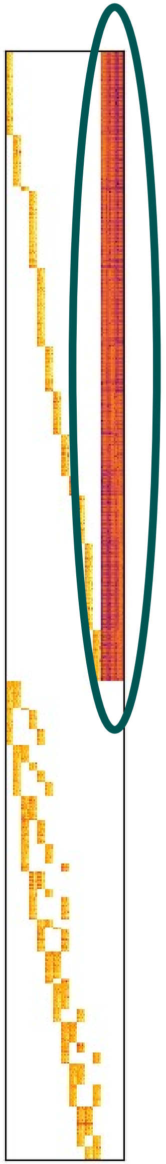
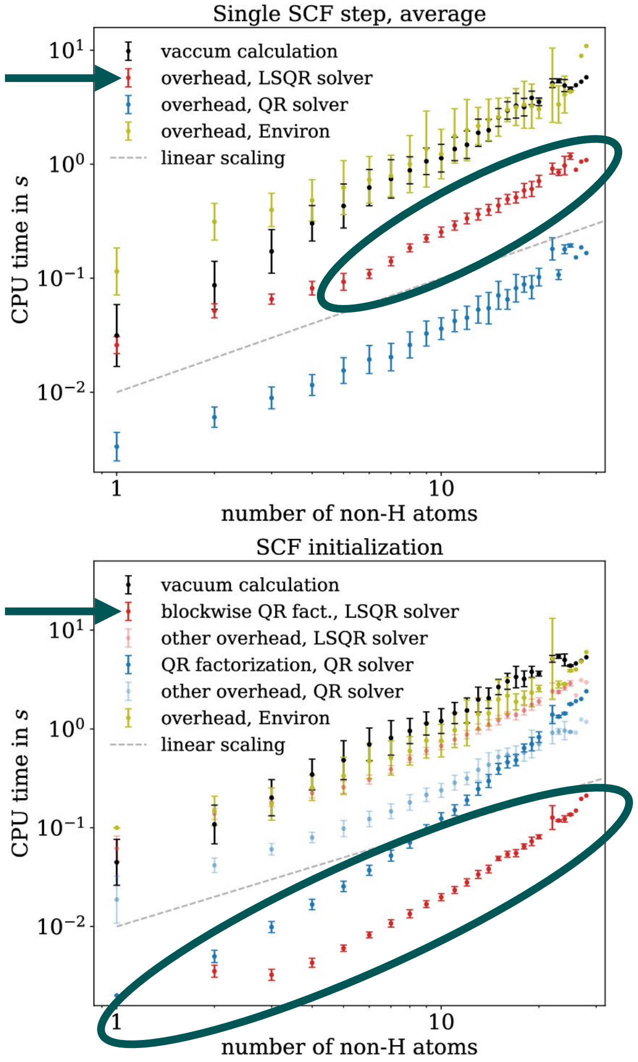


Sparse solver

Sparse solver



Nonlinear scaling

Forces

MPE implicit solvation

Derivatives of …

$$\Delta G_{\text{solv}} = \boxed{\Delta G_{\text{solv}}^{\text{elstat}}} + \Delta G_{\text{solv}}^{\text{non-elstat}}$$

M.Sc. thesis of Daniel Waldschmidt

$$\mathbf{F}_{x_N}^{\text{solv,elstat}} = Z_N \boxed{\nabla_x \Phi_{\text{R}}(\mathbf{r}_N)} + \frac{\varepsilon_{\text{bulk}} - 1}{8\pi} \oint_{c=0} d^2\mathbf{r} \boxed{\mathbf{n} \circ \mathbf{v}} \cdot \boxed{\mathbf{E}_{\text{in}} \circ \mathbf{E}_{\text{out}}}$$

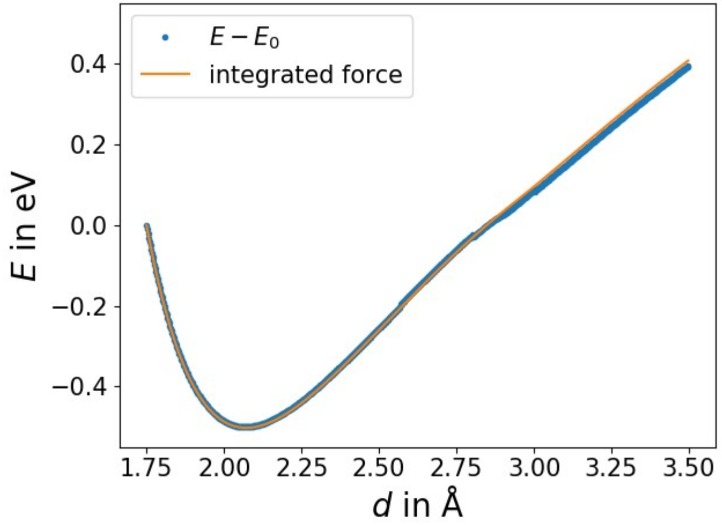
Gradient of solvent potential at nucleus

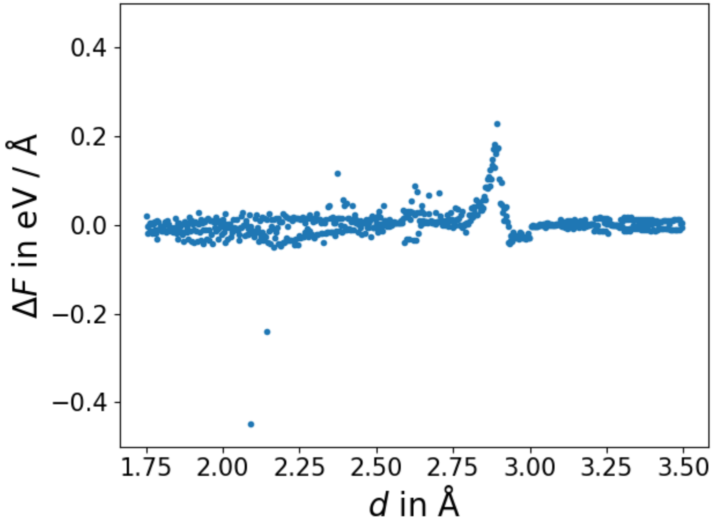
Normal component of nuclear derivative of surface point position

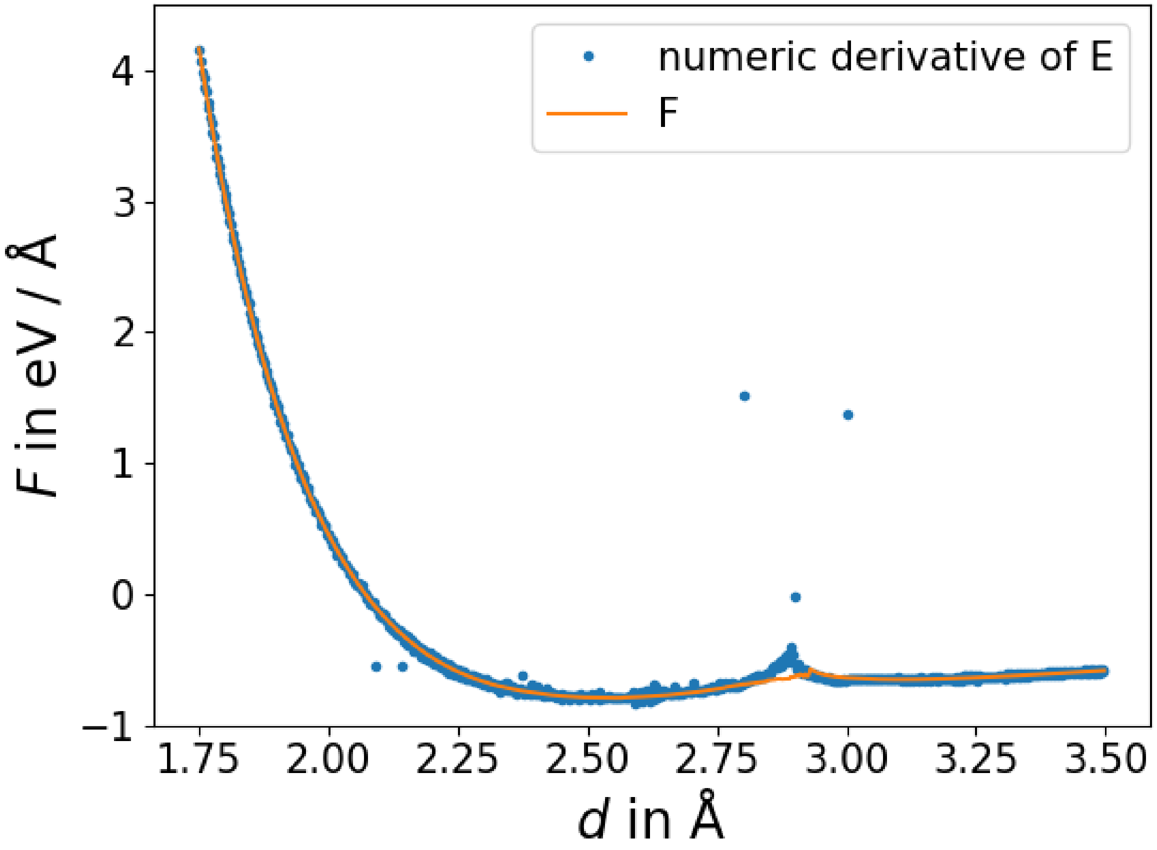
E field at cavity surface in limit from inside and outside

M. Sinstein *et al.*, J. Chem. Theory Comput. **13**, 5582-5603 (2017).

Test system: NaF dimer in ε = 2

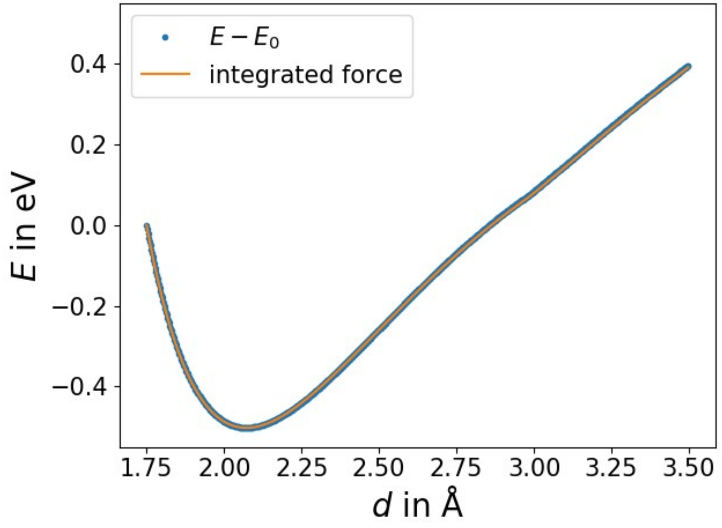


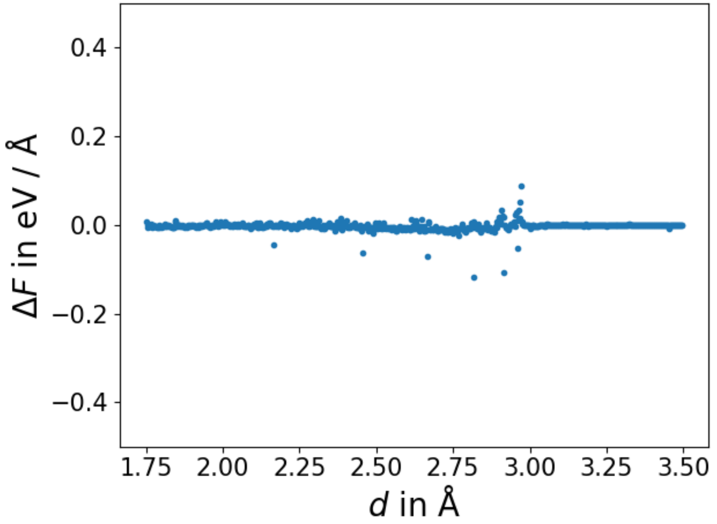


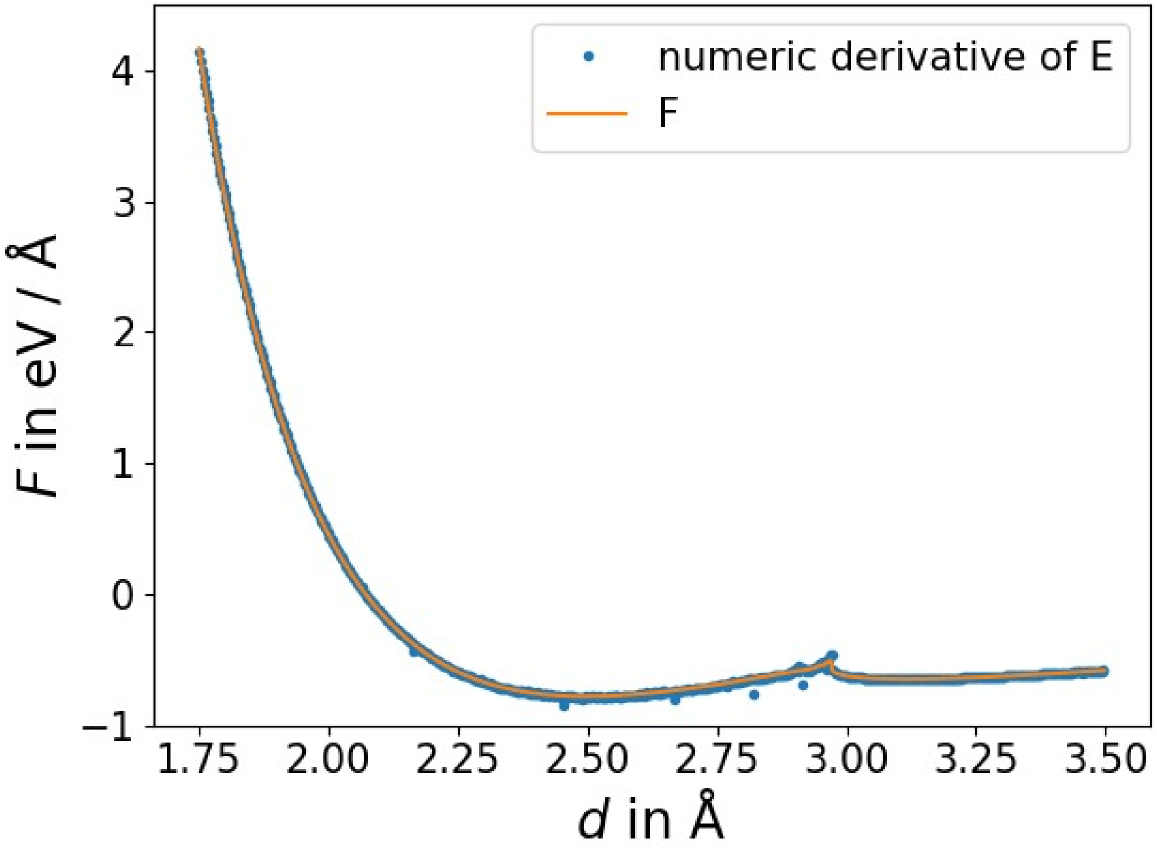


*extreme outliers not shown

Fixing the PES







MPE implicit solvation

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Derivatives of …

$$\Delta G_{\text{solv}} = \Delta G_{\text{solv}}^{\text{elstat}} + \boxed{\Delta G_{\text{solv}}^{\text{non-elstat}}}$$

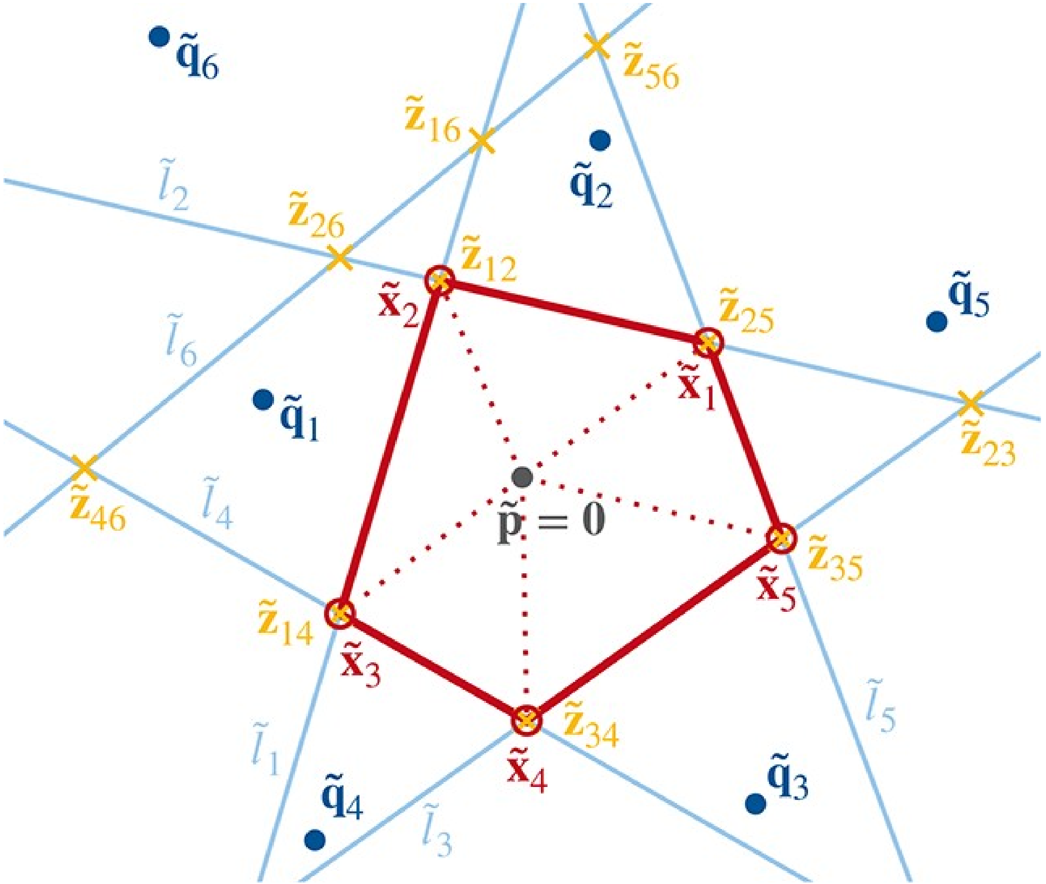
“Everything else“
Post-SCF
correction

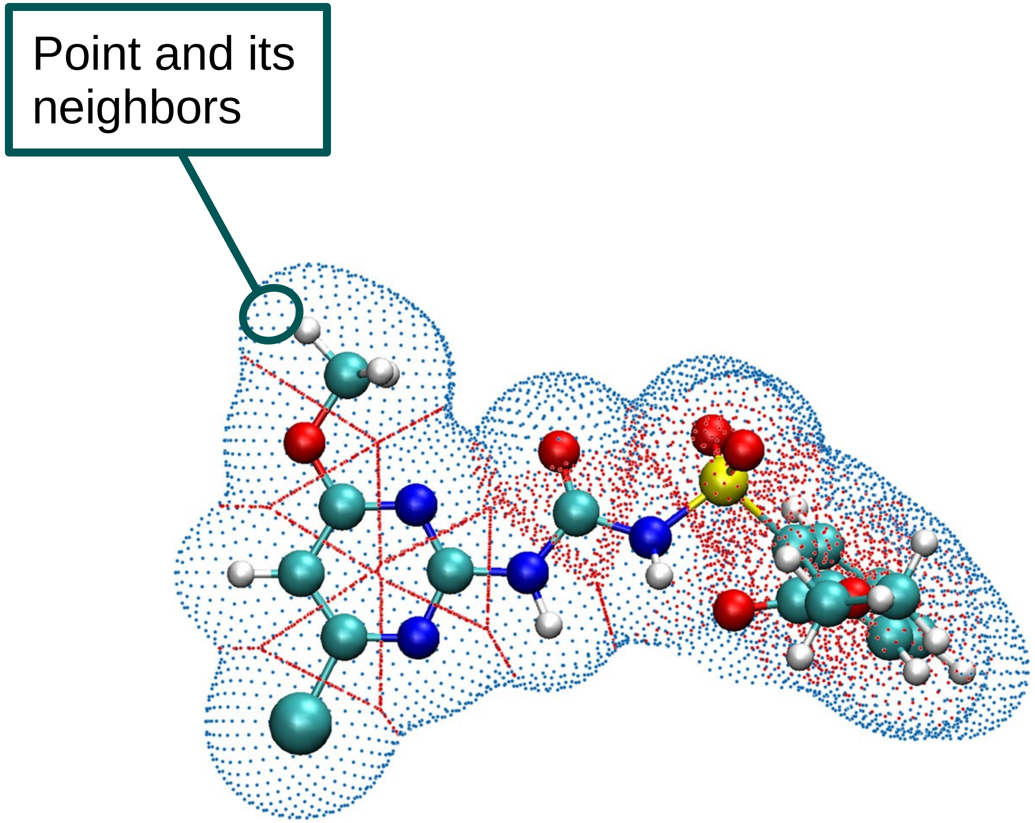
$$\Delta G_{\text{solv}}^{\text{non-elstat}} = \boxed{\alpha}\,\boxed{A}$$

Effective surface tension
Fitting parameter
Depends only on solvent

Cavity surface area

MPE implicit solvation





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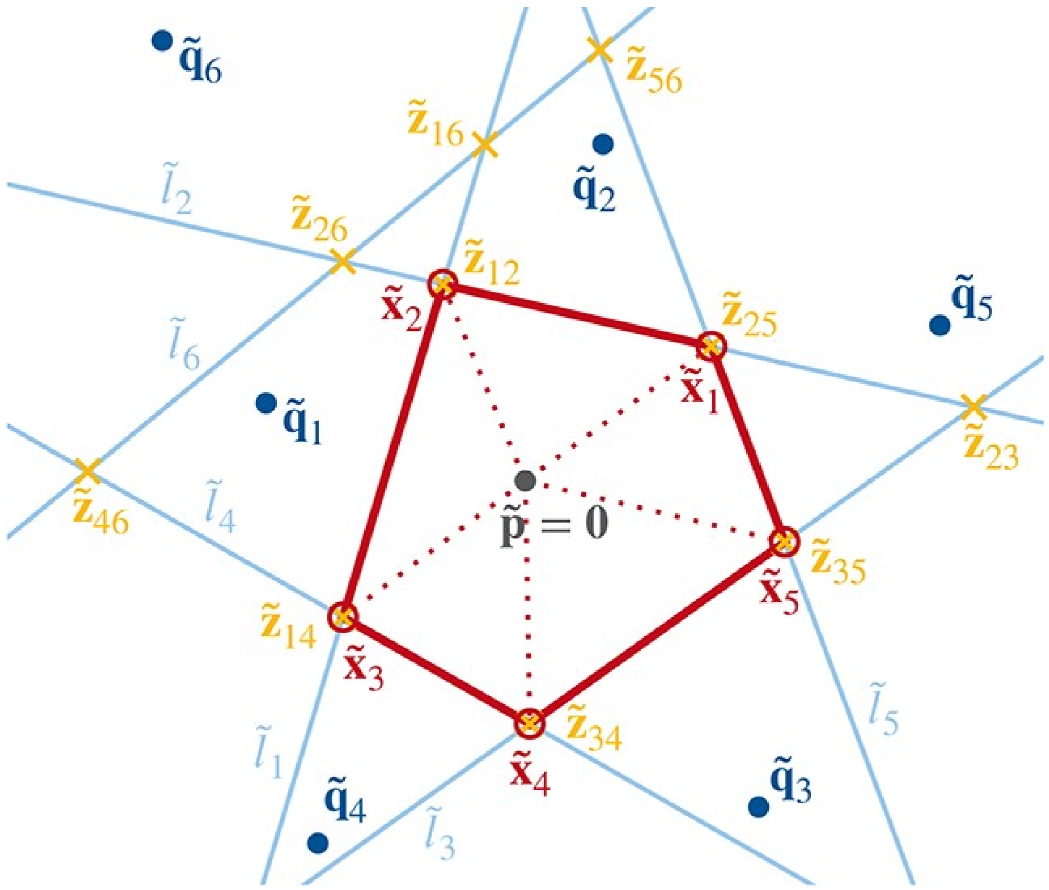
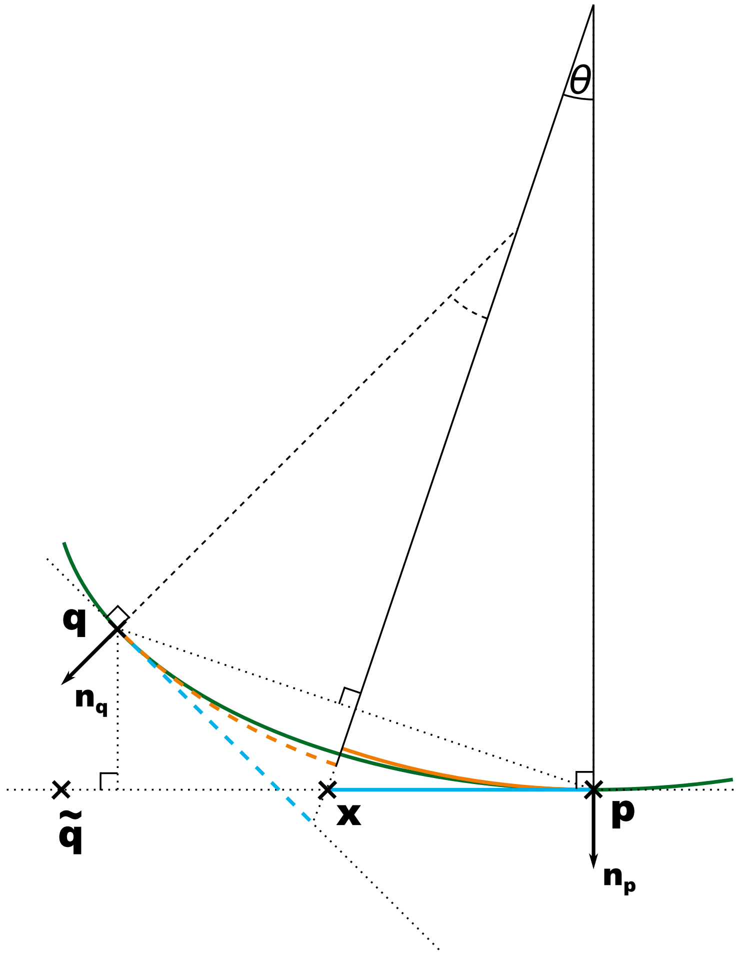
MPE implicit solvation





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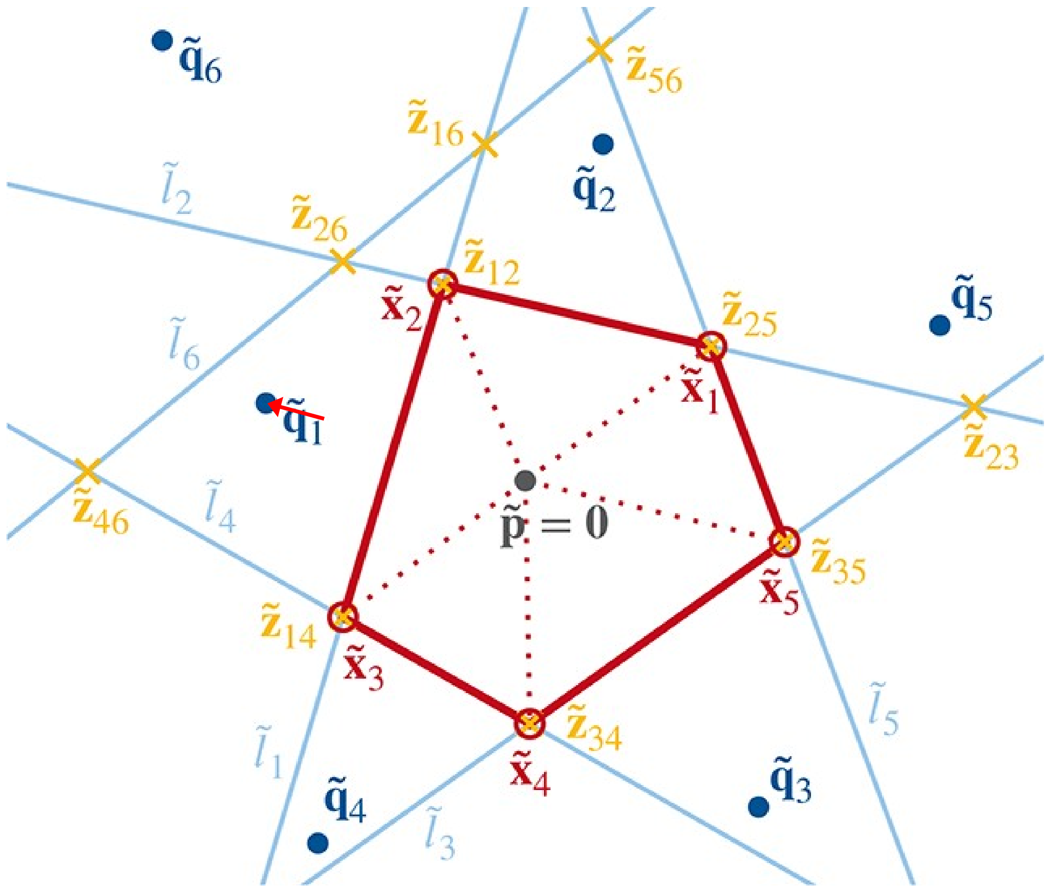

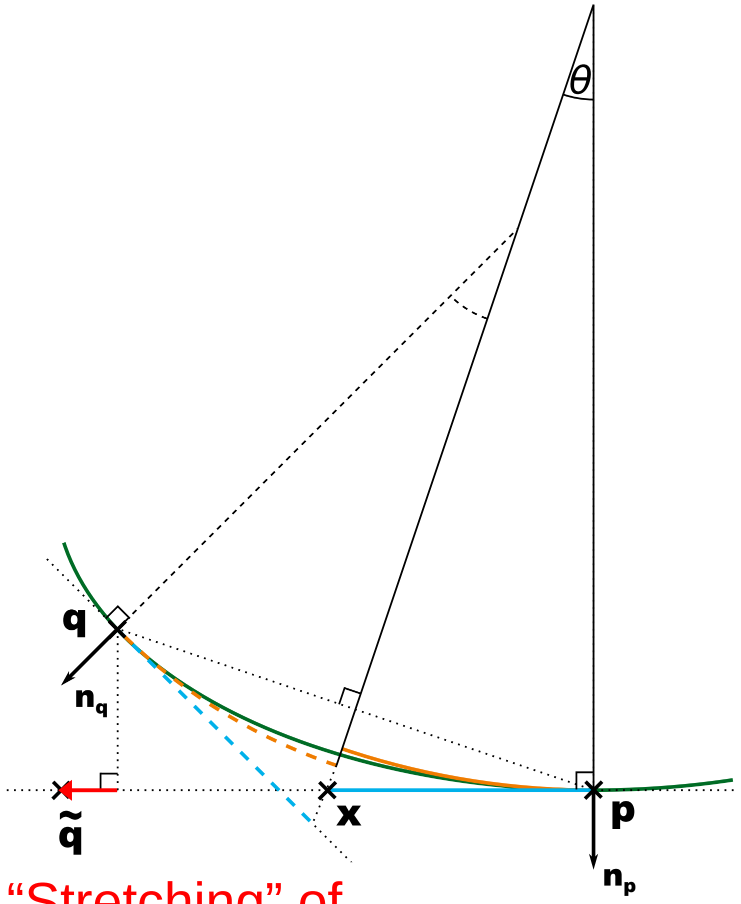

“Stretching” of projected coordinates

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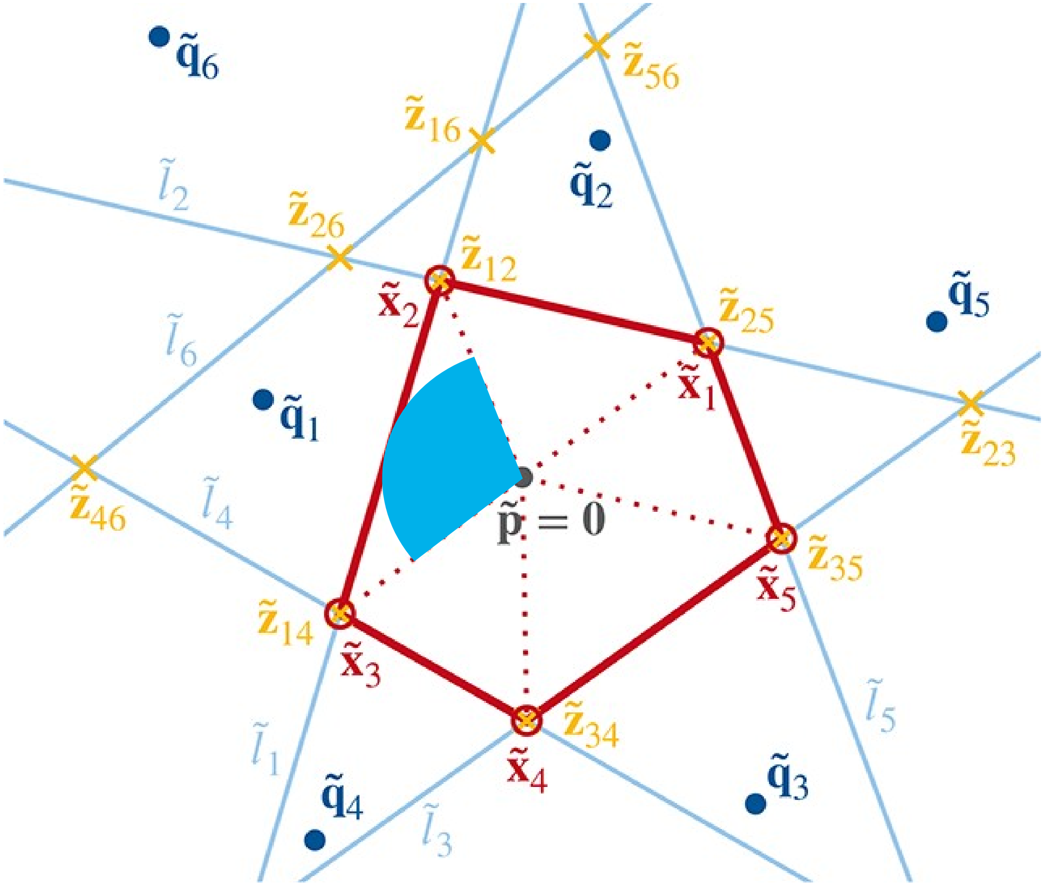
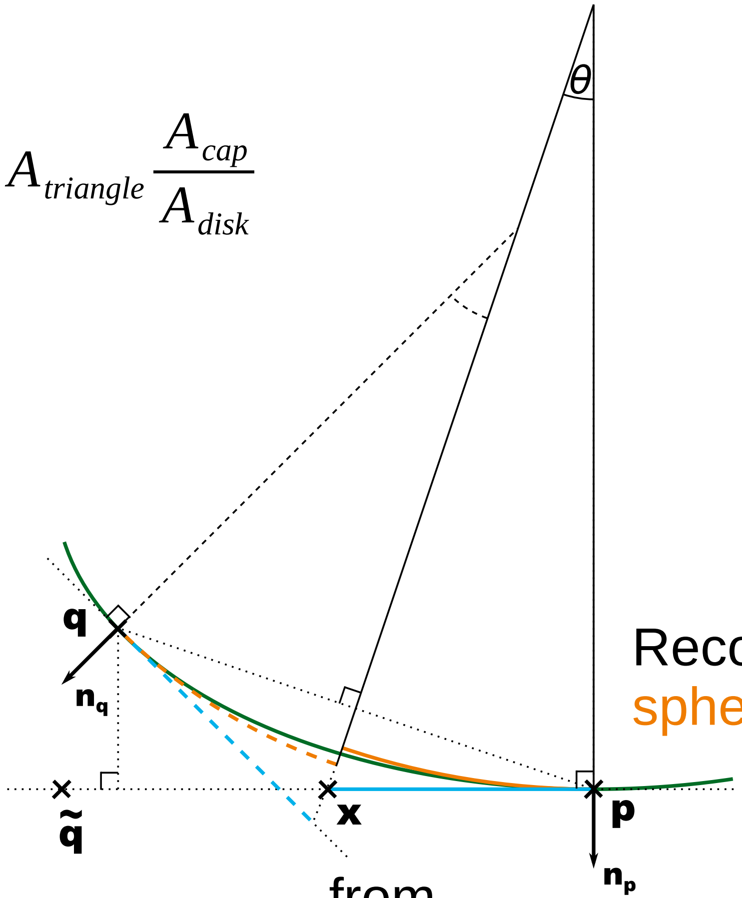
MPE implicit solvation



$$A = A_{triangle} \frac{A_{cap}}{A_{disk}}$$



Recover area of spherical cap …

… from circular disk

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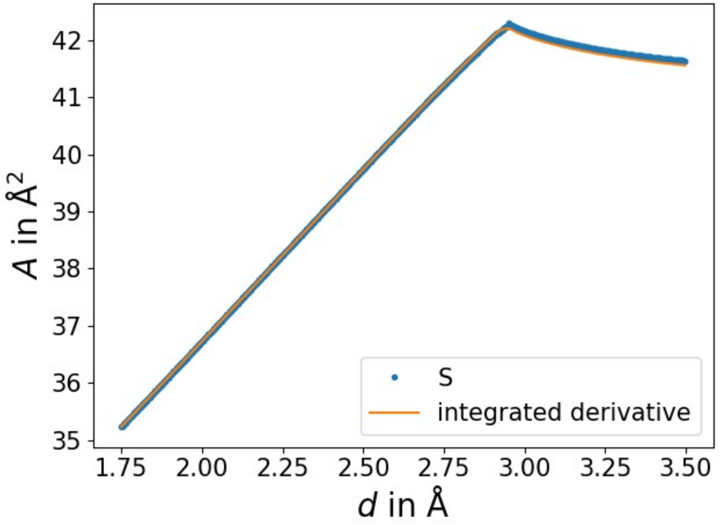
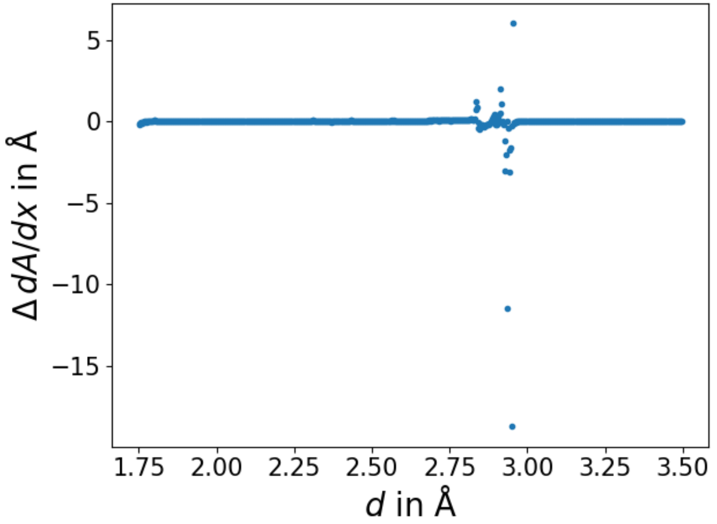
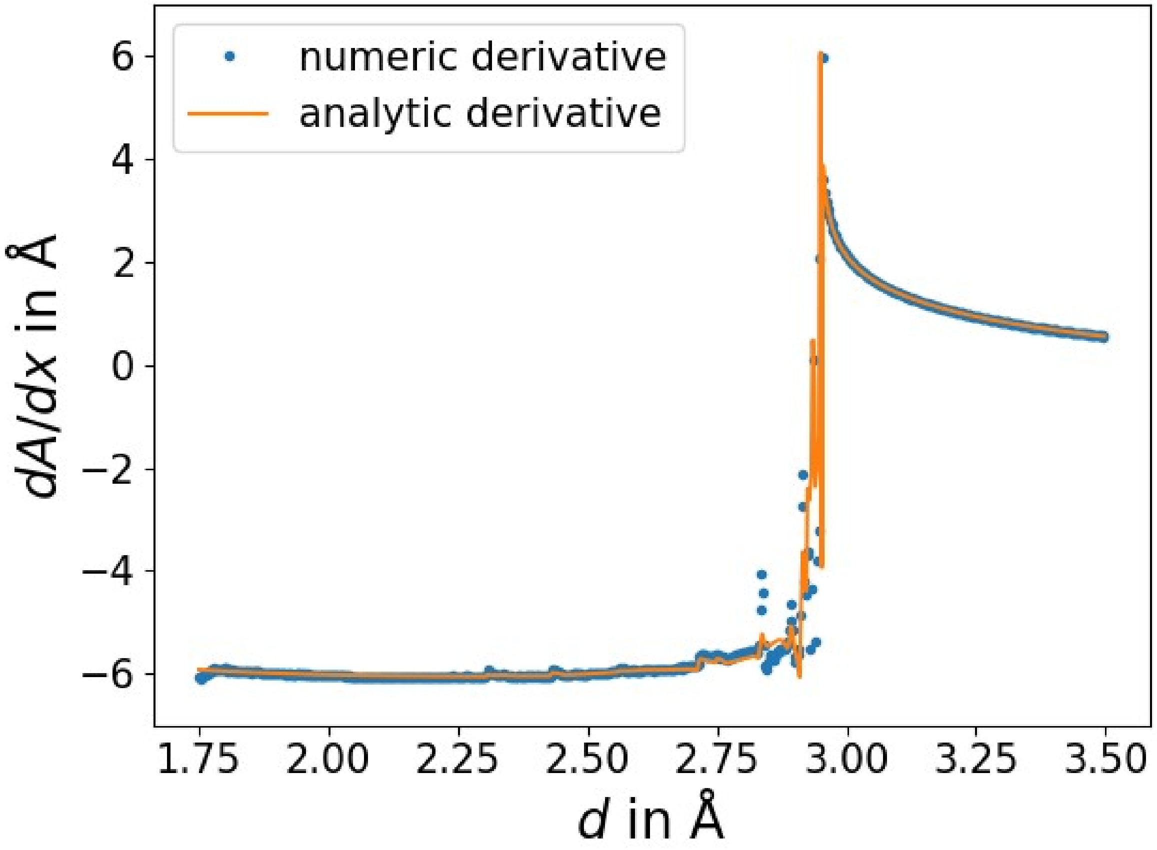
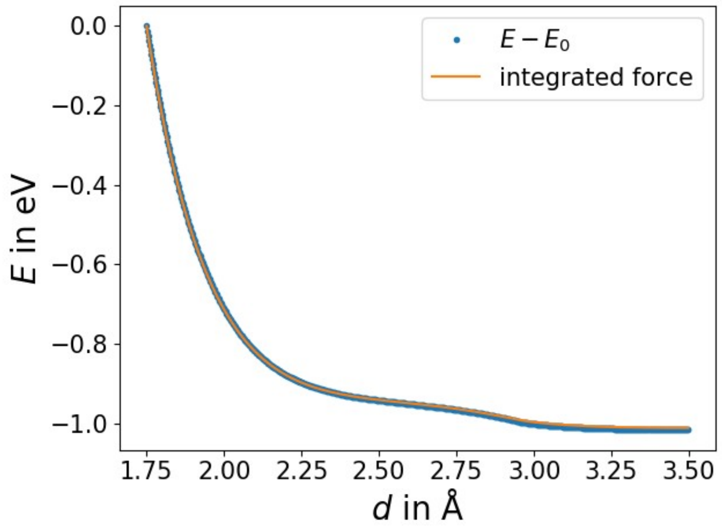
NaF in water, with non-electrostatic contributions

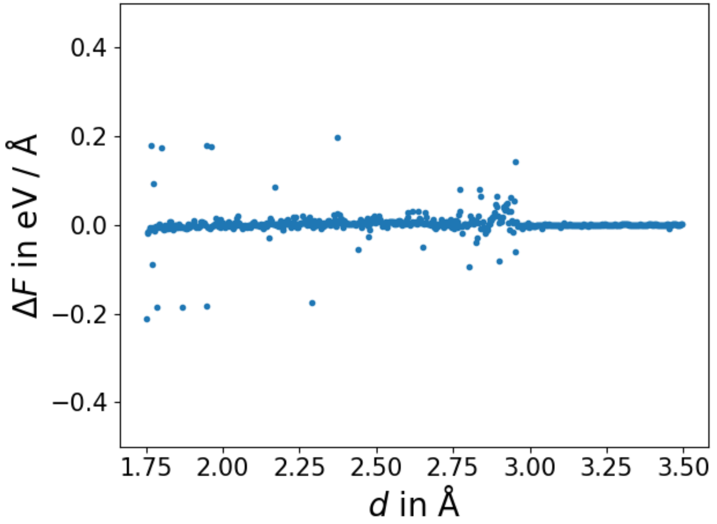


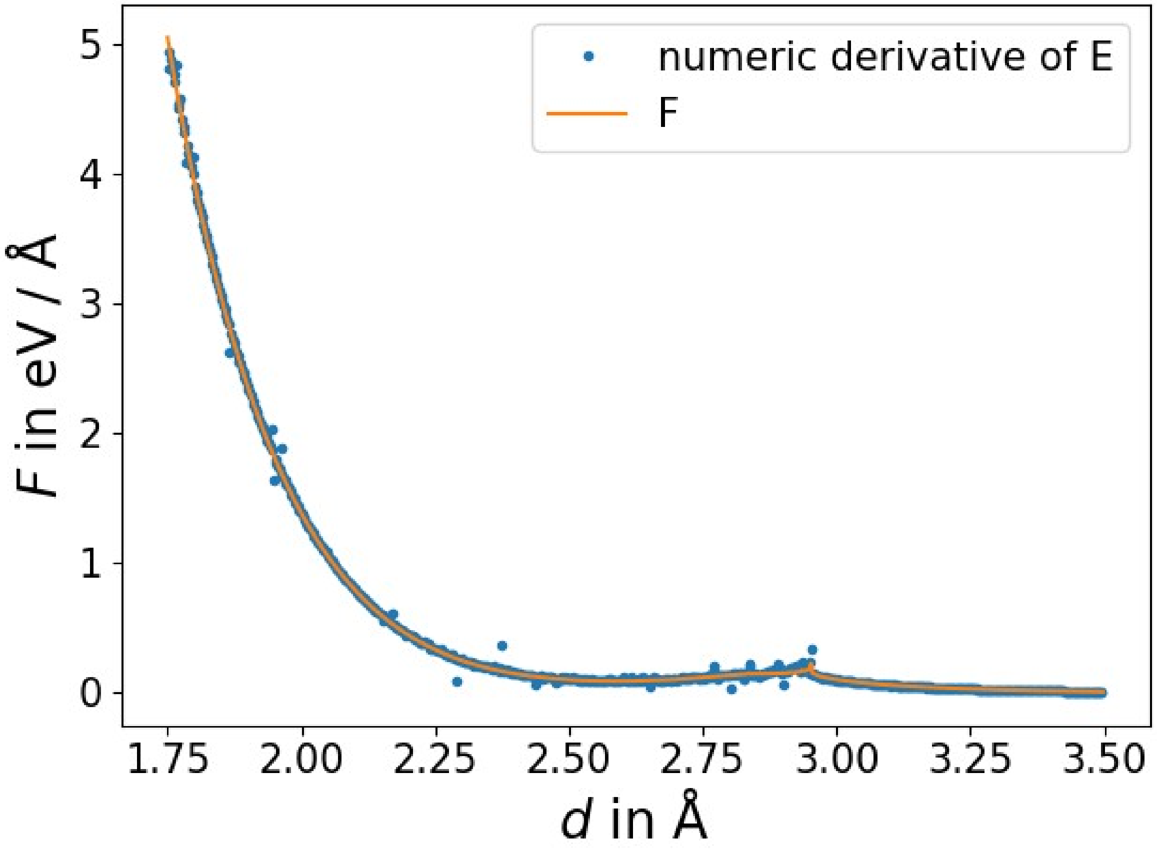




NaF in water, with non-electrostatic contributions







Conclusions

MPE implicit solvation

- One of multiple implicit solvation models in FHI-aims
- Treat neutral, cationic and anionic solutes with same paramter set
- Fast – not bottleneck compared to DFT
- Forces will soon be available

M. Sinstein *et al.*, J. Chem. Theory Comput. **13**, 5582-5603 (2017).

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