Embedding Quantum Regions in Classical Environments

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Why

scaling:

too expensive for large systems

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Why

scaling:

charged systems:

too expensive for large systems
Why

scaling:

![Graph showing relative CPU time vs. number of Ar atoms for different functionals: LDA, PBE, PBE0, XYG3, RPT2. The graph indicates that RPT2 and XYG3 have higher relative CPU times, with RPT2 being the highest.](image)

too expensive for large systems

charged systems:
Why

scaling:

![Graph showing scaling of CPU time with the number of Ar atoms.](image)

- RPT2
- XYG3
- PBE
- PBE0
- LDA

relative CPU time

number of Ar atoms

1000
500
1

too expensive for large systems

charged systems:

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charged systems:
Why

scaling:

number of Ar atoms
relative CPU time

RPT2
XYG3
PBE
PBE0
LDA

too expensive for large systems

charged systems:

PBC charge correction
⇒ finite size effects

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Levels of coarse graining
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Rutile TiO$_2$ cluster w/o embedding
no band-gap, wrong work function
Levels of coarse graining

atomistic embedding
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atomistic embedding
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atomistic embedding

continuum embedding
Levels of coarse graining

atomistic embedding

continuum embedding
Atomistic embedding (QM/MM)

**seamless** coupling between quantum mechanics (QM) and molecular mechanics (MM)

![Diagram of seamless coupling between QM and MM](image)

Structure of a QM/MM simulation

**Example:** Crystal with positive and negative sites

- Cut large cluster
- Designate QM and MM atoms
- Positive sites near QM atoms $\Rightarrow$ charge leakage
- Replace singularities with Pseudo-potentials $\Rightarrow$ transition region
- Still missing: Periodic Madelung potential, correction for multipole moments
- Fitted charges to fix Potential in QM Zone
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Effect of environment polarisability (MM)

IP \((\text{TiO}_2)\)
Effect of environment polarisability (MM)

**IP** \((\text{TiO}_2)\)

**Binding Energy**
\(\text{OH}@\text{TiO}_2\)
Effect of environment polarisability (MM)

**IP** (TiO$_2$)  

Binding Energy  

OH@TiO$_2$

“Seamless embedding” recovers electronic structure  
(DOS of the rutile TiO$_2$ 110-surface)

Example: Rutile TiO$_2$ (110) Surface Oxygen Vacancy

$$G_f(q) \approx E_{\text{defect}}(q) - E_{\text{pristine}}(q) + \mu_O + q\varepsilon_f$$

FHI-aims HSE06, tight settings, polarisably embedded Ti$_{46}$O$_{92}$

Example: Rutile TiO2 (110) Surface Oxygen Vacancy

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\[ V_0^\circ \ 	ext{closed-shell singlet} \]
\[ V_0^2+ \ 	ext{open-shell singlet/triplet} \]

Charged defect stable over wide range of doping (\(\varepsilon_f\)) and oxidation conditions

Charges localise at defects \(\Rightarrow\) photo-electrocatalysis

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Example: Free Energy Barriers

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Initial proton abstraction driven by electron hole:

FHI-aims HSE06, tight settings, umbrella sampling/energy gap reaction coordinate

Basis-set corrected barrier $200 \pm 40$ meV

Continuum embedding

\[ \nabla \cdot [ \nabla \nu(r) ] = -4\pi n_{\text{sol}}(r) \]

Poisson equation in \textit{vacuum}

Parameters:
Continuum embedding

\[ \nabla \cdot \left[ \varepsilon[n_{\text{el}}(r)] \nabla \nu(r) \right] = -4\pi n_{\text{sol}}(r) \]

Parameters:

- \( \{n_{\text{min}}, n_{\text{max}}\} \)  
  solvation cavity shape
- \( \{\alpha, \beta, \gamma\} \)  
  non-electrostatics

Poisson equation in a **dielectric continuum**
Continuum embedding

\[ \nabla \cdot \left[ \varepsilon[n_{el}(r)] \nabla \nu(r) \right] = -4\pi n_{sol}(r) - 4\pi n^{\text{PB}}_{\text{ion}}(r) \]

Parameters:

- \( \{n_{\text{min}}, n_{\text{max}}\} \) - solvation cavity shape
- \( \{\alpha, \beta, \gamma\} \) - non-electrostatics
- \( \{a\} \) - ion size
- \( \{n^{\alpha}_{\text{min}}, n^{\alpha}_{\text{max}}\} \) - ion cavity shape (Stern layer)

(modified) Poisson Boltzmann equation in a dielectric continuum
Continuum embedding

\[ \nabla \cdot \left[ \varepsilon \left[ n_{\text{el}}(r) \right] \nabla \nu(r) \right] = -4\pi n_{\text{sol}}(r) - 4\pi n_{\text{ion}}^{\text{PB}}(r) \]

**Parameters:**

- \( \{n_{\text{min}}, n_{\text{max}}\} \) : solvation cavity shape
- \( \{\alpha, \beta, \gamma\} \) : non-electrostatics
- \( \{a\} \) : ion size
- \( \{n_{\text{min}}^{\alpha}, n_{\text{max}}^{\alpha}\} \) : ion cavity shape (Stern layer)

Ionic "cavity" not necessarily same as solvation cavity \( \Rightarrow 8 \text{ parameters in total} \)

Significance of the parameters

**Example:** Nitrobenzene in H₂O with 1M NaCl
Significance of the parameters

**Example:** Nitrobenzene in H$_2$O with 1M NaCl
Significance of the parameters

Example: Nitrobenzene in H$_2$O with 1M NaCl
With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.

J. von Neumann via E. Fermi
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An elephant pattern.

5 parameter fit output, note the trunk wiggling.

Fixing *solvation* parameters

240 molecule test-set with known experimental solvation free energies

⇒ fit solvation parameters

Fixing solvation parameters

Fixing solvation parameters

Fixing ionic parameters

First approach salt activity coefficients (KCl)

\[
\ln(\gamma_{\pm}) \propto c_s^{1/2}M^{1/2}
\]

Debye-Hückel vs. experiment [1]

Fixing ionic parameters

First approach salt activity coefficients (KCl)

\[ \ln(\gamma^+_{\pm}) \]

Debye-Hückel

MPBE

electrostatics only


Fixing ionic parameters

First approach **salt activity coefficients** (KCl)

\[
\ln(\gamma^+) = \text{fit parameters}
\]

\[
\gamma^+ = \text{physical observables}
\]

\[
c_s^{1/2}M^{1/2}
\]

⇒ ion parameters can be fit to physical observables


Fixing ionic parameters

Molecular test-set, **Setschenow coefficients**

Linear relationship of solvation free energy of (neutral) molecules with salt concentration

\[ \Delta \Delta G_{\text{ion}} \propto k_s c_S \]

Fixing ionic parameters

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Holds for concentrations $\lesssim 2M$.  

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Holds for concentrations \( \lesssim 2M \).

Generally \( k_S > 0 \) ⇒ **salting out**.

Fixing ionic parameters

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Independence of ion parameters

Best results generally found for $a = 0$ (point-like ions), ensures Setschenow linearity.
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Stern layer width $d_\alpha$ versus “softness” $\xi_\alpha$. 
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Stern layer sizes for anions $d^-_\alpha$ and cations $d^+\alpha$.
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Stern layer width $d_\alpha$ versus “softness” $\xi_\alpha$.

Stern layer sizes for anions $d^-_\alpha$ and cations $d^+_\alpha$.

Setschenow coefficients depend only on $d^-_\alpha = d^+_\alpha = d_\alpha$. 
Scaling relation for $d_\alpha$ (Stern Layer width)

What to do with other salts (with often little or no experimental data)?
Scaling relation for $d_\alpha$ (Stern Layer width)

What to do with other salts (with often little or no experimental data)?

$d_\alpha$ correlates with the hydration number.

⇒ predict ionic parameter.

SMPB in practice

Free energy functional

\[ \Omega_{\varepsilon,\alpha_{\text{ion}}}^{\pm}[v, n_{\text{el}}] = T^S[n_{\text{el}}] + E^{xc}[n_{\text{el}}] + \Omega_{\varepsilon,\alpha_{\text{ion}}}^{\text{mf}}[v, n_{\text{el}}] + \Omega_{\varepsilon}^{\text{non-mf}}[n_{\text{el}}] \]

min \(v\)

min \(n_{\text{el}}\)

SMPBE modified KS-eq.

\textbf{Newton-Multipole-Expansion Relaxation Method (MERM)}
Solving the MPBE

Regularisation

\[ v = v^\text{free} + \delta v \]

Rewrite SMPB as root-finding Problem

\[ \mathcal{F}[v] = \nabla \cdot [\varepsilon \nabla v] + 4\pi (n_{\text{sol}} + n_{\text{ion}}[v]) = 0 \]

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Linearise, Newton in function space
\[
\begin{align*}
\mathcal{F}'[v_n](\delta v_{n+1} - \delta v_n) &= -\mathcal{F}[v_n], \\
(\nabla.[\nabla \varepsilon] - \hbar^2[v_n])\delta v_{n+1} &= -4\pi \varepsilon q[v_n]
\end{align*}
\]

Solving the MPBE

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\end{align*}
\]

Solve by relaxation method, recast as screened Poisson equation

\[ (\Delta - \kappa^2)\delta v_{n+1} = -4\pi q[v_n] + \hat{L}_1[v_n] \delta v_{n+1}, \]

\[ \delta v_{n+1}(\mathbf{r}) = -\int d\mathbf{r}' G_1(|\mathbf{r} - \mathbf{r}'|) \left( -4\pi q[v_n(\mathbf{r}')] + \hat{L}_1[v_n(\mathbf{r}')] \delta v_{n+1}(\mathbf{r}') \right), \]

\[ G_1(|\mathbf{r} - \mathbf{r}'|) = \frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{-\kappa |\mathbf{r} - \mathbf{r}'|} \]

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Solve Integral by Multi-centre multipole expansion

MERM

Solving the MPBE

KS-Equation

- SCF update KS-Hamiltonian
- solve eigenvalue problem
- update electron density

Poisson Solver

Solve via multi-centre
Multipole expansion

\( n_{el} \)

\( V \)

Solving the MPBE

**KS-Equation**

- SCF:
  - **update** KS-Hamiltonian
  - **solve** eigenvalue problem
  - **update** electron density

- **MPBE**

  - **rewrite** MPBE: \( F[v] = 0 \)
  - **solve** for \( v \) via Newton method
  - Newton step \( \leftrightarrow \) **solve** "tangent equation"

- **MERM**

  - **recast** "tangent equation" into \textit{Screened Poisson Equation}
  - \textit{to be solved} self-consistently
  - **integrate** SPE via \textit{Multipole Expansion}
  - \textit{ME based Relaxation Method}

**n_{el}**

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