Toward electrocatalysis on metal clusters coupled to an electron reservoir

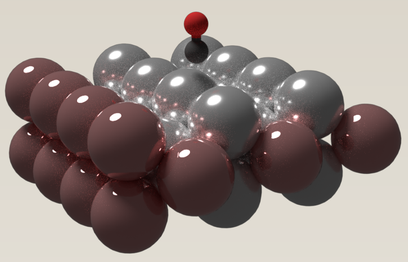
Christopher J. Stein and Martin Head-Gordon

Chemical Sciences Division, Lawrence Berkeley National Laboratory, and,
Department of Chemistry, University of California Berkeley

Green's function coupling to an electron reservoir

Coupling model

Extended molecule model of adsorbate on a nanocluster



electrode atom without coupling

$\Sigma_{jj} = 0$

electrode atom with coupling to electron reservoir

$\Sigma_{jj} = \epsilon + i\eta$

ϵ: energy shift

η: level broadening

Update the density matrix by integrating the retarded Green's function

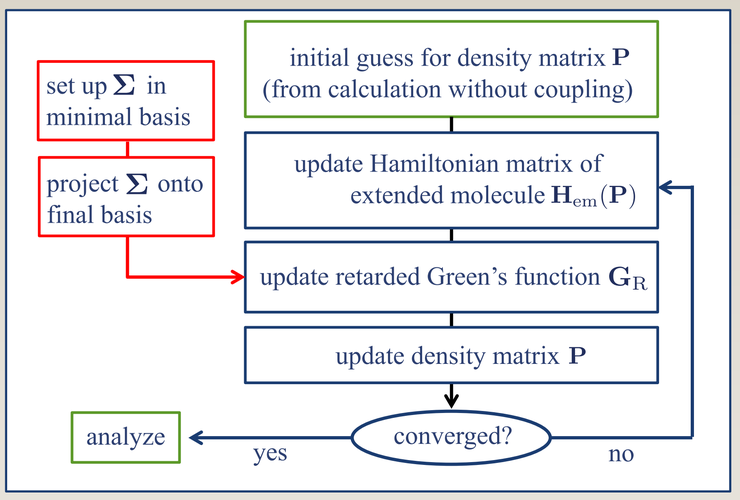
$$\mathbf{G}_\mathrm{R}(E) = (E\mathbf{I} - \mathbf{H}_\mathrm{em}(\mathbf{P}) - \mathbf{\Sigma})^{-1}$$

$$\mathbf{P} = \frac{1}{\pi}\int_{-\infty}^{\mu} \Im\mathbf{G}_\mathrm{R}(E)\mathrm{d}E$$

- The total number of electrons in the system can be controlled by the upper integration limit μ
- Coupling realized in minimal atomic orbital basis and later projected to final basis
- Formalism similar to molecular junctions without second reservoir [1]

Proof-of-principle implementation

Flowchart of the SCF procedure

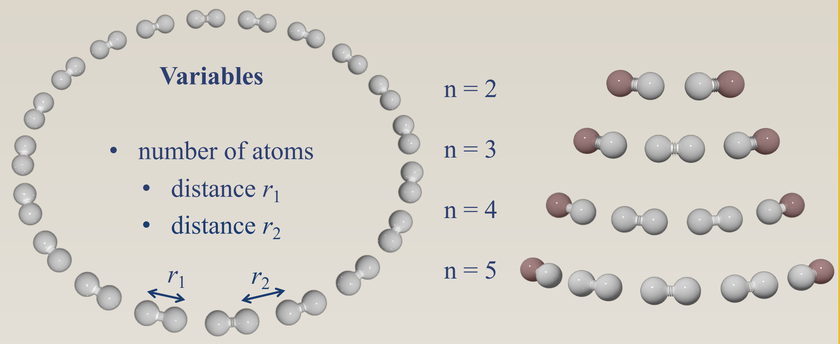


- Convergence acceleration with **density DIIS**
- **Analytical integration** to obtain density matrix

Determination of parameters

Quasi-infinite 1D model system: hydrogen rings

Simulate the full system → with just a few monomers



Optimized parameters to match the energy per fragment of a hydrogen ring with 40 atoms and $r_1 = r_2 = 0.74$ Å under the constraint of uncharged fragments.

n	2	3	4	5
η [a.u.]	0.05093	0.04965	0.04896	0.04871
$\mu - (\epsilon_\mathrm{HOMO} - \epsilon_\mathrm{LUMO})$ [E_H]	-0.24556	-0.18316	-0.14895	-0.12831

- Parameters can be tuned such that the fragments adapt certain properties of the full system
  → Tune parameters of the coupling model to mimick properties of the full nanocluster

Implicit electrolyte solvation model

Formalism

Poisson–Boltzmann equation

$$\nabla[\epsilon(\mathbf{r})\nabla\phi_\mathrm{tot}(\mathbf{r})] = -4\pi[\rho_\mathrm{sol}(\mathbf{r}) + \rho_\mathrm{ions}(\mathbf{r})]$$

with the electrolyte ion charge density for a 1:1 electrolyte

$$\rho^\mathrm{ions}_\mathrm{PB}(\mathbf{r}) = -2ec^b\sinh\left(\frac{e\phi_\mathrm{tot}(\mathbf{r})}{k_\mathrm{B}T}\right)$$

Total electrostatic free energy

$$G^\mathrm{es}_\mathrm{PB} = \int\left(\frac{1}{2}\rho_\mathrm{sol}(\mathbf{r})\phi_\mathrm{tot}(\mathbf{r}) - \frac{1}{2}\rho_\mathrm{ions}(\mathbf{r})\phi_\mathrm{tot}(\mathbf{r}) - \Delta\Pi_\mathrm{PB}\right)\mathrm{d}\mathbf{r}$$

Free energy of solvation

$$\Delta G^\mathrm{solv}_\mathrm{PB} = \frac{1}{2}\int\rho_\mathrm{sol}(\mathbf{r})(\phi_\mathrm{tot}(\mathbf{r}) - \phi_\mathrm{sol}(\mathbf{r}))\mathrm{d}\mathbf{r} - \frac{1}{2}\int\rho_\mathrm{ions}(\mathbf{r})\phi_\mathrm{tot}(\mathbf{r})\mathrm{d}\mathbf{r} + 2c^bk_\mathrm{B}T\int\left(1 - \cosh\left(\frac{e\phi_\mathrm{tot}(\mathbf{r})}{k_\mathrm{B}T}\right)\right)\mathrm{d}\mathbf{r}$$

Solver implementation:

- Extended Multigrid-Poisson solver in Q-Chem [2]
- Strong damping on the ion charge density update for stable convergence

Hierarchy of approximations

1. $q_i\phi_\mathrm{tot}(\mathbf{r}) << k_\mathrm{B}T$ **vs.** $q_i\phi_\mathrm{tot}(\mathbf{r}) \approx k_\mathrm{B}T$

For low ionic concentrations the Boltzmann factor can be approximated as a **linear** function of the electrostatic potential:

$$\exp\left(-\frac{q_i\phi_\mathrm{tot}(\mathbf{r})}{k_\mathrm{B}T}\right) \approx 1 - \frac{q_i\phi_\mathrm{tot}(\mathbf{r})}{k_\mathrm{B}T}$$

2. ⊕ ⊖ **vs.** ⊕ ⊖

Point-like ions accumulate unphysically close to the solute surface
→ Include a **finite ion size** by restricting the maximum local concentration

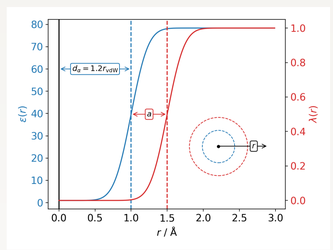
3. Stern-layer thickness

- Offset between dielectric region and ion accessible region to account for Stern layer [3]
- Modeled with error functions

$$\lambda(\mathbf{r}) = \prod_\alpha^\mathrm{atoms}\frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{|\mathbf{r} - \mathbf{R}_\alpha| - d_\alpha - a}{\Delta}\right)\right]$$

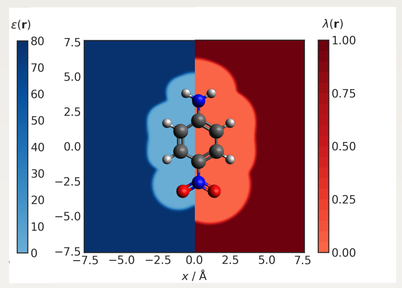
$\lambda(\mathbf{r}) =$ ion exclusion function

$a =$ Stern-layer thickness

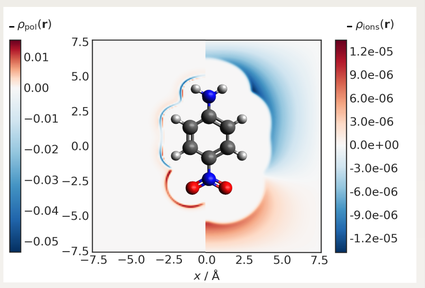


Dielectric function and ion exclusion function for a spherical solule.

Verification of implementation

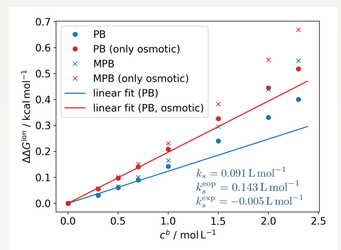


2D-cut of the dielectric function and ion exclusion function for 4-Nitroaniline.



2D-cut of the polarization charge density (the dielectric response) and the electrolyte ion charge density.

- Free energy of solvation changes linearly with electrolyte concentration over a wide range of concentrations (Sechenov coefficients)[4]



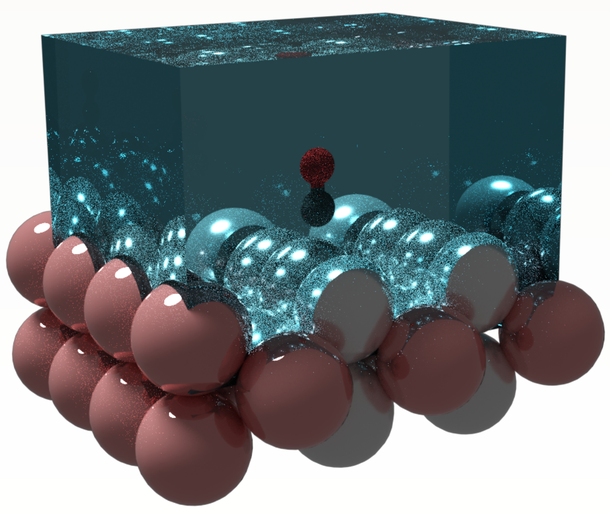
Ion effect on the free energy of solvation for the polar cytosine molecule obtained from the standard (PB) and size-modified (MPB) free energy expressions.

$$k_s = \frac{\Delta\Delta G^\mathrm{ion}}{c^b}\frac{\log_{10}(e)}{k_\mathrm{B}T}$$

- Excellent agreement for nonpolar molecules
- Less satisfying agreement for polar molecules
- Deviation from linear behavior with and without size-modification

Electrocatalysis

Combining both approaches



Combining the Poisson–Boltzmann implicit solvation model with the Green's function embedding model allows to **study electroctalytic reactions on nanoclusters under applied bias**.

Benefits

- Study catalytic reactions at surface structures that are not easily accessible for DFT programs with periodic boundary conditions such as undercoordinated sites [5]
- Applied bias can be naturally included with only one parameter
- Green's function embedding model can by systematically improved (e.g. tight-binding model for the coupling parameters [6])
- Poisson–Boltzmann implementation allows us to systematically analyze ion size effects

REFERENCES

[1] A. Arnold, F. Weigend, F. Evers, J. Chem. Phys. *126*, 174101 (**2007**).

[2] M. Coons, J. M. Herbert, J. Chem. Phys., *148*, 222834 (**2018**).

[3] S. Ringe, H. Oberhofer, K. Reuter, J. Chem. Phys., *146*, 134103 (**2017**).

[4] I. Sechenov, Ann. Chim. Phys. *25*, 226 (**1892**).

[5] Y. Li, F. Cui, M. B. Ross, D. Kim, Y. Sun, P. Yang, Nano Lett., *17*, 1312, (**2017**).

[6] Y. Xue, S. Datta, M. A. Ratner, Chem. Phys., *281*, 151 (**2002**).

This work was supported through the Scientific Discovery through Advanced Computing (SciDAC) program funded by the U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Sciences.