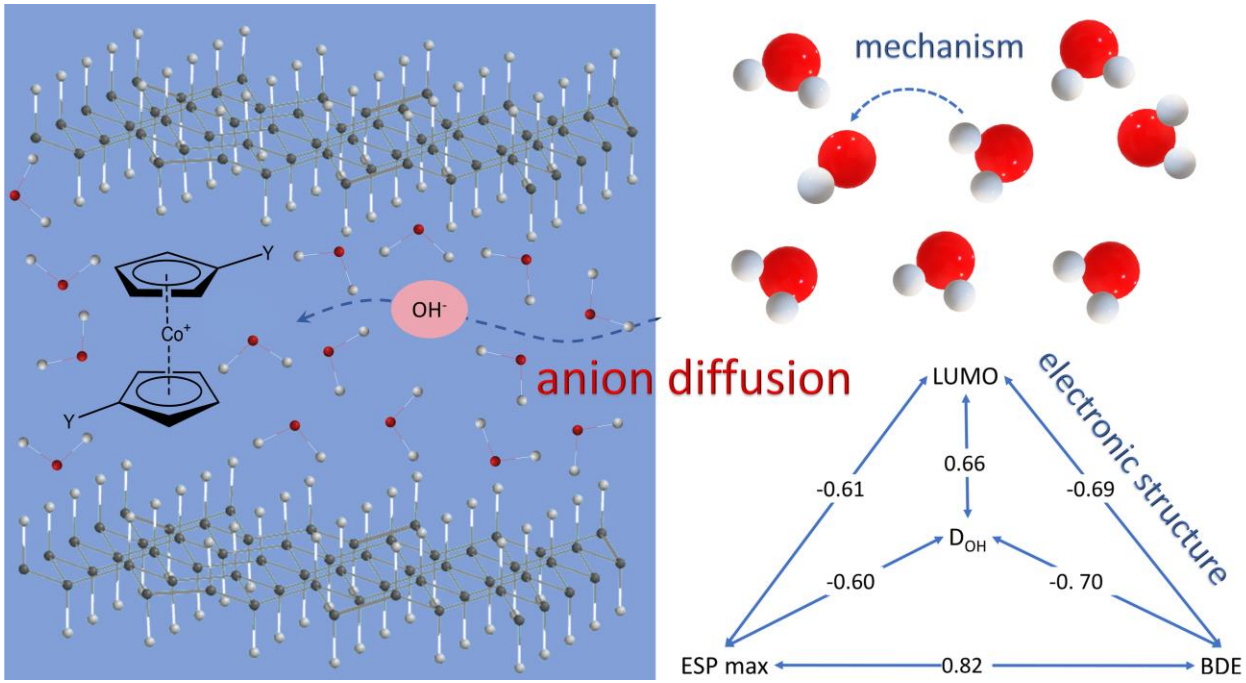
Theoretical Examination of the Hydroxide Transport in Cobaltocenium-Containing Polyelectrolytes



Sachith Wickramasinghe

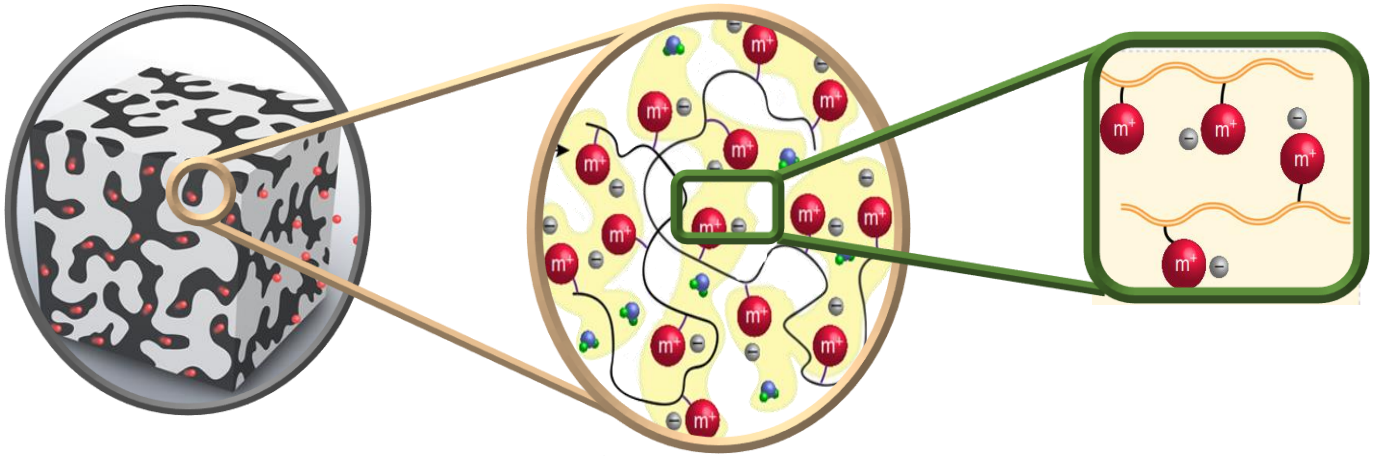
Department of Chemistry and Biochemistry

University of South Carolina

November 22nd, 2023

UNIVERSITY OF SOUTH CAROLINA

Metallo-Polyelectrolytes For hydroxyl Ion Transport



Focus on hydroxyl transport

Enhance the ionic conductivity

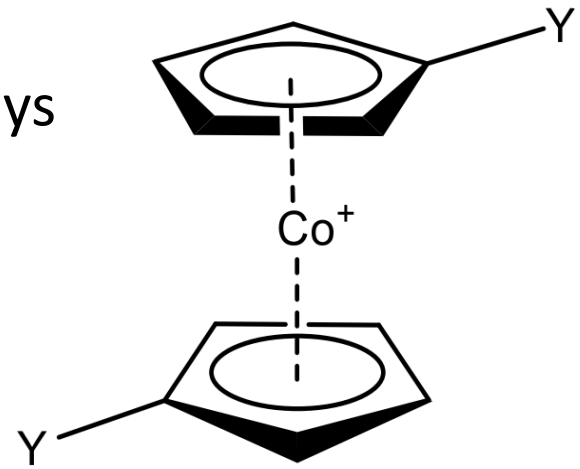
Examine the mechanisms and the pathways

Vehicular and structural diffusion

NQE

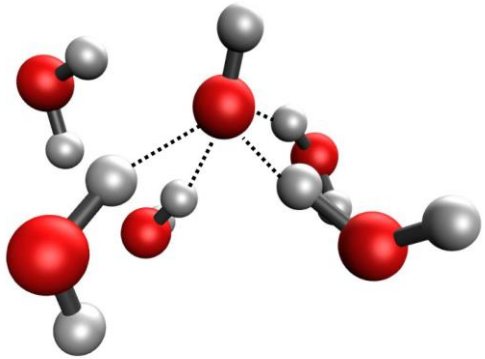
Hydration level

Substituent on the cation

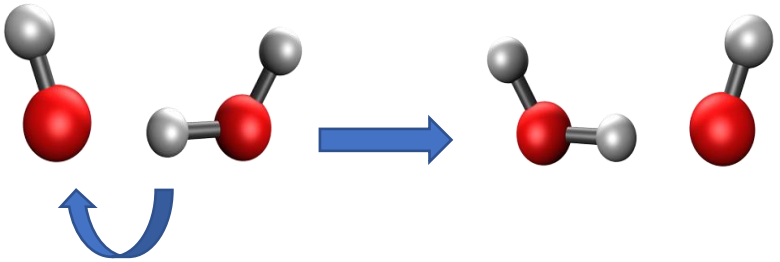


Mechanisms of Diffusion

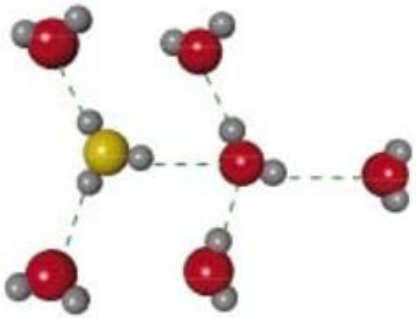
Vehicular diffusion

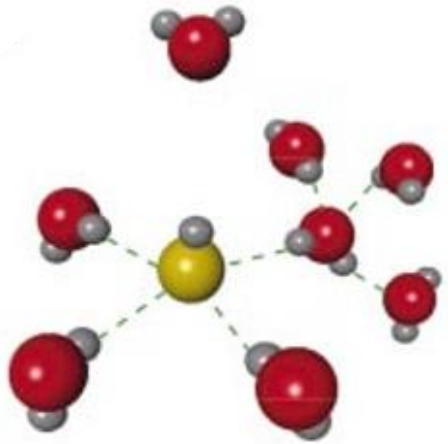


Hopping



Hydroxide vs Proton Hopping

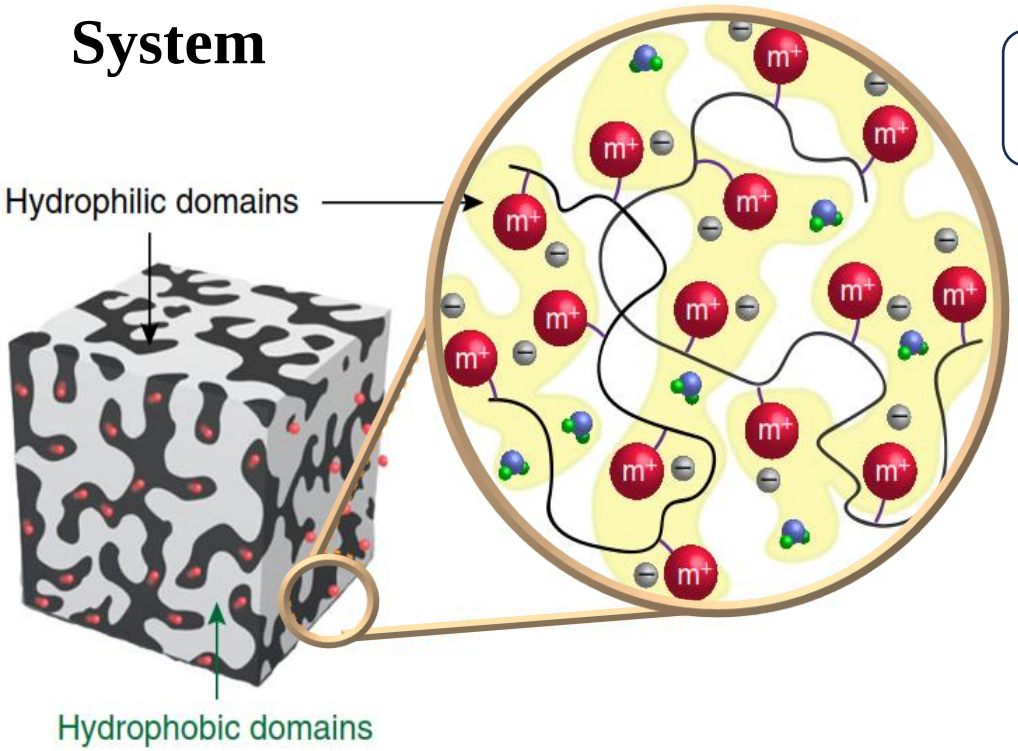




Tuckerman, Mark E., Dominik Marx, and Michele Parrinello. "The nature and transport mechanism of hydrated hydroxide ions in aqueous solution. " *Nature* 417.6892 (2002): 925-929.

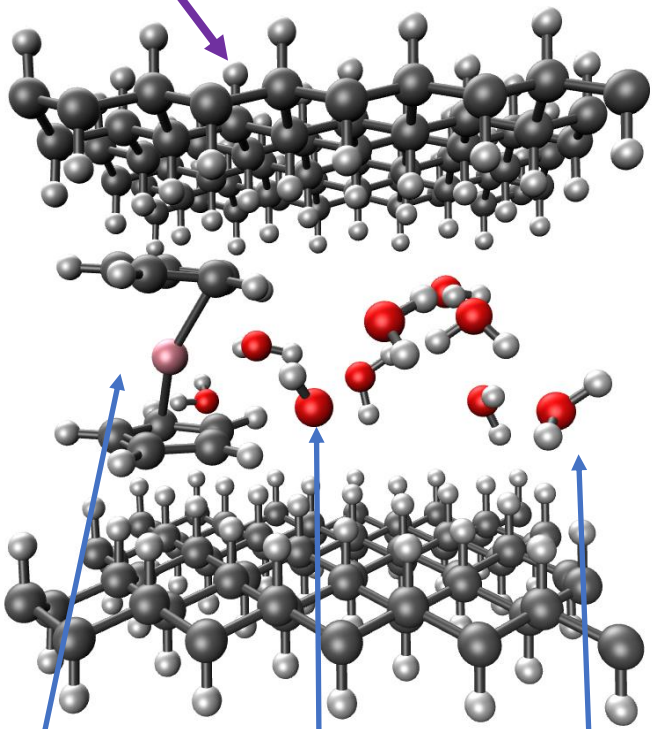
MODELING

System



Molecular model

graphane sheets
mimic polymeric back bone

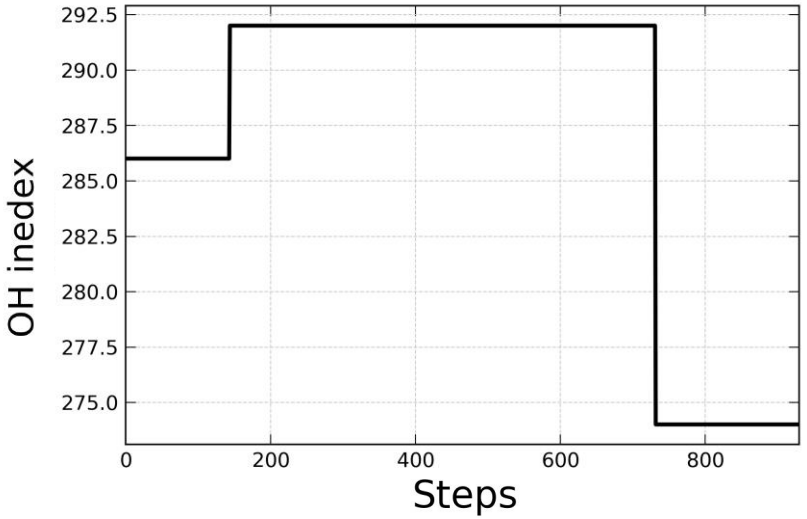


cobaltocenium cation | hydroxide | water

- Molecular Dynamics (**MD**)
- **DFTB**

Estimation of Diffusion Coefficient

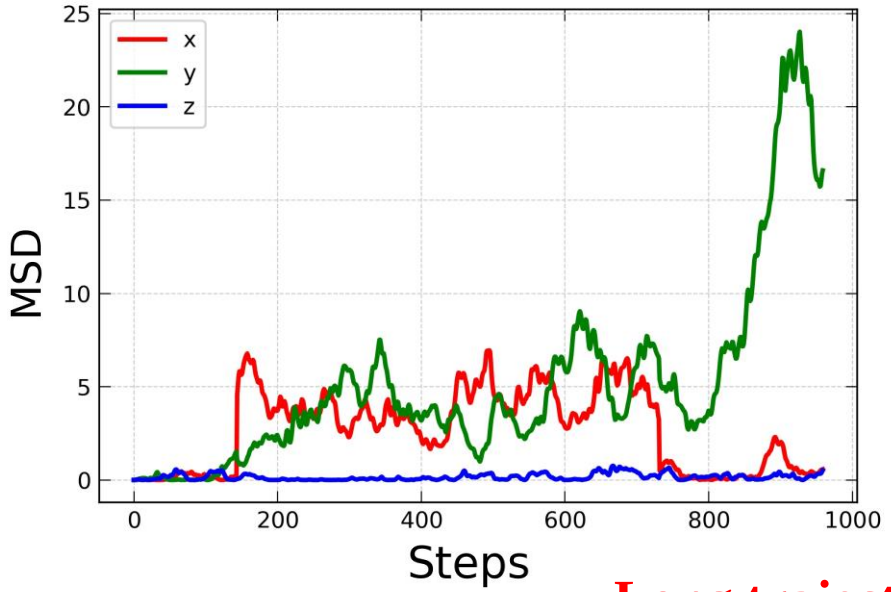
10-40 water molecules
Xbox = 12.66 Å dt = 1fs
Ybox = 13.36 Å 20 ps



Hydroxide moves between cobaltocenium groups

Multiple hops occur

Rattling is removed from the analysis



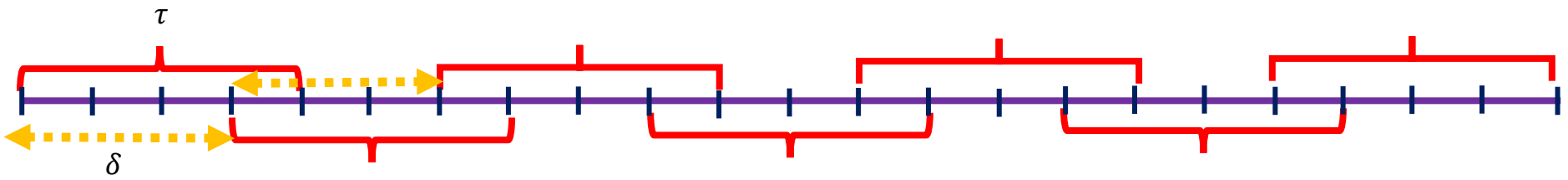
$$MSD(t) = \frac{1}{N}\sum_{n=1}^{N}\left(\vec{r}^{(n)}(t) - \vec{r}^{(n)}(0)\right)^2$$

$$D = \lim_{t\to\infty}\frac{1}{2n_d}\frac{MSD}{t}$$

Long trajectory is needed

Estimation of Diffusion Coefficient

Time-averaged method of calculating D



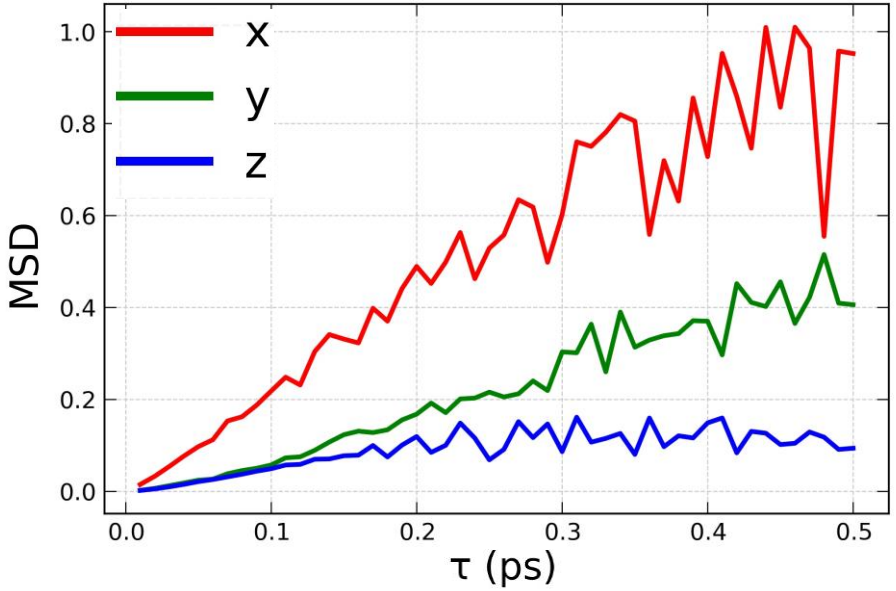
τ : length of a time interval

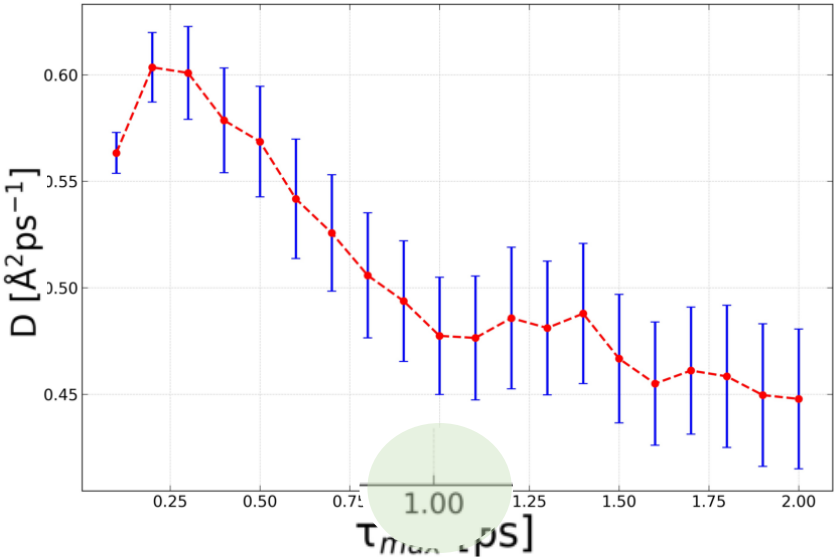
δ : the distance between the time origins of two consecutive time intervals

$$\delta \geq \tau$$

$$MSD(\tau,\delta) = \frac{1}{n_\tau}\sum_{j=0}^{n_\tau}\left(\frac{1}{N}\sum_{n=1}^{N}\left(r^{(n)}(j\delta+\tau) - r^{(n)}(j\delta)\right)^2\right)$$

$$MSD(\tau) = \frac{1}{n_\tau}\sum_{j=0}^{n_\tau}\left(r(j\tau+\tau) - r(j\tau)\right)^2$$





Pranami, G.; Lamm, M. H. Estimating error in diffusion coefficients derived from molecular dynamics simulations. *J. Chem. Theory Comput.* **2015**,11, 4586–4592.

USE OF REPLICAS

MSD OF SINGLE MOLECULE IS NOISY

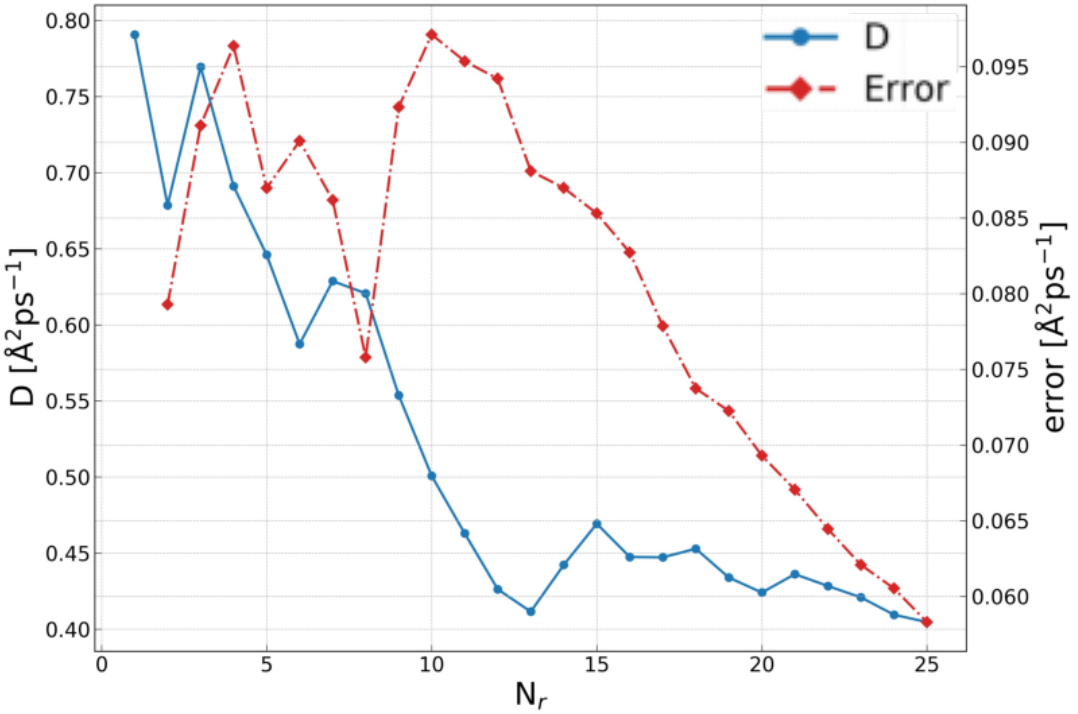
- Same cell geometry
- Same cation separation
- Same number of water

$$\bar{D} = \frac{1}{N}\sum_{n=1}^{N} D^{(n)}$$

$$\sigma_D = \frac{1}{\sqrt{N}}\left(\sum_{n=1}^{N}(D^{(n)} - \bar{D})^2\right)^{1/2}$$

Use Replicas

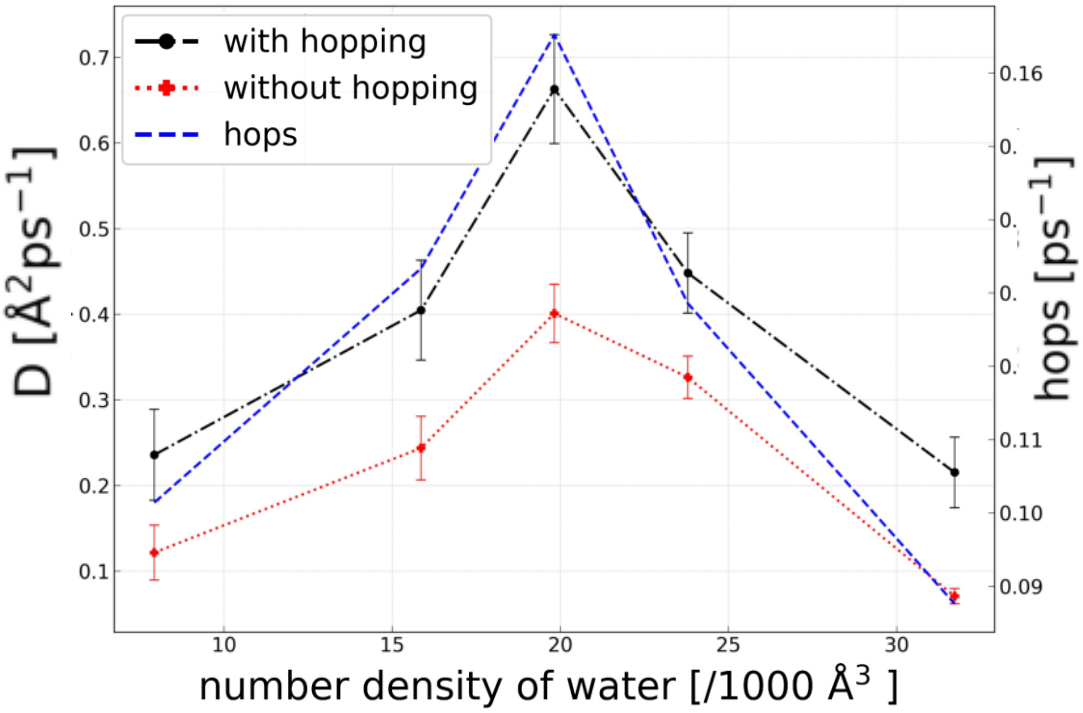
- Different initial position of water and OH^-
- Different initial velocities for thermalization



RUN TRAJECTORIES IN PARALLEL

Diffusion Coefficient at Different Hydration Levels

ρ	D_{OH}	D_O
7.9	0.24	1.06
15.9	0.40	0.86
19.8	0.66	0.72
23.8	0.45	0.48
31.7	0.22	0.07



D_{OH} changes significantly with water density

Lowest and highest densities exhibit low D_{OH}

Maximum D_{OH} (~0.7Å^2/ps) at ~60% of bulk

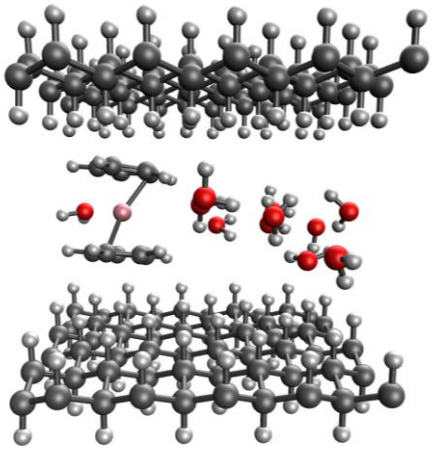
D_{OH} correlates with the number of hops

Low densities: electrostatic interaction
Hopping incurrences D_{OH} by ~2

Wickramasinghe, Sachith, et al. "Theoretical Examination of the Hydroxide Transport in Cobaltocenium-Containing Polyelectrolytes." **J. Phys. Chem. B** (2023).

Diffusion Coefficient with Different Hydration Levels

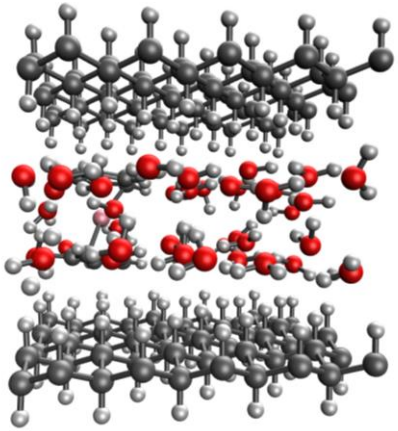
Low water density



Water molecules are nearly free

Hydroxide lacks a well-formed solvation shell, thus low diffusion

High water density

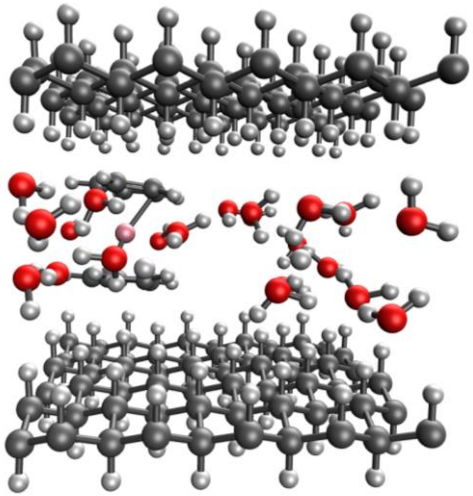


Water molecules form two layers

Domain size and mobility are reduced

Diffusion rates decrease due to increased confinement

Medium water density



Hydroxide is well solvated

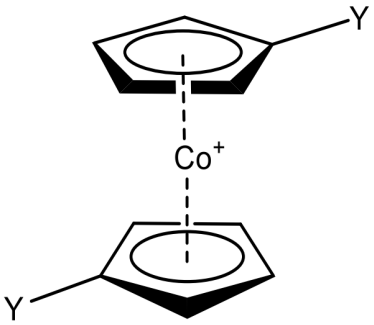
Less coulombic attraction

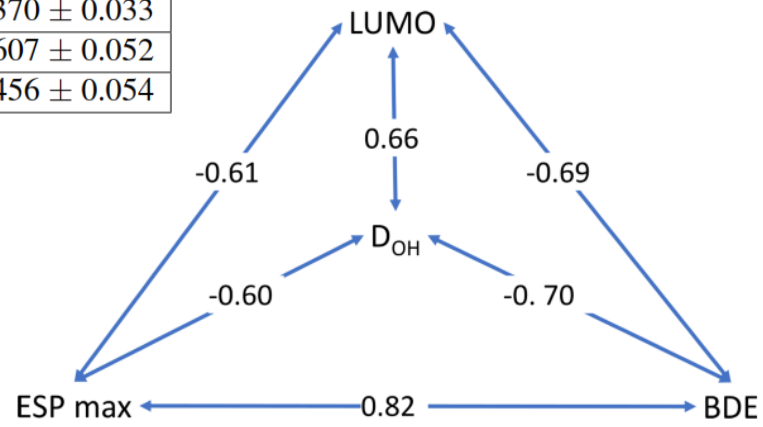
Highest hopping rate

Wickramasinghe, Sachith, et al. "Theoretical Examination of the Hydroxide Transport in Cobaltocenium-Containing Polyelectrolytes." **J. Phys. Chem. B** (2023).

Substituent Effect on Hydroxide Diffusion

Y	D_{OH} [Å^2/ps]
$N(CH_3)_2$	0.609 ± 0.054
OCH_3	0.690 ± 0.075
Ph	0.589 ± 0.063
C_2H_3	0.719 ± 0.063
CH_3	0.773 ± 0.072
H	0.398 ± 0.058
$(CO)NH_2$	0.442 ± 0.050
$(CO)OCH_3$	0.485 ± 0.050
(CO)H	0.527 ± 0.050
CN	0.605 ± 0.064
NO_2	0.370 ± 0.033
C_2H	0.607 ± 0.052
$(CO)CH_3$	0.456 ± 0.054





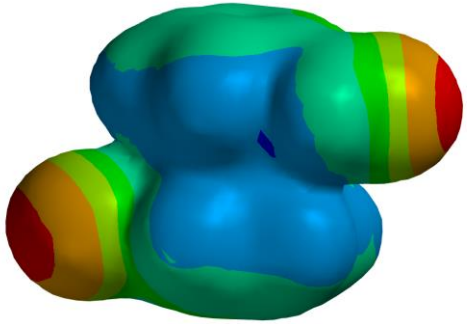
D_{OH} highly correlates with ESP max, cation LUMO, and BDE

No correlation with dipole moment

Positive ESP max indicates strong surface charges attracting hydroxyl ions

Lower LUMO attracts the hydroxide electrons

High BDE values indicate stronger hydroxide binding to cation, reducing mobility

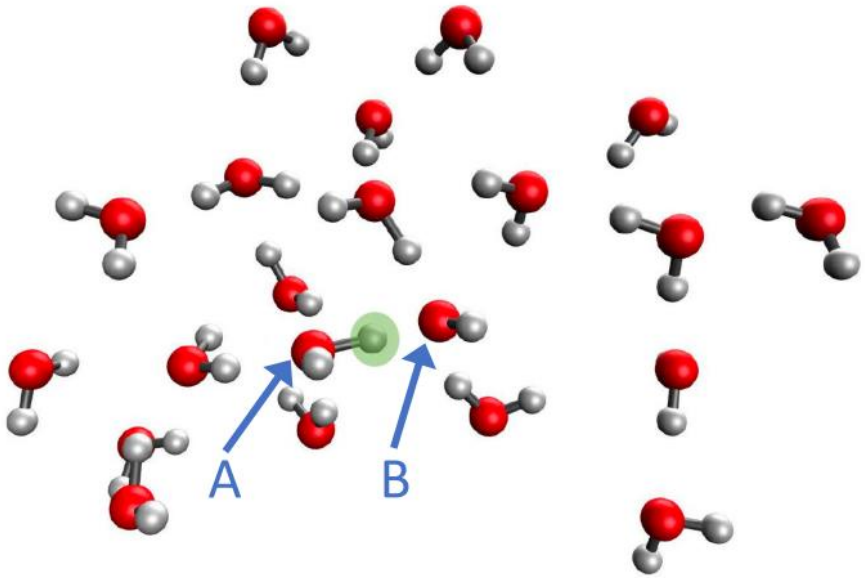


$$BDE = (E_{cation} + E_{hydroxide}) - E_{complex}$$

Modifying the cation can enhance anion mobility

Wickramasinghe, Sachith, et al. "Theoretical Examination of the Hydroxide Transport in Cobaltocenium-Containing Polyelectrolytes." **J. Phys. Chem. B** (2023).

NUCLEAR QUANTUM EFFECTS ON PROTON HOPPING



$$r := |\mathrm{HO}^B| - |\mathrm{HO}^A|$$

Hopping is affected by nuclear quantum effects (NQEs)

Time-dependent PES is constructed using 13 snapshots

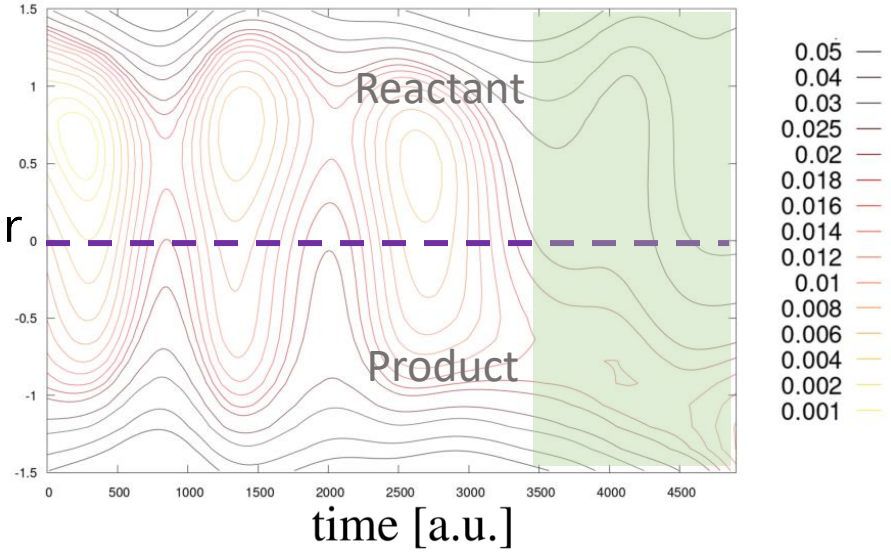
PES is obtained from the partial energy minimization with respect to the positions of the hydrogen atoms attached to the donor and acceptor oxygens

NUCLEAR QUANTUM EFFECTS ON PROTON HOPPING

$$\psi = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\alpha(r-r_0)^2 + \frac{i}{\hbar}p_0(r-r_0)\right)$$

α : harmonic approximation at the initial position

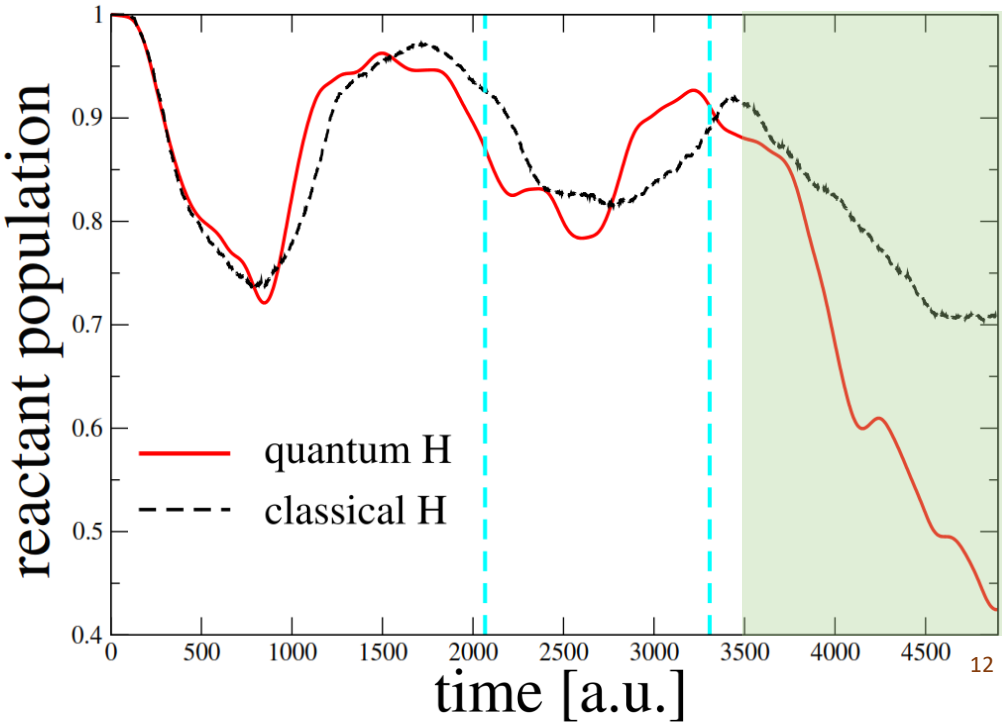
p_0 : translational energy corresponds to 300 K



2000 classical trajectories sampled from the Wigner distribution

60% of the quantum proton wavefunction enters potential energy well

30% of the classical trajectories



SUMMARY

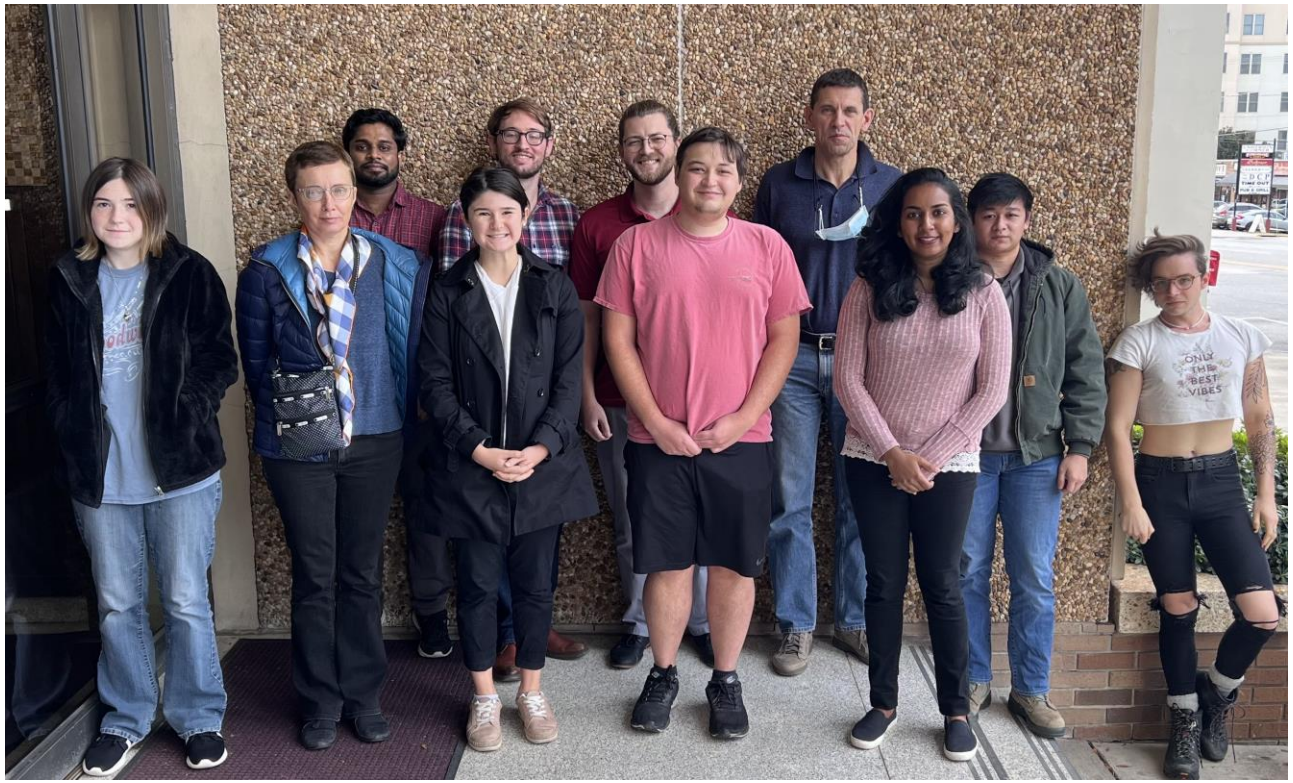
- Both vehicular and structural diffusion mechanisms are important.
  Hopping can incurrences D_{OH} by ~2

- The highest diffusion coefficients (~0.7 $Å^2$/ps) is at moderate hydration levels (~60% liquid water density).
  Sufficient water molecules and space for proton hopping.

- Hydroxide diffusion correlates with electrostatic potential maximum, complex dissociation energy, and energy of the cation LUMO.
  Chemical modification of the cation can enhance anion mobility

- The NQE increases hopping probability by ~ 2 compared to the classical probability.

ACKNOWLEDGEMENT



Special thanks to:
Prof. Sophya Garashchuk
Prof. Vitaly Rassolov

Collaborators:
Prof. Chuanbing Tang
Prof. Qi Wang
Dr. Jacek Jakowski
Dr. Shehani Weththasinghe
Alexandria Hoehn

Funding:

Thank you!