Hybrid Combination of Quantum Mechanics with Quantum-based Polarizable Reactive Force Field for Large Scale Full Solvent Simulations of Electrocatalysis

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Abstract:

To develop new generations of electrocatalysts required for energy and environmental sustainability, we need the accuracy of full solvent QM (free energy barriers to 0.05 eV, onset potentials to 0.05 V) but for practical sized nanoparticles and catalysts (1000's to millions of atoms). We report here a solution to this problem. We start with the RexPoN reactive force field that provides higher accuracy than DFT and combine it with QM to accurately include long-range interactions and polarization effects to enable reactive simulations with QM accuracy in the presence of solvent including 1000's to millions of waters. Here we apply this RexPoN embedded QM (ReQM) to reactive simulations of electrocatalysis demonstrating that ReQM accurately replaces DFT water for computing the Raman frequencies of reaction intermediates during CO_2 reduction to ethylene, with comparisons to operando electrocatalysis experiments and to full solvent QM calculations.

Introduction

The first detailed reaction mechanisms for CO reduction on Cu surface have been predicted from QM (Cheng et al.). We now want to extend such calculations from the QM scale of ~300 atoms and ~5 ps to more realistic models of the electrochemical cell with ~10x10 nm² electrodes and 100 nm of solvent between the electrodes for time scales of milliseconds. We report a hybrid computation framework (ReQM) that efficiently includes accurate long-range interactions and polarization effects at the electrode-electrolyte interface to predict complex reactions in the presence of a realistic description of solvent while retaining the accuracy of full solvent QM. In addition, we combine ReQM with machine learning techniques and use it to identify active sites of disordered Au surfaces including Au nanoparticles and dealloyed Au surfaces. This enables in silico design toward dramatically improved electrocatalysts and many other applications.

Team

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Research Plans

- Development of a polarizable reactive force field (RexPoN) for CO reduction on Cu surface.
- Development of RexPON embedded QM (ReQM) package
- Computing the Raman frequencies of reaction intermediates during CO2RR.
- Combination of ReQM and machine learning for nanoparticles of catalyst

Acknowledgments

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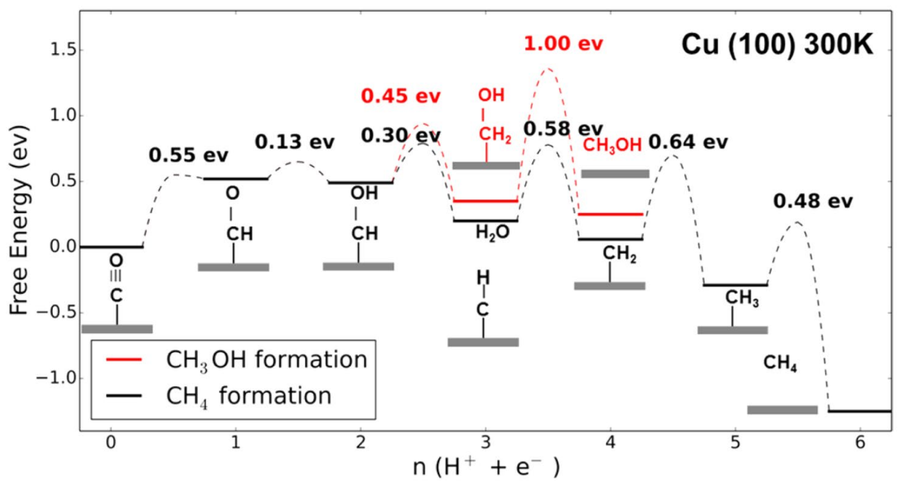
Results, Highlights, and Accomplishments

Quantum Mechanics (QM)

- Lowest-energy pathways for the electro-reduction of CO to methane on Cu(100) at pHo (CH_4, in black) and methanol (CH_3OH, in red)[1].



[1]T. Cheng, H. Xiao, and W. A. Goddard, III, *J. Phys. Chem. Lett.* 2015, **6**, 4767−4773

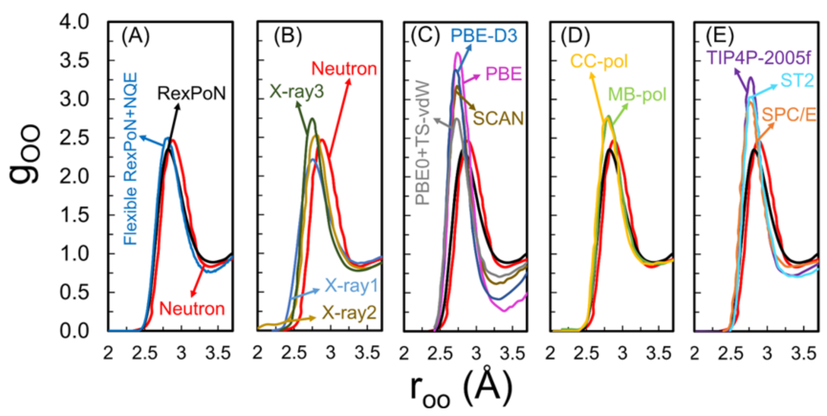
RexPoN: QM-based Polarizable Reactive Force Field

- RexPoN provides the most accurate predictions of water properties **(better than DFT)** compare to any other QM-based or empirical models[2].

Property	Expt.	RexPoN	TIP3P	SPC/E	PBE	MB-pol
Melting temp. (K)	**273.15**	**273.5**	146	215	420	263.5
Entropy (J/mol/K)	**69.9**	**68.43**	72.51	60.30	51.32	-
Density (g/cm³)	**0.9965**	**0.9965**	0.98	0.994	0.944	1.007
Dielectric constant	**78.4**	**76.1**	94	68	112	68.4
Heat of vap. (kcal/mol)	**10.52**	**10.36**	10.05	11.79	6.20	10.93
RDF 1st peak position (Å)	**2.86**	**2.84**	2.79	2.75	2.71	2.81
RDF 1st peak height	**2.50**	**2.34**	2.79	3.05	3.69	2.76

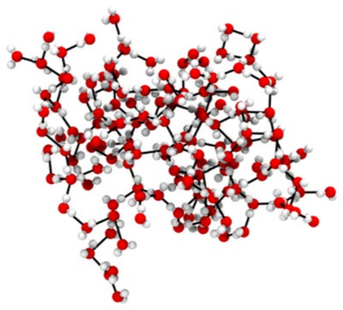
[2] S. Naserifar and W. A. Goddard III, *J. Chem. Phys.*, 149,174502 (2018)

- RexPoN can correctly explain the structure in the first coordination shell.

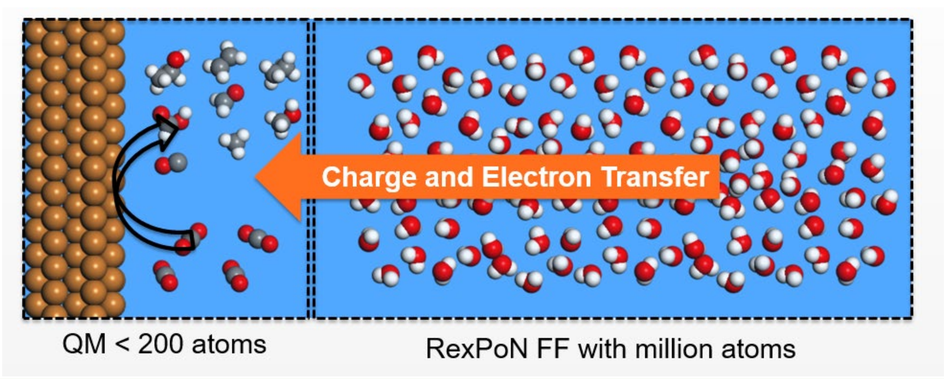


- Liquid Water is a Dynamic Branched Polymer

S. Naserifar and W. A. Goddard, *Proc. Natl. Acad. Sci.*, 116, 1998 (2019)

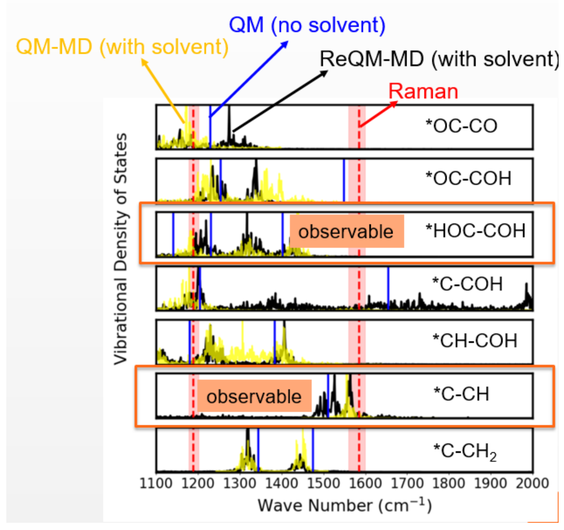


RexPoN Embedded QM (ReQM)



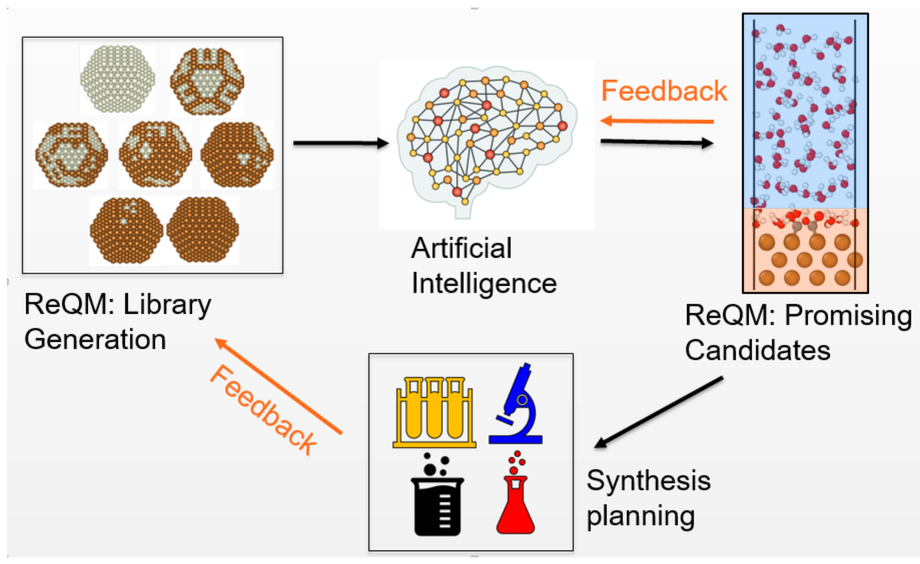
Results

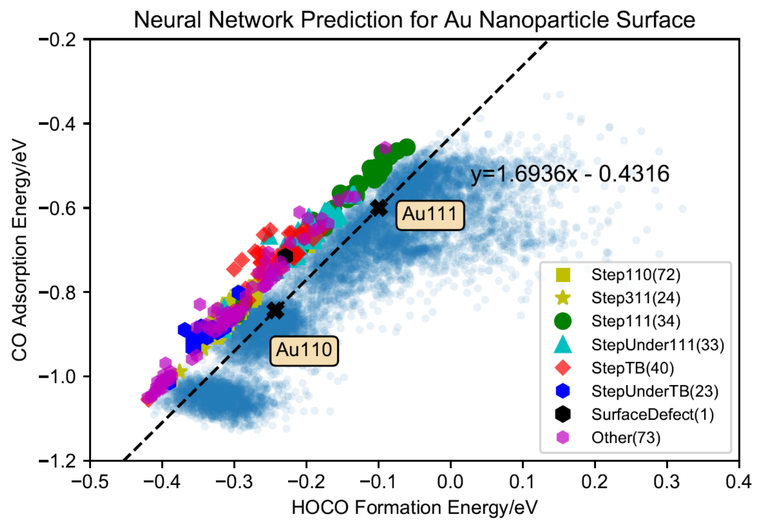
- Identifying reaction intermediates during CO2RR



Moving from Surfaces to Nanoparticles with AI

- Identifying Active Sites of disordered Au surfaces: Au nanoparticles and dealloyed Au surfaces using combination of ReQM and Artificial Intelligence (AI)





- a-Value Mapping and Catalytic Activity Visualization.