BERKELEY LAB

SciDAC
Scientific Discovery through Advanced Computing

SciDAC 4 Scientific Partnership:

Advancing Catalysis Modeling:
From Atomistic Chemistry to Whole System Simulation

Martin Head-Gordon,

Alex Bell, Emily Carter (Princeton), Sharon Hammes-Schiffer (Yale), Teresa Head-Gordon, Khaled Ibrahim, Xiaoye Li, David Limmer, Lin Lin, Esmond Ng, Sam Williams, Chao Yang

Advancing catalysis modeling: Outline

1. **Example: CO2RR catalysis to C2 products on Cu**

Alejandro Garza, A.T. Bell, MHG,
ACS Catalysis 8, 1490 (2018)

2. **Overview of the project and the team**

3. **A deeper look: Electronic structure**

4. **A deeper look: Dynamics and statistical mechanics**

Why is the CO_2RR a challenge for catalysis? Electrocatalytic data

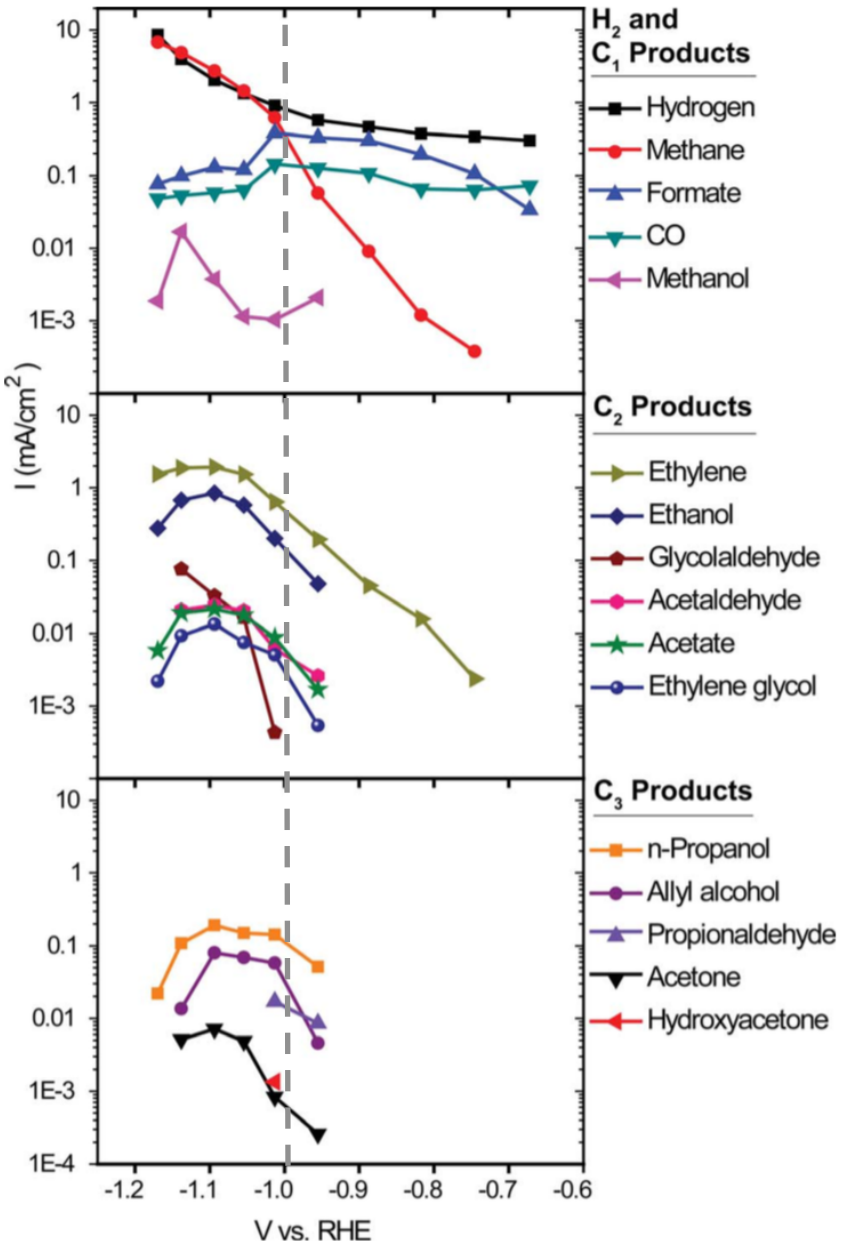
Electrode	Potential (V) vs. *nhe*	Current density ($mA\ cm^{-2}$)	Faradaic efficiency/% CH_4	C_2H_4	EtOH	PrOH	CO	$HCOO^-$	H_2
Cu	−1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5
Au	−1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2
Ag	−1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4
Zn	−1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9
Pd	−1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2
Ga	−1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0
Pb	−1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0
Hg	−1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0
In	−1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3
Sn	−1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6
Cd	−1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4
Tl	−1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2
Ni	−1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9
Fe	−0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8
Pt	−1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7
Ti	−1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7

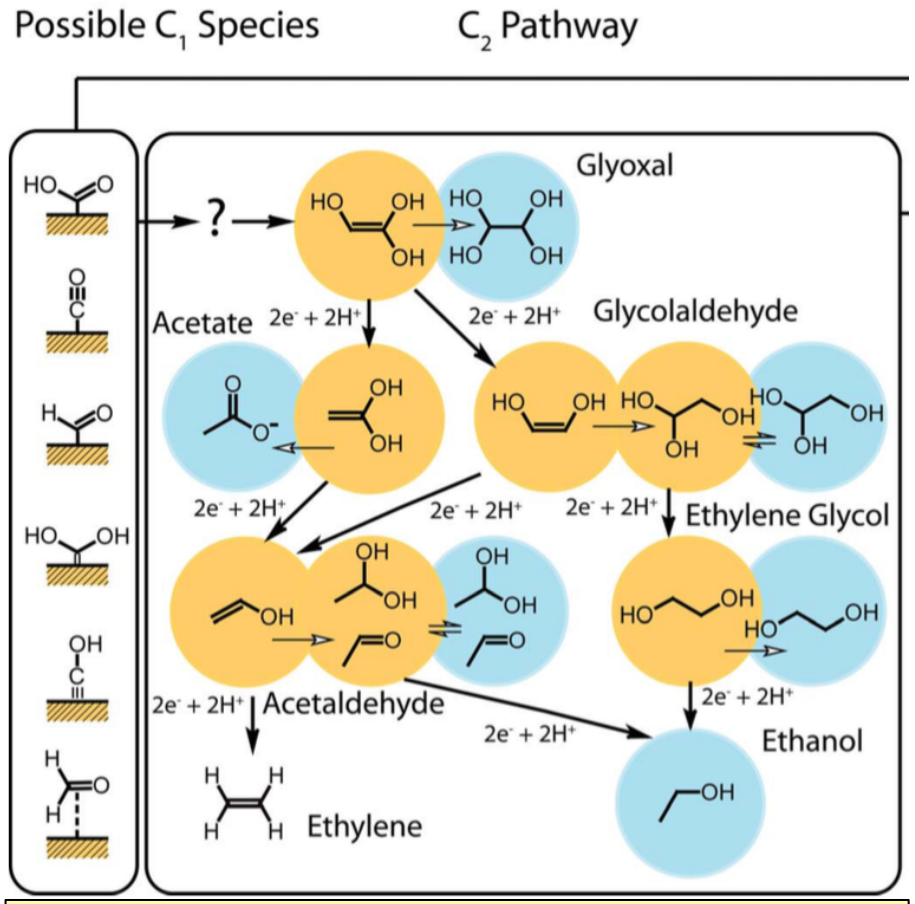
(1) **Only copper** reduces CO_2 to CH_4, C_2H_4, and alcohols. But it has a **high overpotential**, and produces a product **mixture**.

(2) The **Hydrogen evolution reaction** (HER) **competes** with CO_2RR for the input electrical energy.

Hori et al. *Electrochim. Acta* **1994**, 39, 1833

Experimental Constraints on Pathways to Products from CO2RR on Cu(100)





4 C1 products, **6** C2 products

K. Kuhl, E.R. Cave, D.N. Abram T.F. Jaramillo, Energy Environ. Sci., 2012, 5, 7050

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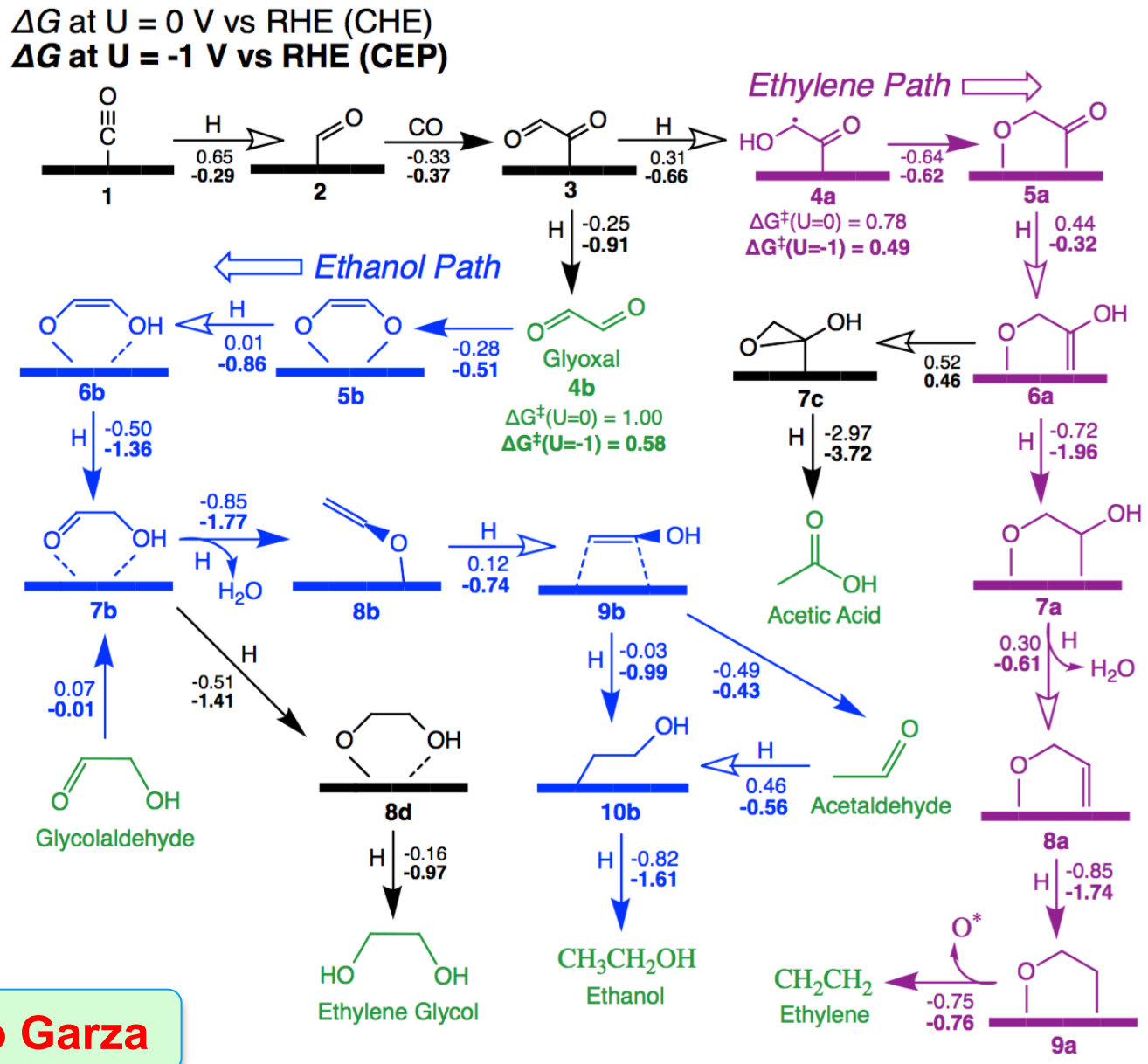
Full Calculated Mechanism for C2 product formation via CO2RR



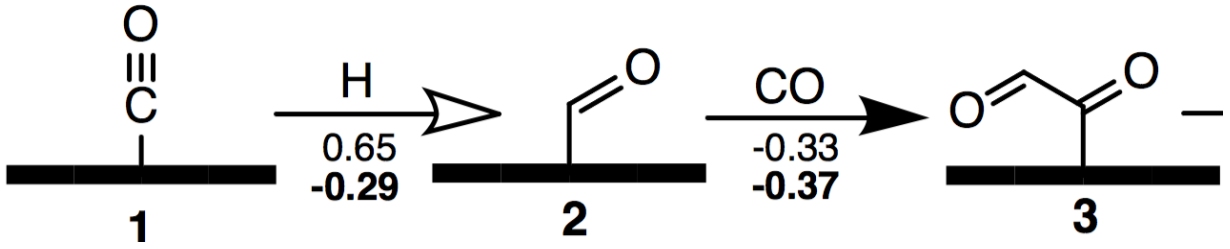
Alejandro Garza

Critical Steps: C-C Bond Formation

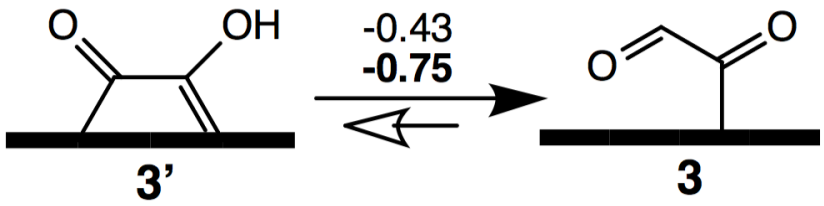
CO dimerization vs CHO/CO coupling vs COH/CO coupling vs CHO/CHO coupling etc.

*CO+*CHO→*COCHO is favored over CO dimerization, more so at high potential.

*CHO dimerization is feasible also, but unlikely due to low surface concentration.



*COCHO, 3, is favored over its tautomer, 3', avoiding double bonds to the surface.



pH dependence suggests that RDS does not involve a proton…

.... which is satisfied if C-C bond formation is the RDS (ie. all pathways allowed)

Alejandro Garza

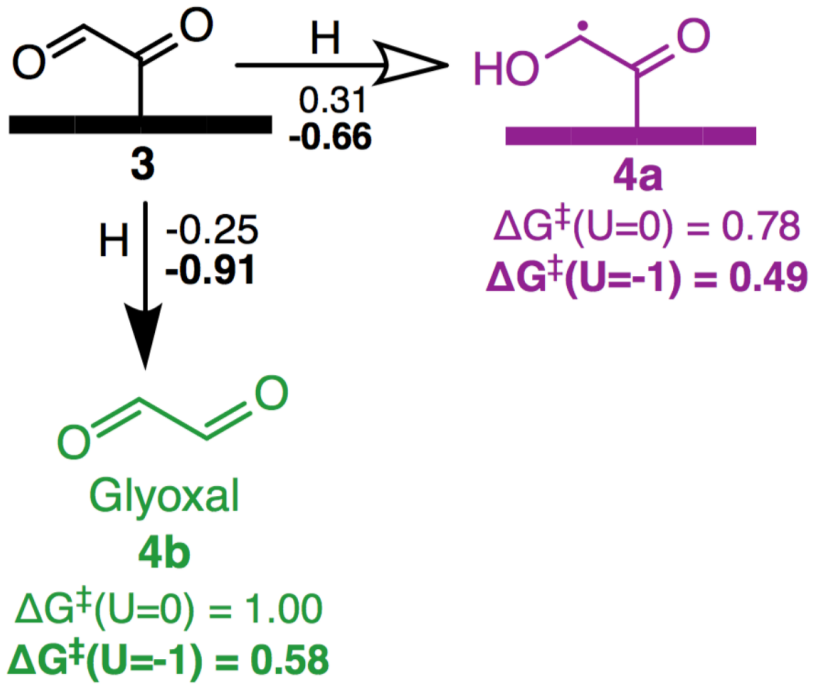
Critical steps: Branching between ethene and ethanol formation

Intermediate 3 can be reduced/ protonated at two sites, one yielding glyoxal, the other giving *COCHOH.

Glyoxal is the gateway to forming ethanol. *COCHOH is the gateway to ethene formation. Consistent with experiments showing no ethene production from feeding glyoxal

The higher barrier to glyoxal determines the observed selectivity for ethene. Barrier height difference is roughly consistent with experimental branching ratio (5:1 ethene to ethanol seen)

Low amounts of glyoxal detected experimentally are consistent with the subsequent path to ethanol being downhill.



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CO2RR on Cu(100) to C2 products: Conclusions

A unified mechanism that can account for all present experimental observations has been developed:

(a) Explains all 7 species detected

(b) Accounts for ethene and ethanol being typically the major products

(c) Accounts for the selectivity to ethene

(d) Explains reduction of glyoxal and glycoaldehyde to acetaldehyde at low potentials

(e) … and to ethanol at high potentials

(f) Can account for why ethylene glycol is not reduced when fed

(g) Can account for the reduction of ethylene oxide to ethene

Alejandro Garza

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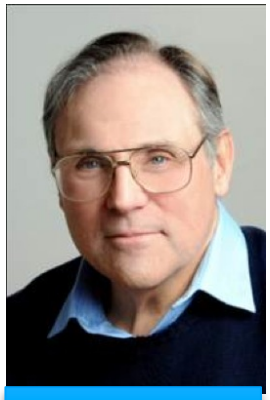
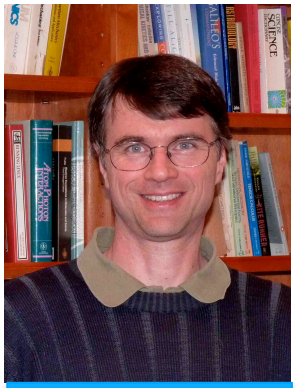
SciDAC-4 Partnership Team



Alex Bell

Emily Carter

Sharon Hammes-Schiffer



Martin Head-Gordon

Teresa Head-Gordon

Khaled Ibrahim

David Limmer

Sherry Li

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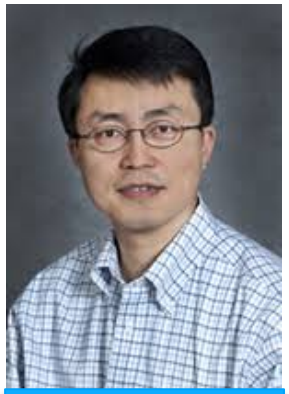
Esmond Ng

Sam Williams



Chao Yang

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Computational methods for CO2RR on Cu illustrate opportunities

a) RPBE density functional. An inexpensive GGA that is far inferior to hybrids, let alone wavefunction theory.

b) A 3-layer slab, with 8 atoms on the Cu(100) surface; Spacing along surface normal was more than 20 Angstroms; 500 eV plane wave cutoff

c) Implicit solvation + electrolyte: 0.1 M "KHCO3". No specific molecular solvation or electrolyte ions.

d) Computational hydrogen electrode, and a more expensive applied bias model (-1 V vs RHE). Partly grand-canonical.

e) The VASP package was used, with the VASPsol extension.

General objectives for the Partnership

Physical sciences objectives:

Advance the level of modeling used for electronic structure theory

Push towards explicit solvent, NQEs and converged statistical mechanics

Integrate microkinetics with transport for whole system modeling

Applied math and computer science objectives:

Deployment of new algorithms/solvers in this application domain

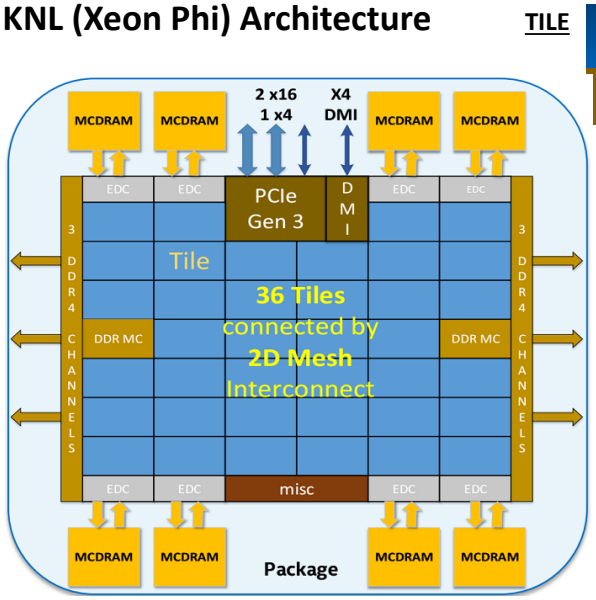
Pursue opportunities for new algorithm development (partnerships)

Improve parallel scaling for deployment on today's leadership computers

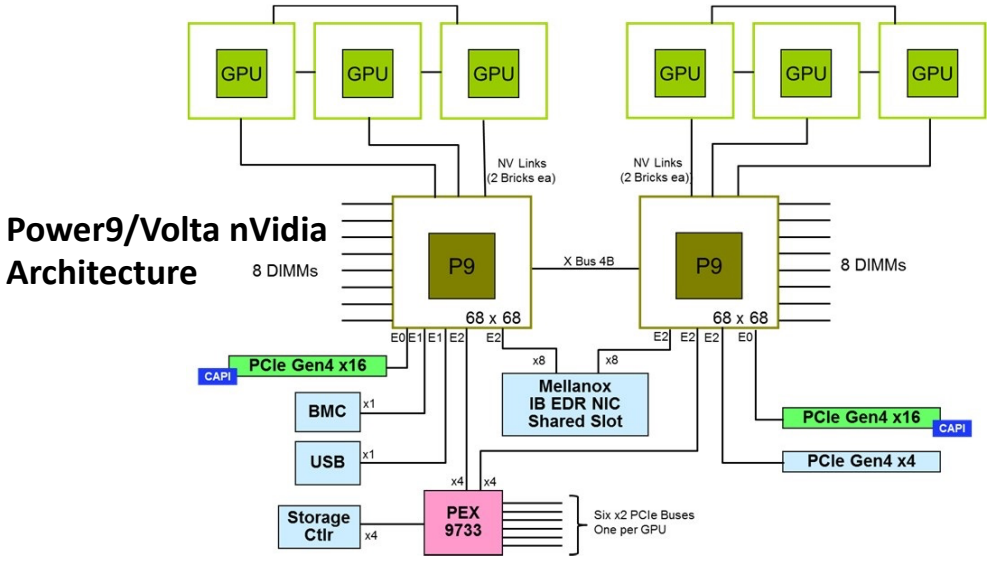
Advise / consult / develop new parallel algorithms with physical scientists

Target HPC architectures (Ibrahim, Williams, and RAPIDS)

KNL (Xeon Phi) Architecture



Power9/Volta nVidia Architecture



- **HPC Architectural heterogeneity**
  - **End of Moore's Law**
  - **Cores**
    - Lightweight cores for throughput **computation.**
    - **Latency optimized complex core.**
  - **Distributed Cache Hierarchy**
    - **Needed for many core architecture.**
  - Memory:
    - **Multiple classes**
    - Capacity/latency/Bandwidth tradeoffs
  - **Accelerators**
- **Target HPC systems (the first two are main focus so far)**
  - **Multi-core architecture (Cori I)**
  - **KNL-based (Cori-II)**
  - **Power/GPU accelerator-based architecture (**Summit)

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DFT: testing 100 functionals across 5000 trusted data points

	RPBE	M06-L-D3	B97M-V	ωB97M-V
NCE	3.4	0.40	0.24	0.18
IE	2.0	0.73	0.27	0.27
TCE	9.7	5.5	3.6	2.5
BH	7.6	6.8	4.4	1.7

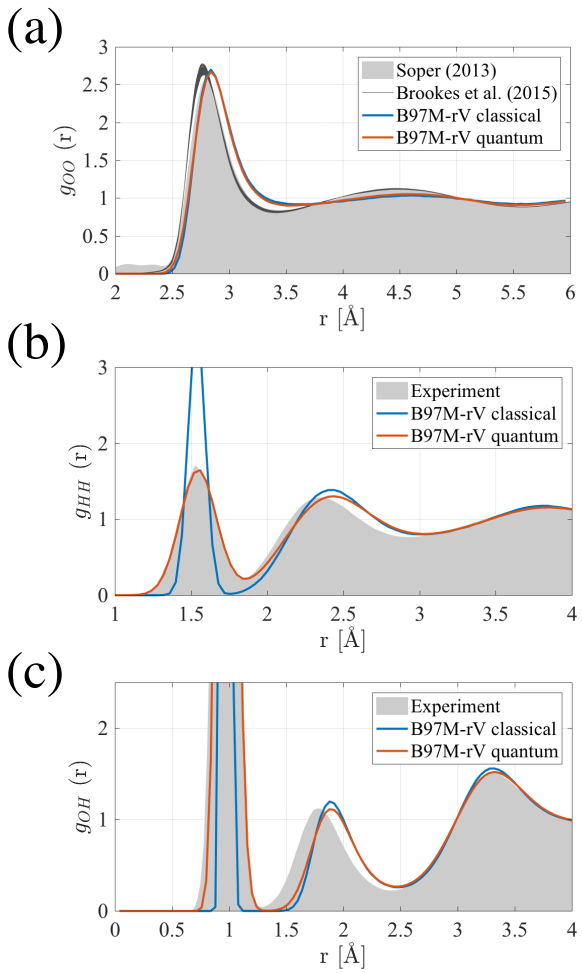
"Easy" RMS errors (kcal/mol).

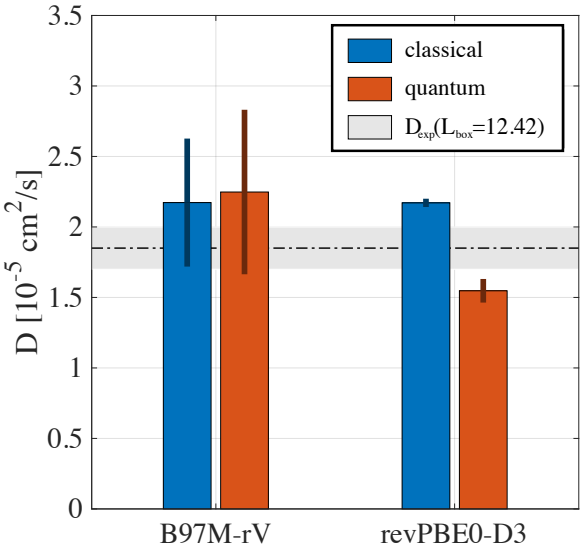
NC = noncovalent, I = isomers, TC = thermochemistry BH = barrier heights.

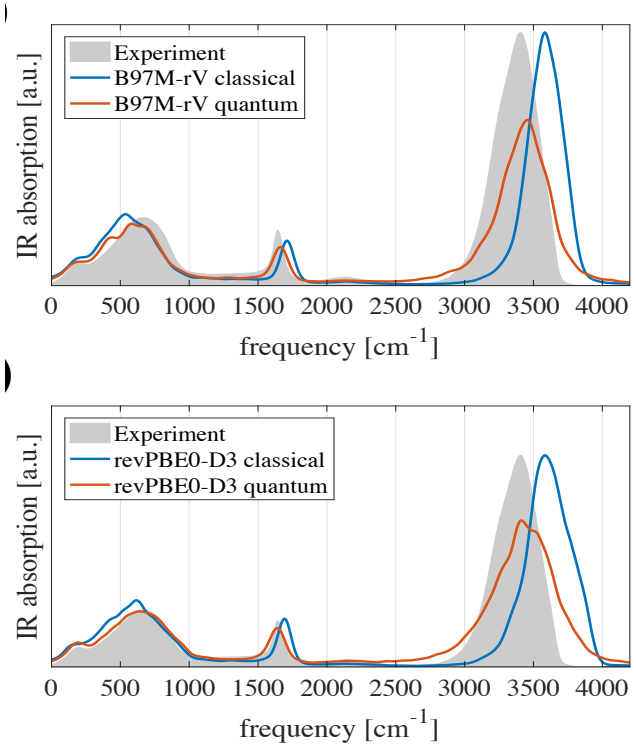
Narbe Mardirossian, MHG, Mol. Phys. 115, 2315 (2017).

Hybrid vs. Meta-GGA: Importance of NQE

B97M-rV is as good as revPBE0-D3; Need at least 100-200ps for convergence; a good functional needs NQEs for dynamics!







L. R. Pestana, O. Marselek, T. Markland, T. Head-Gordon (2018) submitted

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DFT: testing 100 functionals across 5000 trusted data points

	RPBE	M06-L-D3	B97M-V	ωB97M-V
NCE	3.4	0.40	0.24	0.18
NCD	2.4	1.9	2.0	0.98
IE	2.0	0.73	0.27	0.27
ID	9.3	10	6.5	2.1
TCE	9.7	5.5	3.6	2.5
TCD	15	13	4.8	4.3
BH	7.6	6.8	4.4	1.7

"Difficult" RMS errors (kcal/mol).

NC = noncovalent, I = isomers, TC = thermochemistry BH = barrier heights.

Narbe Mardirossian, MHG, Mol. Phys. 115, 2315 (2017).

Results with a new Rung 5 functional: ωB97M(2)

Functional	Rung	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH
ωB97M(2)	5	0.14	0.36	0.32	0.11	0.97	0.96	2.71	0.84
ωB97M-V	4	0.15	0.42	0.53	0.11	1.32	1.56	4.15	1.48
B97M-rV	3	0.18	0.57	1.10	0.24	4.24	1.88	5.47	3.12
B97-D3(BJ)	2	0.45	3.20	1.25	0.62	5.04	3.43	8.88	7.67
SPW92	1	1.91	27.76	5.11	1.26	5.58	10.13	32.20	15.53

RMS error in each category decreases with each step up Jacob's Ladder, as represented by the best functional at each level.

In this statistical sense, DFT is systematically improvable!….

Results are RMS errors in kcal/mol

Electronic structure algorithm & software development plans

Develop algorithms for (more) accurate functionals

Hybrid functionals → large-scale exact exchange
Double hybrid → large-scale PT2/RPA.

Martin Head-Gordon

Basis set limit: Important for accurate functionals!

Are there (more) efficient ways to get there?
Adaptive basis functions.
Low-scaling solvers with high accuracy

Interactions with applied math (FASTMath)

Beyond (simple) DFT: Embedding of an active site

Integration of Emily Carter's methods & codes with Q-Chem
Advances in embedding theory and algorithms
Further applications

Emily Carter

Efficient wavefunction methods for long-range correlation

Numerical experiments that unfold the long-range T2 tensor (right) reveal a striking result (below, right)

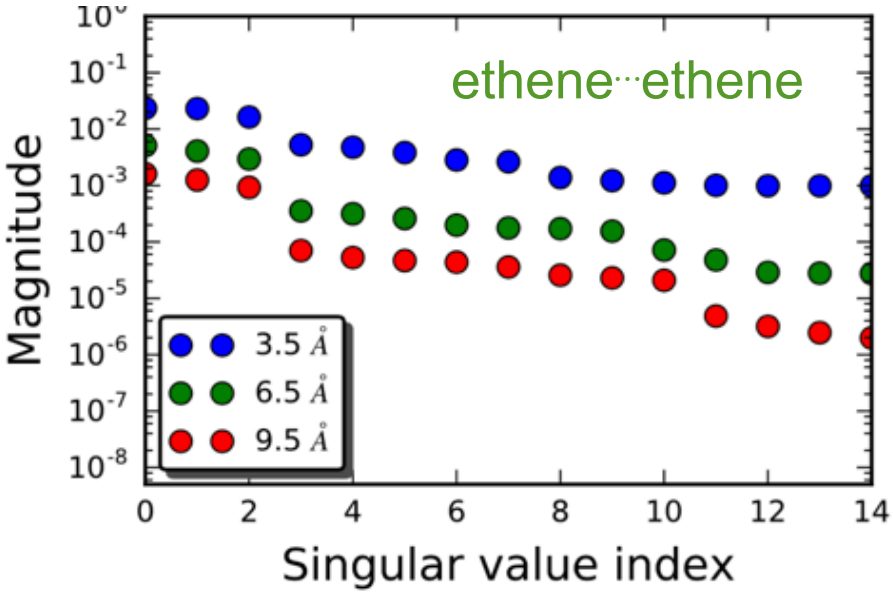
$$\mathbf{T}^{O_A V_A, O_B V_B} = \sum_{P}^{N_{gem}} \mathbf{G}^{A}_{\bullet P} \gamma_P \left(\mathbf{G}^{B}_{\bullet P}\right)^T$$

$$\left(\mathbf{G}^{X}_{\bullet P}\right)^{O_X, V_X} = \mathbf{U}\boldsymbol{\Sigma}\left(\mathbf{V}\right)^T$$

Long-range correlation is controlled by only 3 singular values: *very* low-rank separability! Can be understood on a formal basis (Casimir-Polder for dispersion)

$$C_6^{AB} = \frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)$$

We are starting to design new algorithms that exploit this low-rank separable structure in dRPA



M. Head-Gordon (Cameron Mackie)

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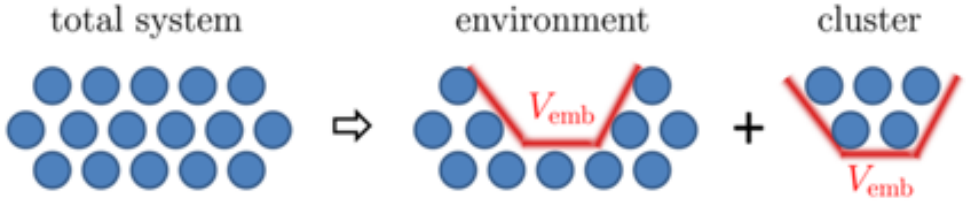
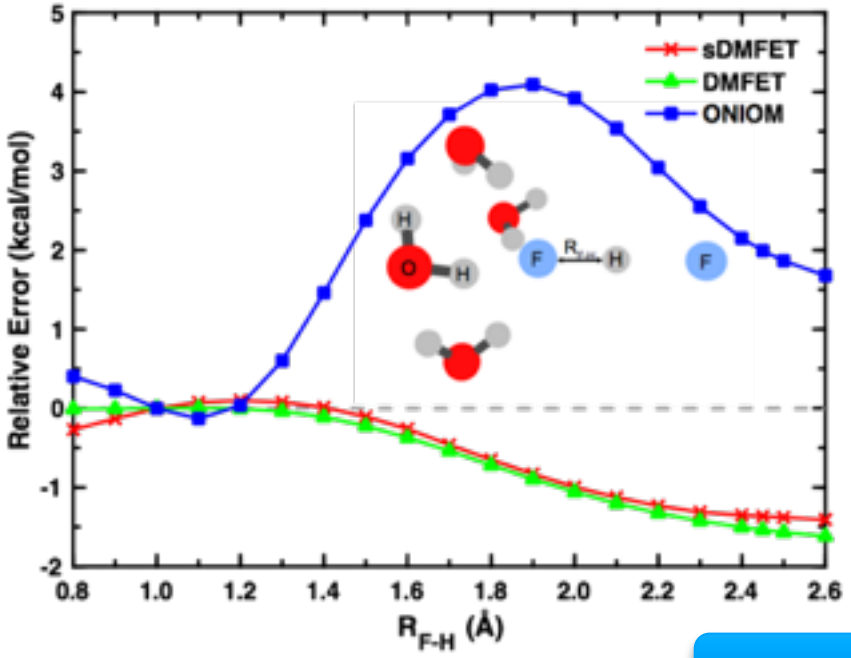
Subspace density matrix functional embedding theory (sDMFET)

$$E_{cluster}^{eDFT}[V_{emb}] + E_{env}^{eDFT}[V_{emb}] \rightarrow \text{OEP}$$

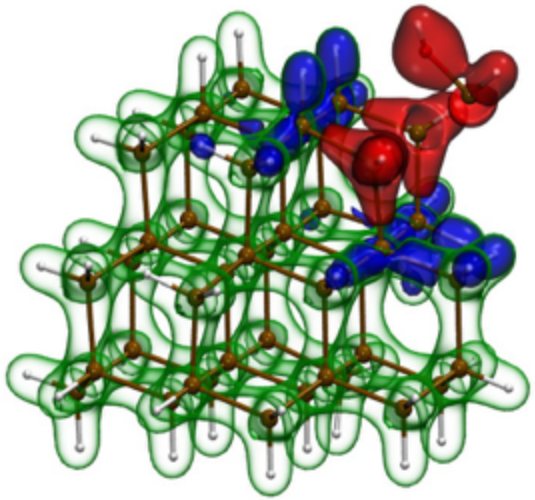
$$\gamma_{cluster}(\mathbf{r},\mathbf{r}') + \gamma_{env}(\mathbf{r},\mathbf{r}') = \gamma_{tot}(\mathbf{r},\mathbf{r}')$$



Performing OEP in a subspace gains efficiency without reducing accuracy, to define sDMFET: an efficient new correlated wavefunction (CW)-in-DFT nonlocal embedding method



$$E_{DMFET}^{eCW/DFT} = E_{tot}^{DFT} + E_{cluster}^{eCW}[V_{emb}] - E_{cluster}^{eDFT}[V_{emb}]$$



Emily Carter

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Natural synergies with applied math (in team, and FASTMath)

Construct a low-rank approximation to the (non-local) exchange potential, Vx, through interpolative separable density fitting (ISDF)

$$\varphi_i(\mathbf{r})\psi_j(\mathbf{r}) \approx \sum_{\mu=1}^{N_\mu} \zeta_\mu(\mathbf{r}) \boxed{\varphi_i(\hat{\mathbf{r}}_\mu)\psi_j(\hat{\mathbf{r}}_\mu)}$$

free!

Use adaptively compressed exchange (ACE) to further reduce the cost of applying Vx to the occupied orbitals in an iterative diagonalization procedure.

Lin Lin

Lin Lin, JCTC 12, 2242, 2016

Robust and efficient DIIS for SCF without constructing full Hamiltonian or density matrices (important in plane-wave codes).

Lin Lin, Chao Yang

W. Hu, L. Lin, C. Yang, JCTC 13, 5458, 2017

Based on tools for sparse linear algebra & preconditioners

Sherry Li, Esmond Ng,

STRUMPACK, symPACK

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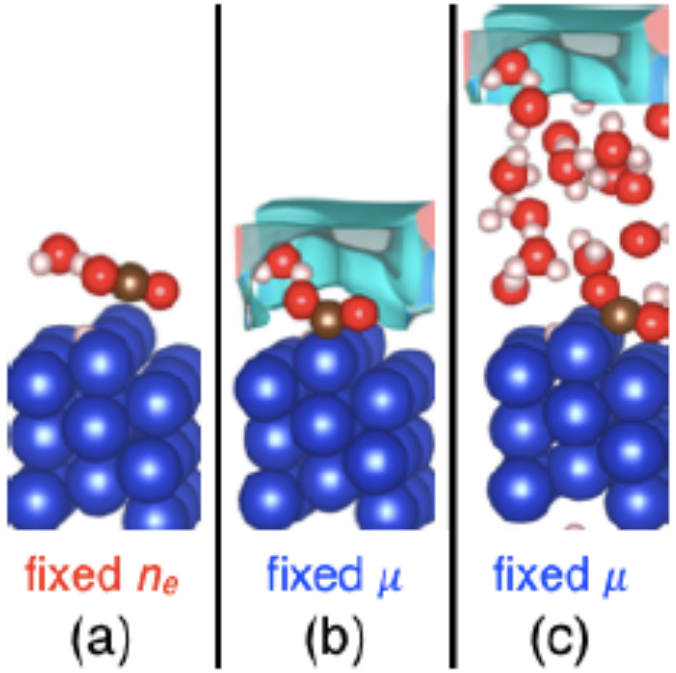
Raising Resolution of (Electro) Catalysis Systems

Electrode-electrolyte interface poses a remarkable series of challenges for computation and modeling at all length and time scales.

(a) Standard electronic structure

(b) and (c) Helmholtz double layer model describing electrolyte as a continuum



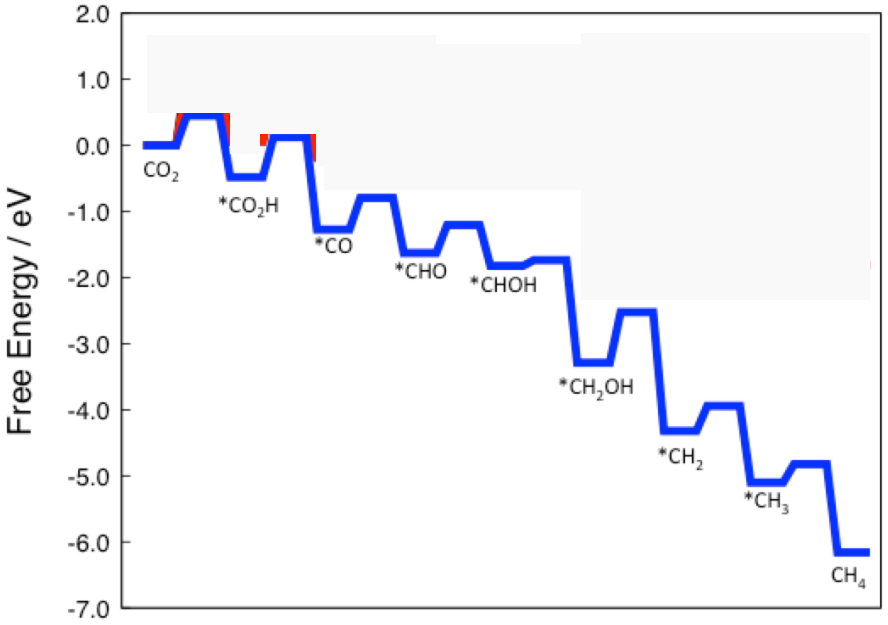
The goal of our sub-task is to raise the resolution of the interface and for full statistical mechanical accounting of explicit solvent, fluctuations, and driven systems with bias (beyond (c) in the figure)

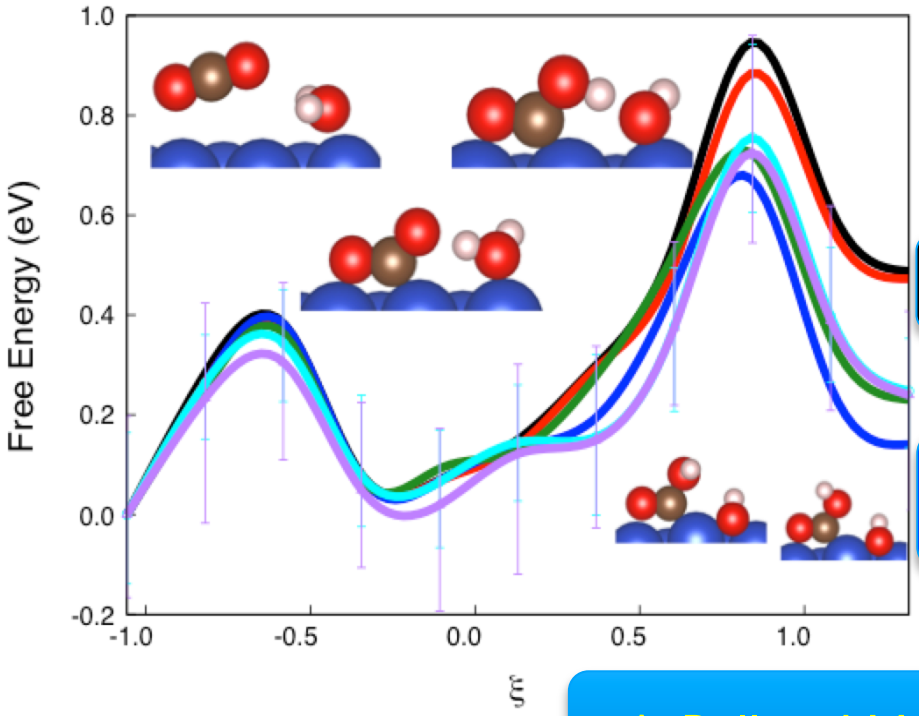
Teresa Head-Gordon,
David Limmer,
Sharon Hammes-Schiffer

Effect of different models on CO2 reduction to CH4 on Cu(100)

Free-energy landscape (right) via applied bias / continuum electrolyte

First exploration of atomistic solvation with applied bias (below)





Vacuum

Continuum

Bias / Continuum

Molecular

Mol. FES

Bias / mol. FES

A. Bell and M. Head-Gordon

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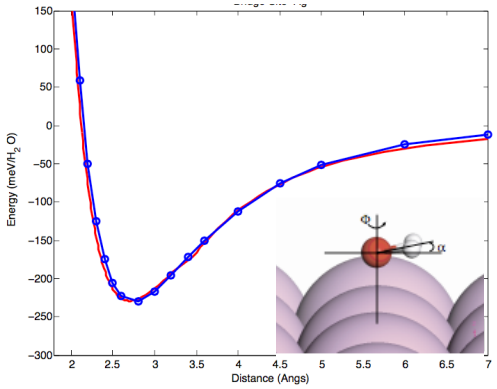
Raising Resolution of (Electro) Catalysis Systems

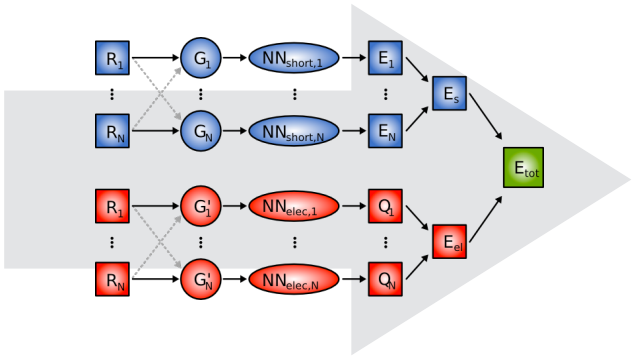
(1) More accurate potential energy surfaces and importance of quantum nuclei for AIMD

- New DFT functionals and NQEs
- Machine learning for reactive FFs

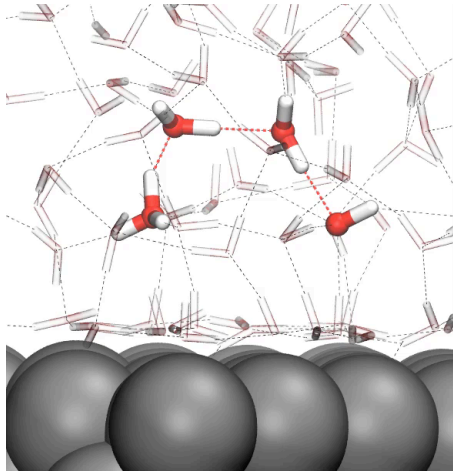
AIMD:
N~100, t_{obs} ~ 100 ps



Neural Networks:
reactive potentials from AIMD



MD:
N~10000, 100ns



Teresa Head-Gordon

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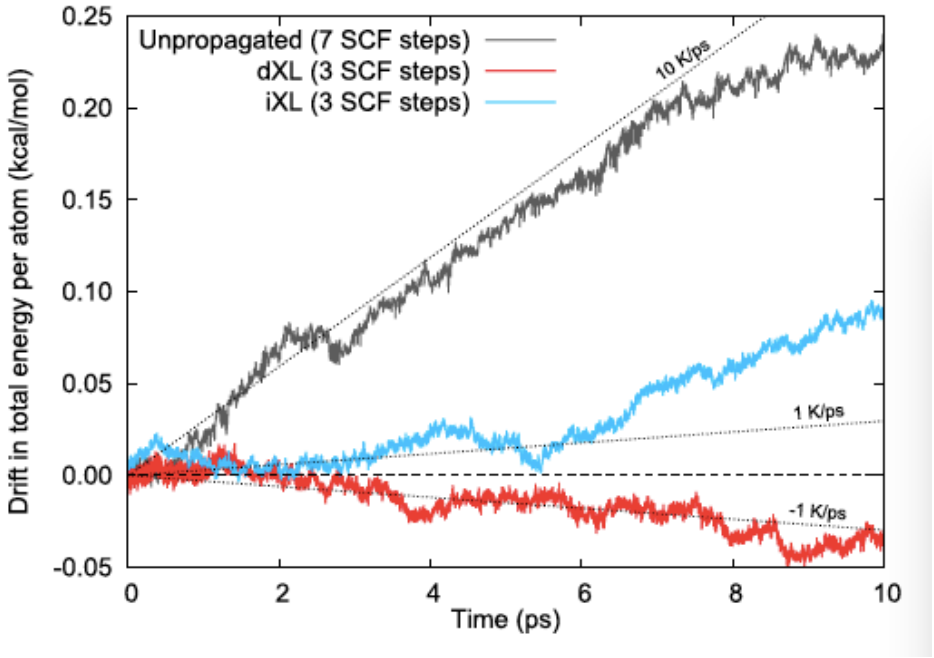
Raising Resolution of (Electro) Catalysis Systems

(2) Lowering cost of pre-factor for SCF solutions in AIMD

- New iEL/0-SCF approaches

$$\mathcal{L}_{\text{hybrid}}^{\text{dipole}} = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\vec{r}}_i^{\,2} + \frac{1}{2}\sum_{i=1}^{N} m_{\mu,i}\,\dot{\vec{\mu}}_i^{\,2} - U\left(\vec{r}^{\,N}, \vec{\mu}_{SCF}^{\,N}\right) - \frac{1}{2}\omega^2 \sum_{i=1}^{N} m_{\mu,i}\left(\vec{\mu}_{SCF,i} - \vec{a}_i\right)^2$$



Challenge for AIMD given first order error in gradient

Teresa Head-Gordon

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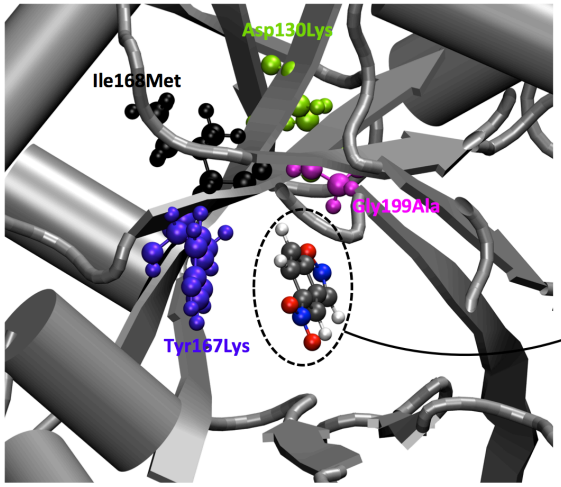
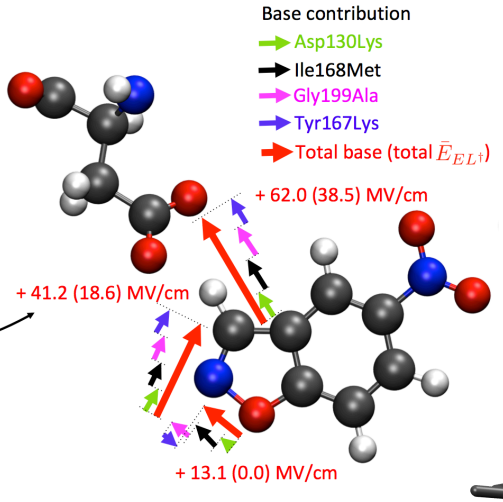
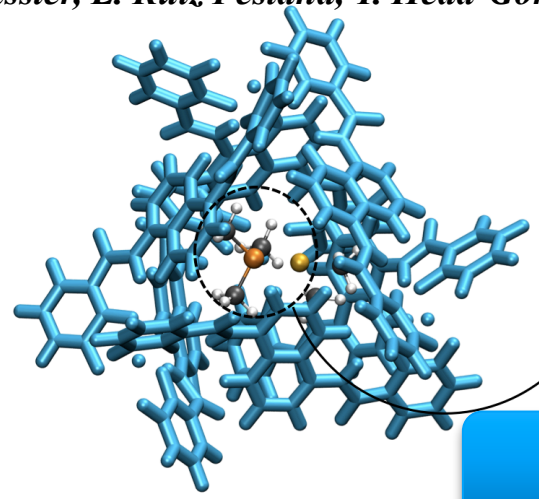
Raising Resolution of (Electro) Catalysis Systems

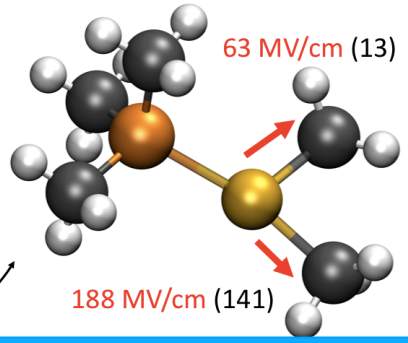
(3) Accurate electric fields and fluctuations in catalysis of large condensed phase heterogeneous and homogeneous systems

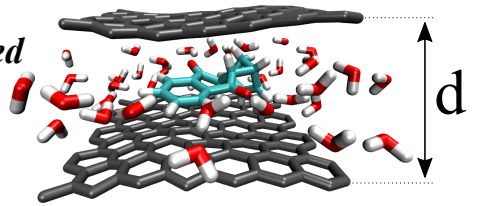


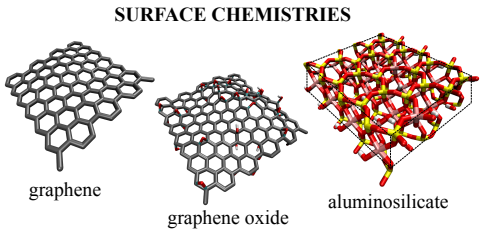


V. Vaissier, L. Ruiz Pestana, T. Head-Gordon (2018) Nature Catalysis Perspective accepted









Teresa Head-Gordon

SciDAC
Scientific Discovery through Advanced Computing

Raising Resolution of (Electro) Catalysis Systems

(4) Non-equilibrium phenomena (rapid changes in pH) and methodology for characterizing driven systems

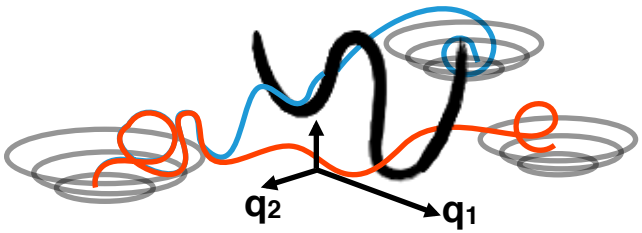
- Extensions to transition path sampling

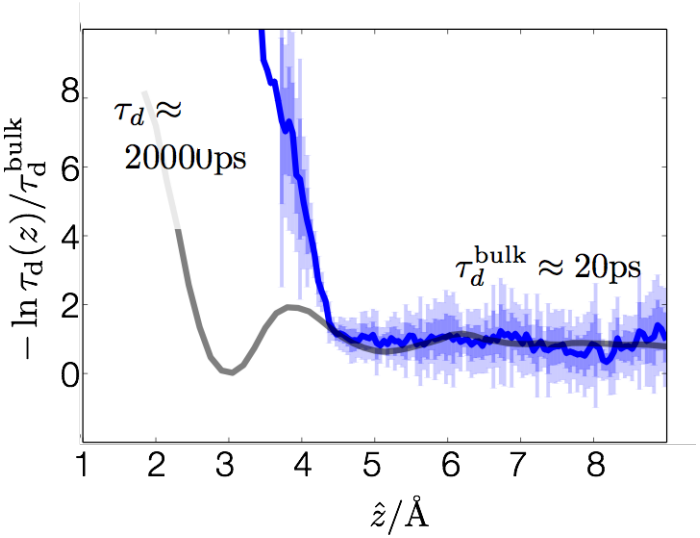
$$C(t) = \frac{\langle h_{\mathrm{A}}[\mathbf{x}_0] h_{\mathrm{B}}[\mathbf{x}_t(\mathbf{x}_0)\rangle}{\langle h_{\mathrm{A}}[\mathbf{x}_0]\rangle} = \frac{Z_{\mathrm{AB}}}{Z_{\mathrm{A}}} = k_{\mathrm{AB}} t \qquad \Delta t < t \ll \tau_{\mathrm{rxn}}$$

rate constant

path partition functions

Umbrella sampling path space for relative rate constants





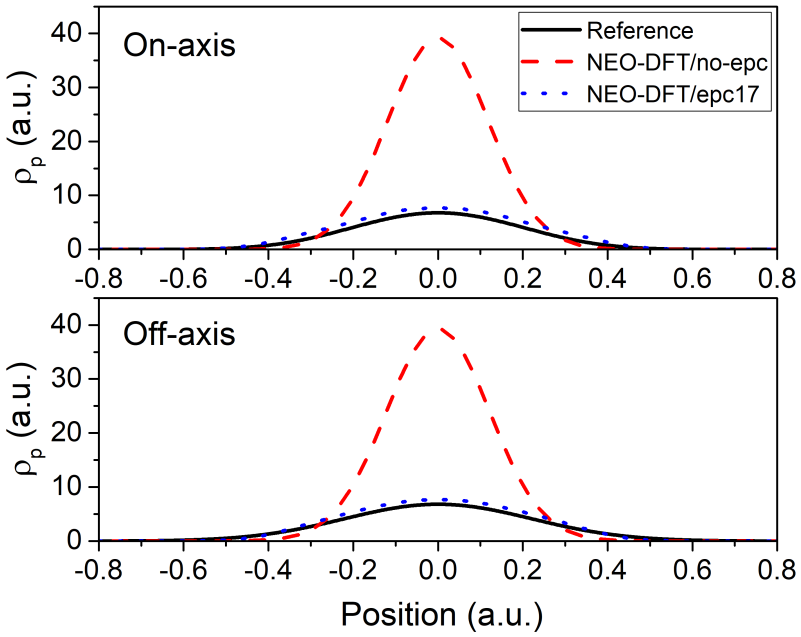
e.g. JA Kattirtzi, DTL, and A P. Willard. "Microscopic dynamics of charge separation at the aqueous electrochemical interface." *PNAS*, 2017

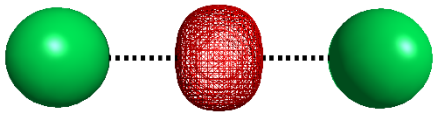
David Limmer

Raising Resolution of (Electro) Catalysis Systems

(5) Utilizing advances in multicomponent density functional theory to treat coupled proton-electron effects.

- SciDAC effort: Port NEO-DFT to Q-Chem and utilize algorithmic advances to improve efficiency and applicability





FHF^-: accurate proton densities

Yang, Brorsen, Culpitt, Pak, and SHS, JCP 2017

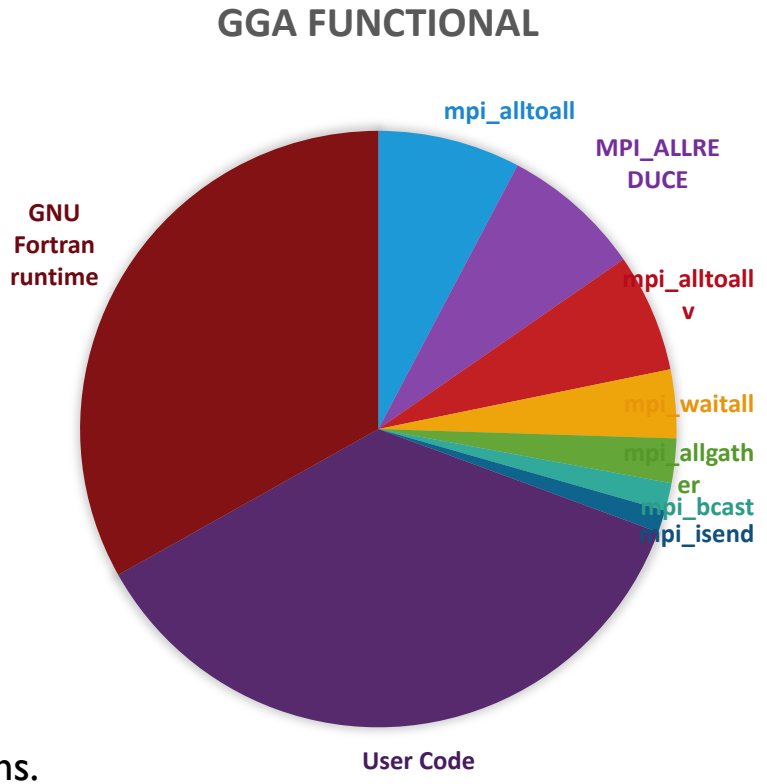
Sharon Hammes-Schiffer

SciDAC
Scientific Discovery through Advanced Computing

Essential CS-based code optimization (Khaled Ibrahim)

Preliminary results for CP2K optimization

- Identified issues regarding interoperability of various components of the software stack that were limiting performance.
- Fixing these issues helped to improve the performance of CP2K for target problems by up to 70% on NERSC (Cori).



Planned / future activities

Exploration of other codes

DGDFT, Q-Chem

Performance of MPI Collective (affects many codes)

Explore collective tuning strategies on the Cray systems.

Performance on KNL architectures (CP2K is not tuned)

Analyze efficiency of vectorization and use of cache hierarchy.

Software package interoperability and threading support.

Strategies for thread concurrency across software stack.

Analyze performance at scale.

Focus on the communication part of the computation.

8 Haswell nodes

64 procs/4 threads

Performance bottlenecks

MPI collectives

BLAS, FFT dominate run time.

Outlook and Acknowledgements: Advancing catalysis modeling

Physical sciences objectives:

Advance the level of modeling used for electronic structure theory
Push towards explicit solvent, NQEs and converged statistical mechanics
Integrate microkinetics with transport for whole system modeling

Applied math and computer science objectives:

Deployment of new algorithms/solvers in this application domain
Pursue opportunities for new algorithm development (partnerships)
Improve parallel scaling for deployment on today's leadership computers
Advise / consult / develop new parallel algorithms with physical scientists

More than enough exciting opportunities and challenges to keep us busy!

Alex Bell, Emily Carter, Sharon Hammes-Schiffer, Teresa Head-Gordon,
Khaled Ibrahim, Xiaoye Li, David Limmer, Lin Lin, Esmond Ng, Sam Williams, Chao Yang