BERKELEY LAB

SciDAC
Scientific Discovery through Advanced Computing

SciDAC 4 Annual Meeting: July 16-18, 2019

Advancing Catalysis Modeling: From Atomistic Chemistry to Whole System Simulation

Martin Head-Gordon,

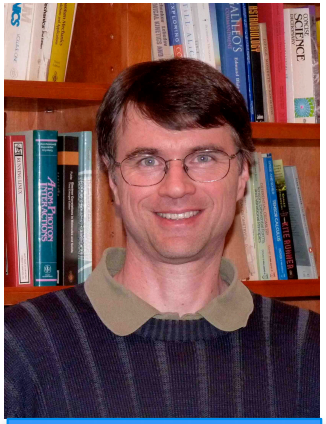
Alex Bell, Emily Carter (Princeton), Sharon Hammes-Schiffer (Yale), Teresa Head-Gordon, Khaled Ibrahim, Xiaoye Li, David Limmer, Lin Lin, Esmond Ng, Sam Williams, Chao Yang

SciDAC-4 Partnership Team

Alex Bell

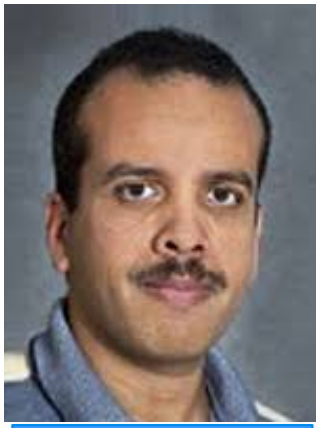
Emily Carter

Sharon Hammes-Schiffer



Martin Head-Gordon

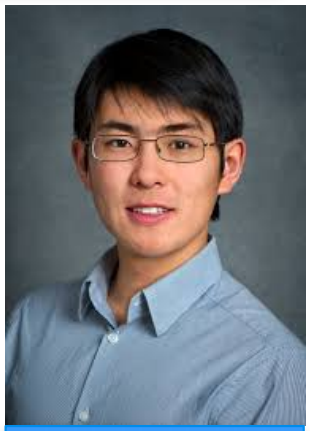
Teresa Head-Gordon



Khaled Ibrahim

David Limmer

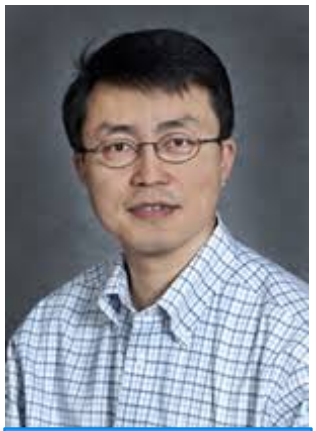
Sherry Li



Lin Lin

Esmond Ng

Sam Williams



Chao Yang

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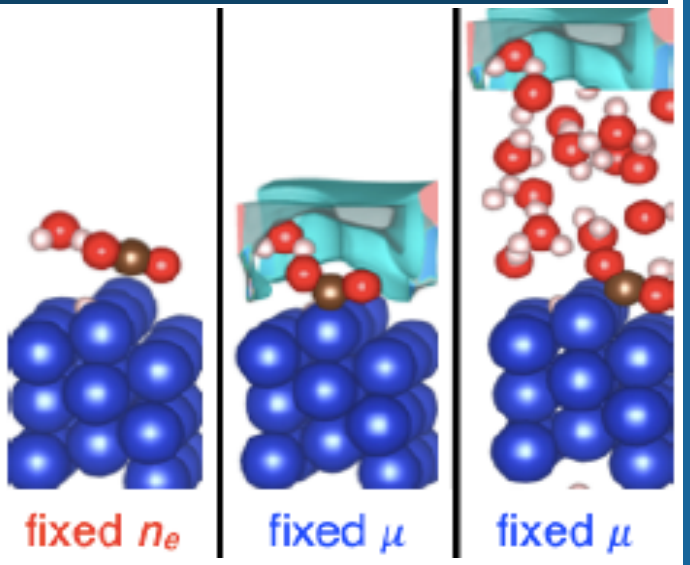
SciDAC 4 Partnership: Advancing catalysis modeling

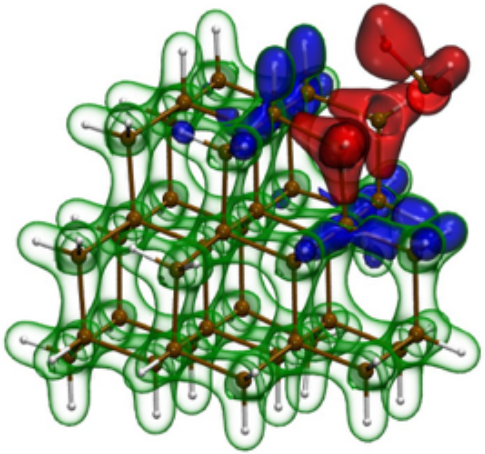


Physical sciences objectives:

Advance electronic structure modeling
Explicit solvent, NQEs and statistical mechanics
Whole system modeling

Applied math and computer science objectives:

New algorithms/solvers for this application domain
New algorithm development (partnerships)
Improved parallel scaling for supercomputers



23 publications over the past year
This talk will cover some highlights.
See also: poster 9 (Christopher Stein and MHG) and poster 3 (David Williams-Young, P. Beckman and C. Yang)

Advancing catalysis modeling: Outline

1. **Electronic structure theory and embedding**

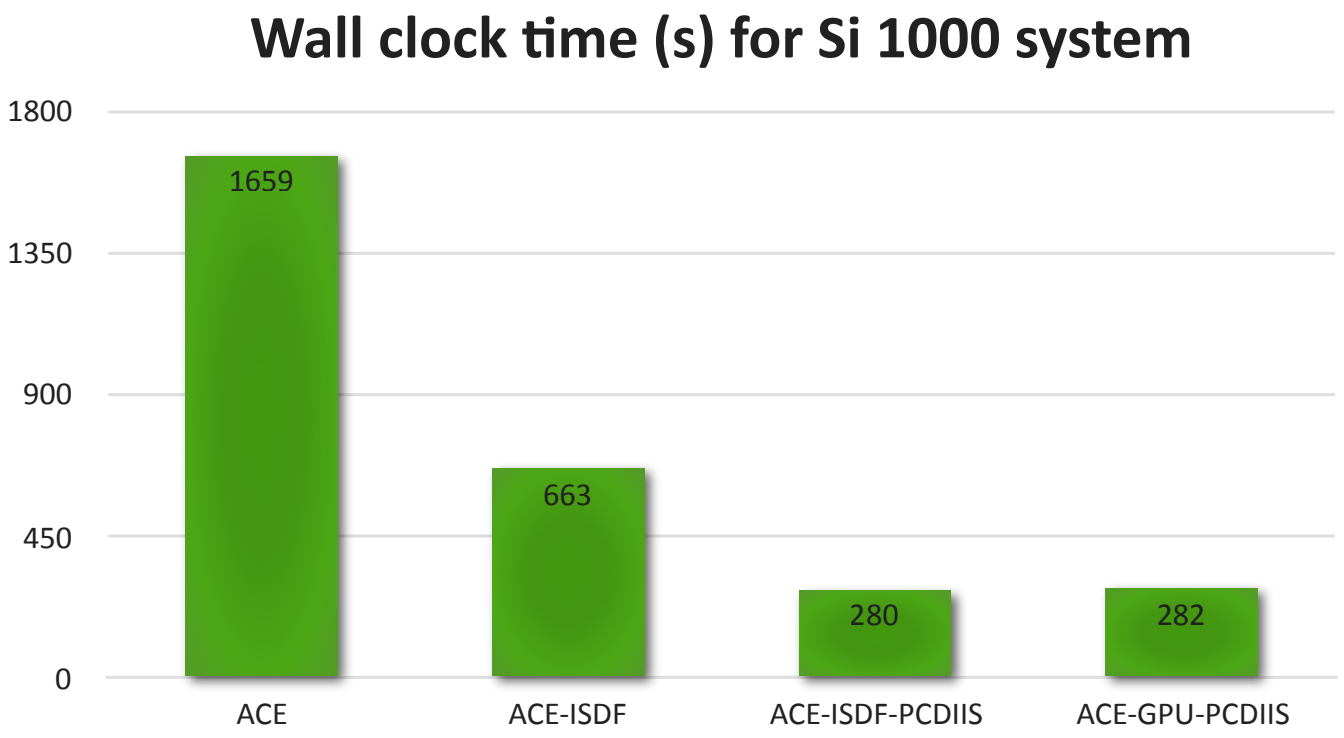
   Martin Head-Gordon, Emily Carter, Lin Lin and Chao Yang

2. **Statistical mechanics & dynamics**

3. **Applied math and CS/HPC**

4. **Whole system modeling**

ISDF and ACE: Accelerating exact exchange DFT



Hybrid(conventional): 12425 s

44 x speed up

~ GGA time (more iterations)

ACE: [Lin, JCTC, 2016] [Hu, Lin, Banerjee, Vecharynski, Yang, JCTC 2017]

ACE-ISDF: [Hu, Lin, Yang, JCTC 2017] [Dong, Hu, L., JCTC 2018]

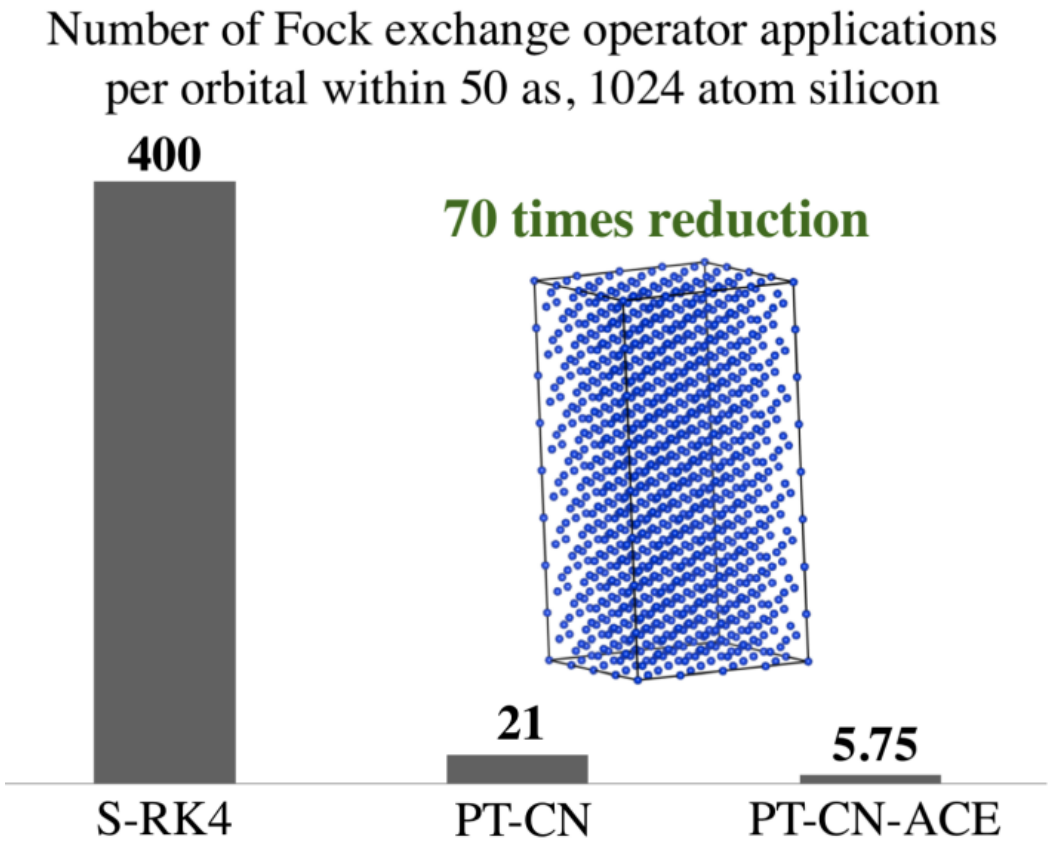
ACE-ISDF-PCDIIS: [Hu, Lin, Yang, JCTC 2017a]

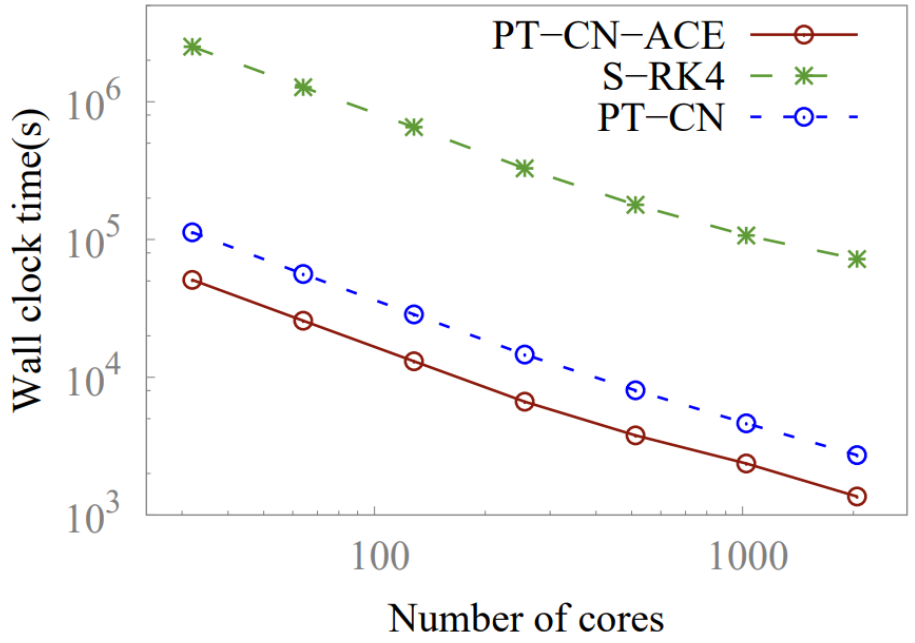
ACE-GPU-PCDIIS: [Jia, Lin, in preparation]

Lin Lin, Chao Yang

Hybrid functional RT-TDDFT

For the first time, practical RT-TDDFT with a large basis set





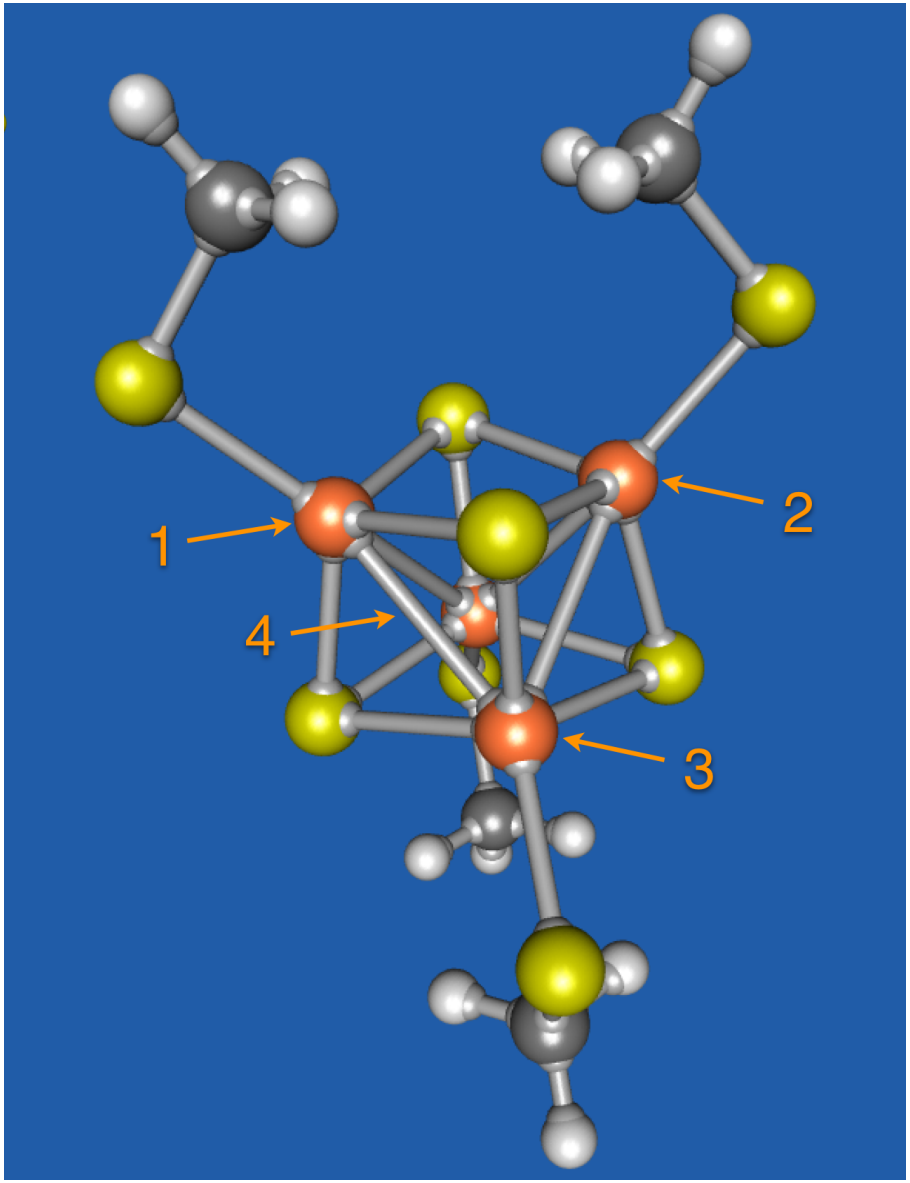
Lin Lin

Strong correlations: Adaptive sampling CI (ASCI) with active spaces

ASCI: selected CI that adaptively chooses most important configurations up to a specified total. Corrected via PT2. Combined with CASSCF permits very large active space calculations (above (50,50)).

Ferredoxin core: 4 irons with oxidation state 2.5. The 20 d orbitals are nominally 2 doubly occupied and 18 singly occupied levels, creating a dense manifold of states. DFT breaks spatial symmetry of this octahedral complex. CASSCF geometry optimization in an active space of 20 d-orbitals, and the 3 orbitals of each sulfur that couple to the d-manifold restores it!

Combined with Emily Carter's embedding! (see subsequent slide)



Daniel Levine

Martin Head-Gordon

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Weak correlations: Uncovering the nature of long-range dispersion

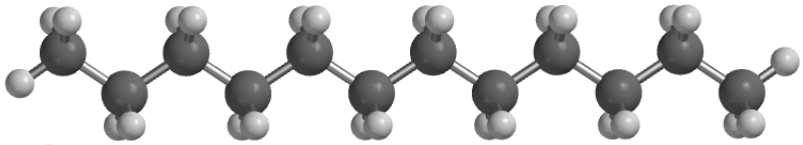
Numerical experiments that unfold the long-range T2 tensor (right) reveal a striking result (below, right)

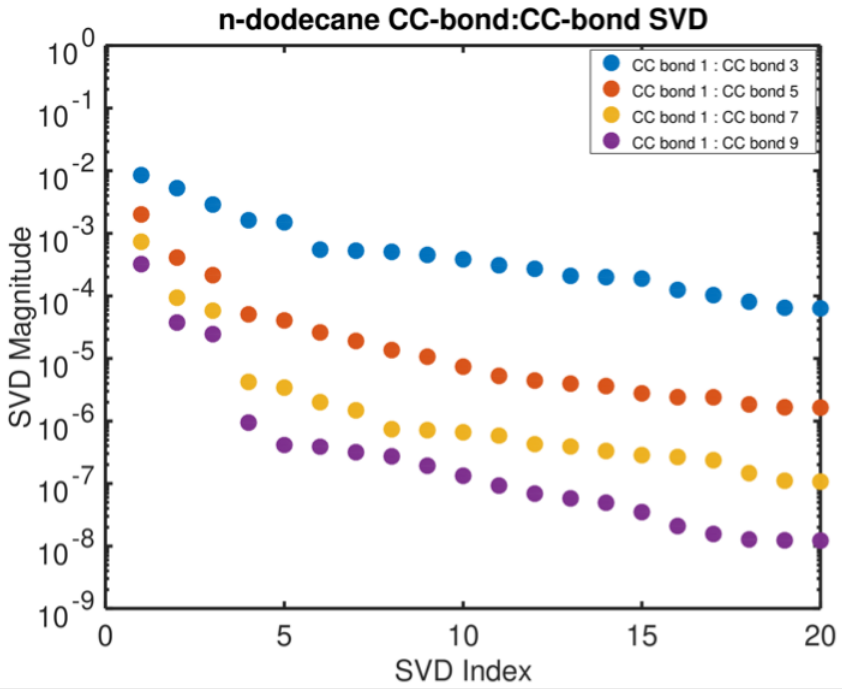
$$\mathbf{T}^{O_A V_A, O_B V_B} = \sum_{P}^{N_{gem}} \mathbf{G}^{A}_{\bullet P} \gamma_P \left(\mathbf{G}^{B}_{\bullet P}\right)^{T}$$

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

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)

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





Cameron Mackie

Martin Head-Gordon

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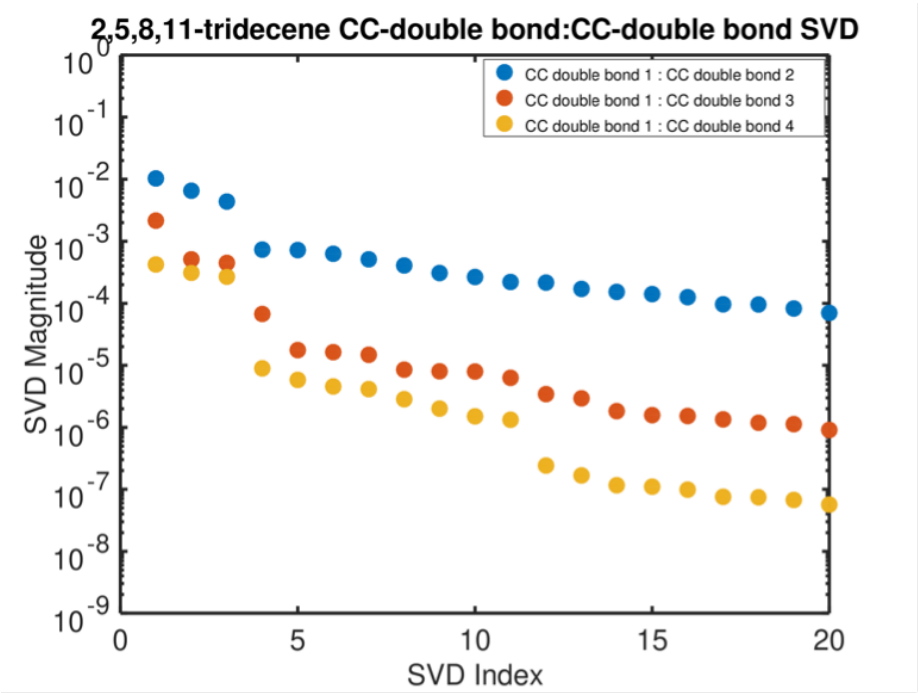
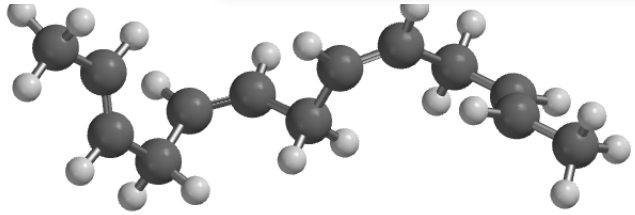
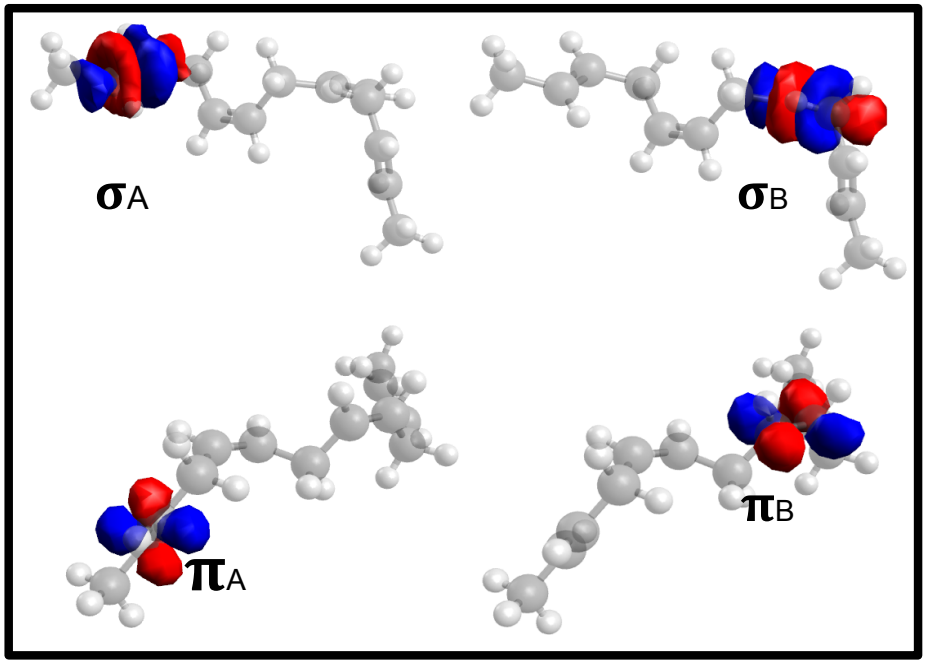
Weak correlations: Uncovering the nature of long-range dispersion



Cameron Mackie



Double-bond/double bond correlation (left, molecule above) show the same rapid decay.



(1) Present results show long-range correlation can be described with 3 dispersion-specific virtuals per occupied.

(2) Future: These virtuals could be optimized to extremize the long-range correlation recovery.

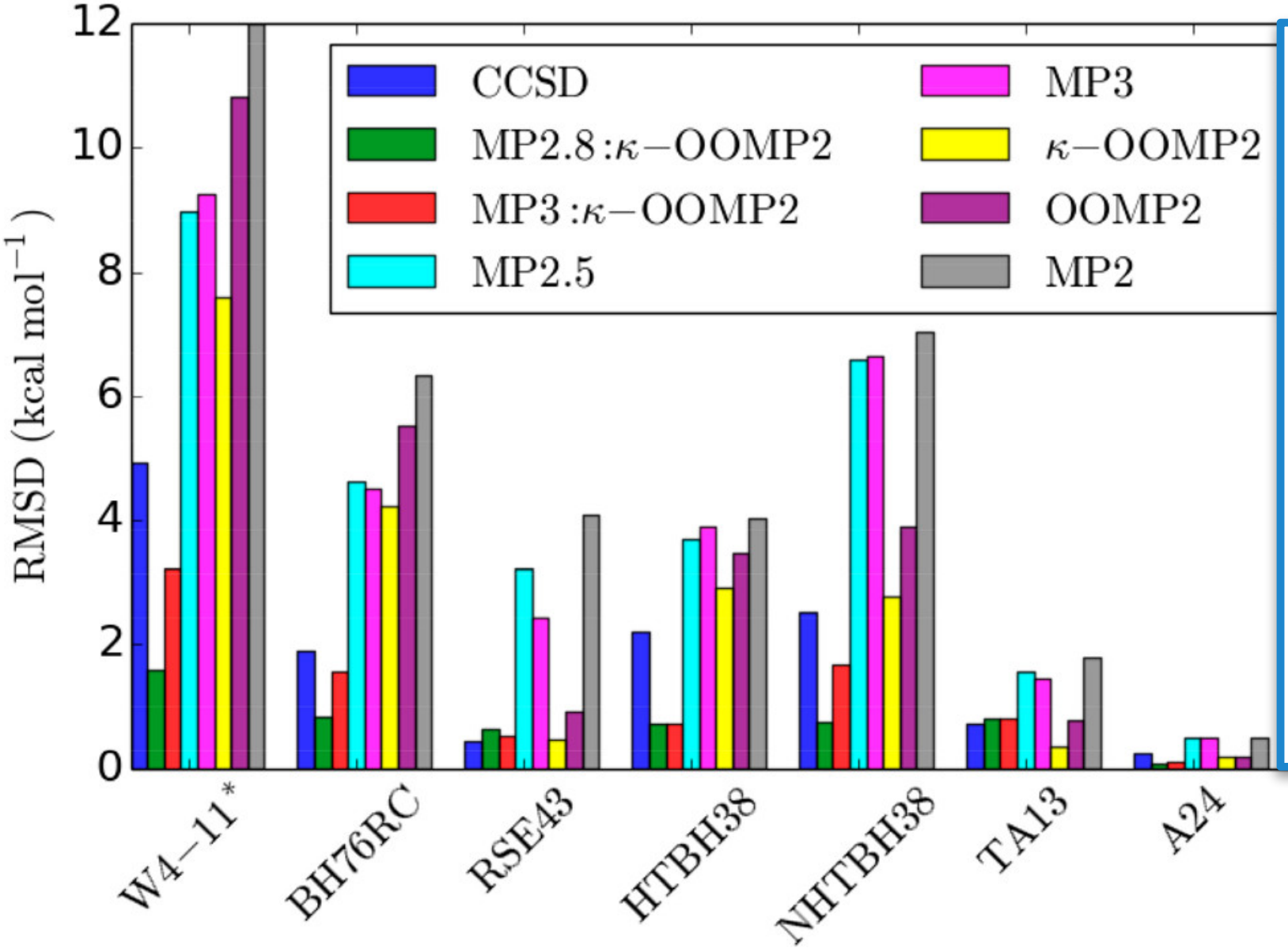
(3) Future: ISDF (Lin Lin) combined with this rank reduction will be a synergistic combination.

Martin Head-Gordon

MP3 made useful? Re-examining a largely abandoned method

Method	Cause of problems	Solution
Mean field (Hartree-Fock): defines a reference problem & a perturbation (fluctuation potential)	Mean-field orbitals often exhibit artificial symmetry-breaking (space &/or spin)	Abandon mean-field orbitals!
MP2: captures leading electron correlations & usually greatly improves observables	… which degrades MP2 results….	Replace by orbitals optimized with regularized PT2 (κ-OOMP2) that usually* restore symmetry.
MP3: beyond pairwise electron correlations but usually does not improve calculated observables	… and makes MP3 even less effective…	**Will the use of these better orbitals affect MP3 results?**

MP3 made useful? Exciting test results.



MP3 (& MP2.5) are not much better than MP2

κ-OOMP2 is better than MP3 and OOMP2

MP2.8 (& MP3) using orbitals from κ-OOMP2 surpass CCSD

L.W. Bertels, J. Lee, MHG, J. Phys. Chem. Lett. 10, 4170 (2019)

Advancing catalysis modeling: Outline

1. Electronic structure theory and embedding

2. **Statistical mechanics & dynamics**

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

3. **Applied math and CS/HPC**

4. **Whole system modeling**

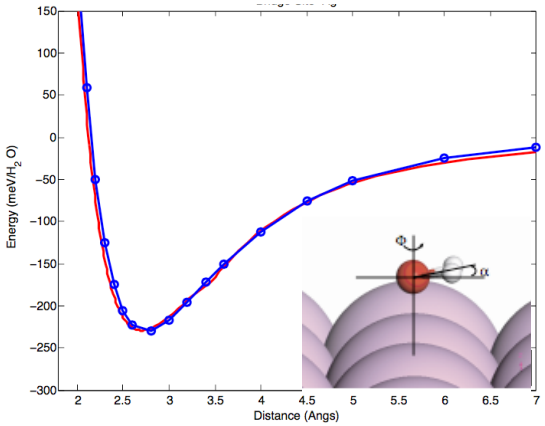
Raising Resolution of (Electro) Catalysis Systems

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

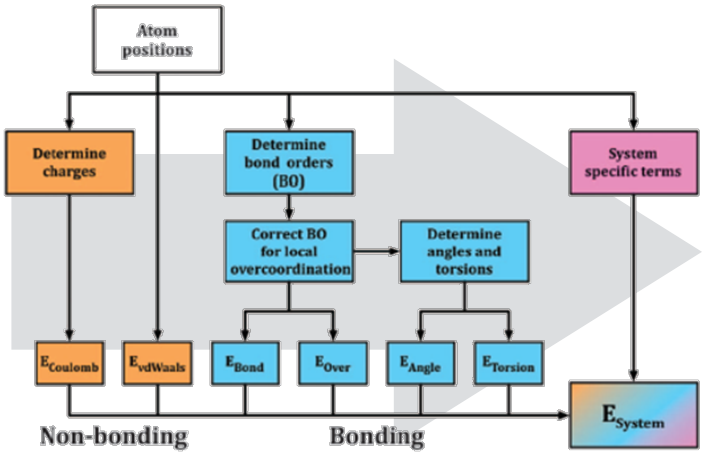
The goal of our sub-task is to raise the resolution of the interface and for full statistical mechanical modeling of solvent, fluctuations, catalysis, and driven systems with bias with development of efficient simulation models and software

AIMD:

N~100, t_{obs} ~ 100 ps



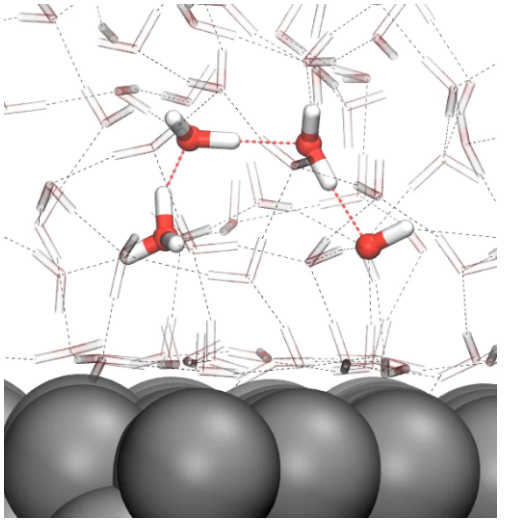
New reactive potentials with improved accuracy and efficiency



Senftle et al. Computational materials (2016): 15011.

Reactive MD:

N~10000, 100-1000's ns



Teresa Head-Gordon

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Electronegativity equalization method (EEM)

Coulomb energy and charge transfer solved self-consistently

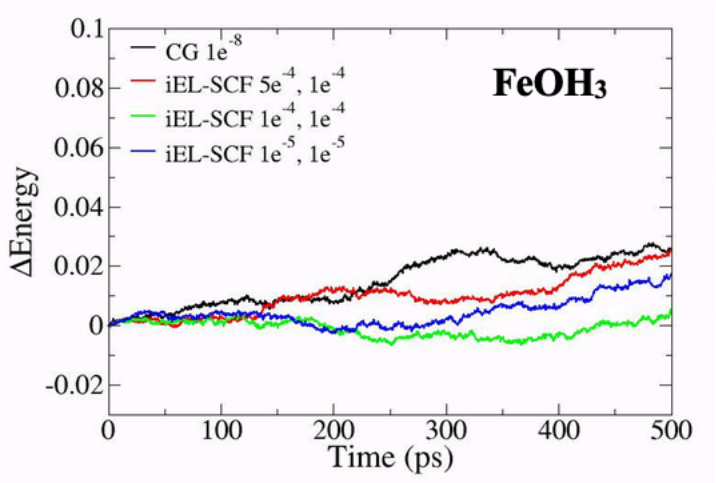
$$\chi_{eq} = \chi_\alpha^* + 2\eta_\alpha^* q_\alpha + \sum_{j\neq i}^{n} \frac{q_j}{R_{ij}}$$

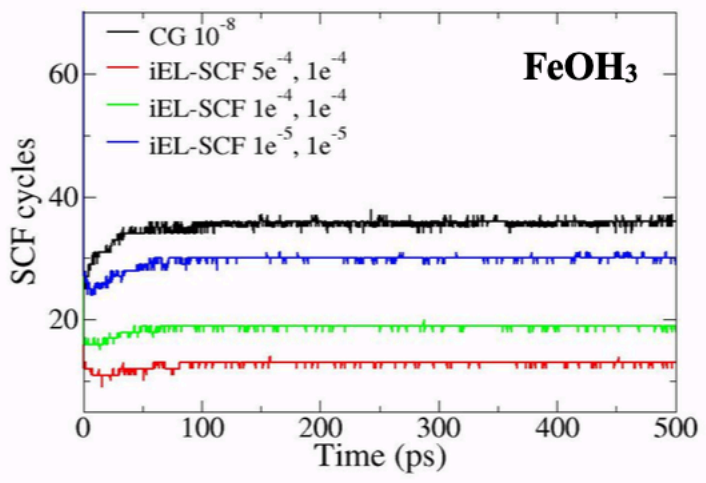
χ^* **–Effective electronegativity**

η^* **–Effective hardness**

Computationally demanding bottleneck for the ReaxFF potential

$$\begin{pmatrix} 2\eta_1^* & 1/R_{12} & \dots & 1/R_{1n} & -1 \\ 1/R_{21} & \cdots & \cdots & \cdots & -1 \\ \vdots & \cdots & \cdots & \cdots & -1 \\ 1/R_{n1} & \cdots & \cdots & 2\eta_n^* & -1 \\ 1 & 1 & 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} q_1 \\ \vdots \\ \vdots \\ q_n \\ \chi_{eq} \end{pmatrix} = \begin{pmatrix} -\chi_1^* \\ \vdots \\ \vdots \\ -\chi_n^* \\ Q_{tot} \end{pmatrix}$$





I. Leven, T. Head-Gordon (2019) (submitted)

Teresa Head-Gordon

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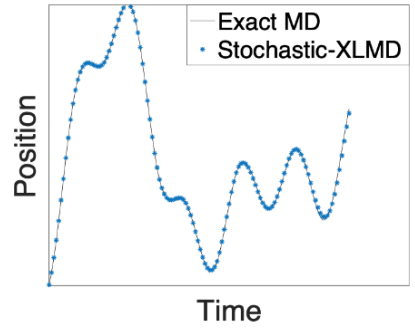
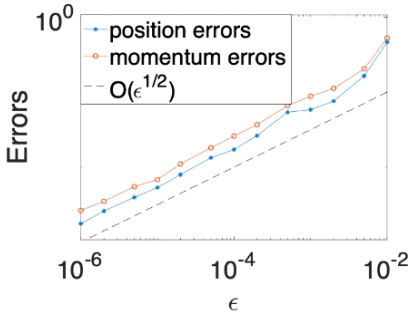
Stochastic-extended Lagrangian molecular dynamics (Stochastic-XLMD)

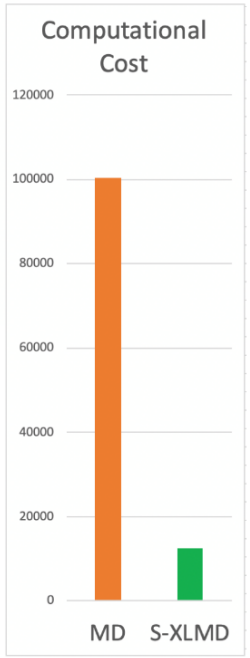
Scientific Achievement: Stochastic-XLMD method builds on the iEL/SCF and iEL/0-SCF methods, and can converge robustly and reduce SCF iterations for model many-body potentials for MD simulations.

Significance and Impact:

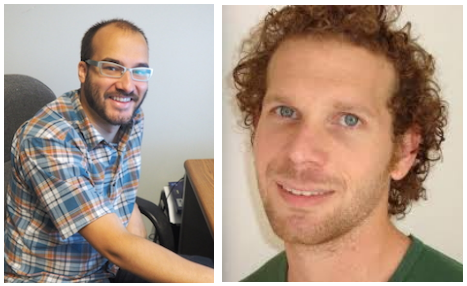
- rigorous proof of convergence beyond linear response regime and demonstrating numerical effectiveness
- generalized the approach of averaging and techniques for analyzing degenerate elliptic operators and proved the error bound for the new method.
- numerically studied scaling of numerical noise, damping factor and perturbation parameter for efficient simulation of non-quadratic interaction energy forms.







D. An, T. Head-Gordon, L. Lin, J. Lu (2019). arXiv: 1904.12082



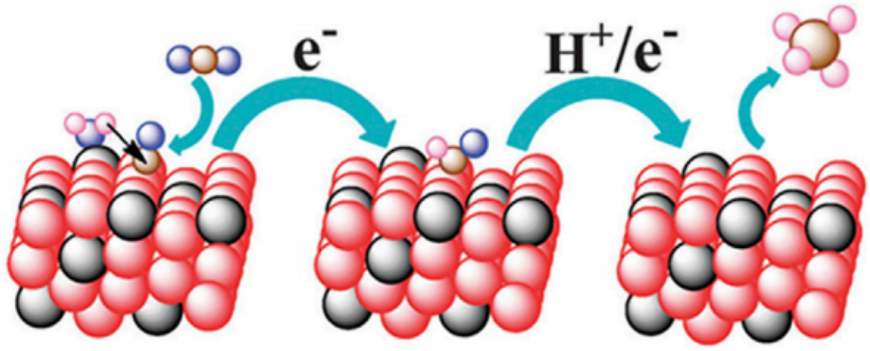
Stochastic-XLMD is currently being extended to AIMD (CP2K) and EEM (ReaxFF in LAMMPs)

Teresa Head-Gordon, Lin Lin

SciDAC Scientific Discovery through Advanced Computing

Charge Transfer Models for Reactive Force Fields

While ReaxFF is sufficient for predicting charge fluctuations in different molecular environments, these models fail to describe redox electrochemical reactions which are accompanied by a flow of charge to/from the anode surfaces.



Vasileff et al (2018) Chem 4, 1809–1831

We have developed a new approach for treating charge flow in reactive force fields through an explicit treatment of electrons. Our model gives improved treatment of charge transfer and also goes beyond the approximation of atomic point charges to account for a more flexible charge distribution in molecules.

I. Leven, T. Head-Gordon (2019) In progress

Teresa Head-Gordon

Charge Transfer Models for Reactive Force Fields

- An atom is partitioned into a core containing the nuclei + core electrons and a shell containing valence electron(s).
- Core and shell are treated as Gaussian charges

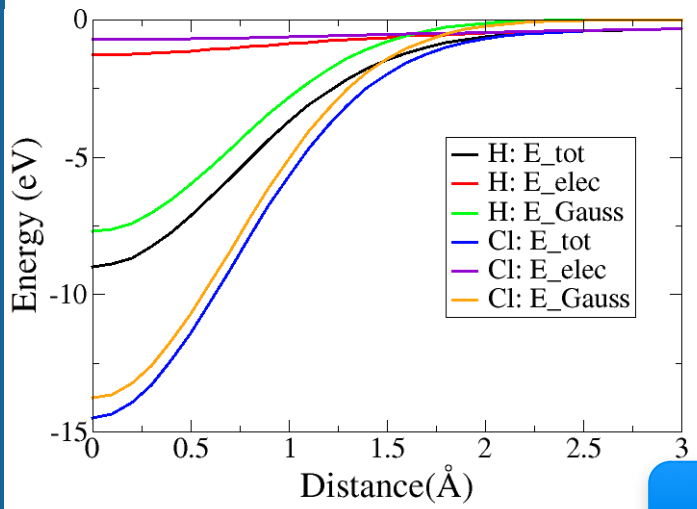
$$\rho_c^i(\vec{r}) = q_c \cdot \left(\frac{\alpha_c^i}{\pi}\right)^{3/2} e^{-\alpha_c^i\left(|\vec{r}-\vec{r}_c^i|^2\right)} \qquad \rho_s(\vec{r}) = q_s \cdot \left(\frac{\alpha_s}{\pi}\right)^{3/2} e^{-\alpha_s\left(|\vec{r}-\vec{r}_s|^2\right)}$$

Resulting interaction potential over core-shell and shell-shell

$$E_{CT} = \sum_{i}^{2n}\sum_{j<i}^{2n}\left(E_{ij}^{elec}(r_{ij}) + E_{ij}^{Gauss}\right)$$

$$E_{ij}^{elec}(r_{ij}) = \frac{q_i \cdot q_j}{r_{ij}} erf\left(\sqrt{\frac{\alpha_i \cdot \alpha_j}{\alpha_i + \alpha_j}} r_{ij}\right)$$

$$E_{ij}^{Gauss}(r_{ij}) = A_{ij} e^{-\gamma_{ij} \cdot r_{ij}^2}$$



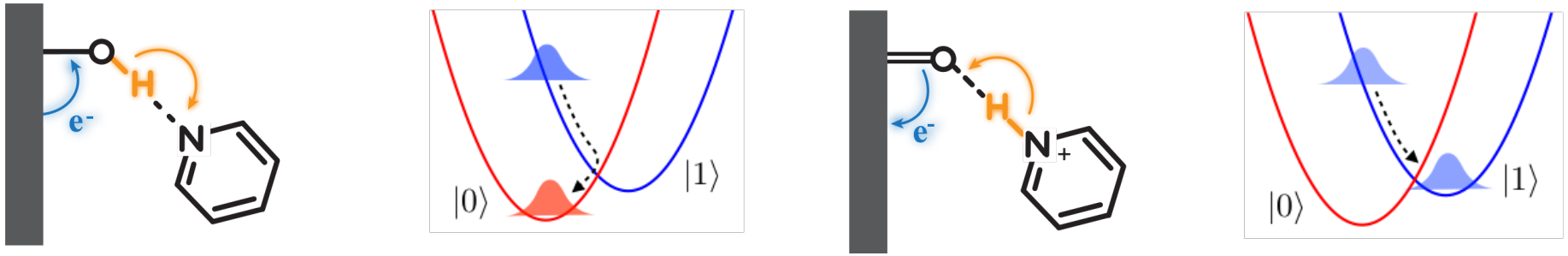
Potential is tuned such that interaction between shell-core and shell-shell yields the ionization potential of core atom type and corresponding electron affinity

I. Leven, T. Head-Gordon (2019) In progress

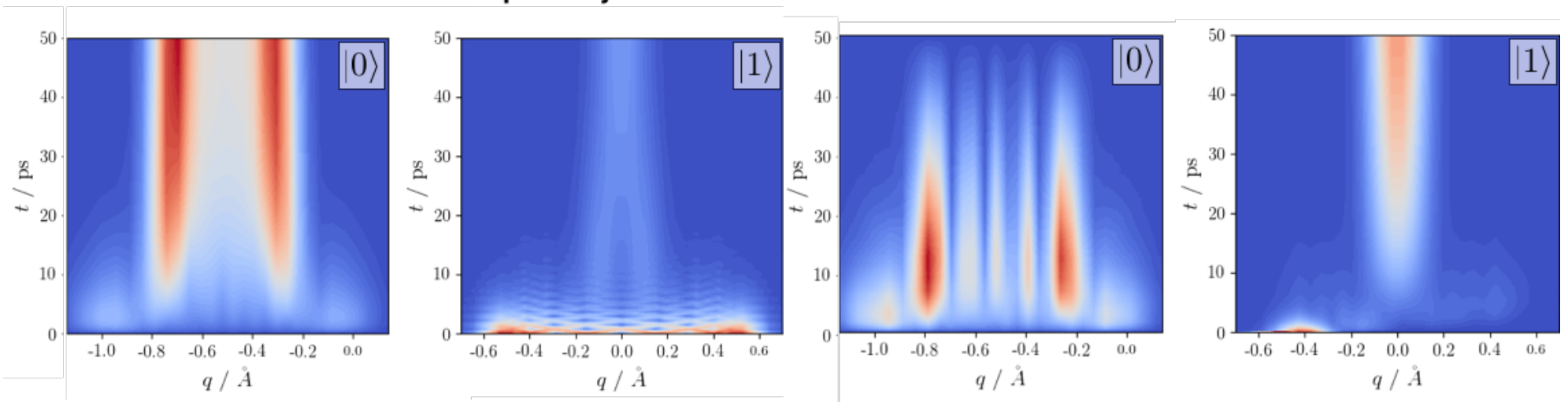
Teresa Head-Gordon

Nonadiabatic Transition Path Sampling (QTPS)

- Transition path sampling quantum nuclei with quantum master equations



Dominate relaxation pathway | **Importance sampling**



Schile, Addison J., and David T. Limmer. JCP 149, 214109 (2018); 151, 014106 (2019)

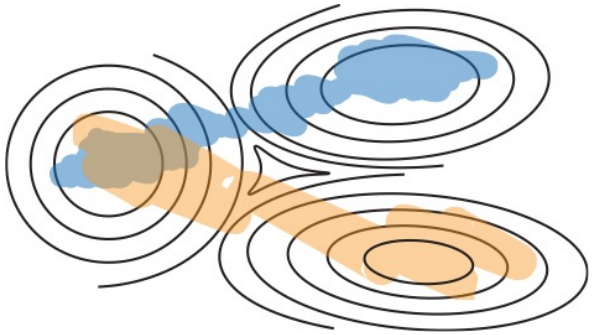
David Limmer

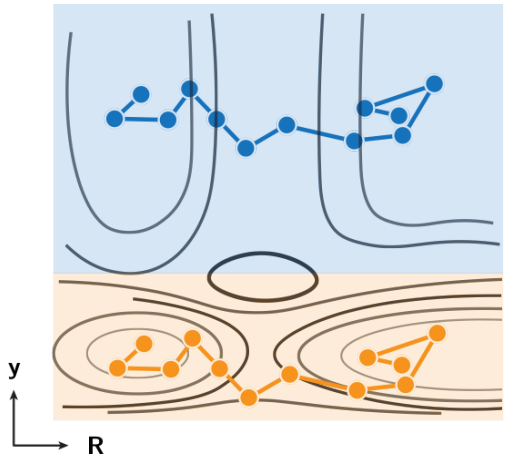
Rate Constants in Inhomogeneous Systems from TPS

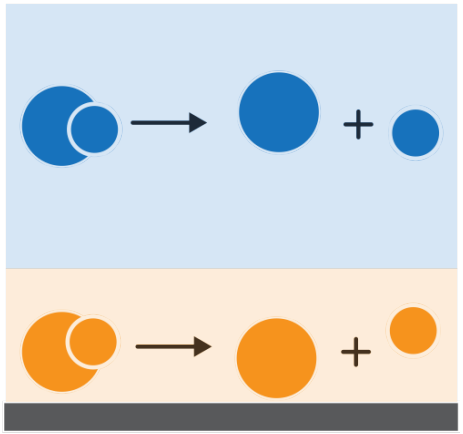
- Transition path sampling for spatial rate dependence

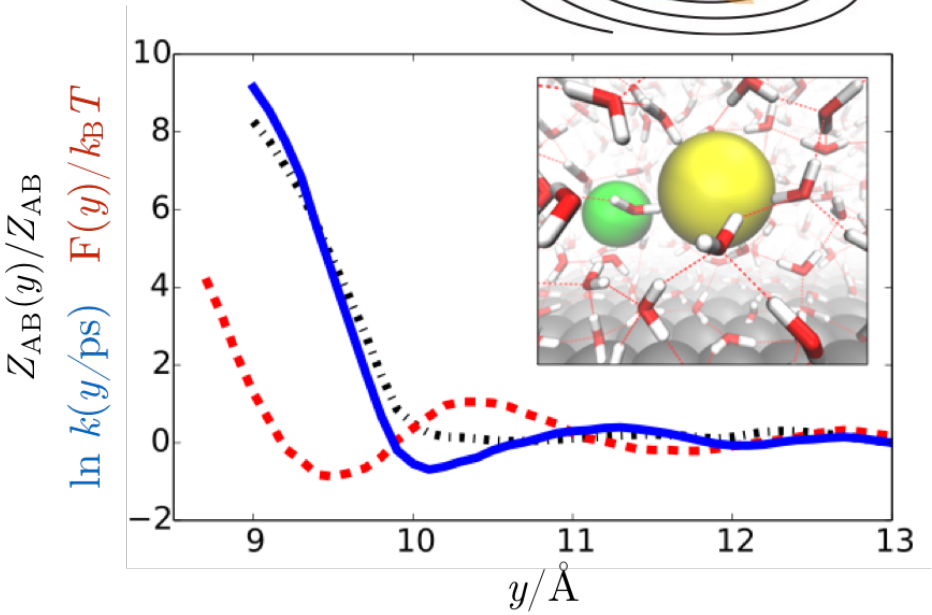
Rate from A to B at fixed y: *Spatially dependent rate constant*

$$Z_{\mathrm{AB}}(y) = \int \mathrm{d}\mathbf{x}_0 \rho[\mathbf{x}_0] h_{\mathrm{A}}[\mathbf{x}_0] h_{\mathrm{B}}[\mathbf{x}_t(\mathbf{x}_0)] \delta(y - y[\mathbf{x}_0]) \propto k_{\mathrm{AB}}(y) e^{-\beta F(y)}$$







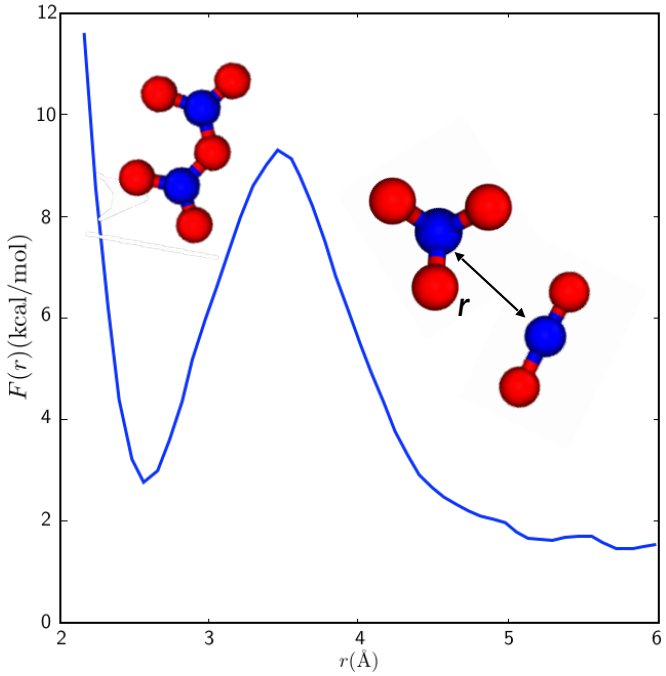


Schile, Addison J., and David T. Limmer. 150, 191102 (2019)

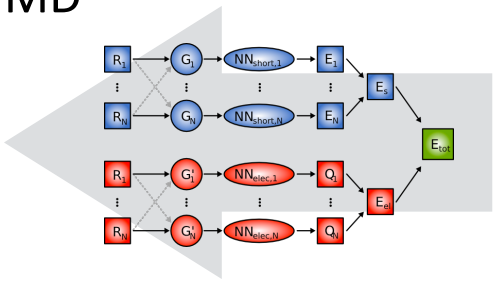
Artificial Neural Network Reactive Molecular Dynamics Potentials

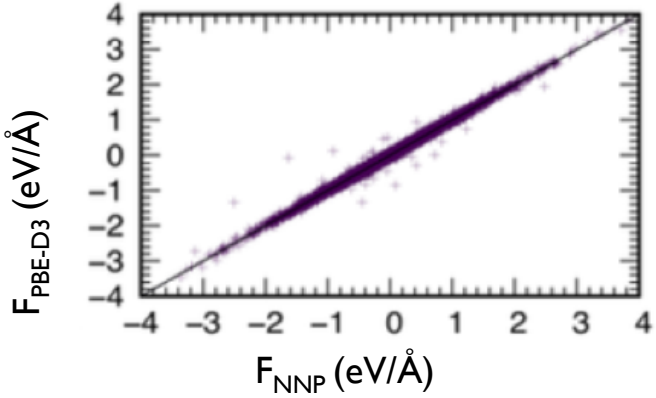
- Machine learning for reactive FFs

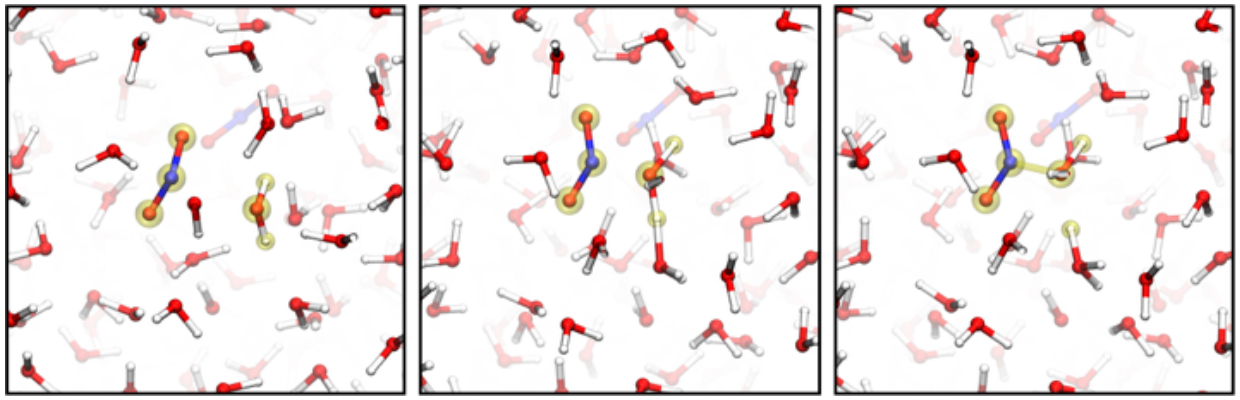
Condensed phase formation and dissociation of nitric acid at the GGA level with neural networks



Neural Networks:
reactive potentials from AIMD







Mirza Galib and David T. Limmer. In preparation

David Limmer

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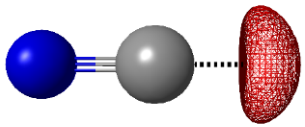
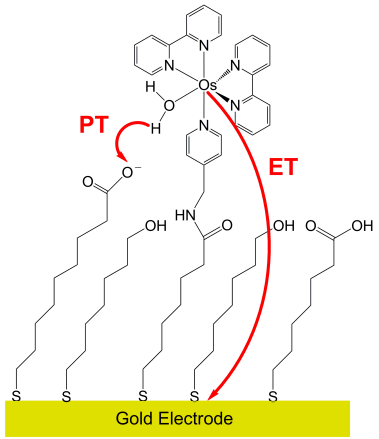
Nuclear-Electronic Orbital (NEO) Approach

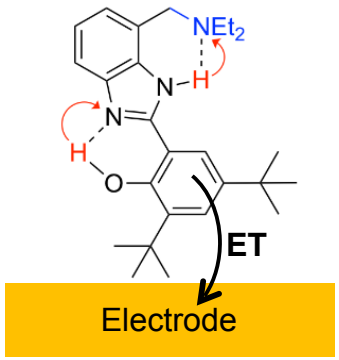
- Solution of mixed nuclear-electronic time-independent Schrödinger equation with molecular orbital methods
- Treat specified nuclei quantum mechanically on same level as electrons
  - treat only key H nuclei QM
  - retain at least two classical nuclei

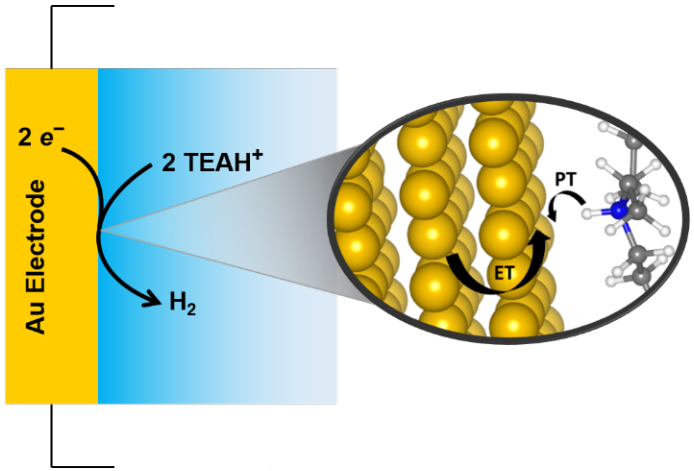
Example: HCN



- Includes proton delocalization and zero point energy during geometry optimizations, reaction paths, and dynamics rather than as corrections
- Avoids Born-Oppenheimer separation between electrons and protons
- Highly suitable for studying proton-coupled electron transfer (PCET) reactions in electrocatalysis systems







Sharon Hammes-Schiffer

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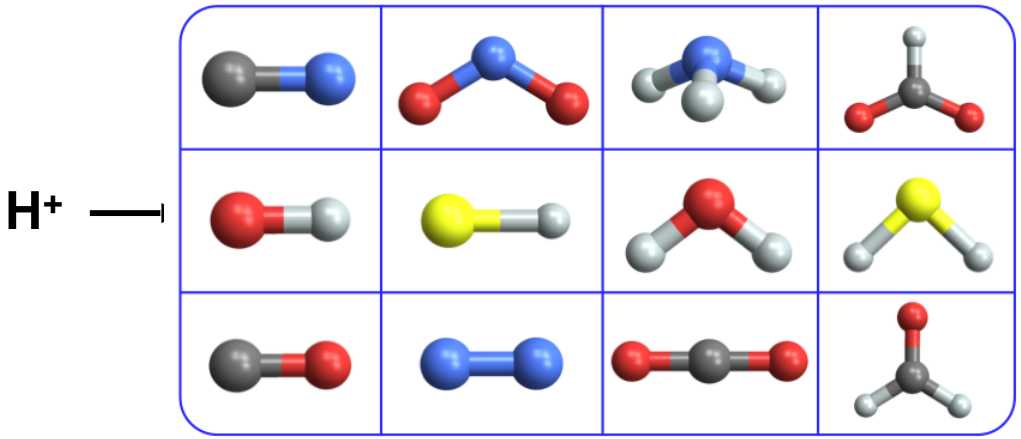
NEO Coupled-Cluster Singles and Doubles Theory

- Derived and implemented NEO-CCSD equations

$$\left|\mathrm{CCSD}\right\rangle = e^{\hat{T}}\left|\Psi_{\mathrm{NEO\text{-}HF}}\right\rangle \qquad \hat{T} = \hat{T}_1^{\mathrm{e}} + \hat{T}_2^{\mathrm{ee}} + \hat{T}_1^{\mathrm{p}} + \hat{T}_2^{\mathrm{pp}} + \hat{T}_2^{\mathrm{ep}}$$

- *T* is the sum of single and double cluster operators for electrons and protons
- Calculated proton densities, proton affinities, and optimized geometries with no parameterization
- NEO-CCSD provides qualitatively accurate proton densities & affinities
- NEO-EOM-CCSD is being developed for excited vibrational states



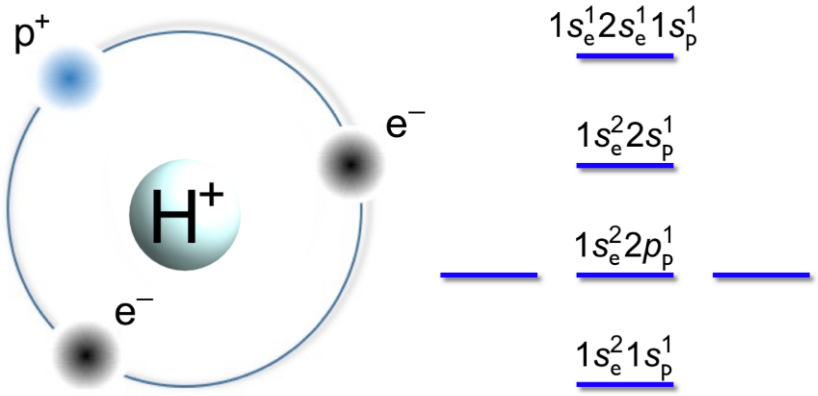
Mean unsigned error wrt experiment for proton affinities: 0.04 eV

Pavošević, Culpitt, Hammes-Schiffer, JCTC **15**, 338-347 (2019).

Sharon Hammes-Schiffer

NEO-EOM-CCSD for Excited States

- NEO-EOM-CCSD equations derived and implemented
- Applied to PsH, where positron and both electrons quantum mechanical
- Applying to quantum protons



state	NEO-FCI	NEO-FCC	NEO-EOM-CCSD	NEO-CISD
ground state	-0.090593	-0.090593	-0.085978	-0.085733
1st excited state	0.156700	0.156700	0.155107	0.179252
2nd excited state	0.165857	0.165857	0.166041	0.187039
3rd excited state	0.242055	0.242055	0.239553	0.254243

Energies in au. Excitation energies are relative to the ground state for each method.

EOM: equation-of-motion

Pavošević, Hammes-Schiffer, JCP 2019.

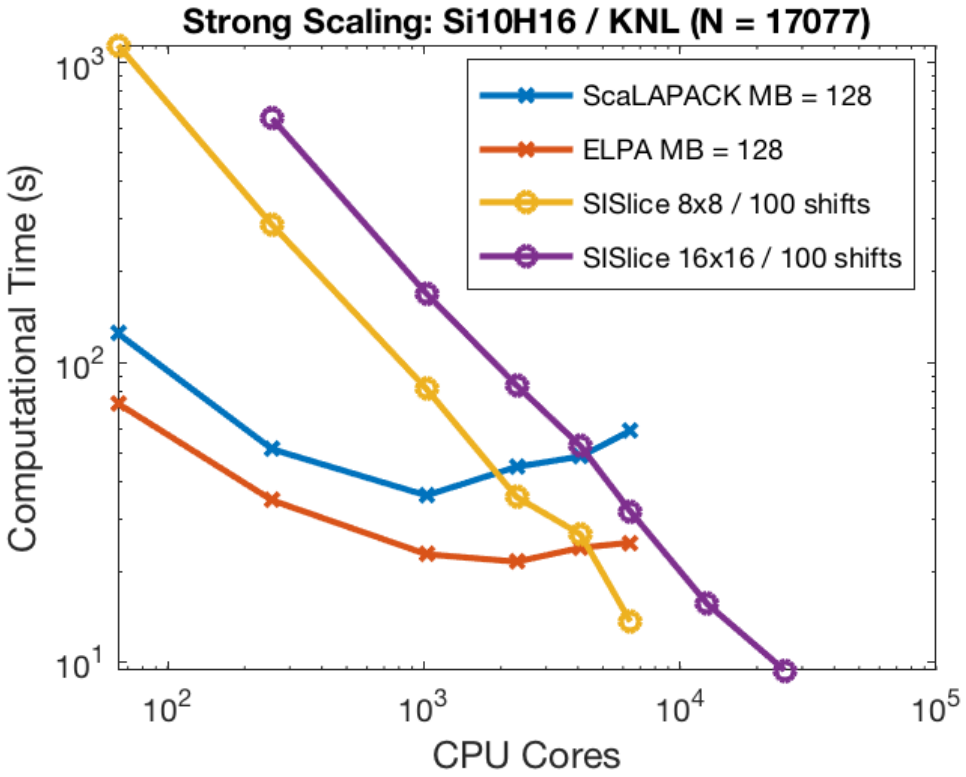
Advancing catalysis modeling: Outline

1. Electronic structure theory and embedding
2. Statistical mechanics & dynamics
3. **Applied math and CS/HPC**

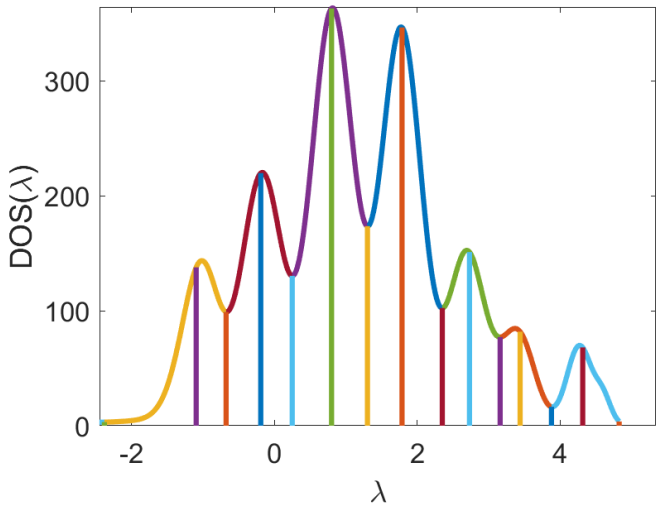
Chao Yang, Xiaoye Li, Lin Lin, Esmond Ng, Khaled Ibrahim, Sam Williams

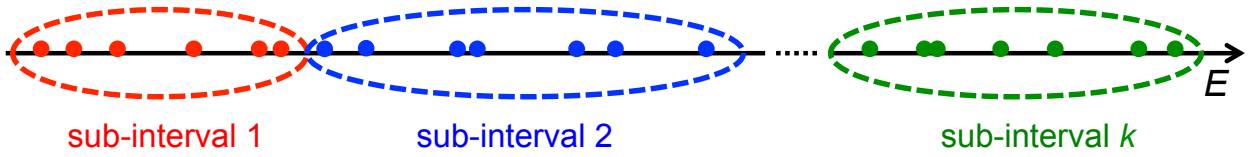
4. **Whole system modeling**

Extending the Scalability of Existing Eigensolvers via Spectrum Slicing



- Existing solvers (ScaLAPACK/ELPA) not scalable beyond a few thousands of cores
- Spectrum slicing has better scalability
  - Initial spectrum partition by Lanczos DOS estimation
  - Refined partition by K-means clustering



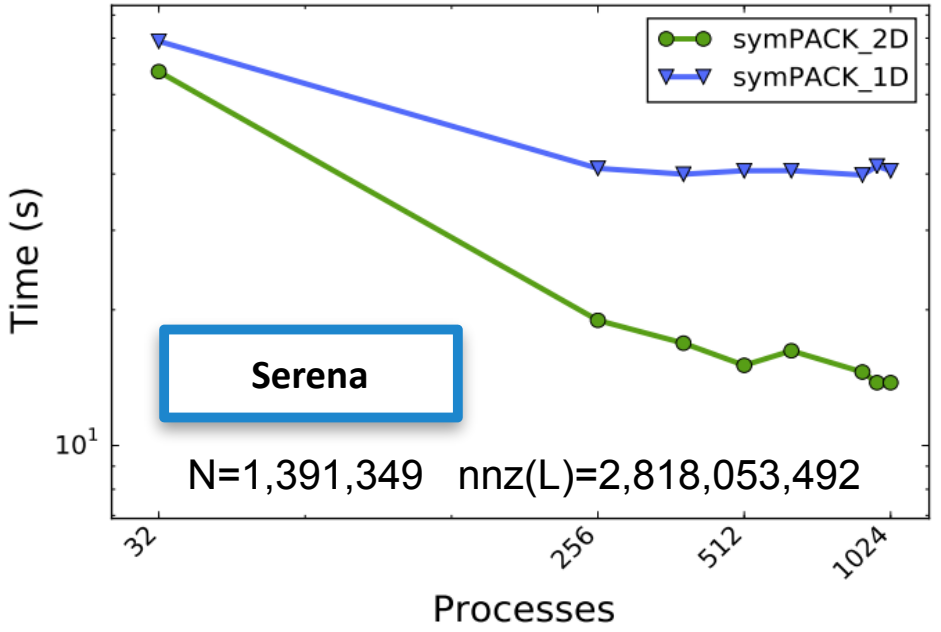


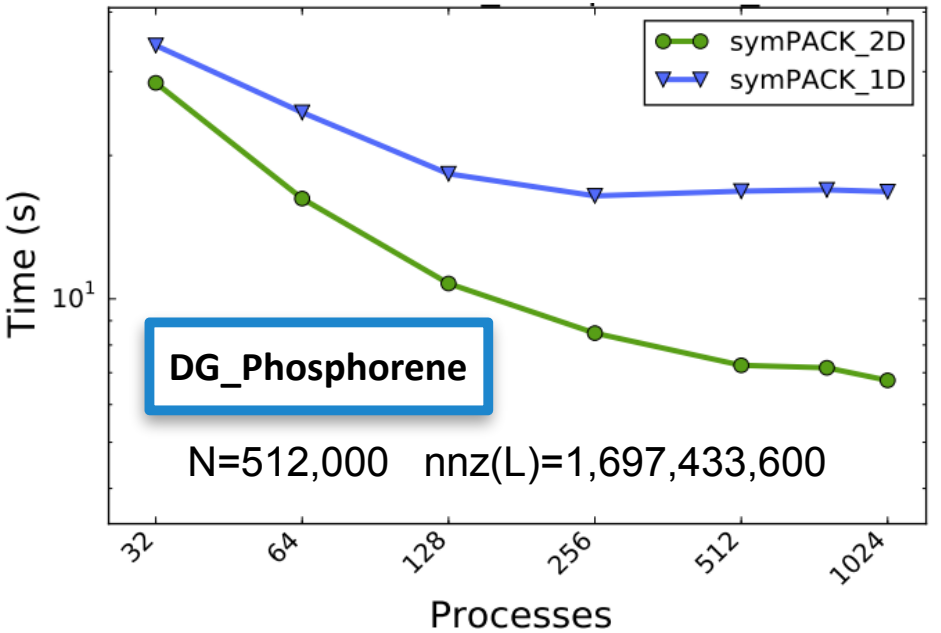
Chao Yang

A new 2D task-based symPACK

- Factorization crucial to PEXSI
- symPACK for symmetric systems
  - 1D supernodal distribution:
    - Balances flops, memory
    - Lacks strong scalability
  - New task-based 2D data distribution
    - Explicit load balancing, not regular block cyclic mapping
    - Balances flops, memory
    - High strong scalability
  - Strong scalability on Cori Haswell:
    - Up to 3x speedup for Serena
    - Up to 2.5x speedup for DG_Phosphorene

www.sympack.org





Sherry Li, Esmond Ng

STRUMPACK – low-rank STRUctured Matrix Package

- Generic direct solvers and preconditioners using hierarchical low-rank compression techniques
  - Nearly-linear complexity O(N polylog(N))

Recent progress

- In addition to HSS, other formats: HODLR, BLR
- Fast rank-detection using adaptive randomized sampling
  - Difficulty: how many random vectors to use?
  - Developed a new stopping criteria based on stochastic norm estimation

Let $A \in \Re^{mxn}$, and $x \in \Re^{n}$ with $x_i \sim N(0,1)$, we proved:

$$\mathrm{E}\left[\left\|Ax\right\|_2^2\right] = \sigma_1^2 + \cdots + \sigma_r^2 = \left\|A\right\|_F^2$$

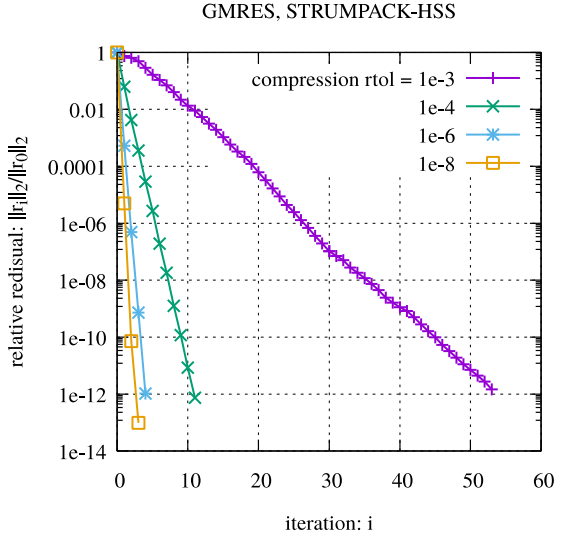
For d sample vectors: $\mathrm{E}\left[\left\|S\right\|_F^2\right] = d\left\|A\right\|_F^2$

- More accurate than commonly-used upper bound estimation (Halko-Martinsson-Tropp)

BEM electromagnetic multi-sphere
Direct solver, N = 27K, dense

	NEW	OLD
Compression	5.50	8.24
Factorization	1.98	2.83
Solve	0.14	0.15

Indefinite Maxwell equations, EM diffusion
Preconditioner to GMRES, N = 331K, sparse



State-of-the-art AMS multigrid preconditioner does not converge

Sherry Li, Esmond Ng

Optimization of DFT Calculation on HPC Platforms

Target platforms

Multi/Many core architectures
(Haswell and KNL)
GPU accelerated architectures

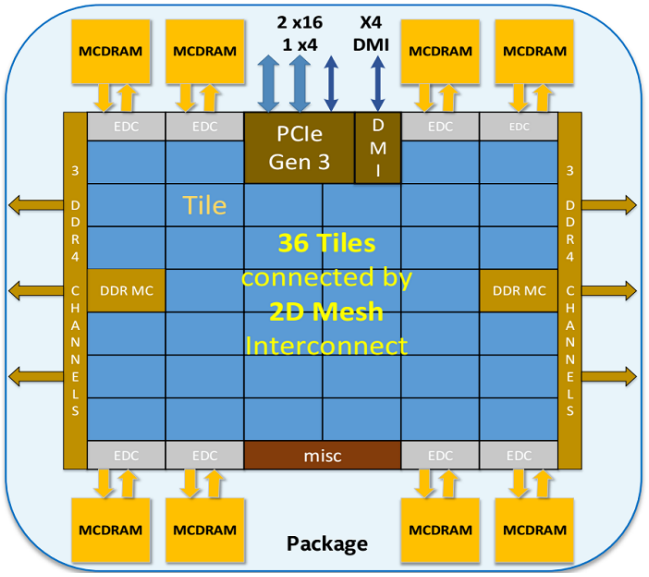
Software tuning challenges:

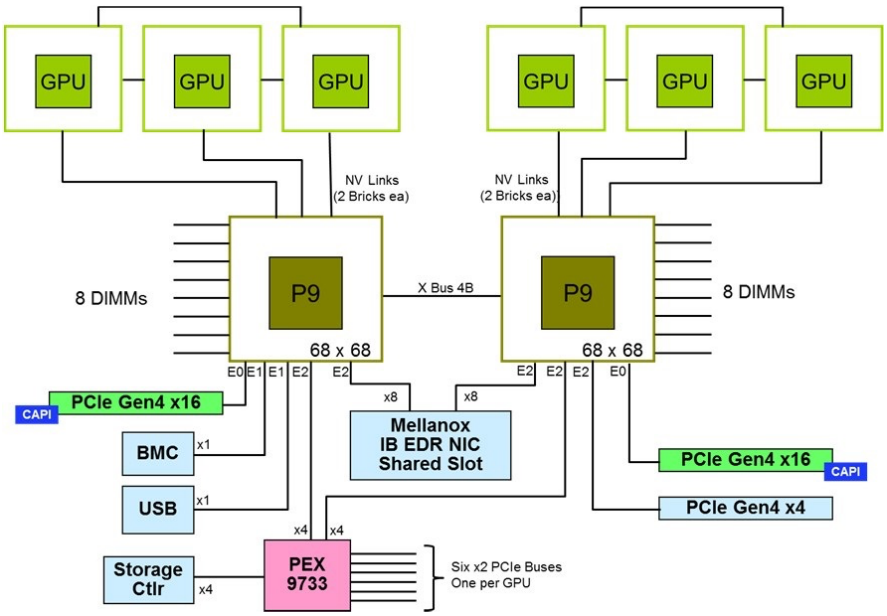
CP2K: Complex software stack,
Thread parallelism across layers.
MPI Communication
DGDFT: MPI Communication
locality in distributed cache
Load imbalance
Improve the use of external.

Accomplishments:

CP2K: Improve CP2K build on Haswell and KNL (up to 1.7x)

DGDFT: Improve communication, load balancing and interaction with external libraries (up to 2x).





Khaled Ibrahim

SciDAC
Scientific Discovery through Advanced Computing

Optimizing Density Calculation

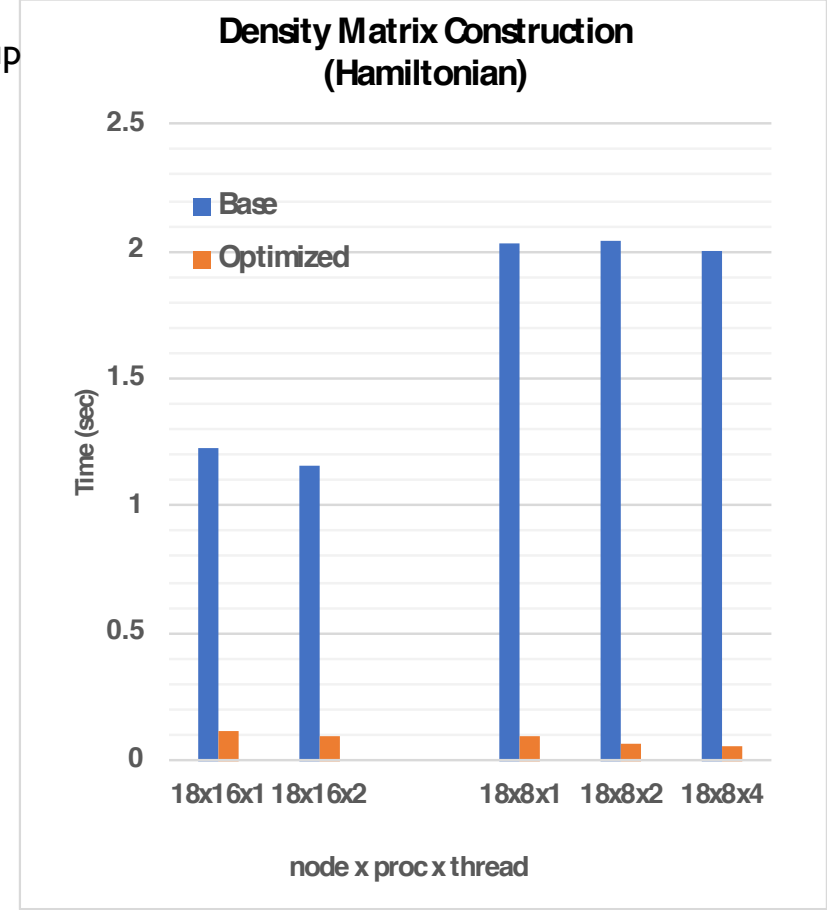
Loop optimizations:

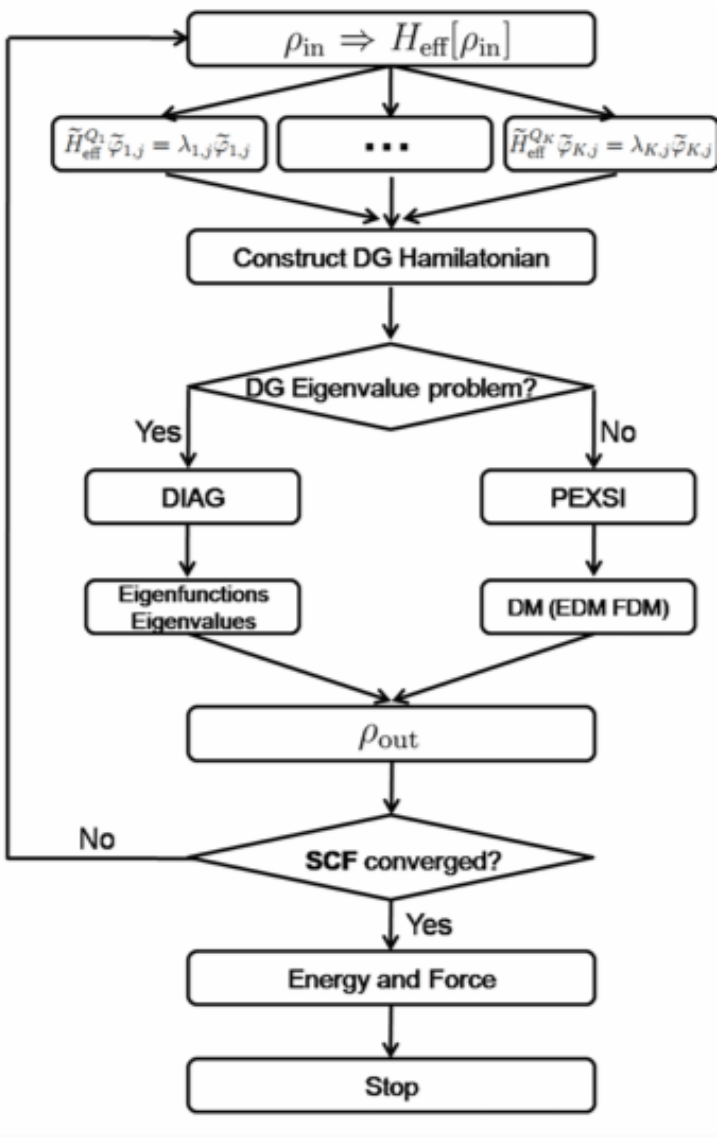
Loop reordering to improve the load balancing
Native indexing, no error checking

Loop parallelization

Performance:

10-37x speedup.
KNL 15x speedup





Khaled Ibrahim

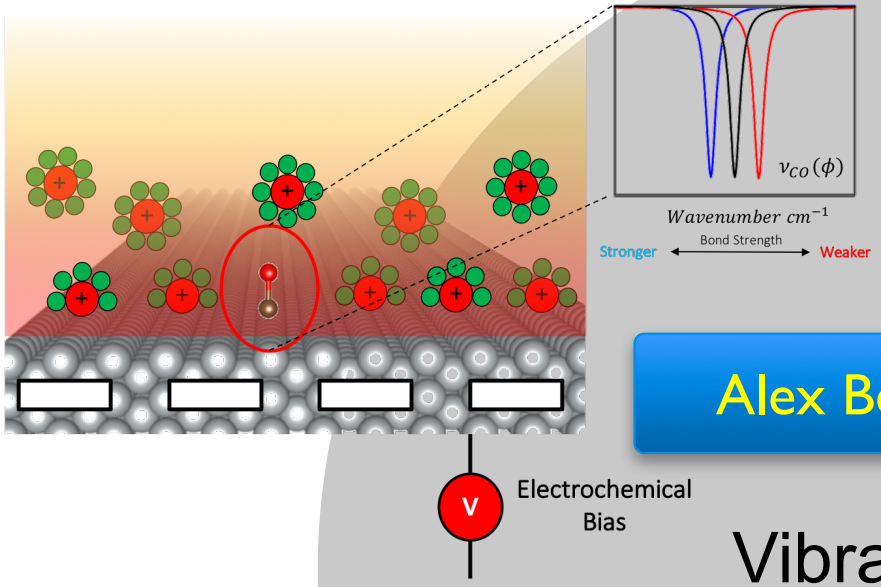
Advancing catalysis modeling: Outline

1. Electronic structure theory and embedding
2. Statistical mechanics & dynamics
3. Applied math and CS/HPC
4. **Whole system modeling**

Alex Bell, Emily Carter, Teresa Head-Gordon, Martin Head-Gordon

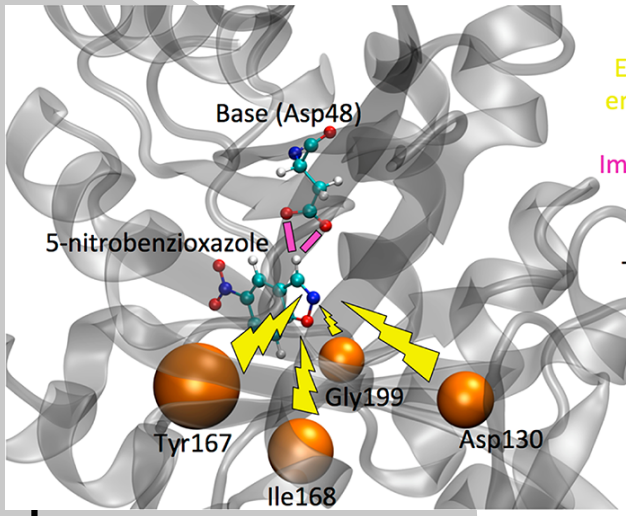
Collaboration within SciDAC on the Vibrational Stark Effect

Vibrational Stark Effect in Heterogenous Catalysis



Alex Bell

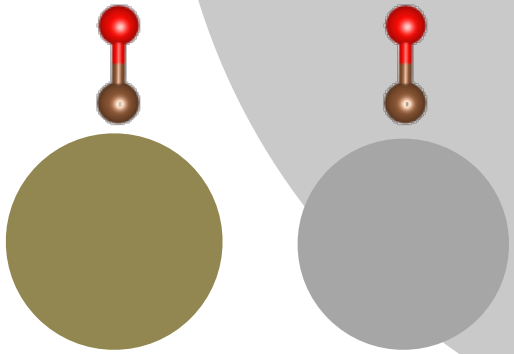
Treatment of Electric Fields in Bio-systems



Teresa Head-Gordon

Vibrational Stark Effect

Vibrational Stark Effect on Noble Metal Atoms



Martin Head-Gordon

Opportunity to investigate the same phenomena in the context of different physical systems.

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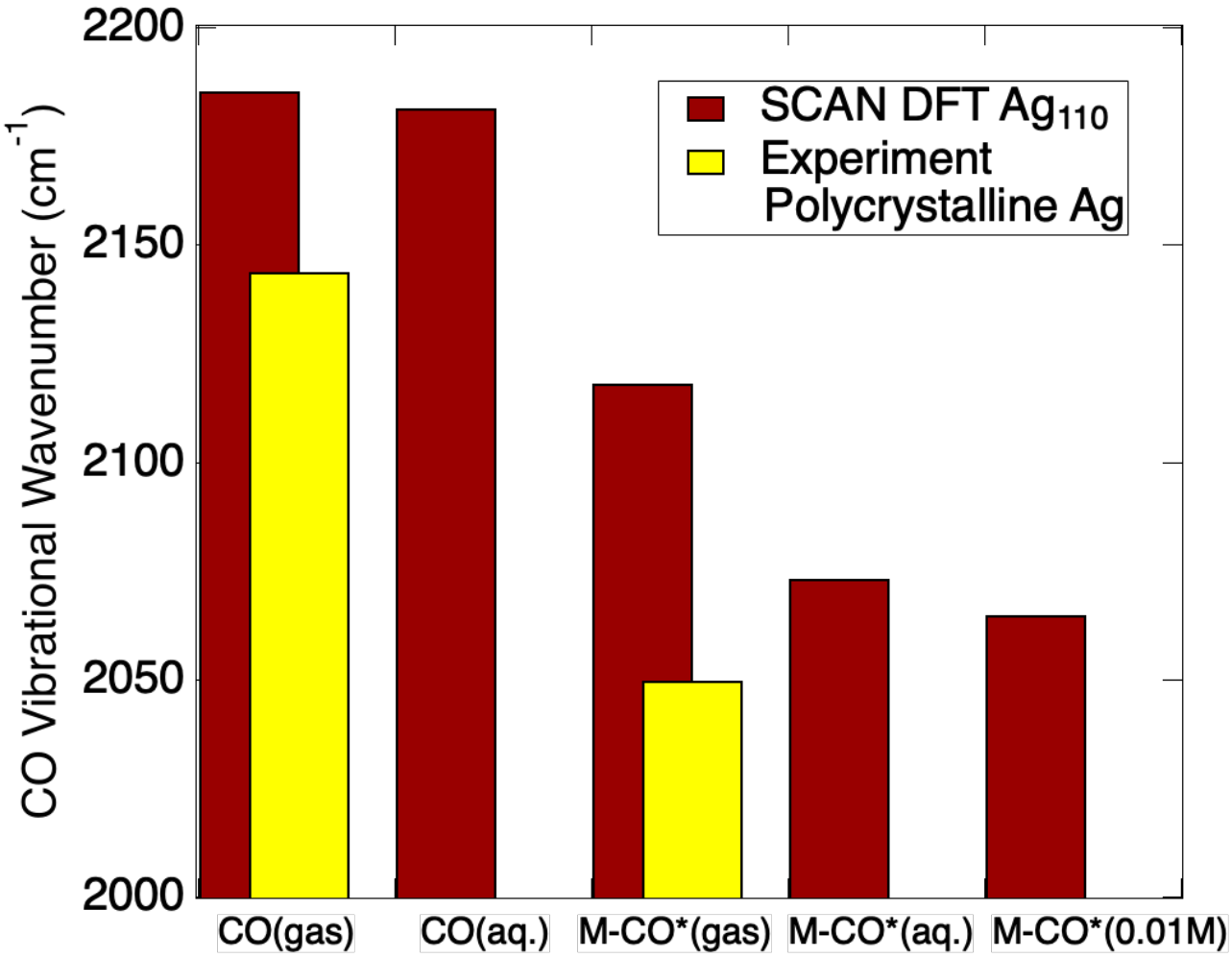
Results: Experimental vs. computed vibrational frequencies

- Calculations: SCAN functional
- Theory predicts red-shift upon adsorption on Ag(110)
- Theory predicts further red-shifting upon aqueous environment
- Origin of discrepancy between experiment and theory: anharmonicity, surface termination, surface coverage, and functional.
- Further experiments underway to assess theoretical predictions.



Christianna Lininger

Experiments: Kun Jiang (LBL) + Xianyin Ma (Fudan)

Alex Bell

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Origin of the Stark effect: Red and blue shifting in M-CO complexes

Physical Stark effect: electric fields due to local charges control frequency shifts via dipole moment changes.

Chemical Stark effect: charge flow due to CO binding controls frequency shifts via dative interactions

Probe by finding the frequency shifts using constraints to prevent charge transfer (and polarization)

E. Rossomme, M. Head-Gordon (2019) In progress

	Frequency Shift (cm^{-1})		
Species	δ_{FRZ}	δ_{POL}	δ_{CT}
$TiCO^-$	1.69	-6.19	-383.87
VCO	-0.81	40.25	-237.00
$CrCO^+$	86.94	25.01	-34.92
VCO^-	-1.03	-6.51	-369.18
CrCO	-0.18	0.04	-119.21
$MnCO^+$	56.05	33.29	8.57

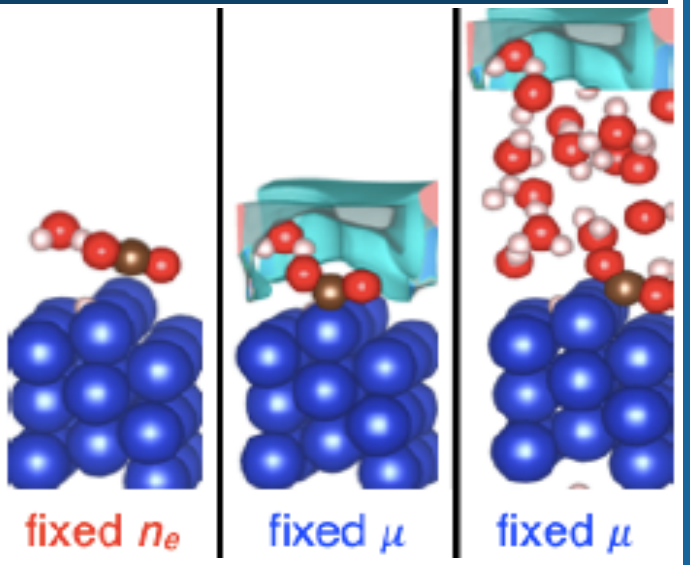
Above results identify charge transfer ("chemical effects") as the origin of red shifting (strongest in metal anions)

Frozen response ("physical effects") is the origin of blue shifting in the cations for above cases: the $^{\delta-}CO^{\delta+}$ dipole increases as bond-length gets shorter.

Martin Head-Gordon

SciDAC 4 Partnership: Advancing catalysis modeling

Martin Head-Gordon (PI)

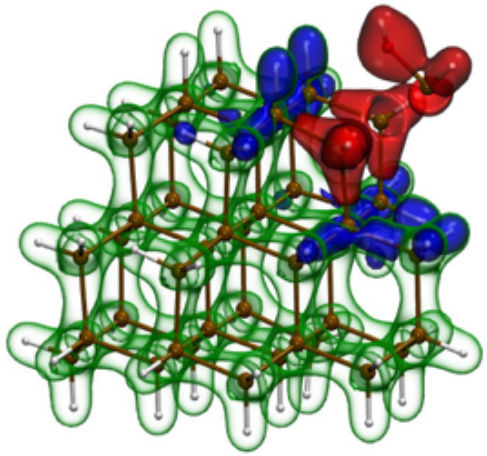


Physical sciences objectives:

Advance electronic structure modeling
Explicit solvent, NQEs and statistical mechanics
Whole system modeling

Applied math and computer science objectives:

New algorithms/solvers for this application domain
New algorithm development (partnerships)
Improved parallel scaling for supercomputers



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

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Scientific Discovery through Advanced Computing