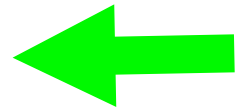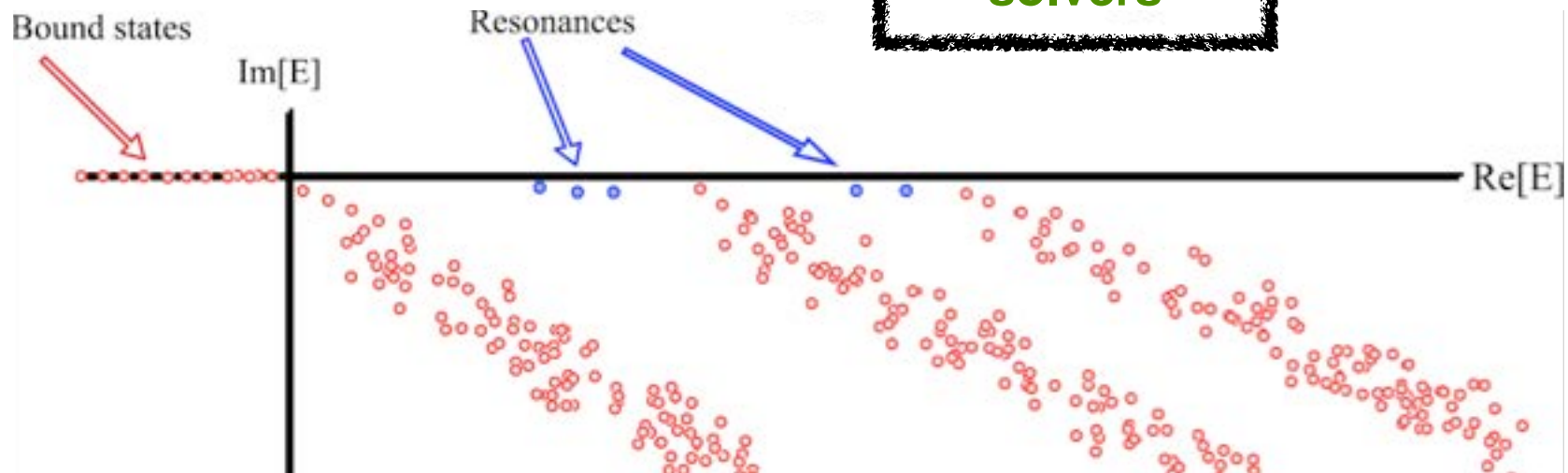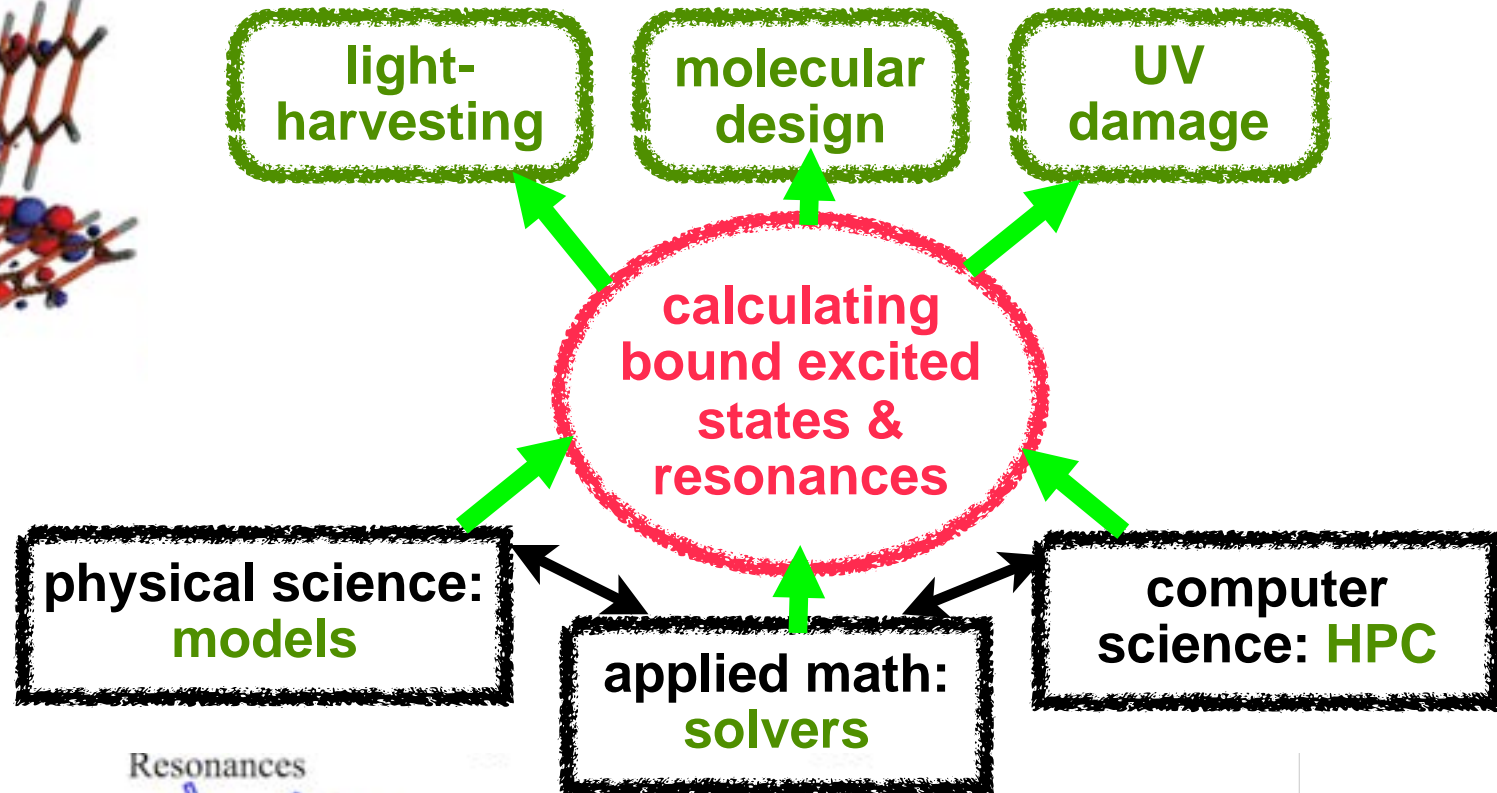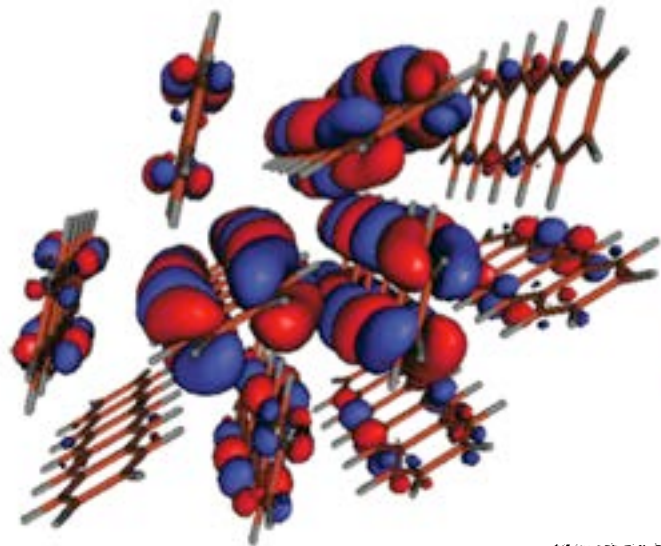# **Simulating the generation, evolution and fate of electronic excitations in molecular and nanoscale materials with first principles methods**

1. Introduction and overview

2. Highlights of progress and interactions

Simulating electronic excitations in molecular and nanoscale materials with first principles methods.

light-harvesting

molecular design

UV damage

calculating bound excited states & resonances

physical science: models

applied math: solvers

computer science: HPC

Bound states

Resonances

Im[E]

Re[E]

Our team: Principal investigators

Daniel Haxton (Chemical Sciences, LBNL).

Martin Head-Gordon (Chemical Sciences, LBNL).

Anna Krylov (Chemistry, USC).

Xiaoye (Sherry) Li (Computational Res., LBNL).

C. William McCurdy (Chemical Sciences, LBNL).

Esmond Ng (Computational Research, LBNL).

Sam Williams (Computational Res., LBNL).

Chao Yang (Computational Research, LBNL).

Our team: Postdocs and students.

Jiri Brabec (EN).

Evgeny Epifanovsky (AIK, MHG).

Khaled Ibrahim (SW).

Jeremiah Jones (DJH).

Ilya Kaliman (AIK).

Nicholas Mayhall (MHG).
Natalie Orms (AIK).
Francois-Henry Rouet (XL).

Eugene Vecharynski (CY).

Alec White (CWM, MHG).

Dmitry Zuev (AIK).

Outline of highlights.

→ **LibTensor developments**
  Anna Krylov, Evgeny Epifanovsky, Ilya Kaliman,
Khaled Ibrahim, Sam Williams, Francois-Henry Rouet,
Sherry Li, Eugene Vecharynski, Dmitri Zuev, Natalie Orms,
Chao Yang, Jiri Brabec, Esmond Ng

Treating resonances using complex scaling
  Alec White, Martin Head-Gordon, Bill McCurdy

Active space spin-flip methods for excited states
  Nick Mayhall, Martin Head-Gordon

Efficient tensor contraction algorithms and codes for wave-function methods

Development of reduced scaling implementations of existing coupled cluster methods for electronically excited states (both bound and resonances).

Approach: Explore matrix and tensor decompositions that reduce data size; exploit locality; combine with efficient parallelization.

Benefits:
- Extend applicability of reliable and proven methods as CC/EOM-CC to larger molecules,
- Apply the same underlying ideas and libraries for reduced scaling to other methods, such as those developed by Head-Gordon and McCurdy.
- Better exploit high-performance computing resources.

Anna Krylov: Progress report.

1. Cholesky decomposition (CD) and RI of ERI is implemented in Q-Chem 4.1(released).
2. Libtensor (tensor library) is extended to handle CD/RI representations (published & released).
3. RI/CD implementation of CCSD and all EOM-CCSD methods (EE, IP, EA, SF) completed and validated (published). RI/CD combined with FNO.
4. New infrastructure in libtensor (expressions eval-n).
5. Shared-memory parallel performance of libtensor is improved following findings by Khaled Ibrahim/Sam Williams (code released, paper submitted).
6. Extension of Davidson solver for interior eigenvalues is implemented.
7. GPLMR is implemented in Q-Chem using libtensor tools (collaboration with Vecharynski & Yang, paper submitted).

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Anna Krylov: Publications

New Implementation of High-Level Correlated Methods Using a General Block Tensor Library for High-Performance Electronic Structure Calculations

Evgeny Epifanovsky,[a,b] Michael Wormit,[c,d] Tomasz Kuś,[a] Arie Landau,[a] Dmitry Zuev,[a] Kirill Khistyaev,[a] Prashant Manohar,[a,e] Ilya Kaliman,[a,f] Andreas Dreuw,[d] and Anna I. Krylov*[a]

General implementation of the resolution-of-the-identity and Cholesky representations of electron repulsion integrals within coupled-cluster and equation-of-motion methods: Theory and benchmarks

Evgeny Epifanovsky,[1,2,3] Dmitry Zuev,[1] Xintian Feng,[1] Kirill Khistyaev,[1] Yihan Shao,[3] and Anna I. Krylov[1]
[1]Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, USA
[2]Department of Chemistry, University of California, Berkeley, California 94720, USA
[3]6601 Owens Drive, Suite 105, Pleasanton, California 94588, USA

New algorithms for iterative matrix-free eigensolvers in quantum chemistry

Dmitry Zuev[a], Eugene Vecharynski[b], Chao Yang[b], Natalie Orms[a], Anna Krylov[a]

[a] Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482
[b] Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

## Analysis and Tuning of Libtensor Framework on Multicore Architectures

Khaled Z. Ibrahim, Samuel W. Williams
Computational Research Division,
Lawrence Berkeley National Laboratory,
Berkeley, CA, USA
{kzibrahim, swwilliams}@lbl.gov

Evgeny Epifanovsky, Anna I. Krylov
Department of Chemistry
University of Southern California,
Los Angeles, CA, USA
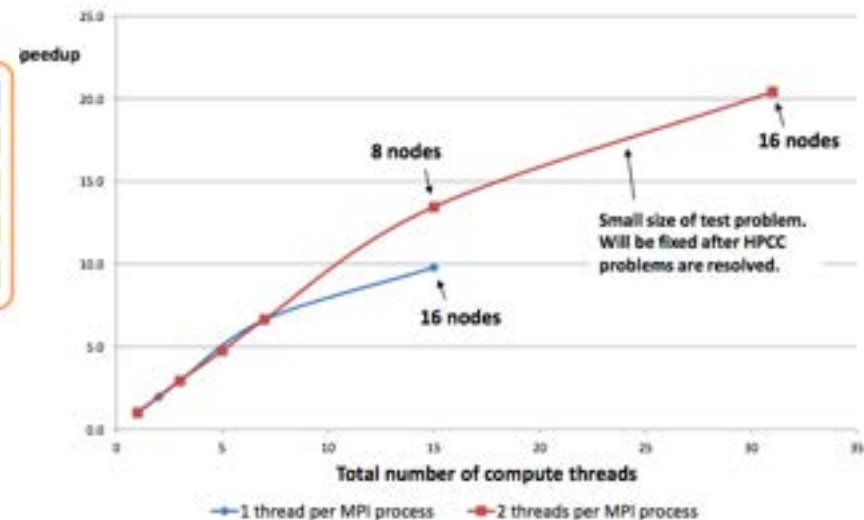{epifanov, krylov}@usc.edu

Anna Krylov: Research highlight

Libtensor developments:

1. Original libtensor: multicore parallel (Khaled and Williams: analyzing/improving performance).
2. Extension to massively parallel (>1000 nodes): via fusion with CYCLOPS (Epifanovsky, Solomonik): Pilot code is ready, performance studies in progress.
3. Extension to intermediate regime (up to 100 nodes): Pilot code is ready, performance studies in progress (Kaliman, **see poster!**). Strategy:
- Replicated memory;
- Known to scale well up to 100s of nodes;
- MPI-1 only (very portable);
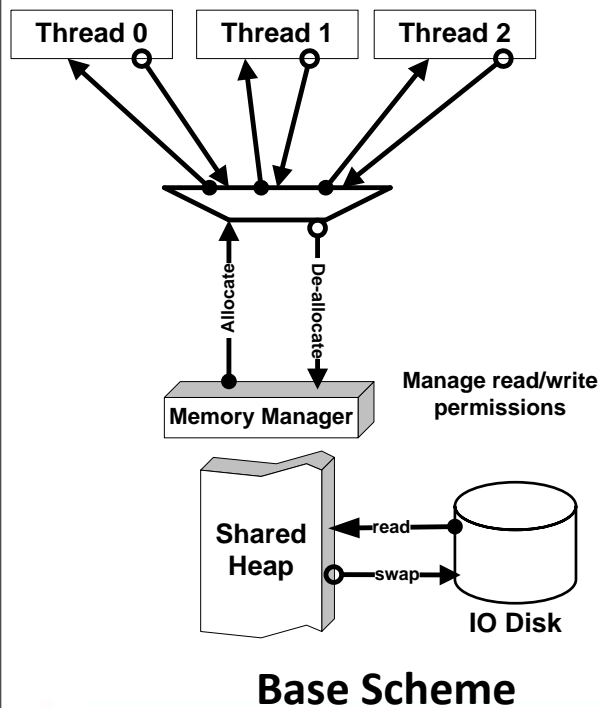- Simple code and algorithms;
- Can reuse existing infrastructure.

USC HPCC, Infiniband network
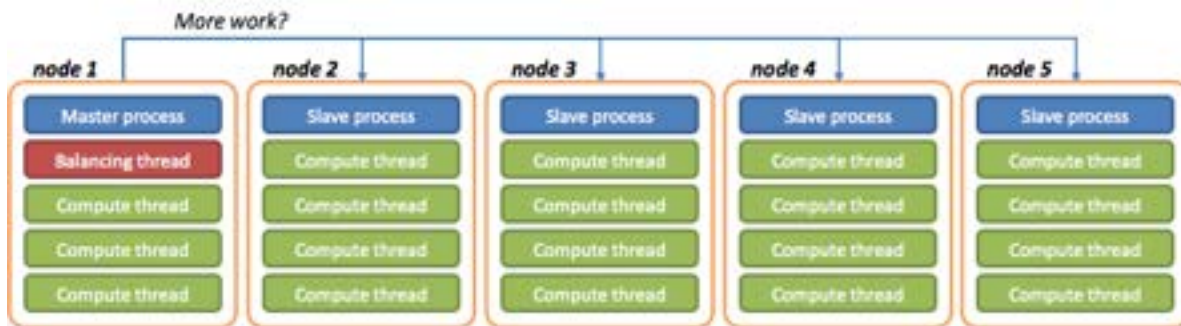
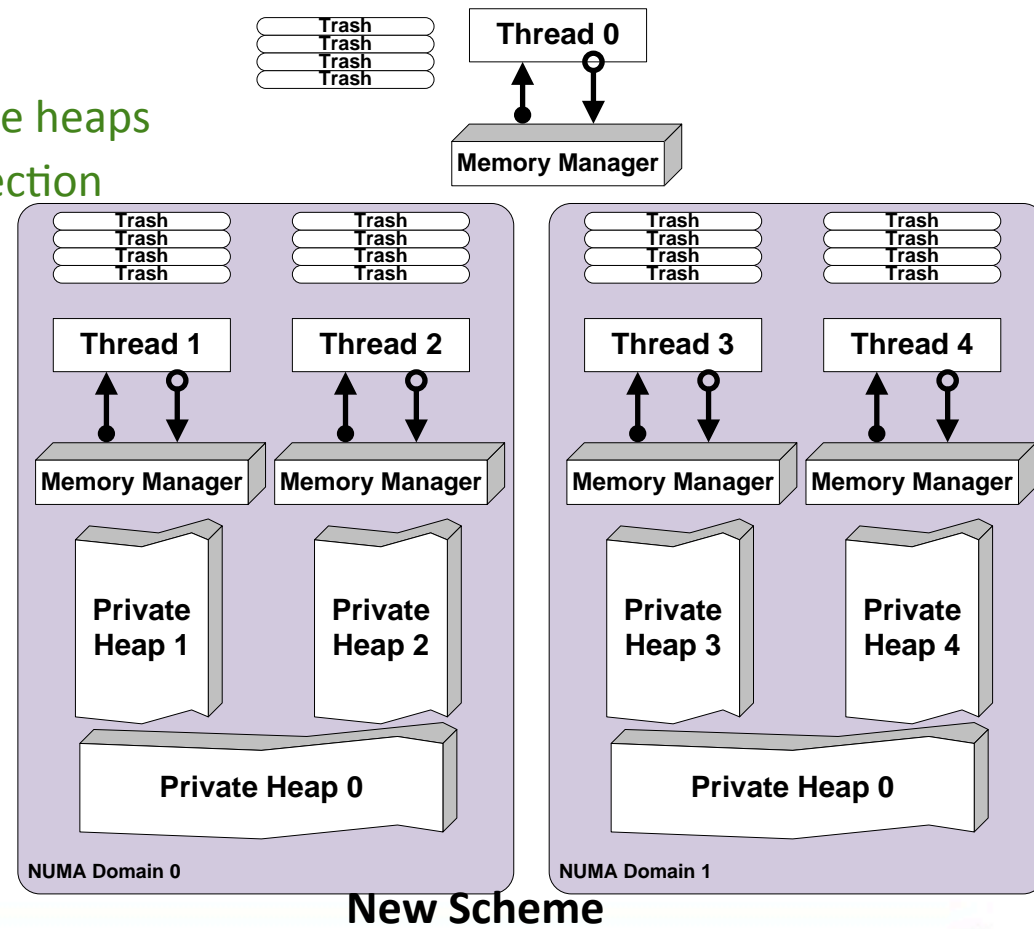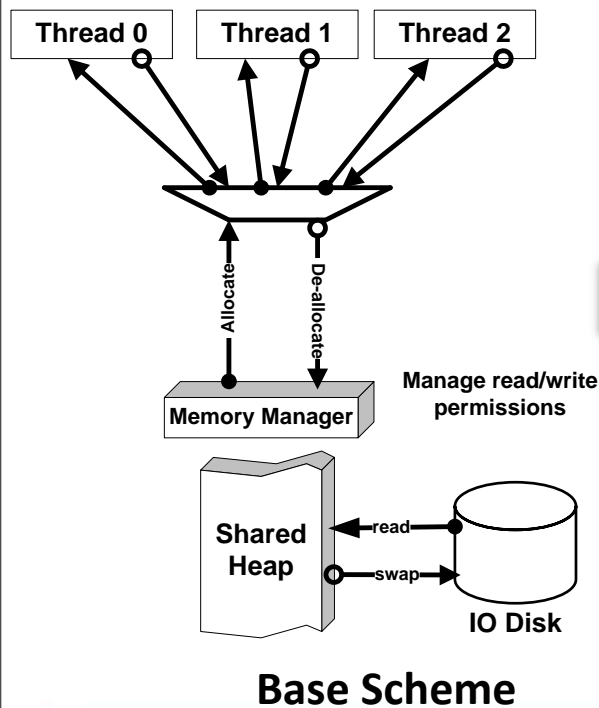Total number of compute threads: $N = N_{thr} * N_{nodes} - 1$

Improving Locality and Parallelization in Libtensor

- Existing Challenges:
  - No inherent management of locality
  - Potential for contention and serialization
- We developed a new memory management scheme:
  - Restrict thread migration
  - Explicit memory affinity allocation
  - Parallelize the allocator by creating private heaps
  - Parallelize deallocator using garbage collection


Base Scheme

Improving Locality and Parallelization in Libtensor

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Base Scheme

New Scheme

Improvement to Libtensor Scaling

- Previous Scalability:
  - 9.5x speedup using 24 cores
- Scalability after Optimization:
  - 15.3x speedup with 24 cores
  - Parallel Efficiency improved from 39.5% to 64%.
- **Ideal scalability is limited by libtensor's tasking model**:
  - Amdhal Effect from master-worker model with barriers
- Further Improvement requires managing task dependencies.
  - Alternatively, concede optimizations for an elegant distributed implementation.

Speedup Edison P1
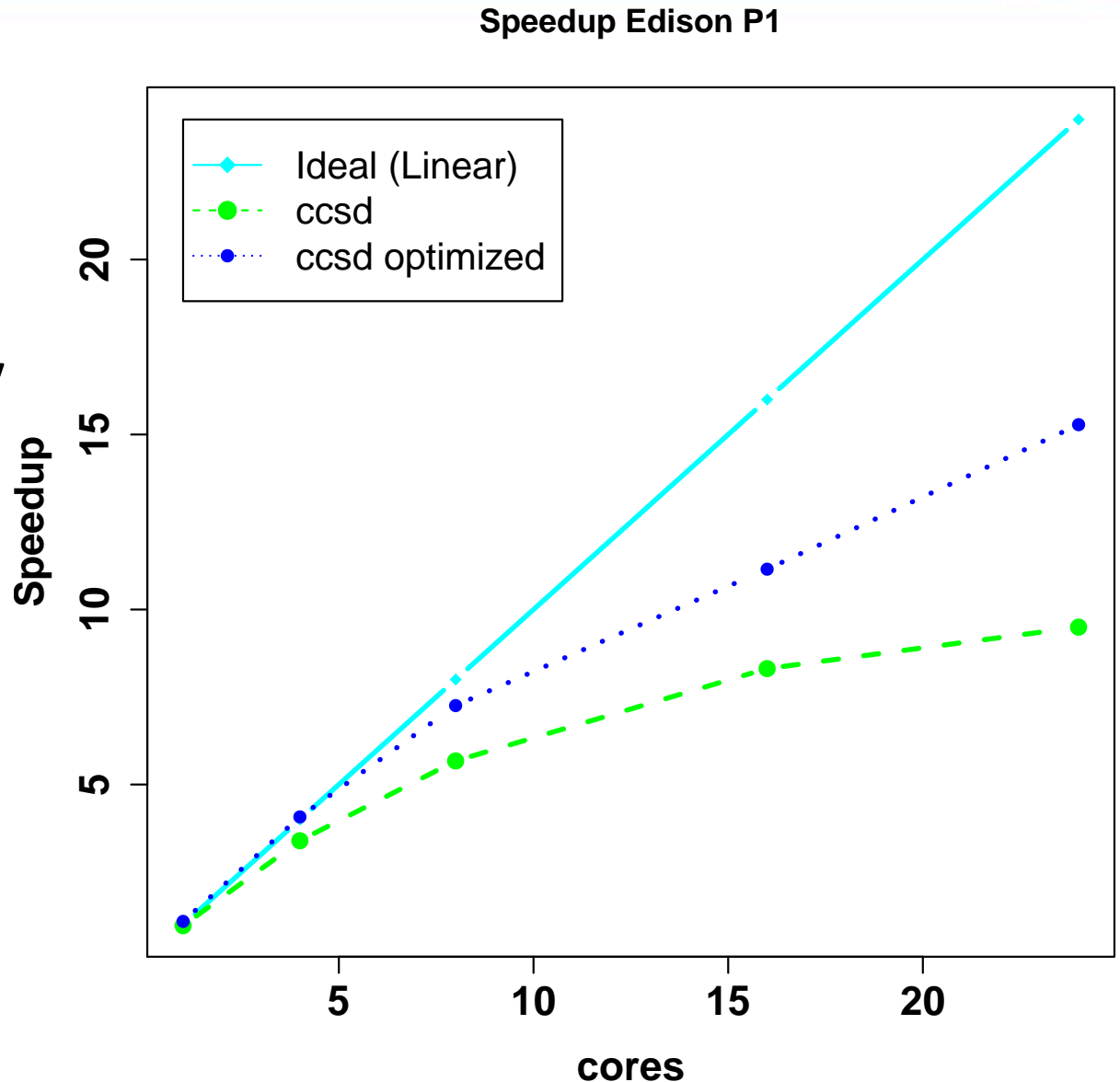
Summary

- Analysis and tuning of Libtensor stack of libraries
  - Identified bottlenecks (locality, serialization, load balancing)
  - Implemented a new memory management system for optimal locality management and to avoid serialization.
  - Searched tuning space for optimal configuration.
  - **attained a 1.8x improvement on Edison, more than 2x on large AMD SMPs.**

- Submitted Publication (under review)
  - Khaled Z. Ibrahim, Samuel W. Williams Evgeny Epifanovsky, Anna I. Krylov "Analysis and Tuning of Libtensor Framework on Multicore Architectures" submitted to the IEEE international Conference on High Performance Computing.

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Benchmarking CD-CCSD
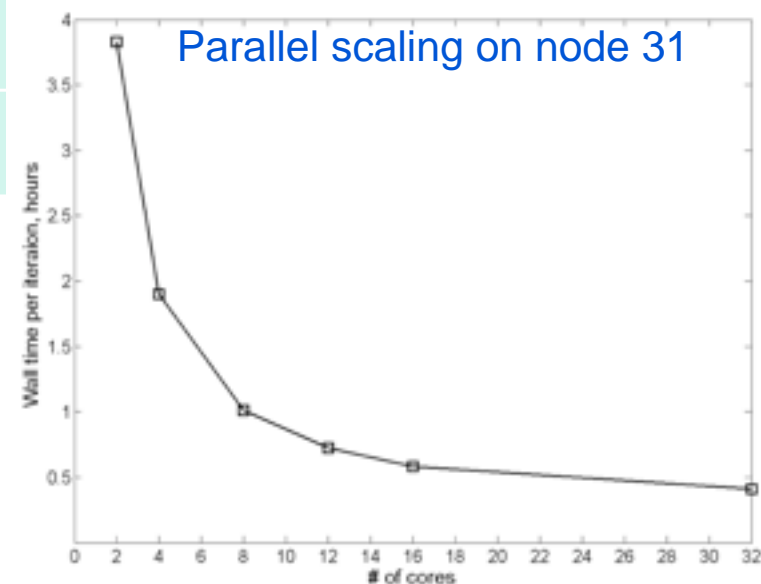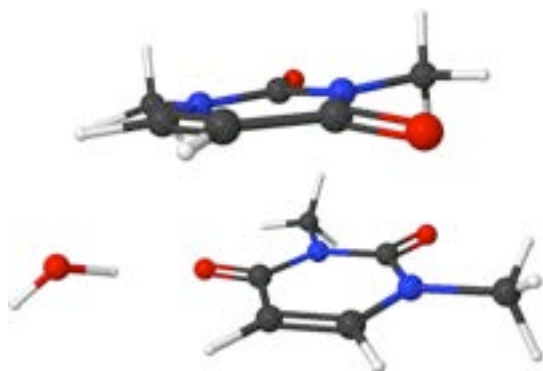Example: $(mU)_2$-H_2O: 158 electrons; C_1 symmetry
6-31+G(d,p) basis: 489 b.f.
cc-pVTZ basis: 882 bf
Calculations on a single Xeon-Dell node (16 cores; node28)

| Method/Basis	Memory	CCSD wall (one iter-n), hours
CD2/6-31+G(d,p)	100 GB	5.1
CD2/FNO/6-31+G(d,p)	100 GB	1.4
CD2/FNO/cc-pVTZ	300 GB	12.2

Parallel scaling on node 31

Anna Krylov: Research highlight

"New algorithms for iterative matrix-free eigensolvers in quantum chemistry", by D. Zuev, E. Vecharynski, C. Yang, N. Orms, A. Krylov

- Different algorithms (modified Davidson procedure and GPLMR by Vecharynski) for interior eigen-states are developed and implemented in production-level code in EOM-CC (released in QChem 4.2);
- Robust performance for high-lying eigenstates (such as highly excited states, core ionized states, etc);
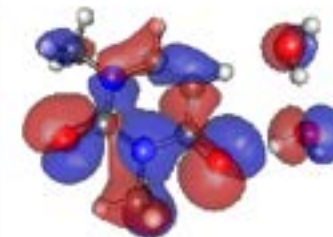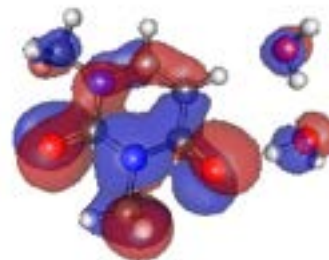- Significant computational savings for valence states.

GLMR converging G2 roots at specified energy shift

Shift, a.u.	N iter	Stored vecs	# of matvec
6.6	4	16	18
9.6	4	16	18
10.1	4	16	18
11.1	4	16	18
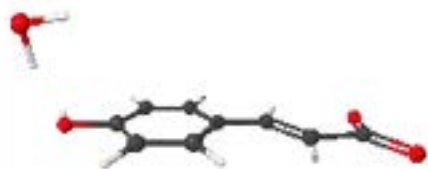
Davidson converging 1 EOM-IP root of a given character

MO	N iter	Max vec	# of matvec	Cost relative to canonical algorithm
46 (2nd IP)	10	22	11	78%
45 (3rd IP)	11	24	12	50%

Anna Krylov: Work in Progress

- RI gradient is nearly completed (coll-n w/Head-Gordon).
- CD gradient is in progress.
- Extension of libtensor to distributed parallel architecture via fusion with CYCLOPS is nearly completed, benchmarks are (collaboration with Solomonik).
- Performance benchmarking and improvements (exploiting data locality) are ongoing (coll-n with Ibrahim and Williams).
- Sparsity/rank reduction explorations are ongoing.

Outline of highlights.

LibTensor developments
  Anna Krylov, Evgeny Epifanovsky, Khaled Ibrahim,
  Sam Williams, Francois-Henry Rouet, Sherry Li,
  Eugene Vecharynski, Chao Yang,
  Jiri Brabec, Esmond Ng

→ **Treating resonances using complex scaling**
  Alec White, Martin Head-Gordon, Bill McCurdy

Active space spin-flip methods for excited states
  Nick Mayhall, Martin Head-Gordon

Computational Quantum Chemistry of Metastable States

The problem: Compute the energies and lifetimes of metastable states of molecules as a function of molecular geometry – complex potential energy surfaces

$$E(\vec{R}) = E_r(\vec{R}) - i\,\Gamma(\vec{R})$$

$$\text{lifetime} = \hbar/\Gamma(\vec{R})$$

Metastable states have complex energies: solutions of the Schrödinger equation with pure outgoing wave scattering boundary conditions

State of the art: No general method exists for applying the tools of modern quantum chemistry to metastable states of polyatomic molecules
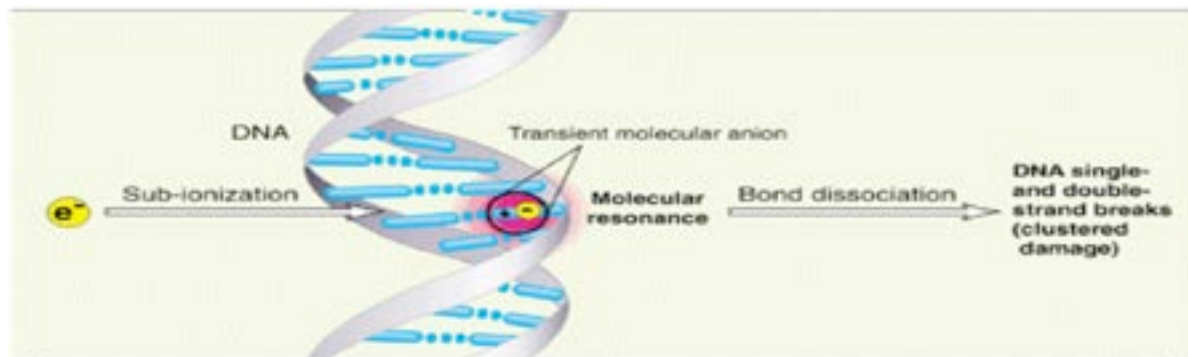
Why is this an important problem?

- Electrons attach to molecules via metastable resonance) states to initiate "Electron-Driven Chemistry"
- Significant for radiation damage

Single and double strand breaks in DNA

Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons
Badia Boudaïffa, et al.
Science 287, 1658 (2000);
DOI: 10.1126/science.287.5458.1658

Most energy deposited in cells by ionizing radiation is channeled into free secondary electrons with energies between 1 eV and 20 eV (B. Boudaï ffa et al., Science 287 (2000) 1658)
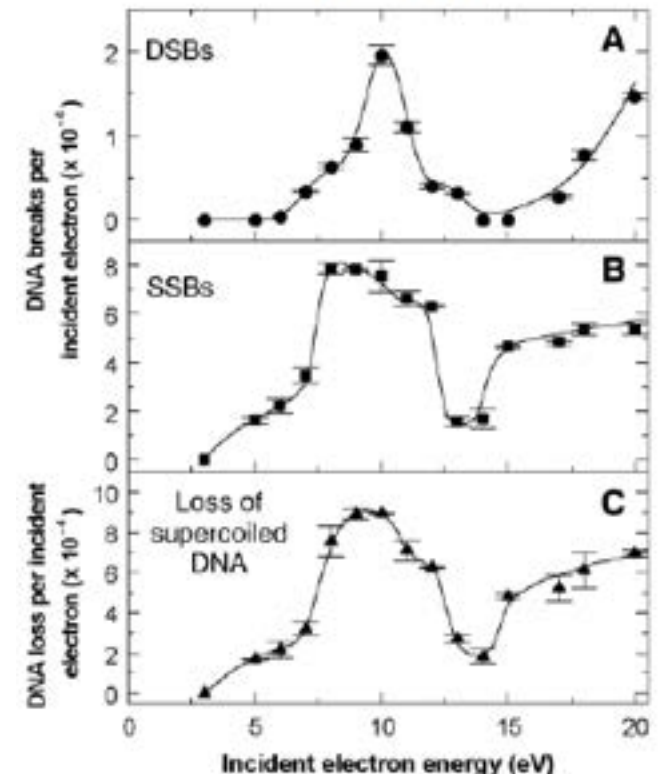
Formal solution is complex scaling of electronic coordinates

- Under complex scaling, wave functions of metastable states are square integrable.

- Hence can be treated with quantum chemistry methods
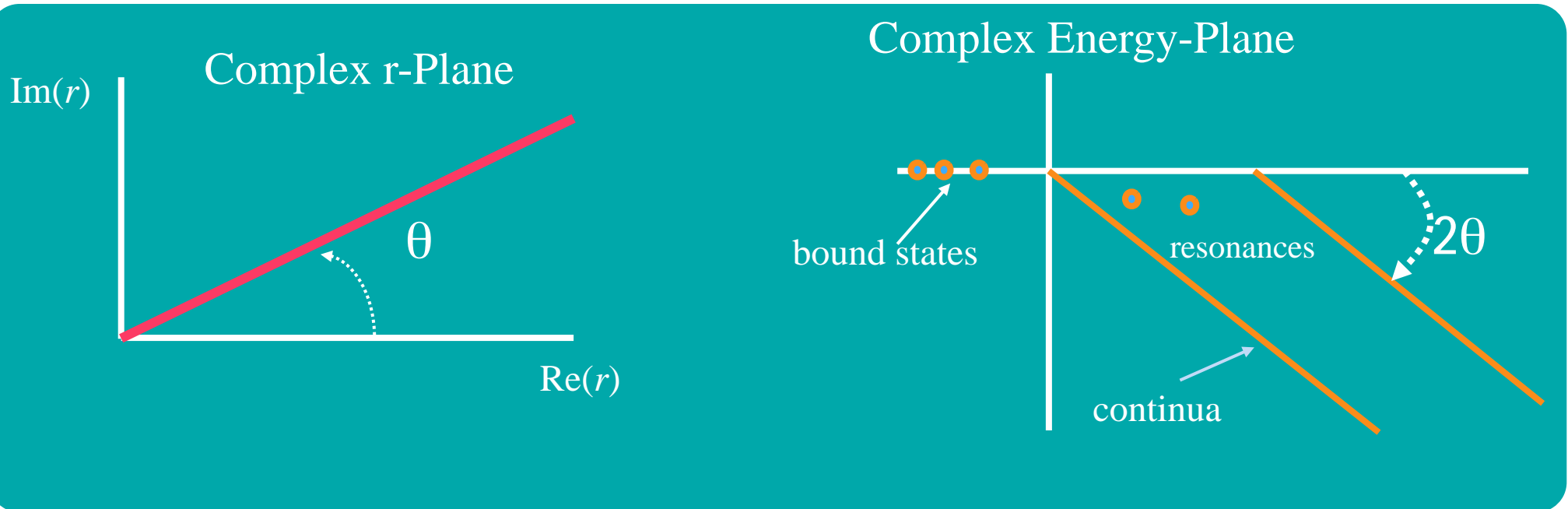
But both formal and practical problems prevent application of this idea to polyatomic molecules

Gaussian basis functions with complex exponents accomplish complex scaling asymptotically

Approach: Implement complex exponents for Gaussian basis functions in the Q-Chem suite of codes to accomplish the effects of *Exterior Complex Scaling*

$$\phi(\mathbf{r}) = N(x - A_x)^l (y - A_y)^m (z - A_z)^n \exp\left[-\alpha e^{-2i\eta}(\mathbf{r} - \mathbf{A})^2\right]$$

Benefit: Renders complex-energy resonance wave functions square-integrable. Allows treatment of polyatomic molecules by SCF, CCSD, CI, and other quantum chemistry methods

$$\langle ij|kl \rangle = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) r_{12}^{-1} \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2)$$

Central Challenge: *Accomplished this year*! Alec White adapted Q-Chem to calculate two-electron integrals over Gaussian basis with mixed real and complex exponents

1st Results: Resonances via static exchange (Alec White)

- Static Exchange Approximation: Finding the complex eigenvalues of an effective one-electron Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{nuc} + 2\hat{J} - \hat{K}$$

Procedure:

1. Determine electron density of the closed shell target in a real basis
2. Diagonalize H in a basis including complex Gaussian basis functions
3. Repeat for many values of η and find stationary value

Nitrogen Molecule Orbital Energies

Im[Energy] (a.u.) vs Re[Energy] (a.u.)
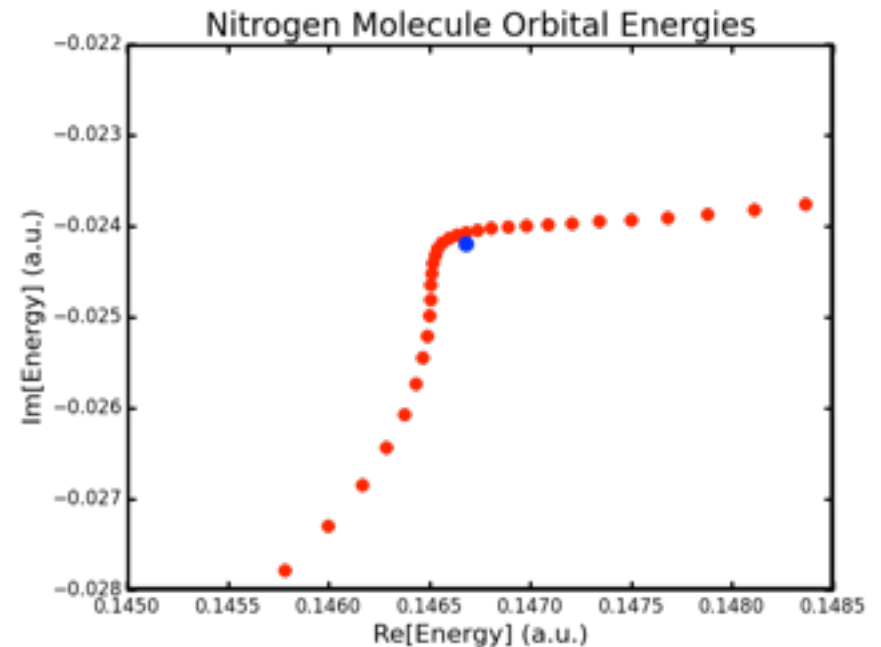
Designing Complex Gaussian Basis Sets: add complex functions to correlation consistent sets (Alec White)

- cc-pvXZ basis sets used for the real calculation.
  - Augmented with even-tempered set of 7 complex diffuse functions
  - For main second row elements, we used spd diffuse functions for dz bases, spdf for tz, and so on.
  - The convergence properties of these basis sets appear to be adequate for small molecules. Results below in eV.

Basis	Nitrogen		Formaldehyde		Carbon dioxide	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
caug-ccpvDZ	3.98980	-0.65830	2.64813	-0.75697	5.80248	-0.00071
caug-ccpvTZ	3.87613	-0.61104	2.64539	-0.80621	5.53680	-0.37414
caug-ccpvQZ	3.85113	-0.61782	2.60813	-0.79131	5.47779	-0.34736

Application to anions of nitrogen-containing aromatics: Only Metastable or Some Bound?
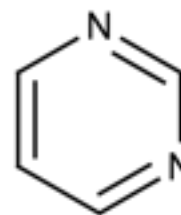
- Nenner and Schulz (1975) reported that pyrazine, pyrimidine, and s-triazine have bound anions, but more recent studies have suggested otherwise.

- CCSD(T) calculations of adiabatic and vertical electron affinities show no bound anions in any of these molecules.
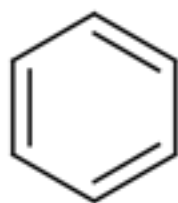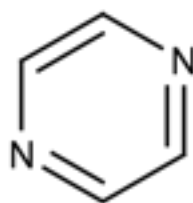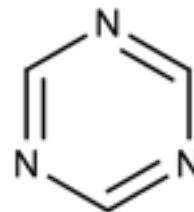

Benzene   Pyridine   Pyrimidine
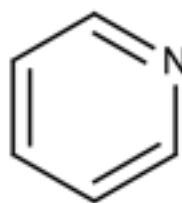
Pyrazine   s-Triazine

Conventional quantum chemistry vs Complex basis function calculations (Alec White)

- CCSD(T) calculations show no bound anion states mol))

EA, kcal/mol	Benzene	Pyridine	Pyrimidine	Pyrazine	s-Triazine
vertical		23.959	15.602	9.194	10.804
adiabatic	18.167	19.016	9.646	3.269	4.647

- Static Exchange calculations give results for lifetimes

Benzene		Pyridine		Pyrimidine		Pyrazine		s-Triazine	
Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
3.1288	-0.2646	2.6459	-0.1897	2.3480	-0.1303	2.0809	-0.1590	2.2580	-0.0803
		3.0219	-0.2291	2.7481	-0.1706	2.8258	-0.1660		
9.4297	-1.2191	9.1366	-1.1151	8.8765	-0.9884	8.8740	-1.2838	8.6586	-0.9917

- Differences between molecules agree with experiment to within 0.2 eV. See Alec's poster for more details!

Current Development: Complex Self Consistent Field Calculations on Metastable Anion States

- Trial function is a determinant of spin orbitals

$$\Phi = |\varphi_1 \,\bar{\varphi}_2 \cdots \varphi_n \,\bar{\varphi}_n \,\varphi_s| \qquad \frac{\delta}{\delta \varphi_i} \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = 0$$

Working SCF equations from complex variational (stationary) principle

- Complex Restricted Open-Shell Hartree-Fock (ROHF) demonstrated by McCurdy et al. in 1980s

- Q-Chem implementation of Complex Unrestricted Hartree-Fock (UHF) with different orbitals for different spins will dissociate polyatomic metastable anions correctly
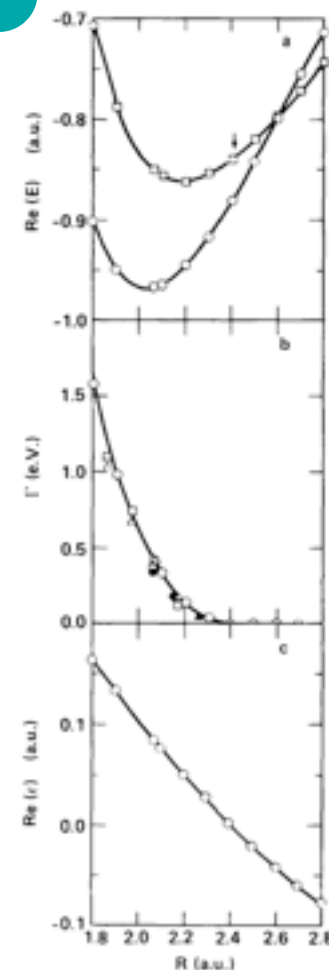
Outline of highlights.

LibTensor developments
 Anna Krylov, Evgeny Epifanovsky, Khaled Ibrahim,
 Sam Williams, Francois-Henry Rouet, Sherry Li,
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Treating resonances using complex scaling
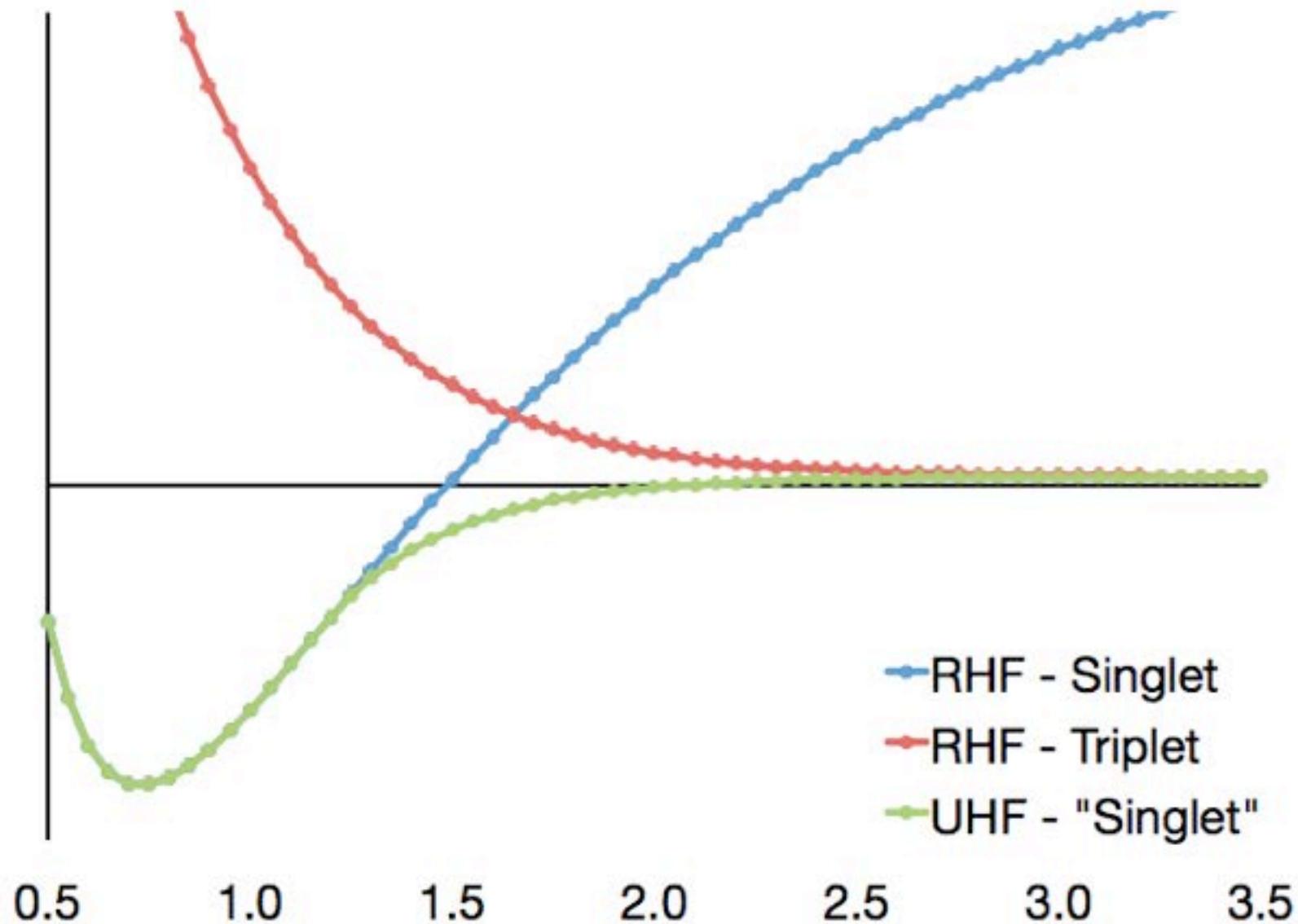 Alec White, Martin Head-Gordon, Bill McCurdy

Active space spin-flip methods for excited states
 Nick Mayhall, Martin Head-Gordon

Spin-flip method
How it works for breaking a single bond

Legend:
- RHF - Singlet
- RHF - Triplet
- UHF - "Singlet"

Spin-flip method
How it works for breaking a single bond

1. RHF configuration is poor at stretched bond-lengths

RHF - Singlet
RHF - Triplet
UHF - "Singlet"

Spin-flip method
How it works for breaking a single bond

2. Triplet is a spin-pure single configuration at all bond-lengths

1. RHF configuration is poor at stretched bond-lengths

- RHF - Singlet
- RHF - Triplet
- UHF - "Singlet"

0.5   1.0   1.5   2.0   2.5   3.0   3.5

Spin-flip method
How it works for breaking a single bond

2. Triplet is a spin-pure single configuration at all bond-lengths

1. RHF configuration is poor at stretched bond-lengths

3. 4 configurations describe H_2 at all bond-lengths: 1 spin flip from $M_s=1$ triplet
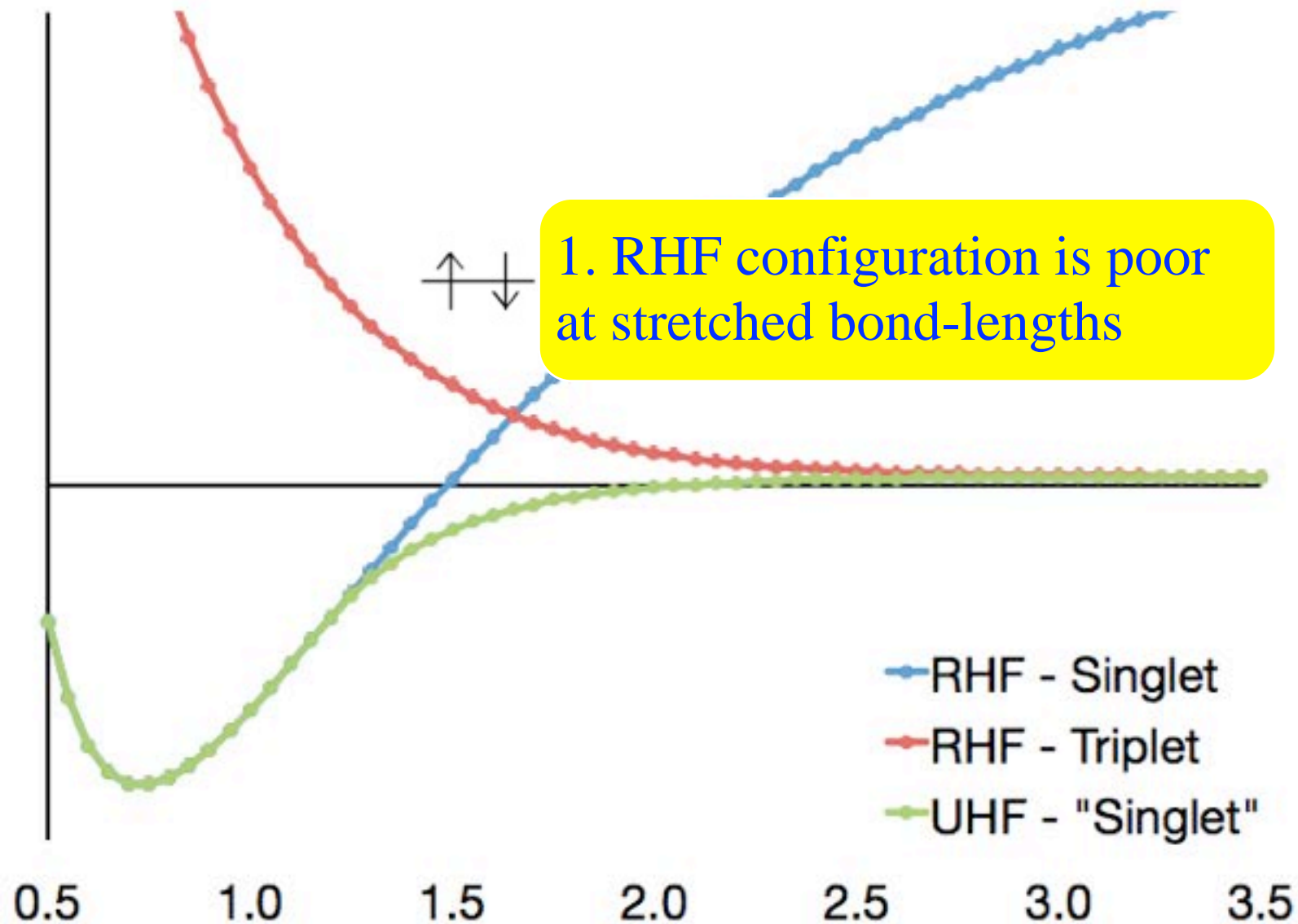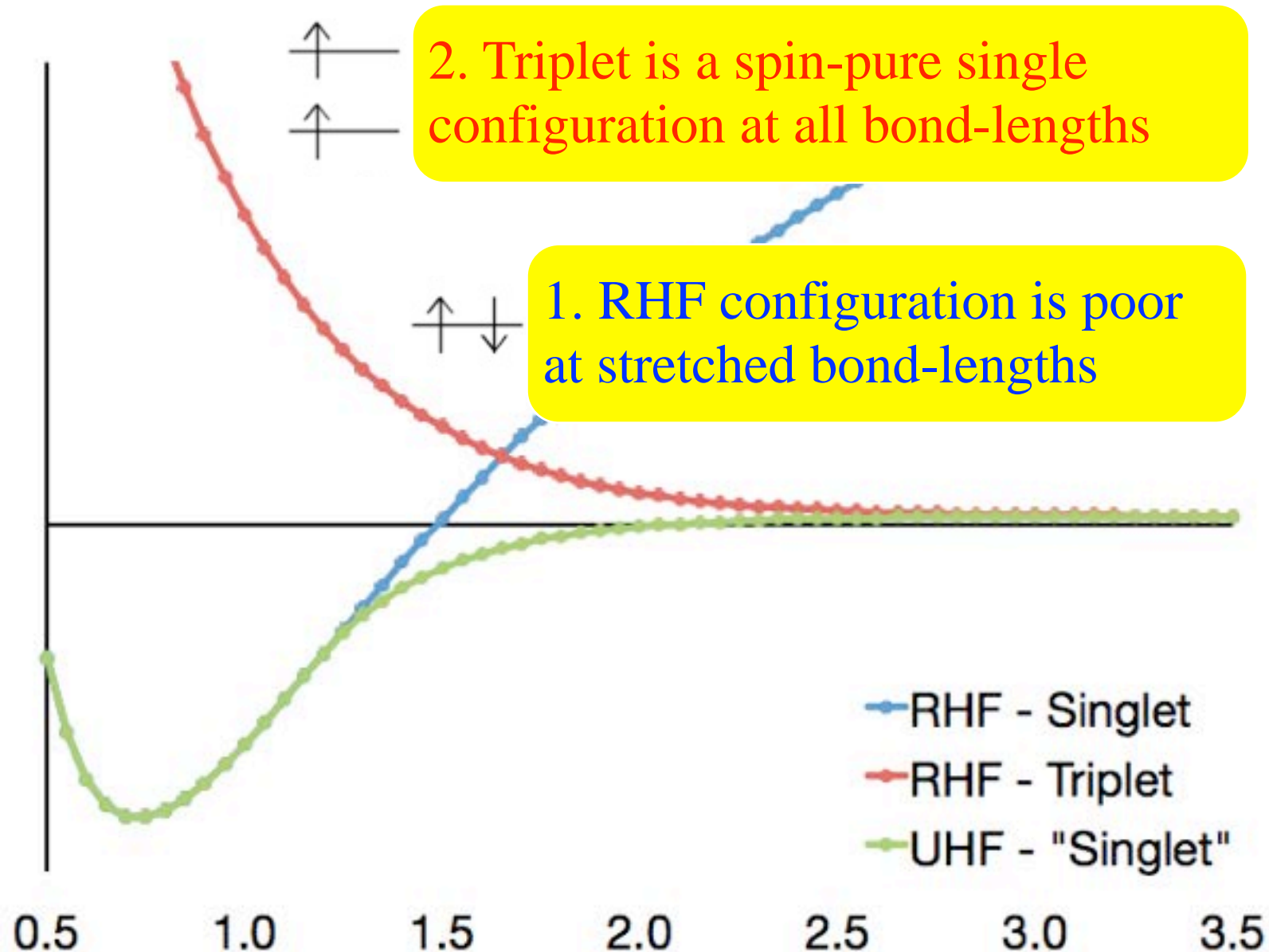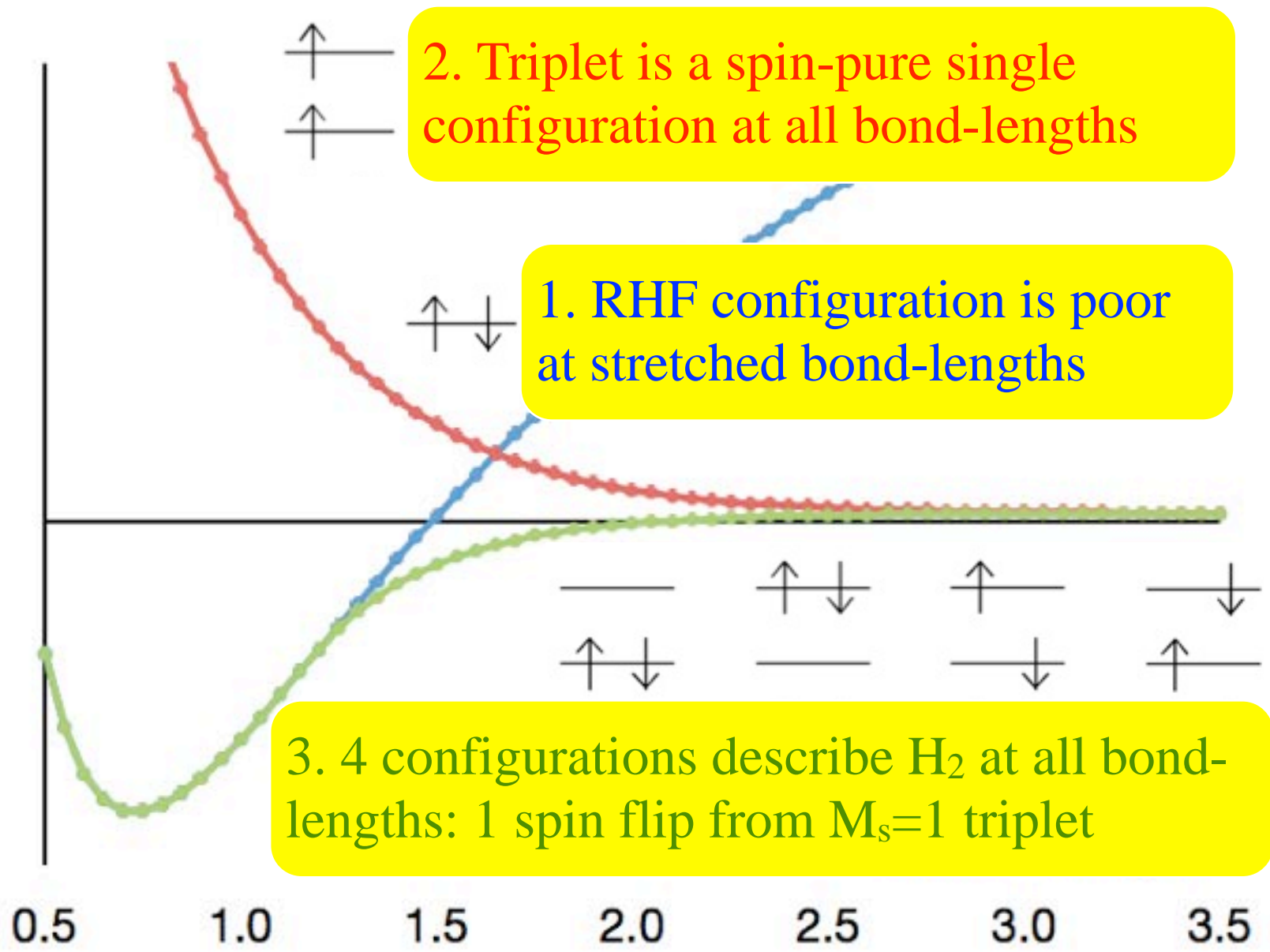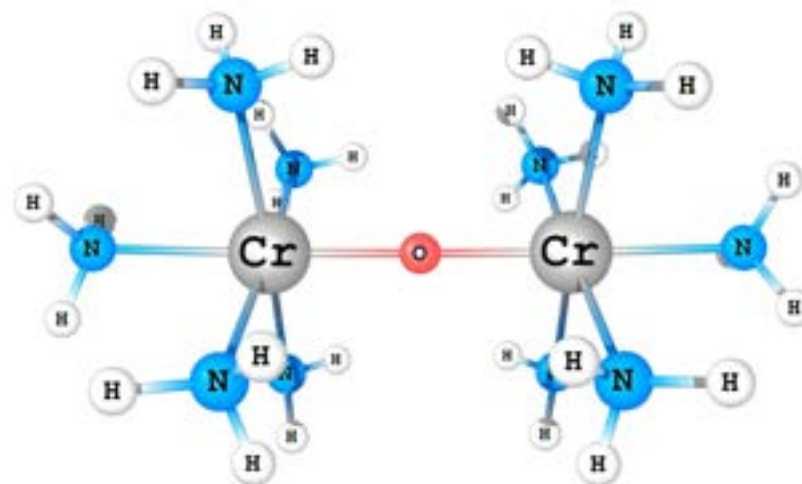
Spin-flipping

- Find the *highest multiplicity low-energy* configuration...

- ... which becomes the *single reference*...

- ... whose half-occupied orbitals define the *active space*

- e.g. $(H_3N)_5Cr^{III}OCr^{III}(NH_3)_5{}^{4+}$
  - Cr(III) $\Rightarrow$ d^3
  - $\Rightarrow$ 6 unpaired e's
  - $\Rightarrow$ heptet single reference

- How do we do the spin-flip electronic structure?
 1. By excitation level (e.g. SF-CCSD etc). Spin impure.
  → 2. As a complete active space (CAS). Spin pure.

SF-CAS methods

- Simplest: full CI in SF active space: SF-CAS
  - Poor performance: orbitals for high spin state
  - Orbital optimization (SF-CASSCF) would help
  - ... but is state-specific.... so we look elsewhere

- Add extra configurations: variationally or perturbatively
  - 1X: RAS-SF   SF-CAS(1x)
  - 2X: SF-CAS(2x)

- 1X: var -- P. Zimmerman, D. Casanova, F. Bell, MHG,
  - JCP 137, 164110 (2012); PCCP 15, 358 (2013)
- 1X: PT -- N. Mayhall, M. Goldey, MHG, JCTC 10, 589 (2014).
- S: PT -- N. Mayhall, MHG, JCP 141, 044112 (2014).

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Accuracy of perturbative approach (Nick Mayhall)

- Quintet reference, cc-pVTZ

- SF-CAS does not even match Hartree-Fock.

- Including 1x (hole, particle) surpasses HF

- Including all singles (partial 2x) recovers significant dynamic correlation
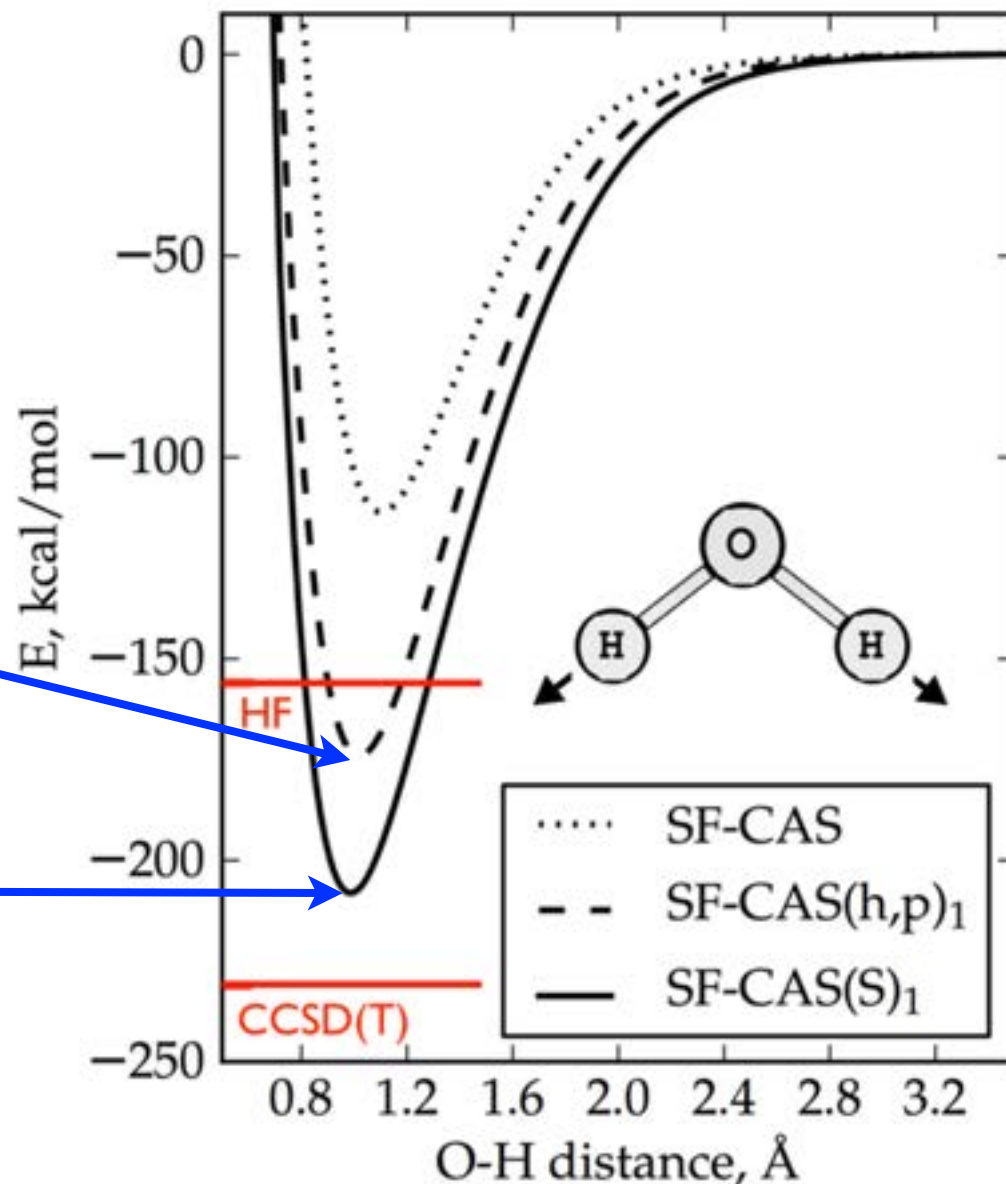
Efficiency of perturbative approach (Nick Mayhall).

Timings via perturbation theory vs variational

Approach

- SF-CAS$(h,p)_1$ solves a dressed non-Hermitian eigenvalue problem in the SF-CAS space.

- For small numbers of spin flips, this can be done by explicit diagonalization giving large speedups for large molecules.

- Example of 6 states (S, T, Q) of a polyradical porphyrin verdazyl derivative.

- 1 cpu, 6-31G basis.
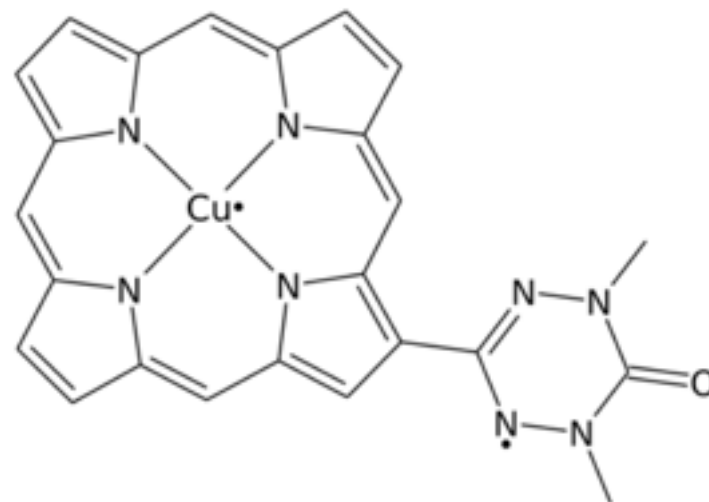
	RAS-SF	SF-CAS$(h,p)_1$
time (s)	7479.392	61.028
relative	100.00%	0.82%

SF-NOCI: non-orthogonal configuration interaction (Nick Mayhall, Eric Sundstrom, Paul Horn)

- ## Starting from SF-CAS
  - 1. Localize active-space orbitals & freeze them
    2. Relax each SF-CAS configuration individually
   3. Diagonalize H in this new "relaxed" determinant basis

- ## A very special form of non-orthogonal CI !!
  - No 2 configurations can coalesce
  - Each relaxation is well-conditioned (large gap)
  - Building the NOCI hamiltonian is highly efficient
  - Rate-determining relaxations are embarrassingly parallel

- N.Mayhall, P. Horn, E. Sundstrom, MHG, PCCP (submitted)
- For NOCI, see: E. Sundstrom, MHG, JCP 140, 114103 (2014).

Ionic / covalent competition in LiF (Nick Mayhall)
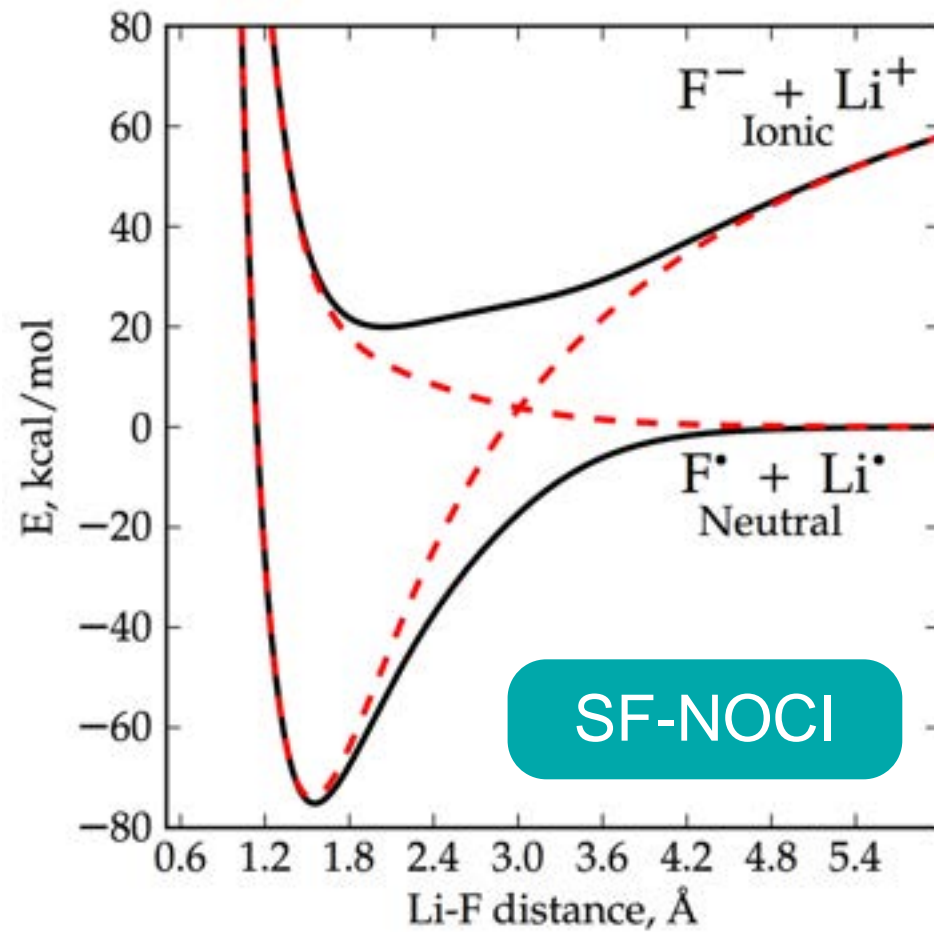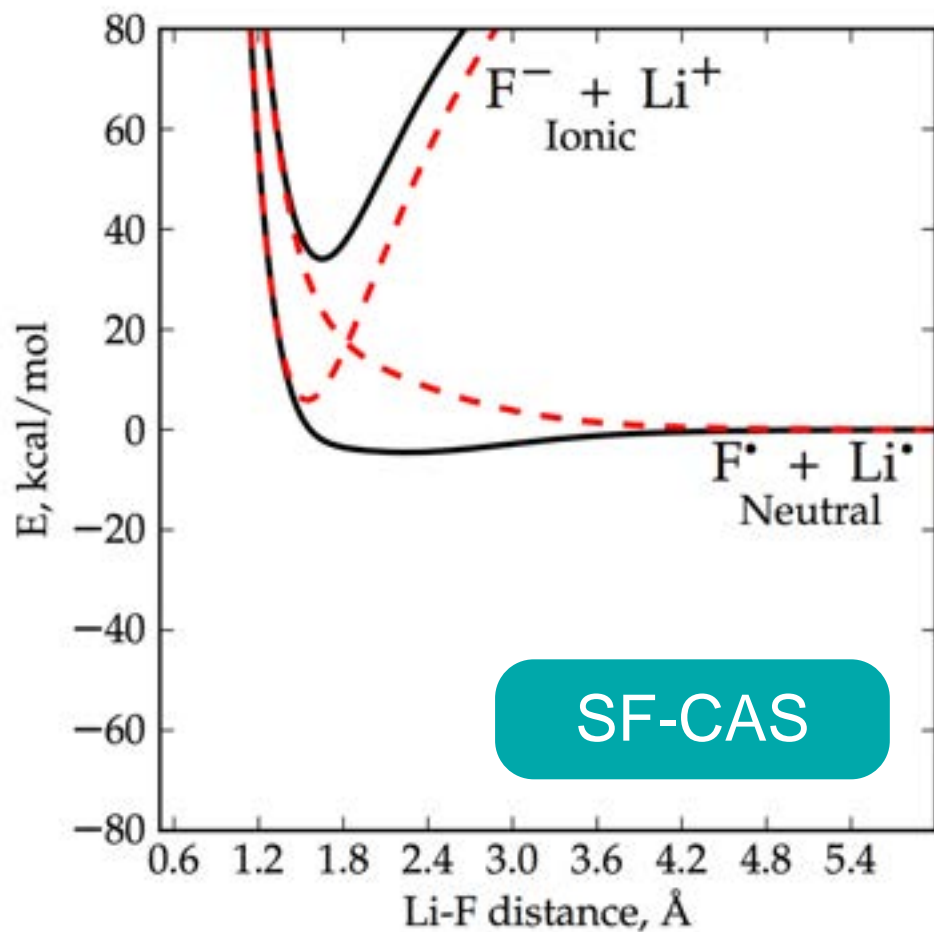
- SF-CAS uses triplet orbitals -- neglects ionic relaxation
- SF-NOCI strongly relaxes the ionic configuration
  - gives a qualitatively correct curve: ΔH_f(expt) = 82 kcal/mol

Low-lying states in $Cu^{II}(^Fsbqdi)_2$ (eV)
(Nick Mayhall)

- **3 unpaired e's in 3 orbitals**
  - Use quartet ROHF single reference
  - 2 low-lying doublets, 1 quartet
  - Higher ionic CT configurations....

$$L^\bullet - M^\bullet - L^\bullet$$

type	config	multiplicity	SF-CAS (eV)	SF-NOCI (eV)
local	αβα	doublet	0.00	0.00
local	ααβ+βαα	doublet	0.05	0.12
local	ααα	quartet	0.07	0.18
LLCT	+α−	doublet	4.6	2.6
LMCT	α−+	doublet	11.4	5.0
MLCT	α+−	doublet	13.8	7.8

Magnetic couplings in Cu^{II}(^{F}sbqdi)$_2$ (Nick Mayhall)

- Even for the low-lying states, SF-NOCI makes a big difference in the magnetic couplings...
  - Expt: J(ML) >> 200 cm^{-1}
  -        J(LL) << J(ML)
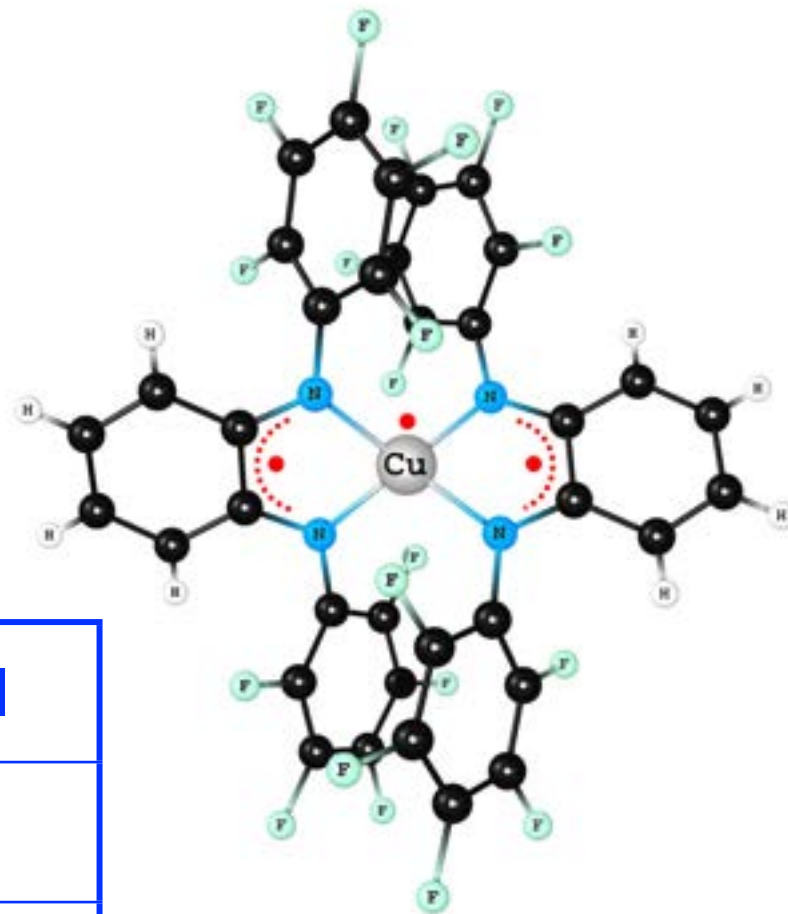
	SF-CAS	SF-NOCI
J(CuL) / cm^{-1}	-231	-548
J(LCu) / cm^{-1}	-165	-434
J(LL) / cm-1	-9	-36

On-going work and future plans

- We are working hard to add dynamic correlation to the new SF-NOCI approach:
    - Density functional theory and perturbation theory are both under investigation

- See Nick Mayhall's poster for exciting progress on how to turn a class of strong correlation problems that involve n spin flips into 1-spin flip problems!

- Gradients for the spin flip CAS methods are underway

- Use of large-scale eigensolvers (Yang, Li) will be needed for large numbers of spin flips.

Summary and conclusions
3 selected highlights

- Developments in the LibTensor framework
  - Enables advanced electronic structure methods
  - Work cuts across physical sciences, math, comp. sci.
  - Major progress in scaling, solvers, new capabilities

- Advances in the treatment of molecular resonances
  - Completed complex 2-electron integral code
  - Preliminary results on basis set convergence
  - First pilot applications to medium-sized aromatic molecules

- New active space spin-flip methods for excited states
  - Development of highly efficient perturbation theory
  - New non-orthogonal framework is highly promising