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

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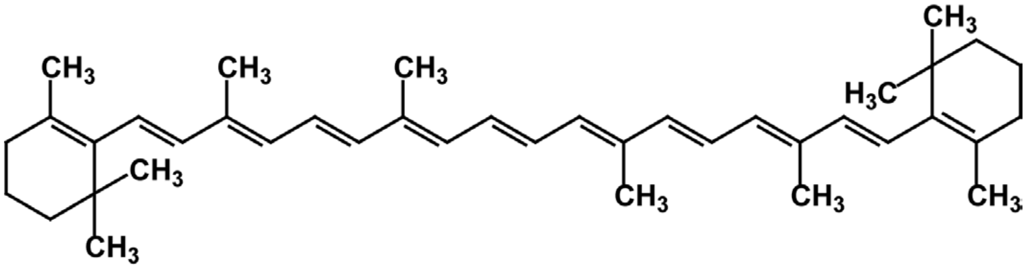
BERKELEY LAB
Lawrence Berkeley National Laboratory

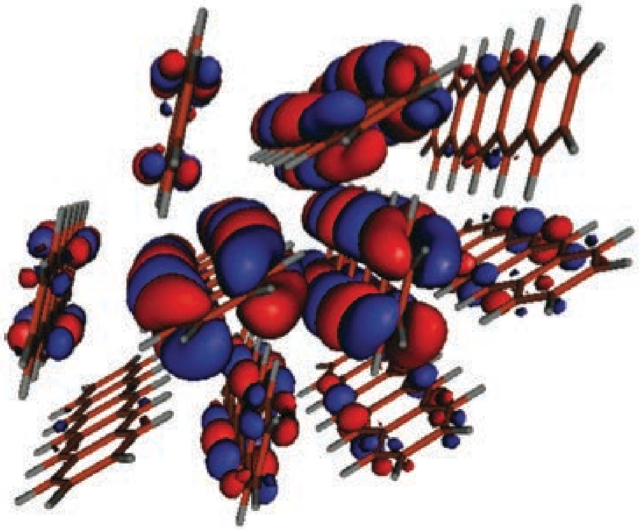
SciDAC
Scientific Discovery through Advanced Computing

Excited states: Physical significance and methodological challenges

Significance:

- Bound states. Light harvesting, photochemistry, …
- Unbound states. Electron attachment / detachment, materials degradation, damage.





Methodological challenges:

- The problems of TDDFT – self-interaction error, failure for strong correlation – are acute.
- Must turn to the “illegitimate concept”, of Ψ….

Outline.

Science highlight: Making Heisenberg Hamiltonians

Nick Mayhall, MHG, J. Chem. Phys. 141, 134111 (2014).
Nick Mayhall, MHG, J. Phys. Chem. Lett. 6, 1982 (2015).

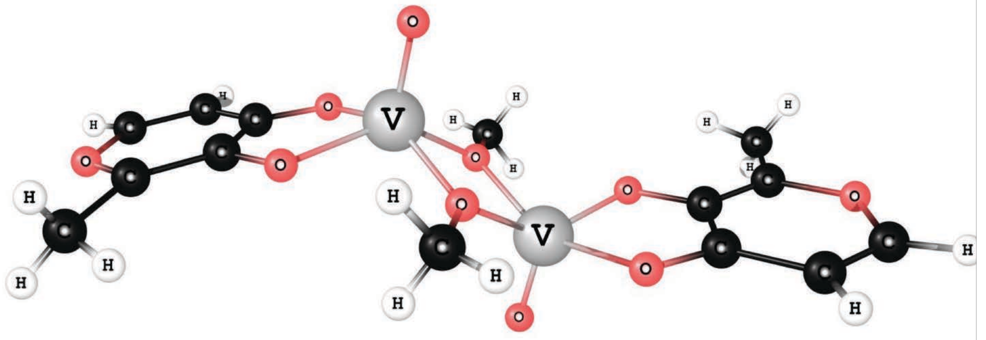
Science highlight: Calculating molecular resonances

Math highlight: Non-hermitian interior eigenvalues

Software highlight: LibTensor

Parallel highlight: LibTensor with distributed memory

Heisenberg spin couplings



- If Heisenberg physics is valid:

$$\hat{H} = -2J\,\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$$

- What is Heisenberg physics?
  - Molecules with 2 (or more) weakly interacting radical centers...
  - ... each has well-localized unpaired electrons (CT small)
  - Strongly correlated low-lying states arise from recoupling of the 2 spins according to Clebsch-Gordon.
  - Lande interval rule: $E(S) - E(S-1) = -2JS$

- Systems which obey Heisenberg physics have strong spin correlations and DFT typically fails
  - Complexity rises steeply with number of entangled spins

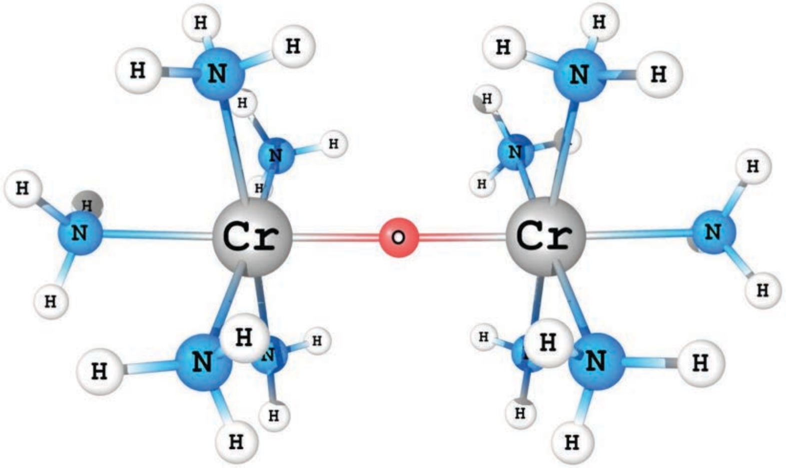
Spin-flipping (invented by Anna Krylov ~2000)

- Avoids the multi-reference problem...
- By finding 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



- Then flip 3 spins to tackle the multireference problem...
  - we have been developing efficient spin-flip methods

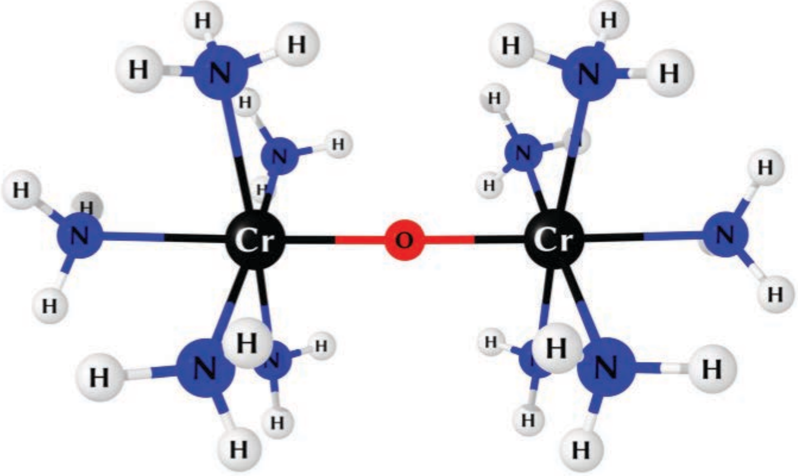
Heisenberg spin couplings from just 1 spin-flip
Nick Mayhall, MHG, JCP 141, 134111(2014)

- If Heisenberg physics is valid:

$$\hat{H} = -2J\,\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$$

- the state separations are:

$$E(S) - E(S-1) = -2JS$$

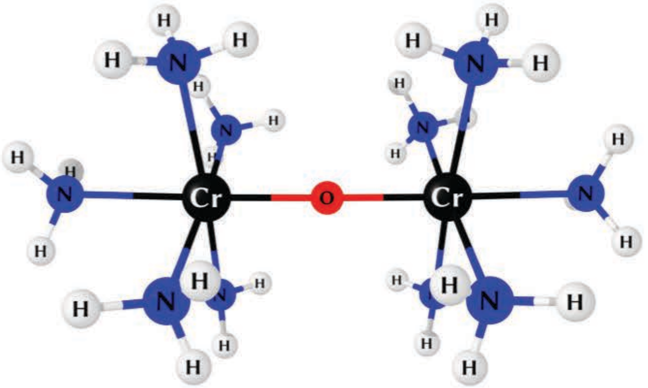


- Spin-pure results can be obtained by flipping only one spin (a great alternative to broken symmetry DFT!!)
  - Start from the high spin single reference: $S_{\max}$
  - Flipping a single spin accesses $S_{\max-1}$.

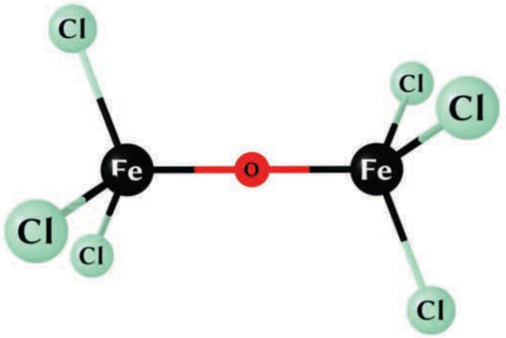
$$J = -\frac{E(S_{\max}) - E(S_{\max}-1)}{2S_{\max}}$$

Applying the 1SF strategy for *J* (cm^{-1})

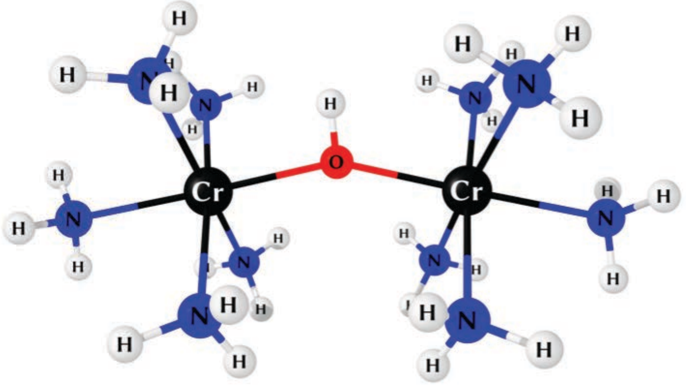
Nick Mayhall, MHG, JCP 141, 134111(2014)



A: Cr-O-Cr



B: Fe-O-Fe



C: Cr-OH-Cr

method	Cr-O-Cr	Fe-O-Fe	Cr-OH-Cr
SF-CAS(S)	-117	-145	-7.9
SF-CCSD	-158	-118	-9.3
DMRG	-166	-117	---
experiment	-225	-112	-15.8

3+3 unpaired e's

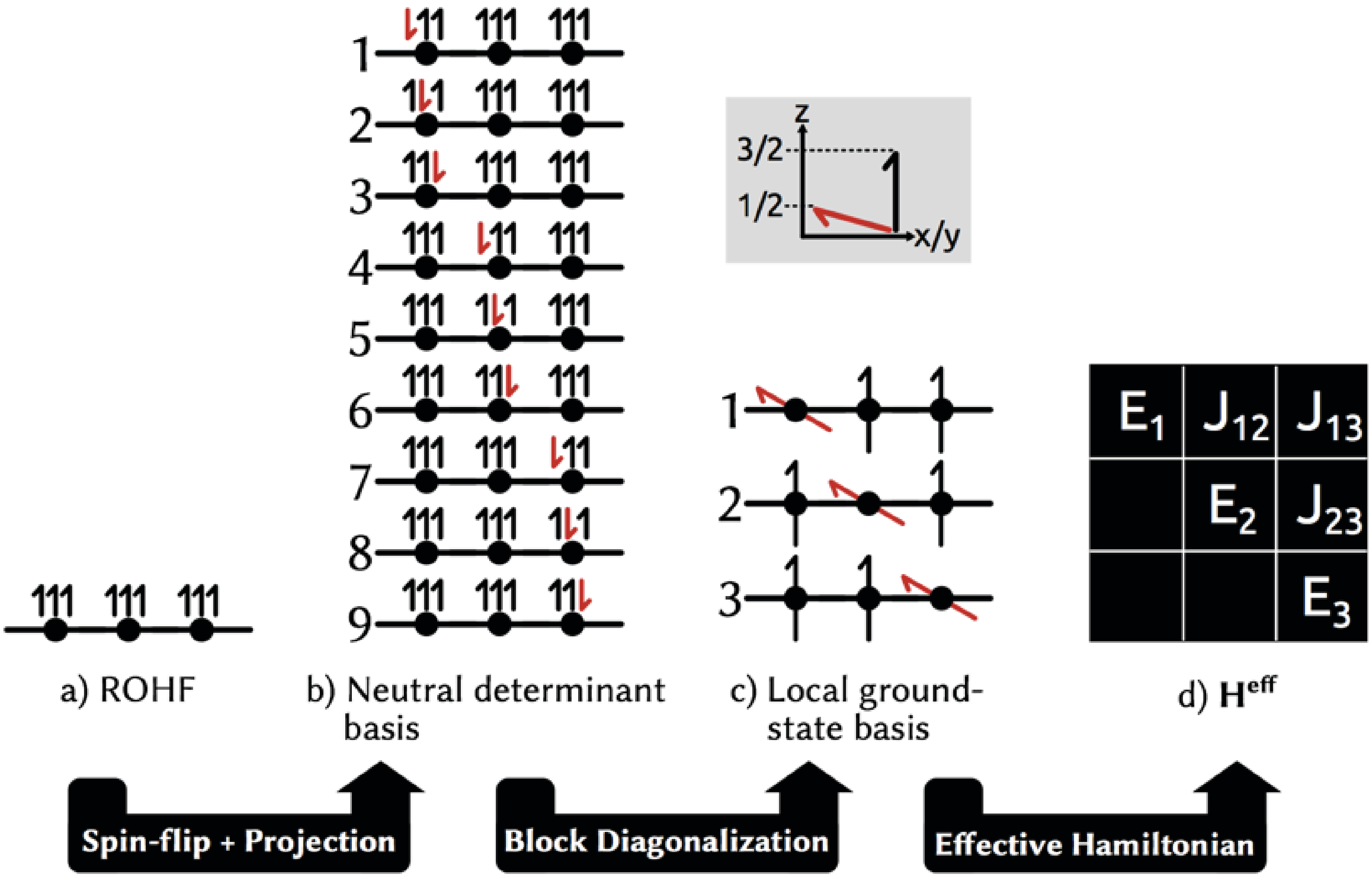
5+5 unpaired e's

3+3 unpaired e's

Generalizing to n-site Heisenberg physics

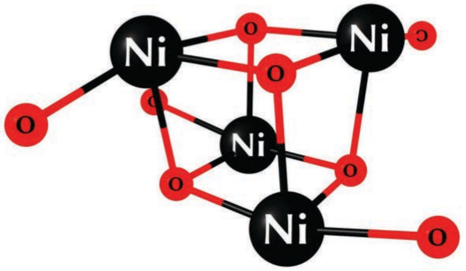
Nick Mayhall: J. Phys. Chem. Lett. 6, 1982 (2015).

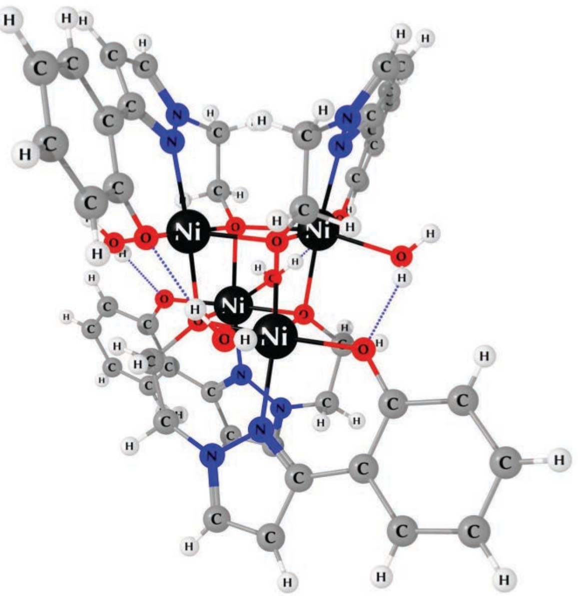
- Make the Heisenberg Hamiltonian from 1 spin-flip states.
- Diagonalizing Heisenberg Hamiltonian for energy levels.

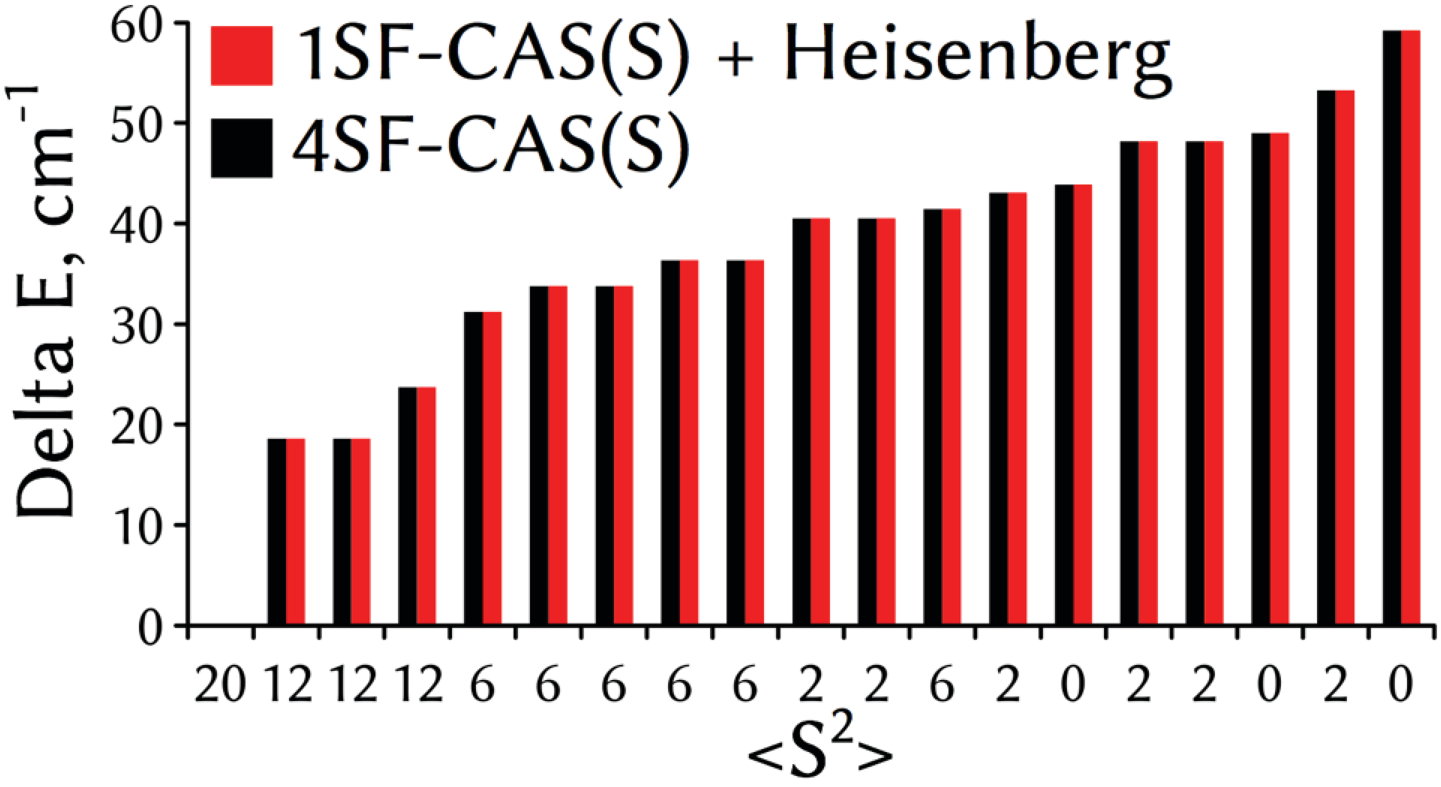


Test case: Explicit vs implicit

Nick Mayhall: J. Phys. Chem. Lett. 6, 1982 (2015).







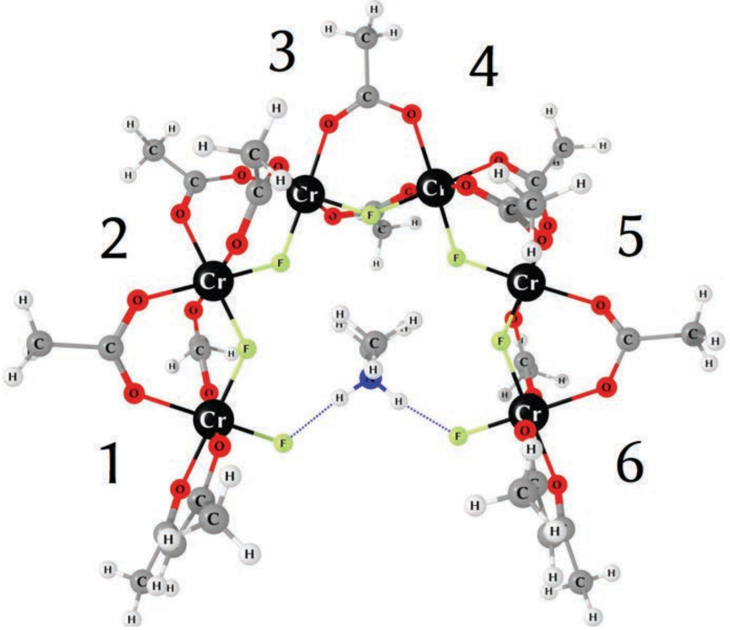
Ni$_4$ cubane: 8 entangled e's

Explicit: 4 spin flips for all levels

Implicit: 1 spin flip for all levels

Cr_6 horseshoe complex

Nick Mayhall: J. Phys. Chem. Lett. 6, 1982 (2015).



6 Cr atoms: 18 entangled e’s
Would have been 9 spin flips
But actually only 1 is needed

		Spin-Pure		
	SF-CAS	SF-CAS(h,p)	SF-CAS(S)	Exp.
J_{12}	0.51	-0.64	-2.30	–
J_{23}	0.52	-0.59	-2.20	–
J_{34}	0.57	-0.64	-2.37	–
J_{45}	0.42	-0.53	-1.90	–
J_{56}	0.43	-0.54	-1.94	–
J_{Outside}	0.47	-0.59	-2.12	-5.65
J_{Inside}	0.50	-0.59	-2.15	-5.89

Summary and outlook

- Spin-flip approach to strong electron correlations is under active development, starting from SF-CAS
  - adding out-of-active-space excitations: 1X, 2X, ...?
  - relaxing the orbitals of each configuration: SF-NOCI
- Spin-flip methods map very naturally to molecular magnetism problems with Heisenberg hamiltonians
  - For either 2 or *n* sites, only 1 spin-flip is sufficient for *J*
  - Gives an exponential reduction in effort!!
- Lots of challenges ahead
  - Forces and non-adiabatic couplings
  - Two key challenges are as yet not fully resolved ;-))

Outline.

Science highlight: Making Heisenberg Hamiltonians

Science highlight: Calculating molecular resonances

Alec White, MHG, Bill McCurdy, J. Chem. Phys. 142, 054103 (2015)
Alec White, Bill McCurdy, MHG, J. Chem. Phys. (submitted) (2015).

Math highlight: Non-hermitian interior eigenvalues

Software highlight: LibTensor

Parallel highlight: LibTensor with distributed memory

Quantum Chemistry of Metastable States

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

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

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

- Complex basis function method:

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

Makes resonance wavefunction square integrable: allows use of quantum chemistry methods/codes for scattering states... but:

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

Central Challenge: *Accomplished*! Alec White adapted Q-Chem’s integral engine to calculate complex two-electron integrals.

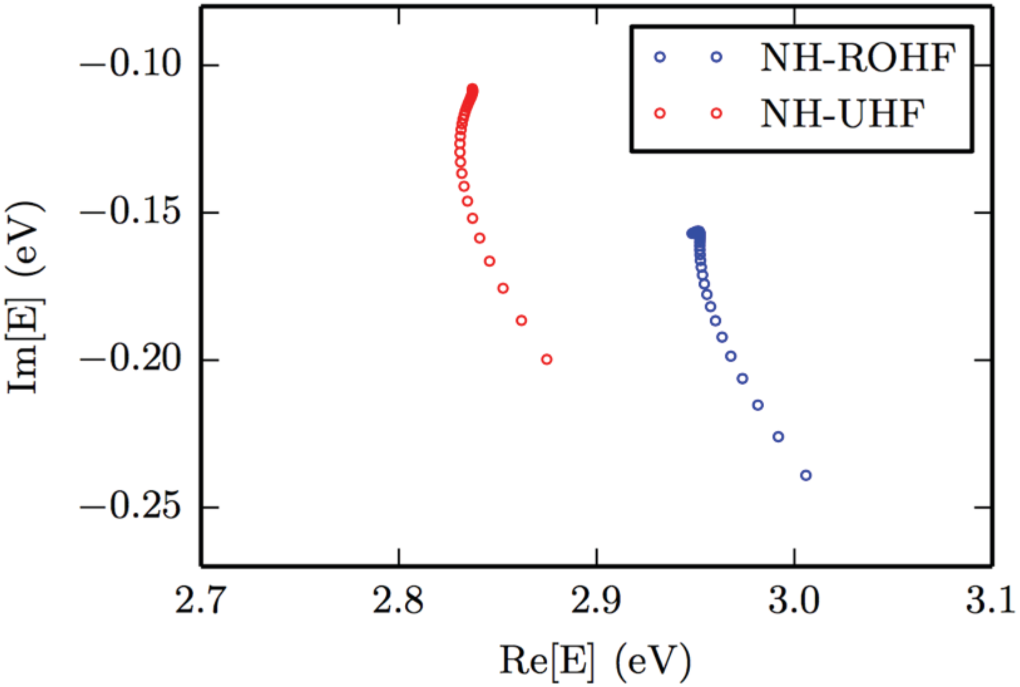
Non-Hermitian (NH) Hartree-Fock (HF) Theory for Metastable Anion States

- Trial function is a determinant of spin orbitals

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

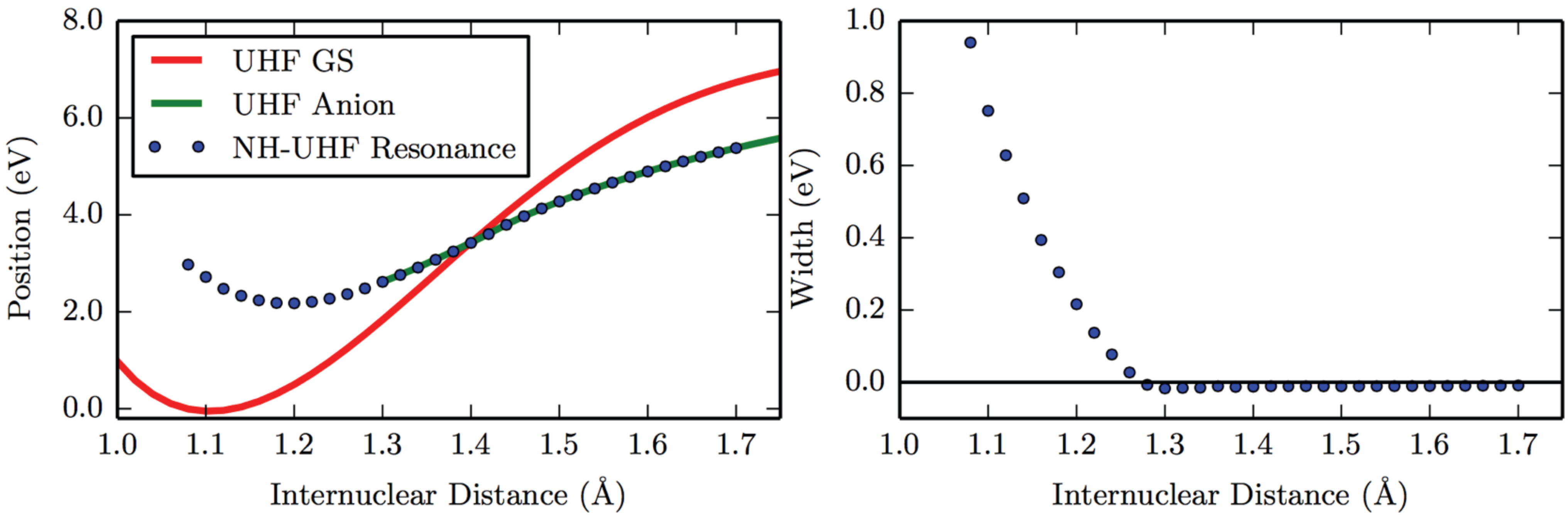
SCF equations from complex variational (stationary) principle

- NH Restricted Open-Shell HF (ROHF) was piloted in the 80's
- NH Unrestricted HF (NH-UHF) is new and can dissociate polyatomic metastable anions
- Find stationary points of theta trajectories (varying scaling)
- Standard basis sets are augmented with very diffuse functions at the center of mass.

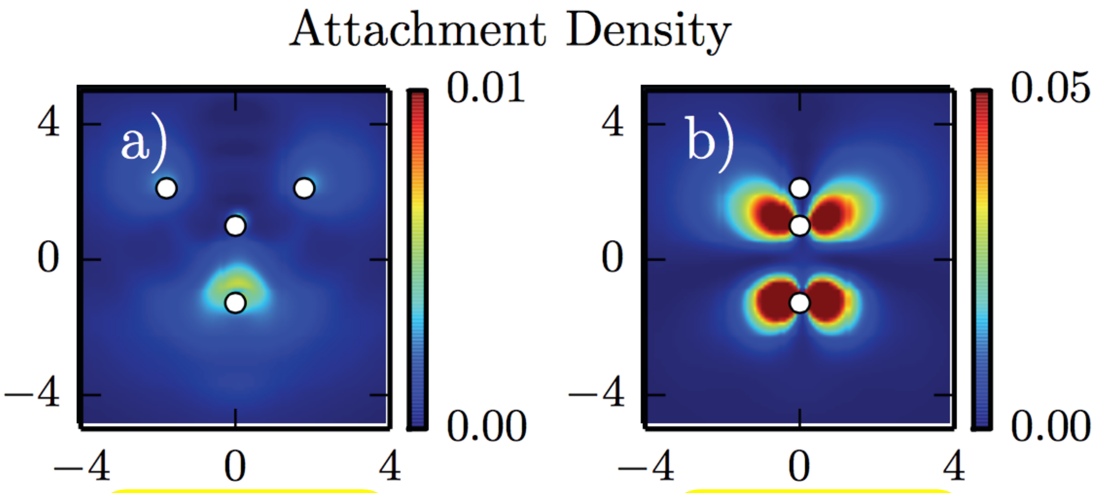


First application of NH-UHF to a complex potential energy surface: carbon monoxide

- CO$^-$ pi* resonance:
  - unbound in the equilibrium region (blue dots, left panel)
  - NH-UHF lifetime is zero for r > 1.3 Angstroms (right panel)
  - NH-UHF curve coalesces with UHF anion curve for r > 1.3
  - could enable prediction of vibrational structure in scattering



Examples of larger polyatomics: formaldehyde and carbon tetrafluoride



xz plane

yz plane

real part of the alpha spin attachment density of pi* symmetry resonance of CH_2O

T_2 symmetry resonance of CF_4 with caug-cc-pVTZ basis

method	center	width
NH-SE	11.1	2.0
NH-ROHF	9.1	0.8
NH-UHF	8.9	0.8

On-going work and future challenges

- NH-SCF calculations are really tough to converge.
  - We will be seeking help on this problem!
  - There may be scope for reformulating NH-SCF.
- Matrix elements are calculated in the c-norm.
  - Orbitals are c-orthogonal. It is not a metric space
- We're implementing a more numerically stable orthogonalization (SVD-based)
- With Anna Krylov, we will use the complex basis function method with coupled cluster theory (EOM-EA-CCSD).
  - Allows assessment of correlation effects, and direct comparison with complex absorbing potentials (CAPs)

Outline.

Science highlight: Making Heisenberg Hamiltonians

Science highlight: Calculating molecular resonances

Math highlight: Non-hermitian interior eigenvalues

Dmitry Zuev, Eugene Vecharynski, Chao Yang, Natalie Orms, Anna I. Krylov, J. Comput Chem. 36, 273–284 (2015).

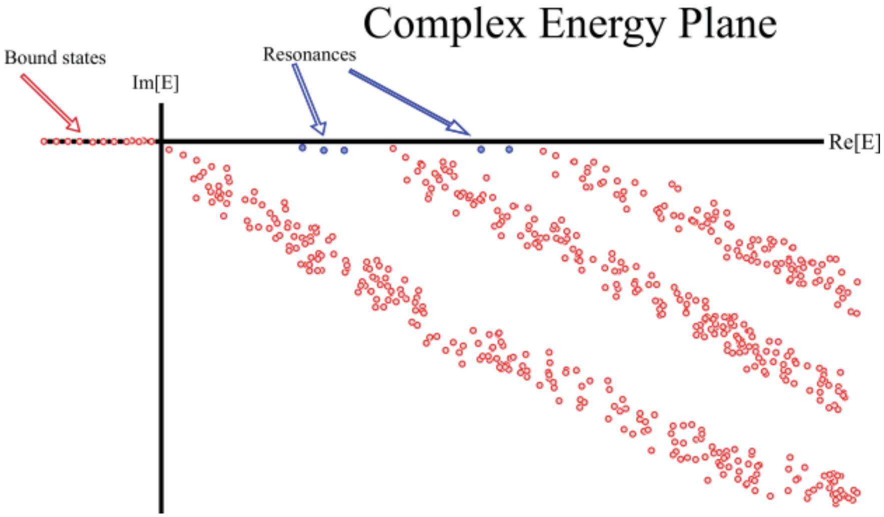
Software highlight: LibTensor

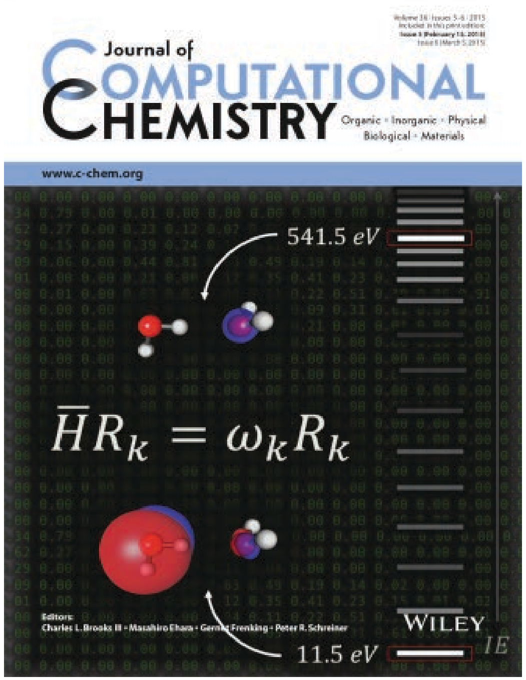
Parallel highlight: LibTensor with distributed memory

GPLHR: A Non-Hermitian Eigensolver

- Generalized Preconditioned Locally Harmonic Residual method (GPLHR) is useful for:
  - Coupled cluster Equation-of-motion calculation
  - Complex scaled configuration interaction calculations

- Algorithm designed by Eugene Vecharynski & Chao Yang. Implemented in LibTensor for production calculations & comparison against Davidson.





GPLHR basics

- A matrix-free approach (i.e. do matrix-vector products)

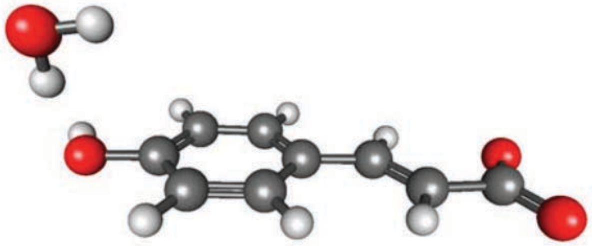
- Reuse information generated from the iterative solution to Newton correction equation for the eigenvectors (or Schur vectors) to construct the search space

- Use Harmonic Ritz projection (suitable for approximating interior eigenvalues/vectors)

- More robust than Davidson for interior eigenvalues

Example: EOM-IP-CCSD for PYPa-Wp/6-31+G(d,p) interior roots near 11 a.u

- Both algorithms work well for the lowest roots, but for a higher interior eigenvalue, GPLHR is far more robust.



- We're excited about using GPLHR for EOM-EA-CCSD calculations of resonances

Davidson

nroots	niters	Max. # of stored vectors	# matvec
1	DNC	–	–
2	DNC	–	–
3	DNC	–	–
5	DNC	–	–

GPLHR

nroots	niters	m	Max. # of stored vectors	# matvec
1	4	1	8	9
2	4	1	16	18
3	4	1	24	27
5	8	1	40	63

Outline.

Science highlight: Making Heisenberg Hamiltonians

Science highlight: Calculating molecular resonances

Math highlight: Non-hermitian interior eigenvalues

Software highlight: LibTensor (& Q-Chem)

> **LibTensor: E. Epifanovsky, K. Ibrahim,** S. Williams, A. Krylov
> J Comp Chem. 2013;34:2293–2309, HIPC 2014
> **Q-Chem:** Mol Phys. 113, 184–215 (2015)

Parallel highlight: LibTensor with distributed memory

What is Q-Chem? What is LibTensor?

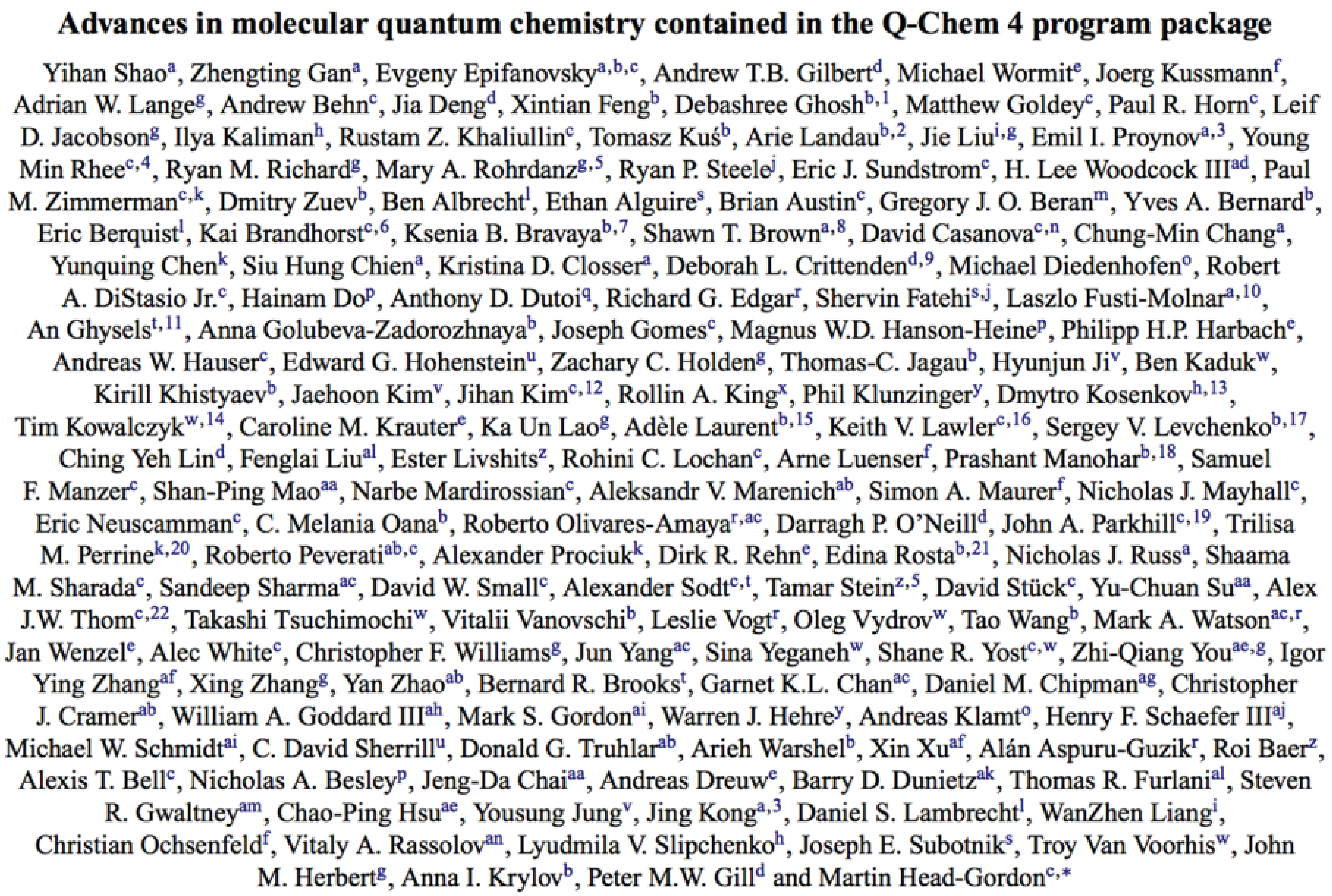
- Q-Chem is a widely used electronic structure program.
    - Est 1993. Commercial code, academic control.
    - Over 4 million lines of code: C++ and Fortran.
    - Over 200 active developers: Open TeamWare.
    - Over 55,000 distributed copies.

- Where does LibTensor fit?
    - A C++ library for doing tensor contractions & compactly expressing coupled cluster electron correlation methods
    - Open source release (permissive BSD) as well as a key component of Q-Chem
    - Main focus of SciDAC development

Q-CHEM™

A Quantum Leap Into the Future of Chemistry

Q-Chem 4.2 (2014) & 4.3 (2015) include SciDAC features



Advances in molecular quantum chemistry contained in the Q-Chem 4 program package

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Q-CHEM™
A Quantum Leap Into the Future of Chemistry

We face a great range of software challenges!

- How do we meet open source mandates in a commerical code?
- Q-Chem is helping to create public domain libraries of general use....
    - libtensor: many-body contractions (Anna Krylov)
    - libefp: effective fragment potential (Lyudmila Slipchenko)
- Synergisms: We do mid-scale computing (limited parallel scalability).
    - disruptive computer architectures (gpu/MIC) are quite disruptive...
    - we hope to avoid need for domain-specific solutions
- Limited interoperability? standardized data interchange
    - GUI interfaces, QM/MM...
- We’re a single job code: but our users do projects.
- Managing software renewal? for medium term (& esp. long term) sustainability

Outline.

Science highlight: Making Heisenberg Hamiltonians

Science highlight: Calculating molecular resonances

Math highlight: Non-hermitian interior eigenvalues

Software highlight: LibTensor & Q-Chem

Parallel highlight: LibTensor with distributed memory

Khaled Ibrahim, S. Williams, (E. Solomonik),
E. Epifanovsky, A. Krylov

Motivation and background

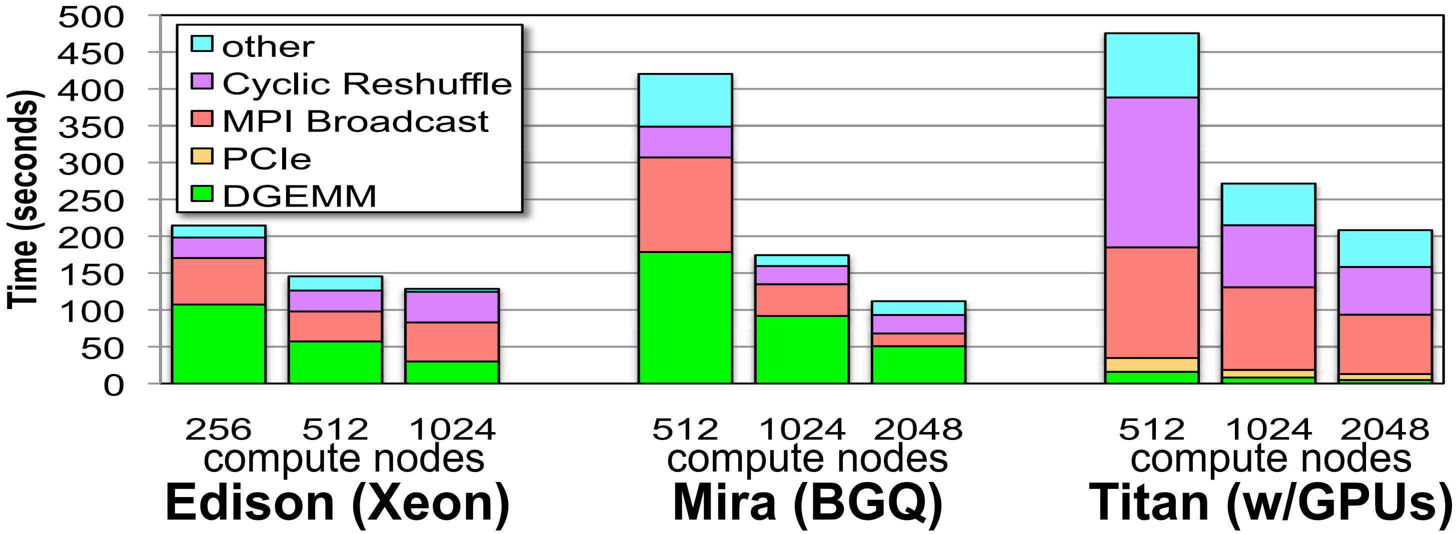
- LibTensor is very powerful (i.e. large range of CC methods rapidly and efficiently implemented).
  - Its roots were in mid-scale computing
  - Not designed for distributed data or massively parallel
- We decided to leverage the Cyclops Tensor Framework (CTF) as a backend for LibTensor…
  - Scalable on distributed-memory supercomputers
  - Created at UC Berkeley by Solomonik et al. in 2013
  - Uses a cyclic distribution of tensor elements to allow for a regular parallel distribution (avoids MPI All-to-All stresses)
  - Distributed SUMMA-based matrix-matrix multiplication (MPI row broadcasts plus calls to highly-tuned vendor BLAS routines)

Khaled and Sam took LibTensor where it had never gone before....

- Edison (Cray XC30 at NERSC) up to 16,384 cores
- Mira (IBM Blue Gene/Q at Argonne) up to 32,768 threads
- Titan (Cray XK7 w/GPU's at Oak Ridge) up to 2048 GPUs
- Strong-scaled methylated uracil water dimer test problem with 302 basis functions and C_s symmetry
- Modified to exploit tuned BLAS routines (including CULA for GPUs)
- Tuned MPI vs. OpenMP (or CUDA) to balance MPI vs. compute

Strong scaling test highlights

- More than 150x faster on 2000 nodes of Mira than on a large, multi-socket, big-memory SMP at NERSC.
- GPU-acceleration reduced DGEMM to 3% of the run time.
- Mira's network provided the best overall performance and scalability, although local DGEMM was slowest
- Future work will examine customized MPI collectives to improve performance and scalability on Edison and Titan.



Summary and perspective

- We’ve been having a great time building new tools and software through new collaborations
    - Math & chemistry, CS & chemistry, chemistry & chemistry...
- There is other exciting progress that I had to skip, such as:
    - Jiri Brabec & Esmond Ng: sparse tensors in CC theory
    - Francois Rouet & Sherry Li: STRUMPACK, low-rank structured factorization preconditioners
    - Shane Yost & MHG: new dynamical correlation correction to spin-flip methods
    - Jan Roden & Birgit Whaley: excited states & tensors
- Thank-you to all my team members & to you for listening!