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Chemistry

Charge Transfer and Charge Transport in Photoactivated Systems

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite

Bert de Jong

SciDAC Meeting, July 2015

Pacific Northwest
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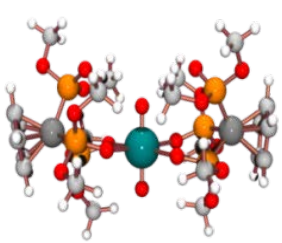
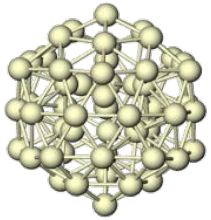
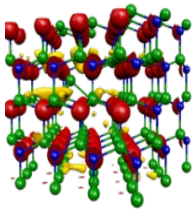
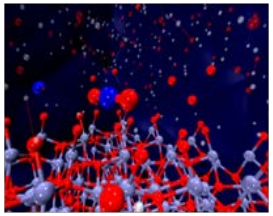
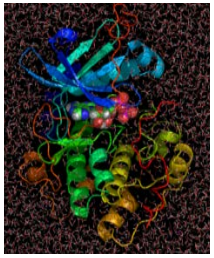
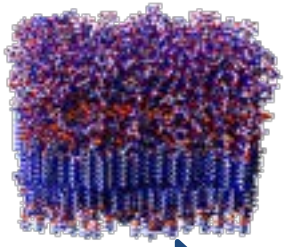
Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite

QM-CC/CAS | QM-DFT | AIMD | QM/MM | MM

Implement a suite of methods in the NWChem software suite in order to perform electronically excited-state dynamics in solution and to provide improved capabilities for excited-state dynamics in the gas phase.

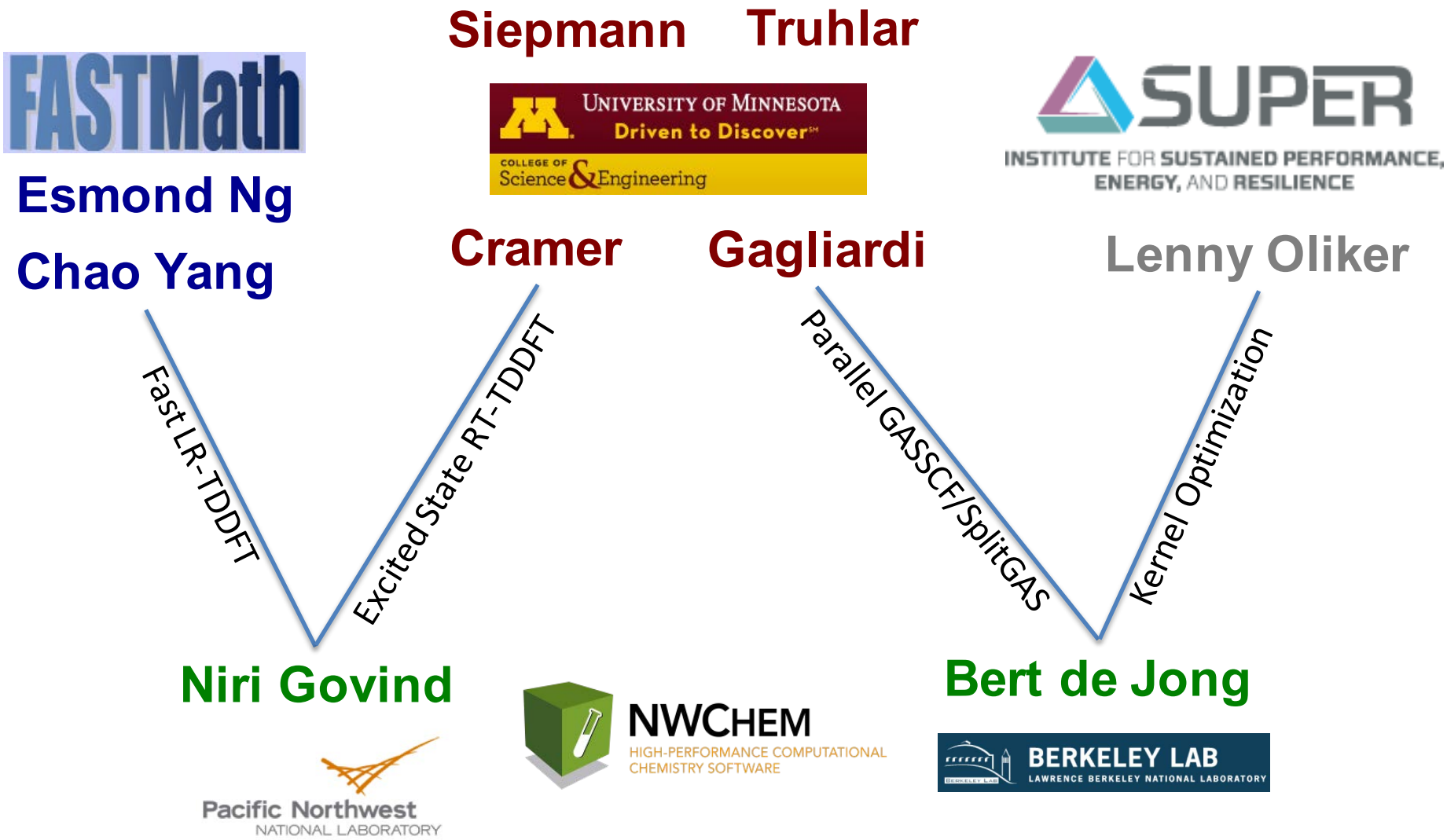
NWChem
High-Performance Computational Chemistry Software

Pacific Northwest National Laboratory

University of Minnesota Driven to Discover℠
College of Science & Engineering

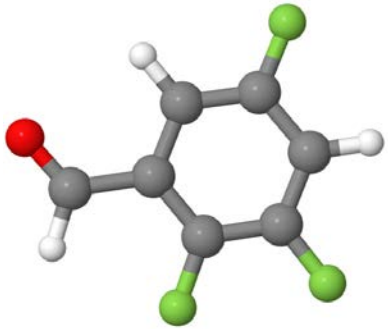
Berkeley Lab
Lawrence Berkeley National Laboratory

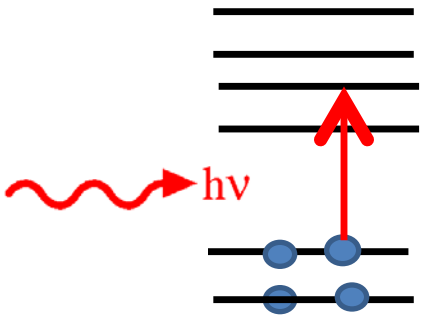
Team and Collaborative Efforts Discussed Today

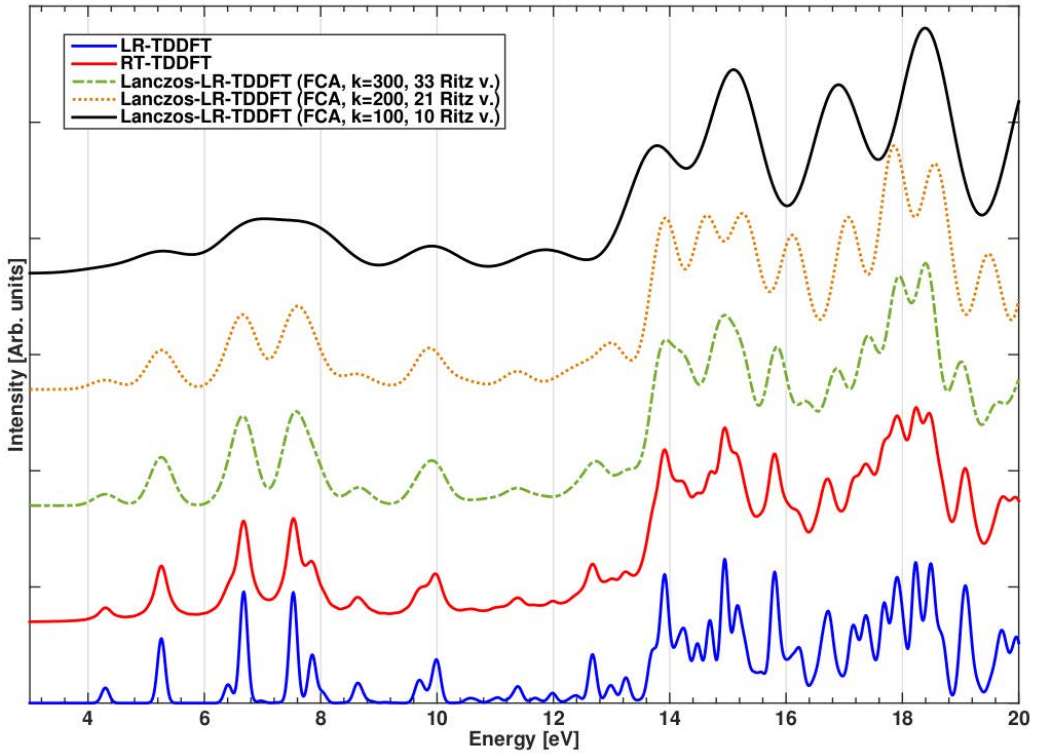


New Mathematical Approaches to Solving Linear-Response Time-Dependent DFT

C. Yang, L. Lin, J. Brabec, M. Shao, E. Vecharynski, E. Ng, N. Govind







Linear-Response Time-Dependent DFT (LR-TDDFT)

- Casida working equations

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix}$$

Matrix dimension
$N_{occ}N_{virt}$ x $N_{occ}N_{virt}$

$$KM(X+Y) = \omega^2(X+Y)$$
$$MK(X-Y) = \omega^2(X-Y)$$

where $K = A - B$, $M = A + B$

- $\alpha_{xx} = 2\hat{x}_1^T K\delta(\omega^2\, I - KM)\hat{x}_1$

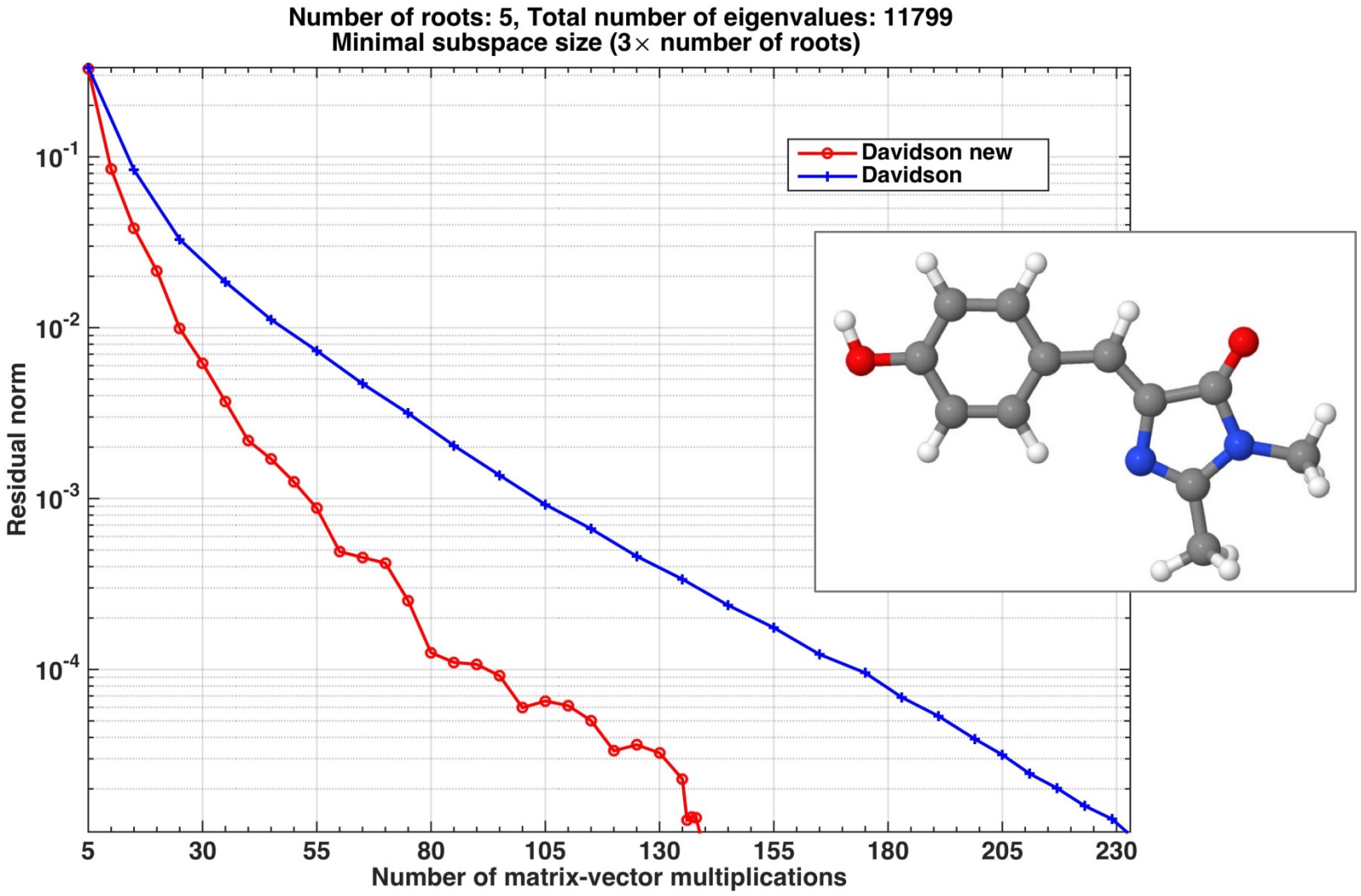
Solving Time-Dependent DFT

- Compute all eigenvalues and eigenvectors of large KM matrix $(O(N^6))$
- Improvement to Davidson for lowest few eigenvalues and eigenvectors
- Lanczos method to estimate absorption spectrum for a large frequency interval
- Time domain simulation

Improvements to Davidson Algorithm

- State-of-the art
  - Project K and M into a subspace S separately: $\widehat{K} = S^T K S$ and $\widehat{M} = S^T M S$
  - Solve the projected problem $\widehat{K}\widehat{M}U = U\Omega$
  - Expand the subspace: $S \leftarrow \{S, R_K, R_M\}$, where $R_K = KSU - SU\Omega$, $R_M = MSU - SU\Omega$
- New algorithm
  - Project MK into a subspace S in K-inner product: $G = S^T K M K S$
  - Solve a projected symmetric eigenvalue problem: $GU = U\Omega$
  - Expand the subspace $S \leftarrow \{S, R_{MK}\}$, where $R_{MK} = MKU - U\Omega$
  - Left eigenvectors can be easily recovered from the right eigenvectors through a cheap post-processing procedure
  - **Save half of the storage and matrix vector multiplications!**

Linear Response TDDFT



Full Spectrum Utilizing Lanczos Method

- MK is symmetric with respect to the K inner product
- k-step Lanczos factorization using K inner product

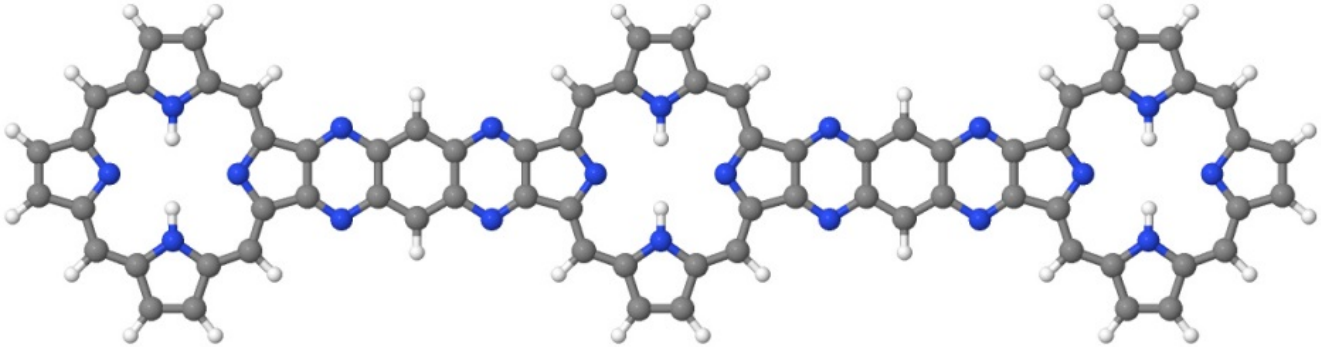
$$MKV_k = V_k T_k + f_k e_k^T, \qquad V_k^T K V_k = I_k, \qquad V_k^T K f_k = 0$$

- Choose $V_k e_1 = \hat{x}_1 / \|\hat{x}_1\|$

$$\alpha_{xx}(\omega) \approx e_1^T \delta(\omega^2 I - T_k) e_1$$

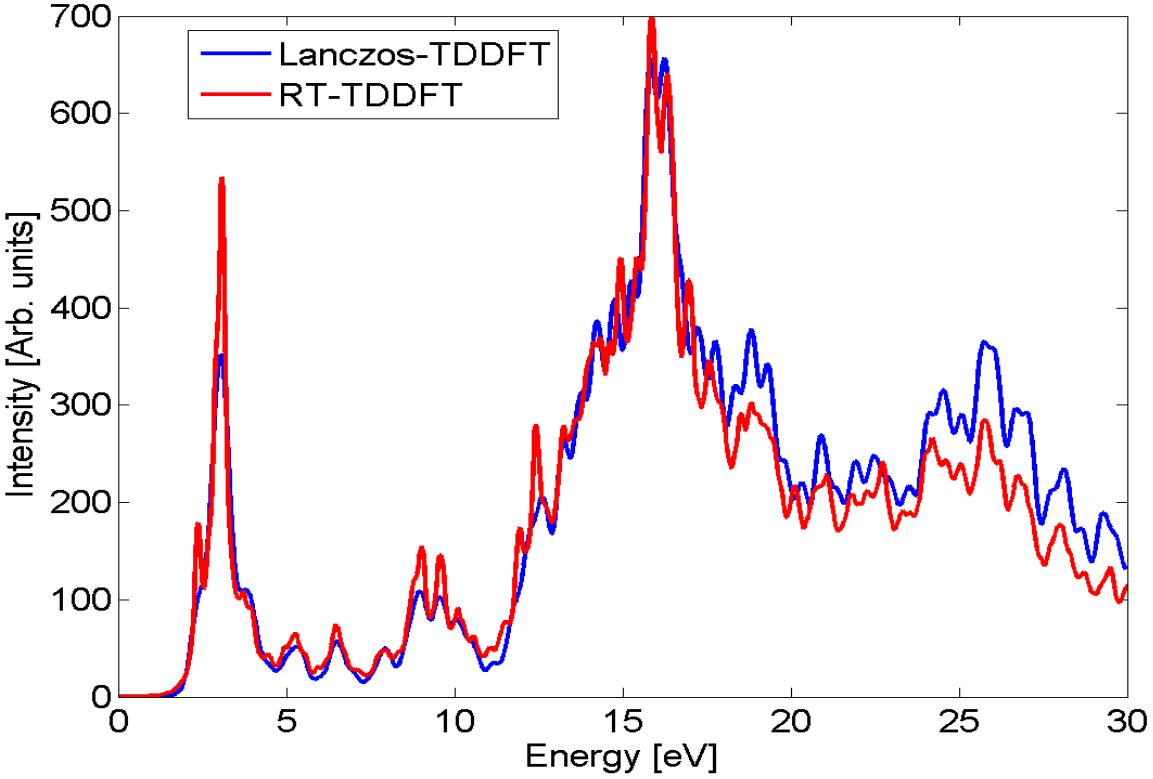
- Effectively, the number of eigenvalues resolved depends on number of steps in Lanczos
  - Use Lorentzian or Gaussian to approximate width

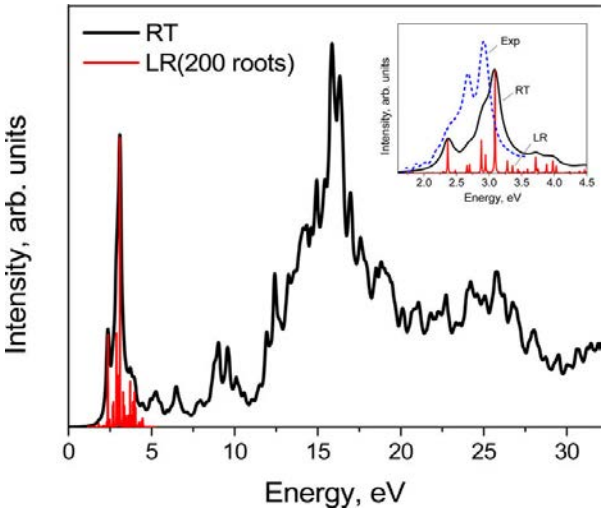
Demonstration Case for Lanczos Approach



- P_3B_2 ($C_{72}H_{32}N_{20}$) molecule
- Using B3LYP and $6{-}31\mathrm{G(d)}$ basis with dimension $n = 1364$
- $n_o = 305, n_v = 1059$, dimension of matrix is: $2n_o n_v = 645{,}990$
- Lanczos steps $k = 400$
- Time domain simulation: $\Delta t = 0.0048$fs, $T = 25$ fs (~5200 steps)

Demonstration of Lanczos





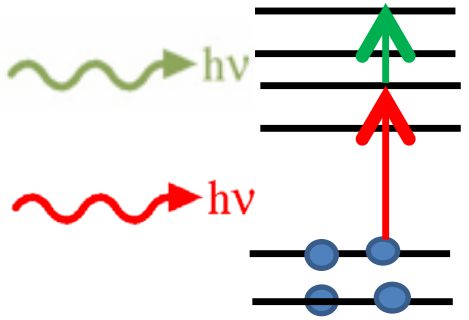
Tussupbayev, Lopata, Cramer, Govind, JCTC, 11, 1102 (2015)

- RT-TDDFT: **96 hours** on 1376 cores
- Lanczos-TDDFT: **5 hours** on 1536 cores
- Davidson-TDDFT: **13 hours** for first 200 roots out of 645,990 on 1536 cores (Or >40,000 hours to do the whole spectrum 200 roots at a time)

Excited State Absorption (ESA)

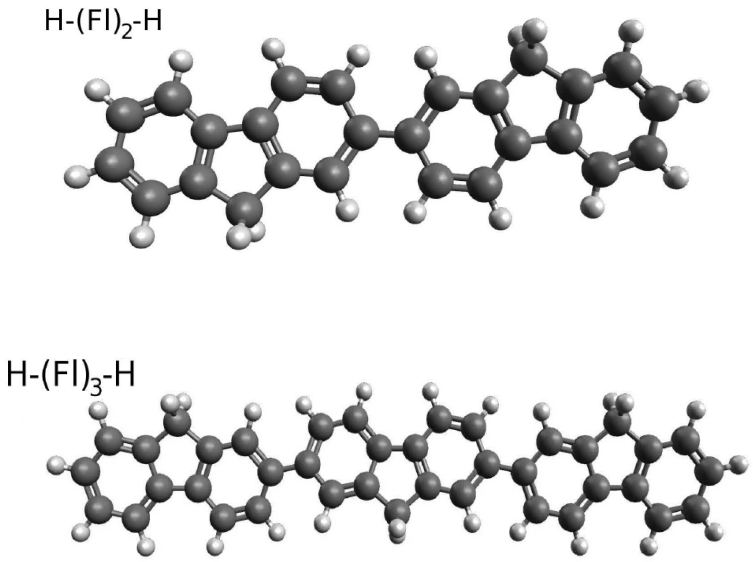
N. Govind, S. Fischer, C. Cramer

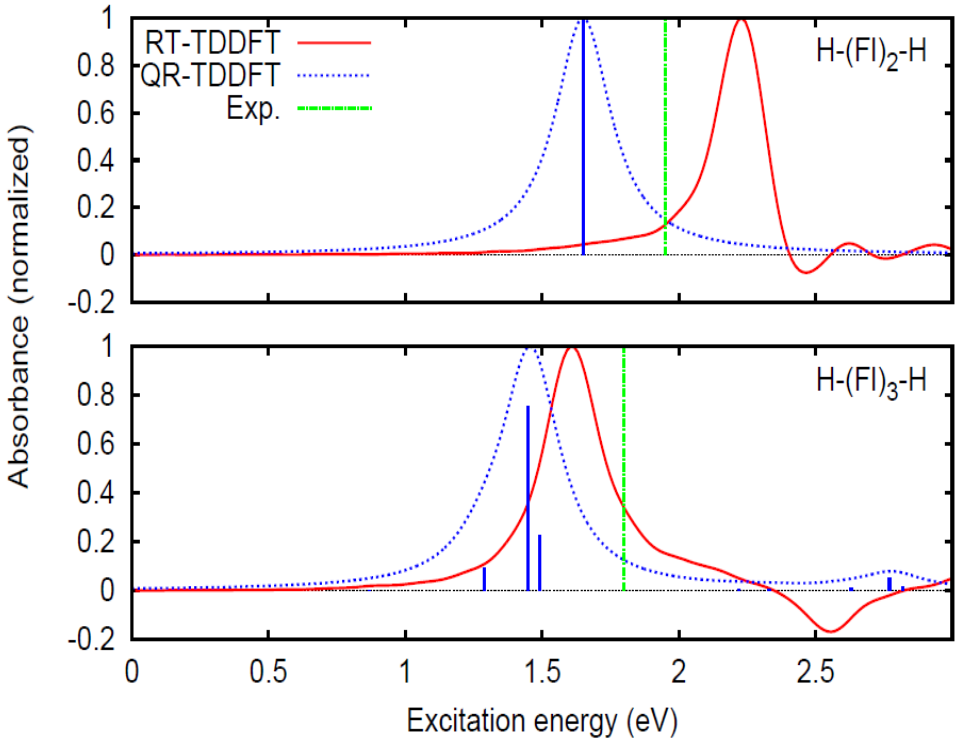
- ESA simulations can model pump-probe experiments, transient absorption and non-linear optical properties
- Calculation of quadratic response (QR-TDDFT) prohibitively expensive for large systems
- Excited state absorption is calculated with RT-TDDFT by propagating the excited state density obtained from LR-TDDFT



Fischer, Cramer, Govind, JCTC (in review)

ESA Testcase: Oligofluorenes

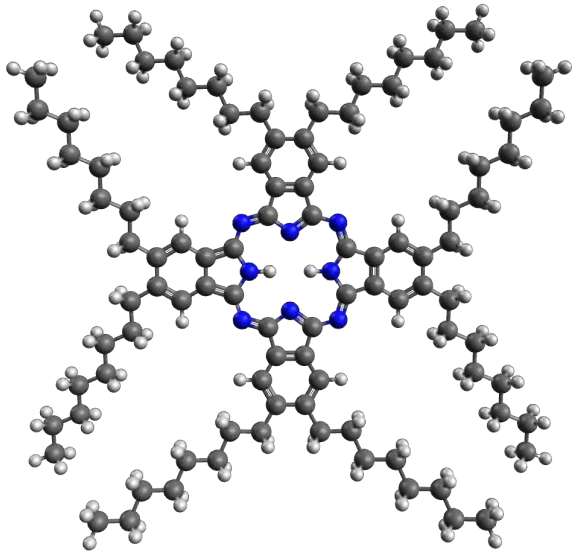


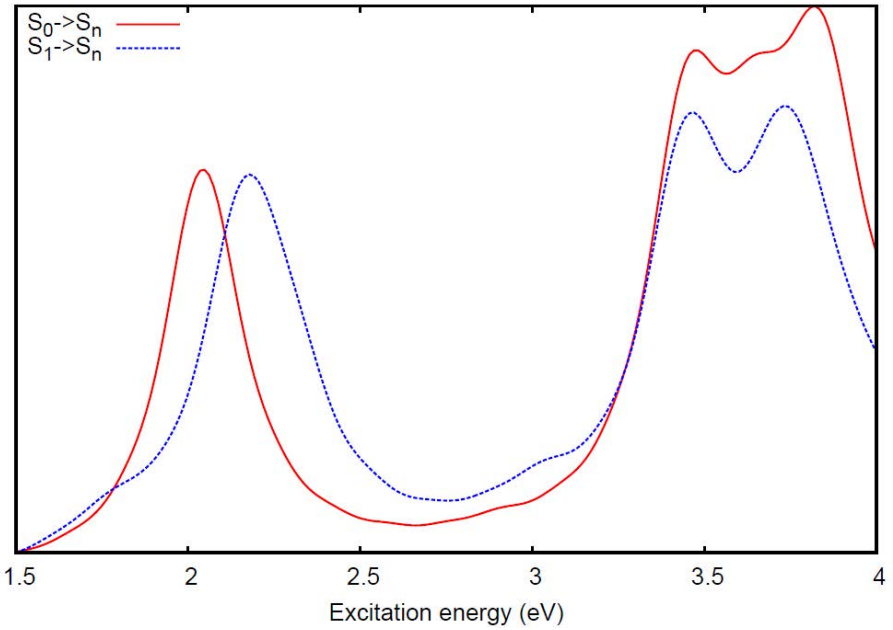


- Excited state absorption from real-time TDDFT and quadratic response TDDFT at CAM-B3LYP/6-31G level
- Vertical green line experimentally measured absorption maximum

Fischer, Cramer, Govind, JCTC (in review)

Large Scale ESA Simulations: Phtalocyanine Complex





- For ground and excited state absorption of phthalocyanine, 250 atoms at the B3LYP/6-31G* level
- Experimental measurements from the group of Prof. David Blank at the University of Minnesota ongoing

Improving Performance of Fock Kernel

H. Shan, W.A. de Jong, S. Williams, L. Oliker

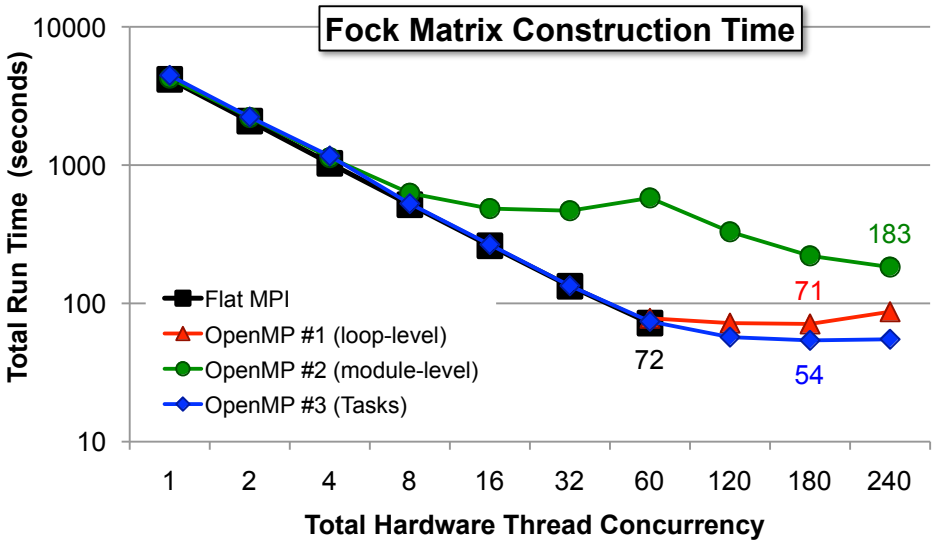
- Fast Fock build essential for RT-TDDFT

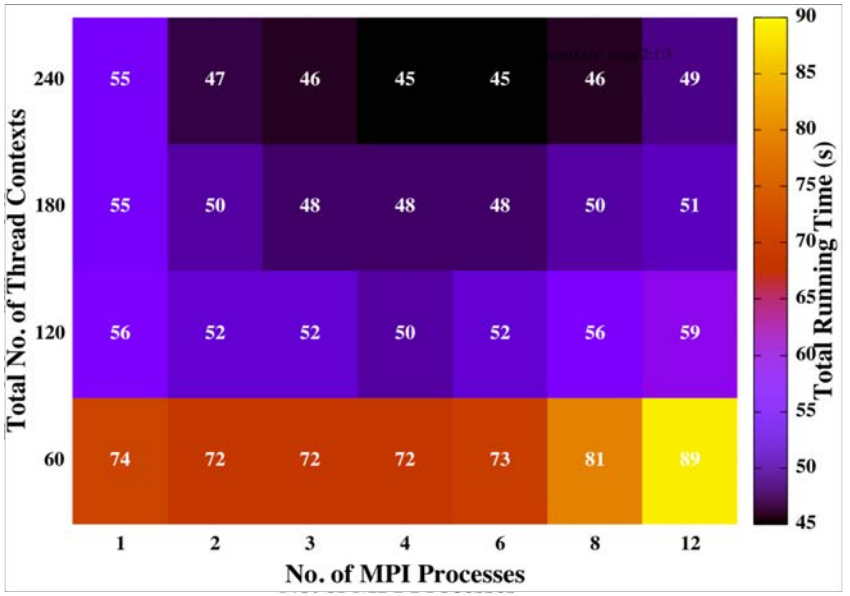
$$F_{ij} = h_{ij} + \sum_{kl}^{N} D_{ij} \left[(ij|kl) - \tfrac{1}{2}(ik|jl) \right]$$

- Optimization leads to 2.5x performance improvement components
  - 2-electron integrals: Increased data locality
    Reordering of loops
  - Fock matrix assembly: Tuning of task level granularity
    Vectorization
    Multi-threading

Shan, Austin, de Jong, Oliker, Wright, Apra, PMBS, pp 261 (2014)

Understanding Multi-Threading on Intel Knights Corner





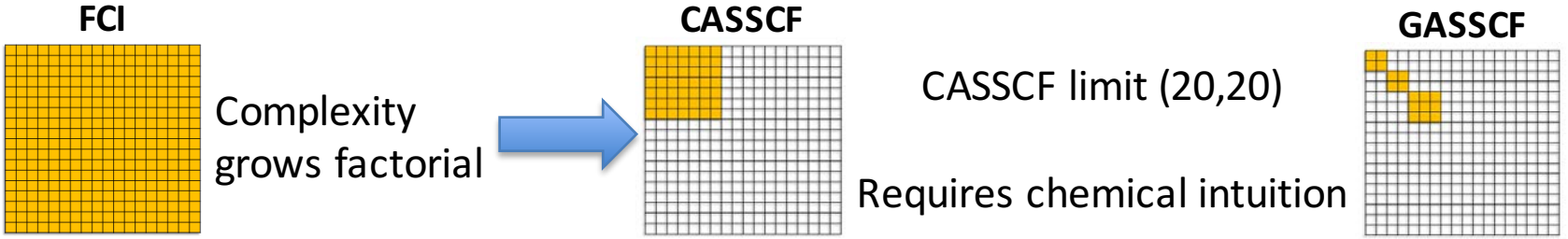
- Limit of 60 MPI ranks due to memory pressure
- OpenMP task parallelism scales to 180 threads
- Hybrid MPI-OpenMP achieves 1.6x speed up

Shan, Williams, de Jong, Oliker, PMAM 2015, pp 58 (2015)

Developing Parallel GASSCF and SplitGAS

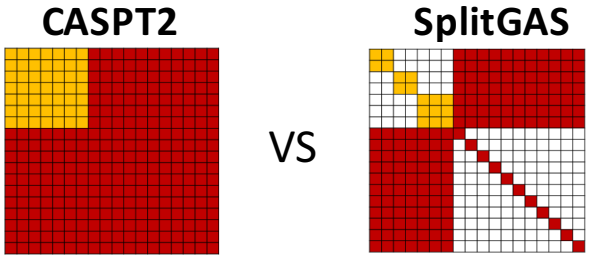
W.A. de Jong, K. Vogiatzis, D. Ma, G. Li Manni, L. Gagliardi

- Handle non-dynamical correlation due to orbital degeneracies



- Bringing dynamical correlation back into the equation

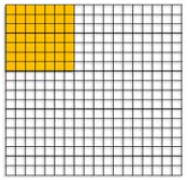
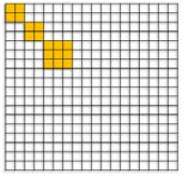
Parametric shift zeroth-order Hamiltonian needed



Löwdin's partitioning technique
Parameter free

Computational Cost Driven by Direct-CI

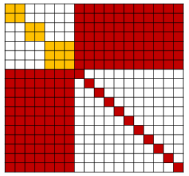
- CASSCF and GASSCF

 and 

$$H_{IJ} = \sum_{ij} h_{ij} \langle \Psi_I | \varepsilon_{ij} | \Psi_J \rangle + \frac{1}{2} \sum_{ijkl} (ij|kl) \left[\left(\sum_K \langle \Psi_I | \varepsilon_{ij} | \Psi_K \rangle \langle \Psi_K | \varepsilon_{kl} | \Psi_J \rangle \right) - \delta_{jk} \langle \Psi_I | \varepsilon_{il} | \Psi_J \rangle \right]$$

- SplitCAS (P=1) and SplitGAS

$$U_{IJ} = \sum_J^P \left(H_{IJ} - \sum_M^Q \frac{H_{IM} H_{MJ}}{H_{MM} - E} \right)$$



- Solving eigenvalue problem $Hv = Ev$ using Davidson algorithm
  - Most time consuming step is generation of sigma vector $\sigma_I = H_{IJ} c_J$

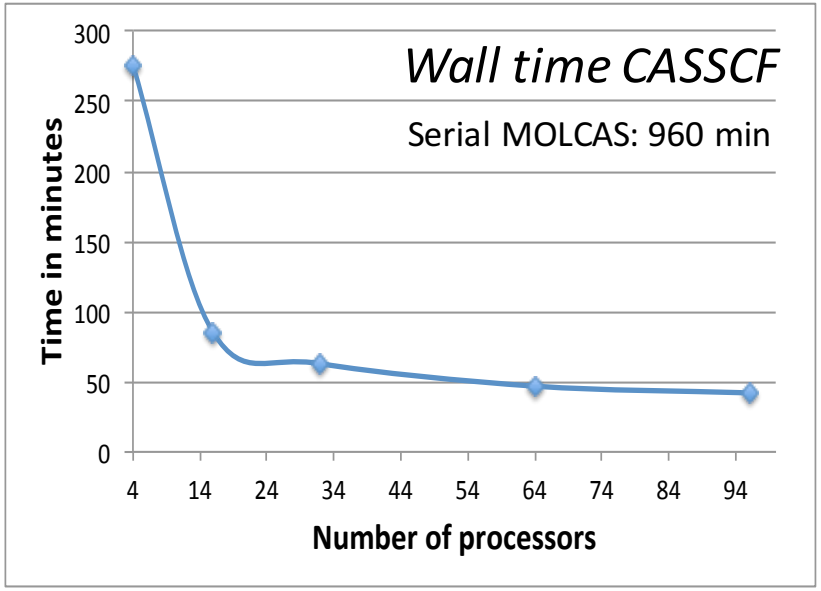
Li Manni, Aquilante, Gagliardi *J. Chem. Phys.* **2011**, *134*, 034114.
Li Manni, Ma, Aquilante, Olsen, Gagliardi *J. Chem. Theory Comput.* **2013**, *9*, 3374.
Vogiatzis, Li Manni, Stoneburner, Ma, L. Gagliardi *J. Chem. Theory Comput. Accepted*.

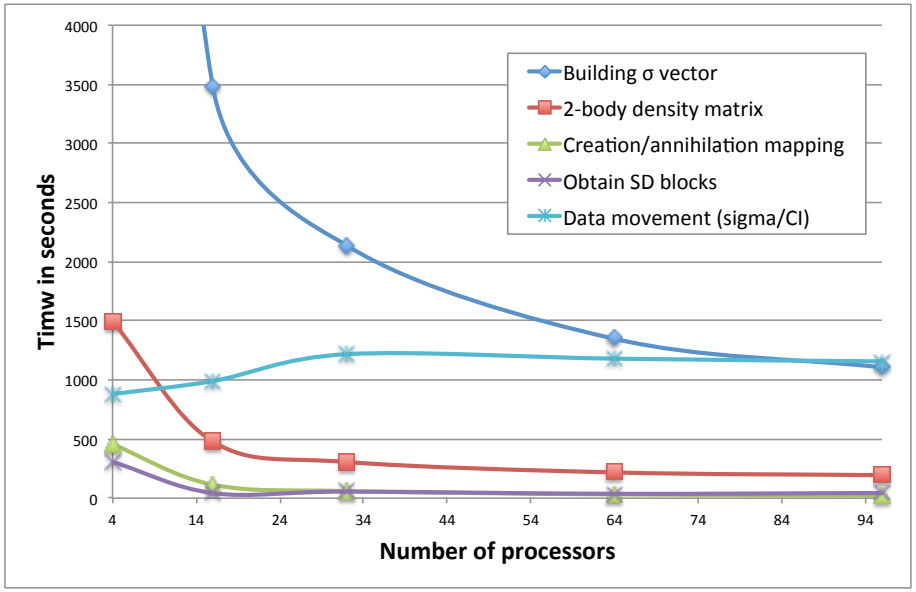
LUCIA, From Serial Code to Parallel

- NWChem GASSCF/SplitGAS implementation via parallelization of widely used LUCIA code (Jeppe Olsen, Aarhus University)
  - Utilized in MOLCAS, DALTON, DIRAC, …
- Native NWChem data handling
  - Large CI and Sigma vectors are stored globally using Global Arrays
    - Global Arrays can be stored on disk using parallel IO
  - Two-electron integrals replicated to reduce global communication
  - Local data stored using NWChem memory allocator
- Parallel scheme for building sigma vector
  - All procs get same block of CI vector (requires communication)
  - All procs build part of sigma vector block (long loops and lots of compute)
  - Global reduction and store sigma block in global sigma vector

Note: Everything done in SD instead of CSFs to avoid transformations!

Scaling Results CASSCF

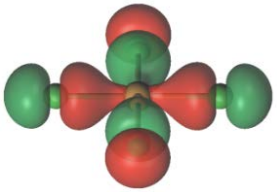


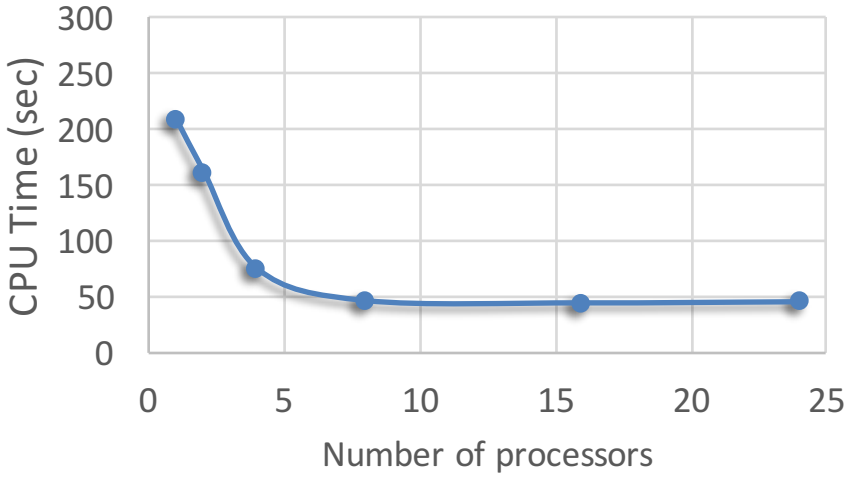


- Compute intensive work scales well
- Communication of data becomes bottleneck with increased processor count

Cr_3 ^1Ag state
CAS: 18 elec, 18 orb
147 784 110 SDs
Basis set: 6-31G*

First Scaling Results SplitGAS

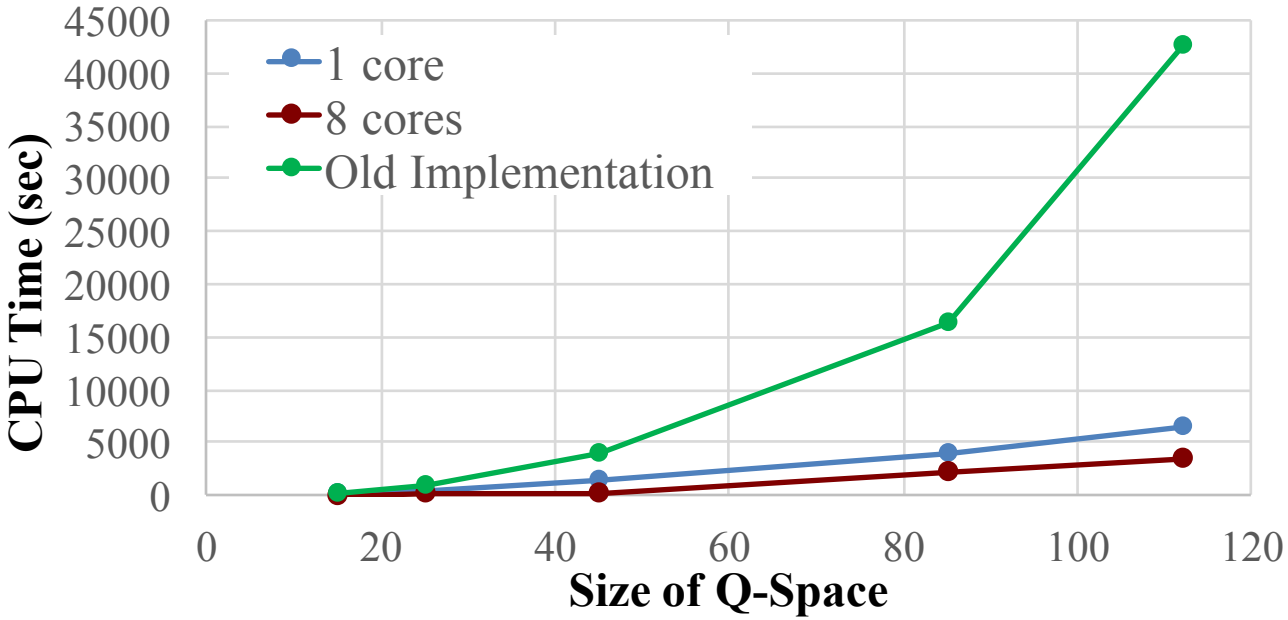




$[CuCl_4]^{2-}$
P-space: (11,11)
P/Q-space: (11,26)
aug-cc-pVDZ

SplitGAS with 123 orbitals correlated

CSFs: 168 163 896
SDs: 424 526 732



Improving Parallelism and Memory Use

- Ongoing code development work

- Moving from one to two-level parallelism
  - Reduce memory footprint by storing two-electron integrals stored once per node
  - Split CI vector into smaller logical blocks by internally creating large number of CI spaces
  - New parallel scheme for sigma vector
    - Each node works on a local CI block (eliminates communication step)
    - All processors in node accumulate sigma block locally (less compute)
    - Store in global sigma vector
  - OMP style, not sure if OMP directives will suffice
    - Collaboration with SUPER key here

Summary

- Discussed developments to compute excited states
  - FastMATH/PNNL collaboration advances greatly accelerate TDDFT calculations
  - PNNL/UMN collaboration leads to new excited state absorption approach
  - SUPER/LBNL collaboration accelerates Fock build algorithm
  - LBNL/UMN collaboration develops parallel GASSCF and SplitGAS implementations

- All developments are available for download in NWChem development version (http://nwchem-sw.org)