Very large scale linear algebra for bound and unbound electronic states

Computational Research, LBNL
- Chao Yang
- Samuel Williams
- Esmond Ng
- Xiaoye (Sherry) Li

Chemistry, USC
- Anna Krylov

Chemical Sciences, LBNL
- **Martin Head-Gordon** **Team Leader**
- **Daniel Haxton** **Me**
- C. William McCurdy

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

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POSTERS: BOARD 30, PLAZA 1

A perturbative approximation to RAS-nSF for excited states and strong correlations
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Scientific introduction

We are developing methods to calculate excited electronic states of molecules.

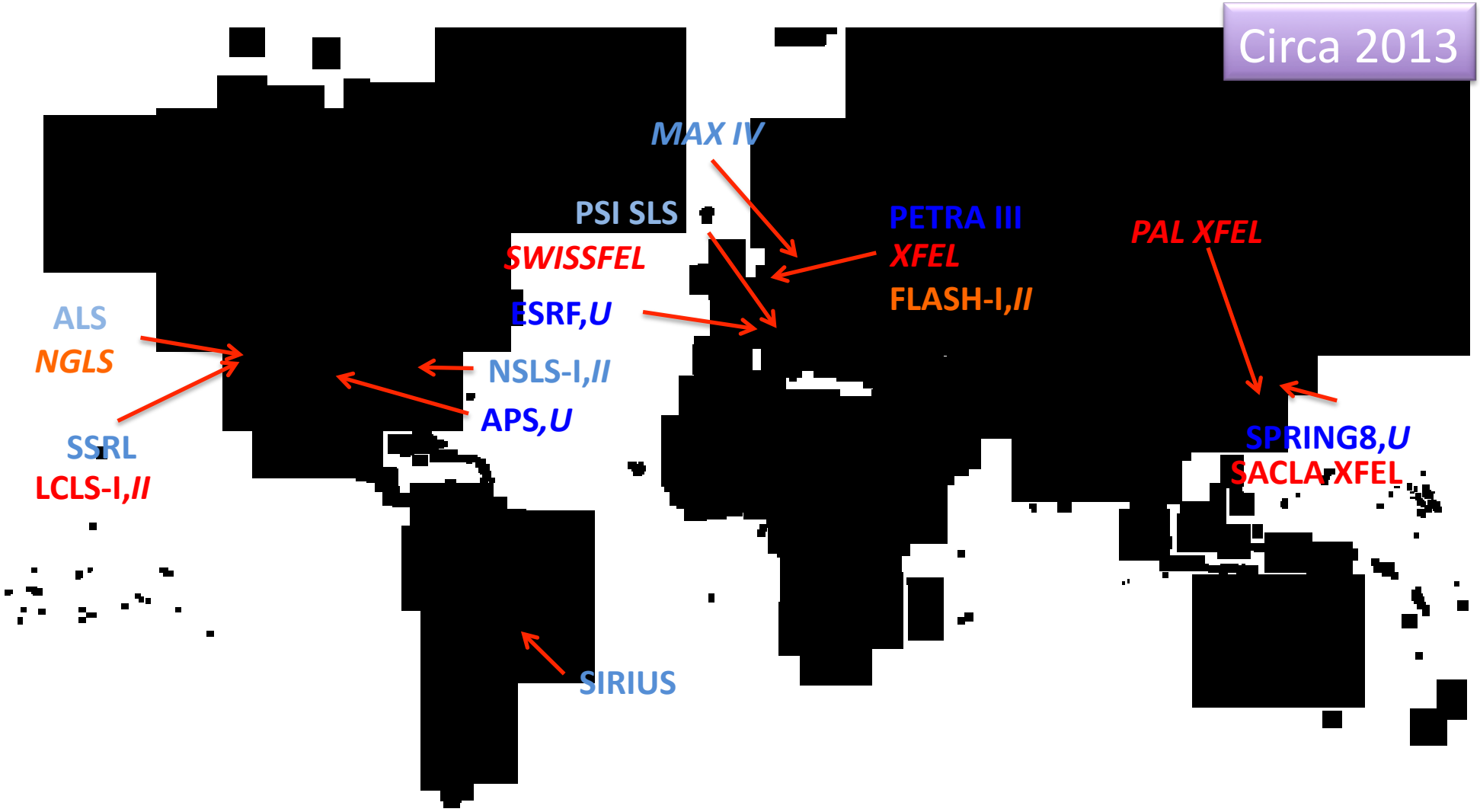
Excited states are involved in important physical processes including photochemistry.

Highly excited states may decay via ionization, ejection of an electron – they autoionize.

Autoionizing states require extension of current numerical capabilities.

Excited and autoionizing states are relevant for current and next generation light source experiments.

BES Light Sources & Key Worldwide Competitors



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Our Tools Include

1) Q-CHEM Quantum chemistry program, Martin Head-Gordon et al

   Over 3 million lines of code. Over 55,000 copies distributed. Over 100 active developers. Small scale parallel, mostly mid-scale computing, current focus on OpenMP.

2) LIBTENSOR Library for tensor algebra, Evgeny Epifanovskiy

   http://iopenshell.usc.edu/downloads/tensor

   Used for all correlated methods in Q-CHEM

Two Computational Challenges

1) Scalable electronic structure

2) Linear algebra with complex symmetric matrices

I will describe these CHALLENGES, the TASKS involved, and our STRATEGIES for each task.

Challenge 1: Scalable Electronic Structure

Quantum chemistry: **Gaussian basis functions**.

→ Order N^4 two electron matrix elements ($1/r_{12}$) to compute,
N=number of Gaussian basis functions (size of molecule).

A) Makes transformations of these integrals slow, which fact is relevant to methods that optimize orbitals and that form the core of this project e.g. EOM-CCSD, equations of motion coupled cluster with single and double excitations.

Two index transformations performed in Order N^6 operations, rate limiting step for CCSD / EOM-CCSD

B) Matrix diagonalization (Configuration Interaction): Matrices to diagonalize are not very sparse and have nontrivial structure.

Tensor Decompositions for two electron integrals

Want to make an approximation by which we can reduce the effort required to store and manipulate the two electron matrix elements.

Like representation of a nonseparable operator as a sum of separable terms.

$$1/r \approx f_1(x)f_1(y)f_1(z) + f_2(x)f_2(y)f_2(z) + ...?$$

Not really.

Tensor Decompositions for two electron integrals

Resolution of the identity

$$\langle ij|\frac{1}{r_{12}}|kl\rangle \approx \sum_{\alpha\beta} p_{ik\alpha}\ q_{\alpha\beta}\ p_{jl\beta}$$

More than one resolution of the identity approximation satisfies the above equation.

SVS approximation

$$\left\langle \varphi_i(1)\varphi_j(2)\left|\frac{1}{r_{12}}\right|\varphi_k(1)\varphi_l(2)\right\rangle \approx \sum_{mn}\langle\varphi_i\varphi_k|\phi_m\rangle\langle\phi_n|\varphi_j\varphi_l\rangle \int d^3r_1 d^3r_2 \phi_m(1)\frac{1}{r_{12}}\phi_n(2)$$

V approximation

$$\left\langle \varphi_i(1)\varphi_j(2)\left|\tfrac{1}{r_{12}}\right|\varphi_k(1)\varphi_l(2)\right\rangle \approx \sum_{mn}\left[\int d^3r_1 d^3r_2 \varphi_i(\vec{r}_1)\varphi_k(\vec{r}_1)\tfrac{1}{r_{12}}\phi_m(\vec{r}_2)\right]\left[\int d^3r_1 d^3r_2 \phi_m(\vec{r}_1) r_{12}\phi_n(\vec{r}_2)\right]\times \left[\int d^3r_2 d^3r_2 \phi_n(\vec{r}_2)\tfrac{1}{r_{12}}\varphi_j(\vec{r}_1)\varphi_l(\vec{r}_1)\right]$$

Tensor Decompositions for two electron Integrals

Canonical decomposition

Symmetry of two electron matrix elements not naturally accounted for

$$\langle ij|\frac{1}{r_{12}}|kl\rangle \approx \sum_{\alpha} w_{i\alpha}\ x_{j\alpha}\ y_{k\alpha}\ z_{l\alpha}$$

Cholesky decomposition

$$\langle ij|\frac{1}{r_{12}}|kl\rangle \approx \sum_{\alpha} L^{\alpha}_{ik}\ L^{\alpha}_{jl}$$

Formula equivalent to resolution of the identity

Resolution of the identity or Cholesky decomposition:

Permits keeping two electron matrix elements in memory.

But currently no reduction in scaling (still N^6 for CCSD) due to certain terms

Math has to be done to carry tensor decompositions through and achieving better scaling of calculation with respect to basis functions is not straightforward.

Tensor Decompositions for two electron Integrals

TASK: Improve scaling of CCSD to less than N^6

STRATEGIES:

1) Working on problematic terms.

2) Canonical decomposition of Cholesky factors. Nonlinear fitting problem.

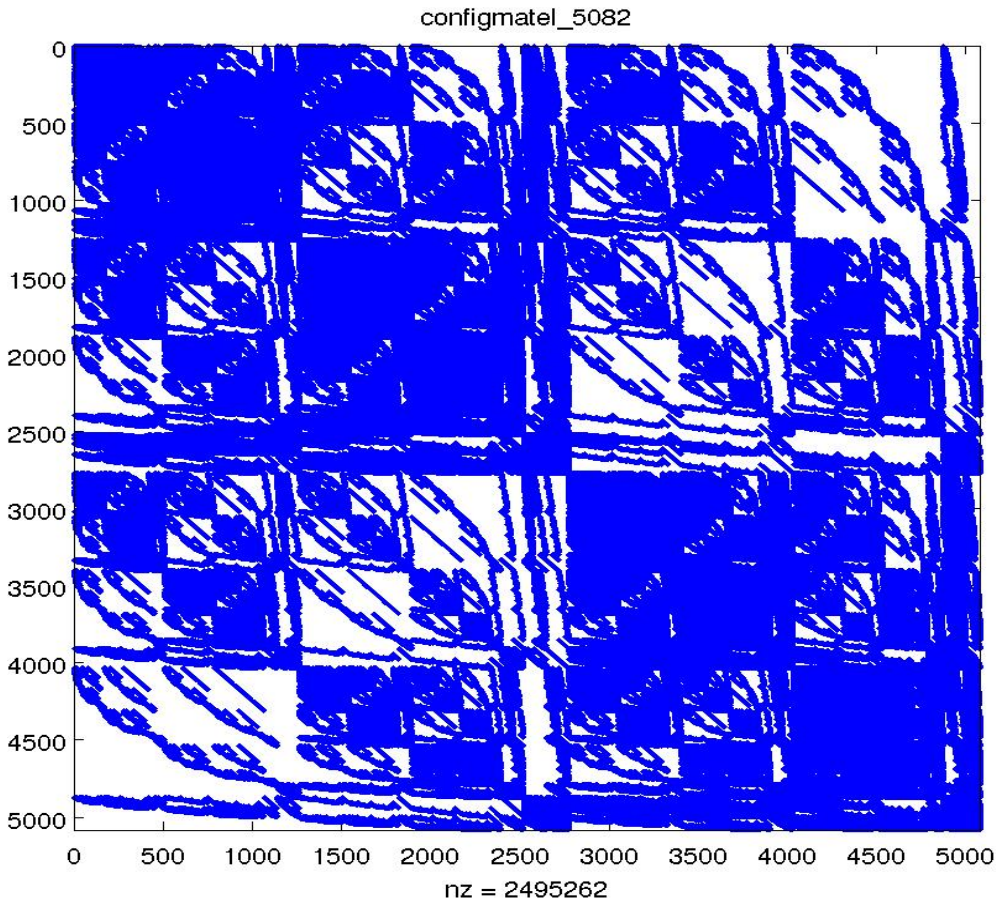
$$L_{ij}^{\alpha} \approx \sum_{\gamma} x_{\alpha\gamma}\ y_{i\gamma}\ z_{j\gamma}$$

In order to find the optimal decomposition, sample approach of
Friedland S, Mehrmann V, Miedlar A and Nkengla M
Fast low rank approximations of matrices and tensors

3) Tensor hypercontraction algorithm of Hohenstein, Parrish, Martinez & coworkers

Tensor Decompositions for Preconditioning Hamiltonian Matrix

Algebraic preconditioner via low-rank approximate factorization
Using low rank approximations to Hamiltonian matrix in order to precondition Hamiltonian matrix. Work of Xiaoye (Sherry) Li



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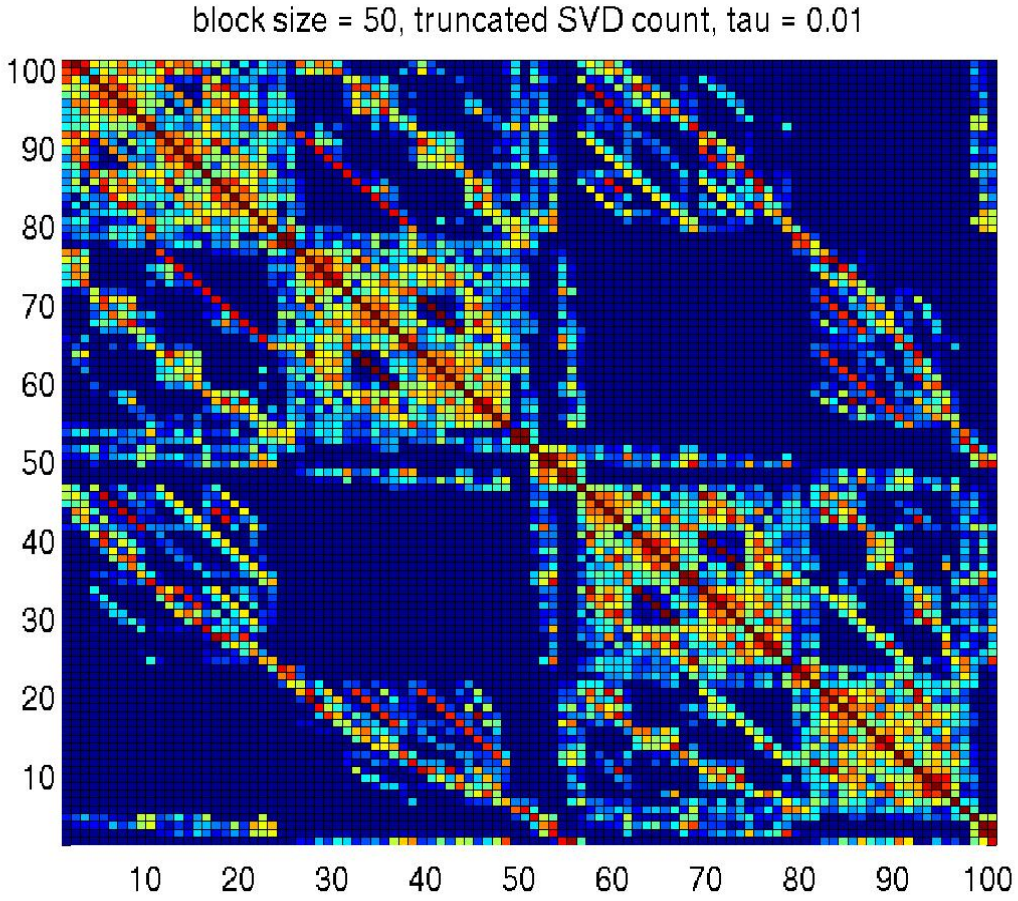


Challenge 1: Scalable Electronic Structure

Hybrid grid/Gaussian method:

Combined method with both grid basis functions and standard Gaussians.

Appropriate for arbitrary excitation and ionization of up to two electrons (with all other electrons active as well).

Goal is an accurate description of metastable states of small systems for new ultrafast light source experiments.

Hybrid method: Grid basis: Key ``approximation''

Two electron matrix elements are DIAGONAL and TRANSLATIONALLY INVARIANT just like the potential, $1/r_{12}$

$$\langle ij|\frac{1}{r_{12}}|kl\rangle \approx \delta_{ik}\ \delta_{jl}\ v_{(i-j)}$$

Four index tensor → one index tensor (size similar to that of wave function vector)

The operation of the two electron part of the Hamiltonian can always be done locally (no communication).

Hybrid method: Grid basis: Key ``approximation''

Works unnaturally well.

Hydrogen, grid spacing **0.6 atomic units** (Bohr radii)

E= -0.494 Atomic units (hartree) -0.5 atomic units actual

Helium, grid spacing **0.4 atomic units**

E= -2.866 Atomic units -2.903 atomic units actual

Hybrid method: Tensor Structure

Large Hamiltonian matrices naturally expressed as tensor decompositions.

E.g.

$$\left\langle ij\alpha\beta \left| \frac{1}{r_{12}} \right| kl\gamma\delta \right\rangle = \sum_{\vec{P}} \epsilon_{\vec{P}} \Big[\delta_{\alpha A}\delta_{\beta B} \ll ij||ab \gg$$
$$+ \delta_{\alpha A}(1-P)_{ia}\Big(\ll j\beta||bB \gg - \ll j\beta||Bb \gg \Big)$$
$$- \delta_{\beta A}(1-P)_{ia}\Big(\ll j\alpha||bB \gg - \ll j\alpha||Bb \gg \Big)$$
$$- \delta_{\alpha A}(1-P)_{ja}\Big(\ll i\beta||bB \gg - \ll i\beta||Bb \gg \Big)$$
$$+ \delta_{\beta A}(1-P)_{ja}\Big(\ll i\alpha||bB \gg - \ll i\alpha||Bb \gg \Big)$$
$$+ (1-P)_{ia}(1-P)_{jb} \ll \alpha\beta||AB \gg \Big]$$

$$P_{ij} = \sum_{\alpha} v_{i\alpha} v_{j\alpha}$$

Hybrid method: Tensor Structure

Kinetic energy

$$[\mathbf{T}\Psi]_{ijklmn} = \sum_{Q} t_{(i-Q)}\Psi_{Qjklmn} + t_{(j-Q)}\Psi_{iQklmn} + \cdots$$

For two electrons, we operate with the 1D kinetic energy six times.

Hybrid method: Tensor Structure

TASK: Effectively precondition linear equations for iterative solution of eigenvector/eigenvalue equation, accounting for tensor structure.

STRATEGY: Incorporate Algebraic Preconditioner via low-rank approximation into hybrid method.

Challenge 2: Linear Algebra for Complex Symmetric Matrices

For metastable states our Hamiltonian matrices are complex symmetric.

Standard quantum chemistry eigensolvers designed for Hermitian problems are not applicable to complex symmetric matrices.

TASK: Develop and deploy cutting edge methods for eigenvectors and eigenvalues that are appropriate for complex (symmetric) matrices

STRATEGY: Implement methods under development by C. Yang within Q-CHEM and within the hybrid method.

Methods That Fail for Complex Symmetric Matrices

Implicitly restarted Arnoldi:

Needs ``implicit filtering'' for good convergence with restarts.

Implicit filtering removes unwanted spectral components from starting block of vectors of Arnoldi algorithm.

However there are too many unwanted spectral components to filter because we are dealing with interior eigenvalues.

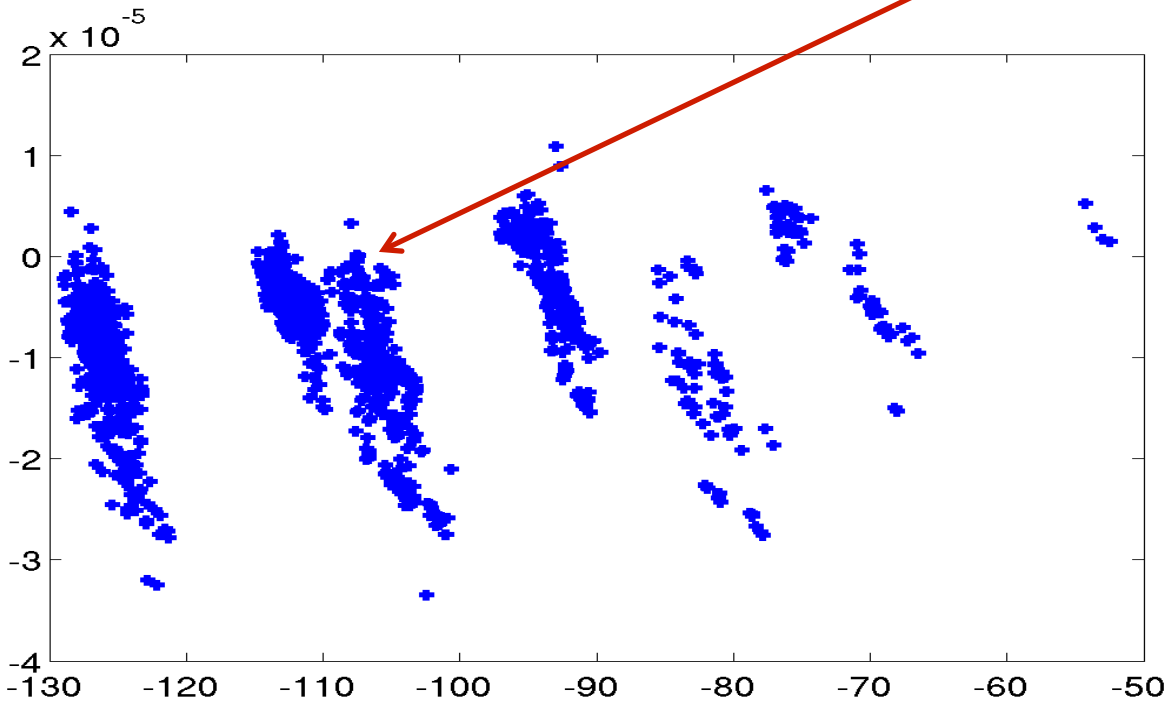
Davidson diagonalization is the basis of many quantum chemistry configuration interaction codes including Q-CHEM. Steepest descent method not directly applicable to complex matrices

Methods That May Work for Complex Symmetric Matrices

Inverse subspace iteration: underlying linear equations need to be solved accurately

Makes it harder for interior eigenvalues

$E = -114.68 - 10^{-6}i$



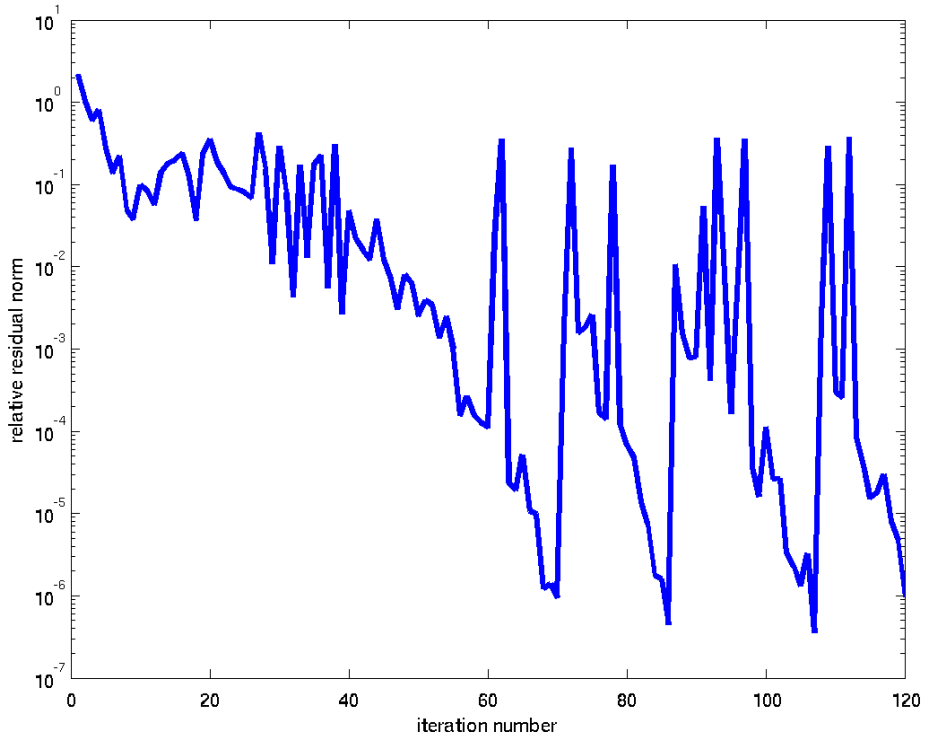
Im(E)

Re(E)

Methods That May Work for Complex Symmetric Matrices

Jacobi Davidson: Applicable to complex symmetric matrices. One eigenpair is computed at a time; a block algorithm is more desirable.

Residual error



Four eigenvalues Computed.

Iterations

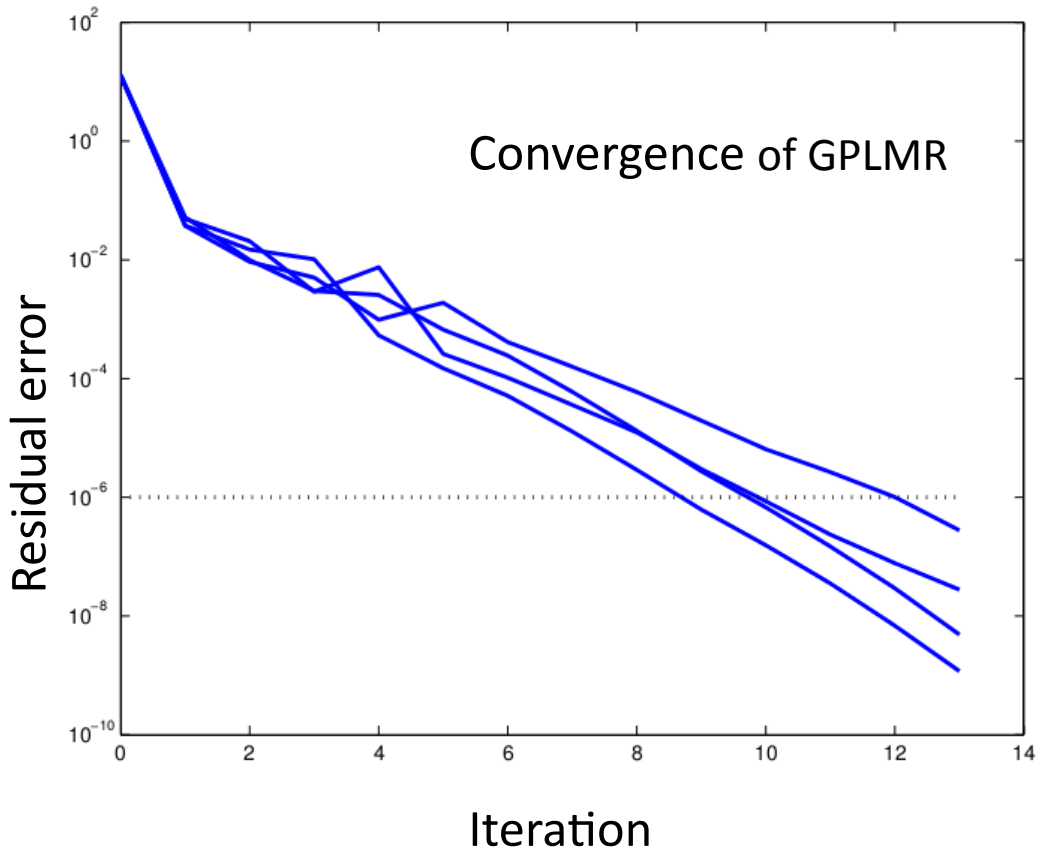
Methods That May Work for Complex Symmetric Matrices

Generalized Preconditioned Locally Minimum Residual Method

PLMR developed by Eugene Vecharynski, PhD thesis.

Surprisingly good convergence for both real and complex symmetric problems.

Uses Krylov space for preconditioned (always nonsymmetric) linear equation.



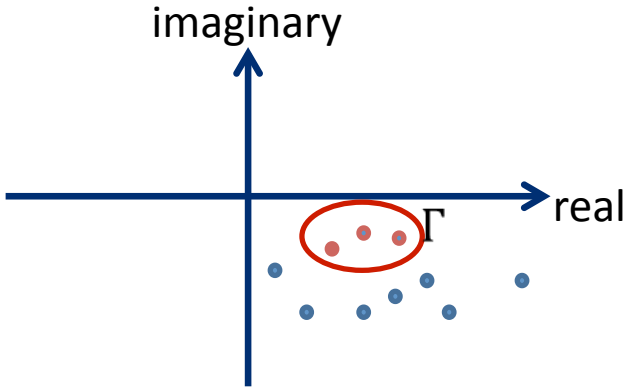
- Block algorithm
- Multiple levels of parallelism
- Easy to incorporate a preconditioner

Methods That May Work for Complex Symmetric Matrices

Complex contour integral idea for calculating eigenvectors V

- Pick an orthonormal basis *V*
- While no convergence

1. $W \leftarrow PV$
2. $V = qr(W)$
3. Check convergence



$$P = \frac{1}{2\pi i}\oint_{\Gamma} (A - zI)^{-1} dz \approx \sum_{i=1}^{n_p} (A - z_i I)^{-1} \omega_i$$

Fin

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