

Advanced Software for the Calculation of Thermochemistry, Kinetics and Dynamics

<http://www.mcs.anl.gov/scidac/beskinetics>



ANL BES-SciDAC program has two inter-related projects

- Parallelization of Cumulative Reaction Probabilities (**CRP**)
- Parallel Implementation of Subspace Projection Approximate Matrix (**SPAM**) method

CRP (Stephen Gray and Al Wagner)

- computationally intensive core of reaction rate constants
- mathematical kernel (all matrices are sparse with some structure):
 - method 1: - iterative eigensolve (imbedded iterative linearsolves)
 - clever preconditioning important
 - portability based on ANL PETSc library of kernels
 - method 2: - Chebyshev propagation (=> matrix vector multiplies)
 - novel finite difference representation (helps parallelize)
- programming issues:
 - parallelization
 - exploiting data structure (i.e., preconditioning)

Advanced Software for the Calculation of Thermochemistry, Kinetics and Dynamics



SPAM (Ron Shepard and Mike Minkoff)

- **novel iterative method to solve general matrix equations**
 - eigensolve
 - linear solve
 - nonlinear solve
- **applications are widespread**
 - in chemistry: CRP, electronic structure (SCF, MRSDCI,...)
- **mathematical kernel:**
 - related to Davidson, multigrid, and conjugate gradient methods
 - subspace reduction (requiring usual matrix vector multiplies)
 - projection operator decomposition of matrix vector product
 - substitution of user-supplied approximate matrix in computationally intensive part of decomposition
 - sequence of approx. matrices => multilevel method
- **programming issues:**
 - generalization of approach (only done for eigensolve)
 - incorporation into libraries (connected to TOPS project part at ANL)
 - test of efficacy in realistic applications (e.g., CRP)

Parallelization of Cumulative Reaction Probabilities (CRP)

Stephen Gray and Al Wagner (Argonne National Laboratory)

- **Cumulative Reaction Probabilities (CRP)**
 - computational core of reaction rate constants
 - exact computation computational intensive
 - approximate computation underlies all major reaction rate theories in use

=> efficient exact CRP code will

 - give exact rates (if the computed forces are accurate)
 - calibrate ubiquitous approximate rate methods
- **Two methods:**
 - Time Independent (Miller and Manthe, 1994, and others)
 - Time Dependent (Zhang and Light, 1996, and others)
- **Highly parallel approaches to both methods being pursued**

Parallelization of **C**umulative **R**eaction **P**robabilities Time Independent Approach

- $N(E) = \sum_k p_k(E, J)$

where $p_k(E, J)$ = eigenvalues of Probability Operator:

$$P(E) = 4 \varepsilon_r^{1/2} (H+i\varepsilon-E)^{-1} \varepsilon_p (H-i\varepsilon-E)^{-1} \varepsilon_r^{1/2}$$

where $i\varepsilon_x$ = absorbing diagonal potentials
= imaginary potentials

H = hamiltonian (differential operator)

=> for realistic problems

size $\sim 10^5 \times 10^5$ or much larger

number of eigenvalues < 100

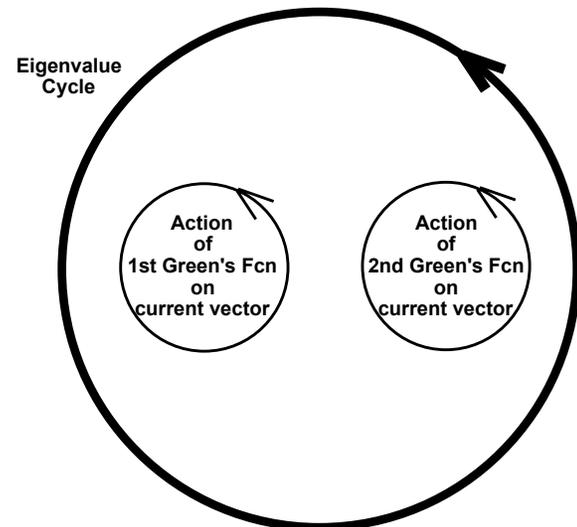
- iterative approach

macrocycle of iteration for eigenvalue

microcycle of iteration for

action of Green's function $(H-i\varepsilon-E)^{-1}$

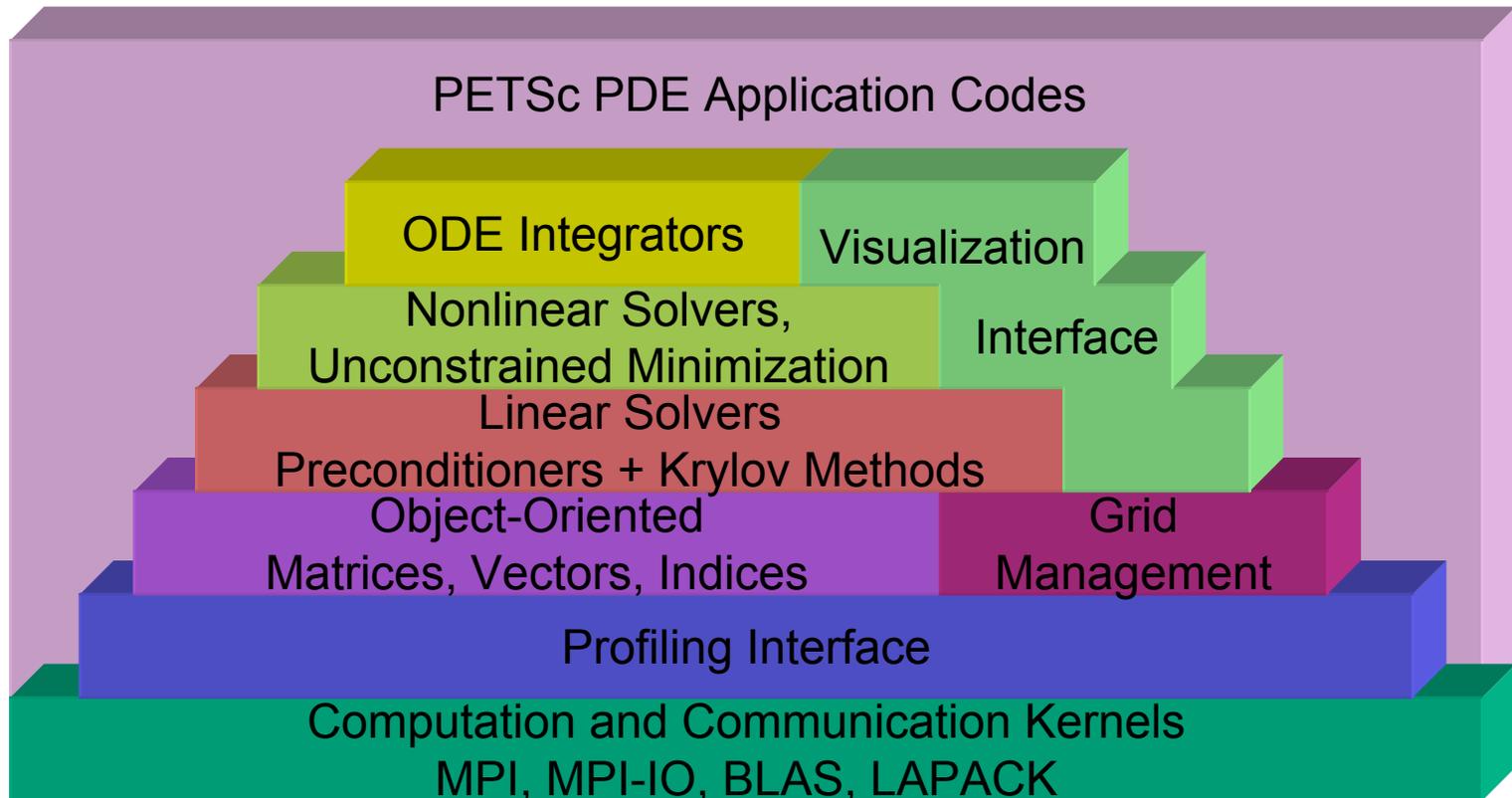
=> linear solve



Parallelization of Cumulative Reaction Probabilities

Time Independent Approach

- Code built on PETSc (<http://www.mcs.anl.gov/petsc>) -> TOPS
- PETSc: data structure, GMRES linear solve, preconditioners
USER: Lanczos method for eigensolve
- Future: user supplied preconditioners



Parallelization of **C**umulative **R**eaction **P**robabilities

Time Independent Approach

Performance:

-model problem

- Optional number of dimensions
 - Eckhart potential along rxn coord.
 - parabolic potential perpendicular to reaction coord.
- DVR representation of H

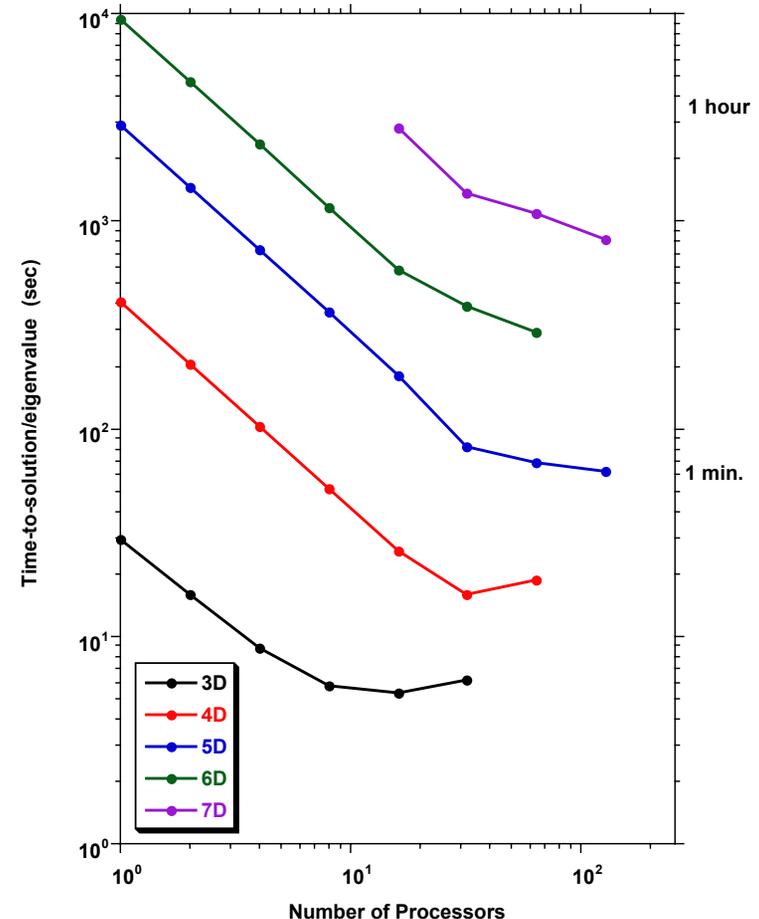
-Algorithm options

- Diagonal preconditioner
- other PETSc preconditioners slower

-Computers

- NERSC SP
- others include SGI Power Challenge, Cray T3E

Performance vs. processors for model with increasing dimensions

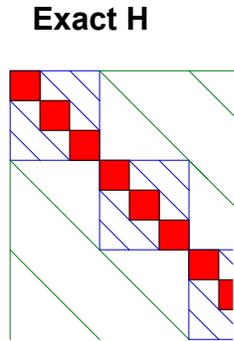


Parallelization of Cumulative Reaction Probabilities

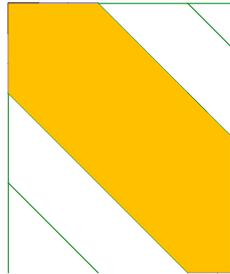
Time Independent Approach

Future Preconditioners:

- SPAM (see next poster)

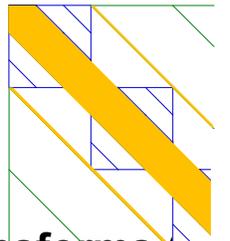


fat band
precond.



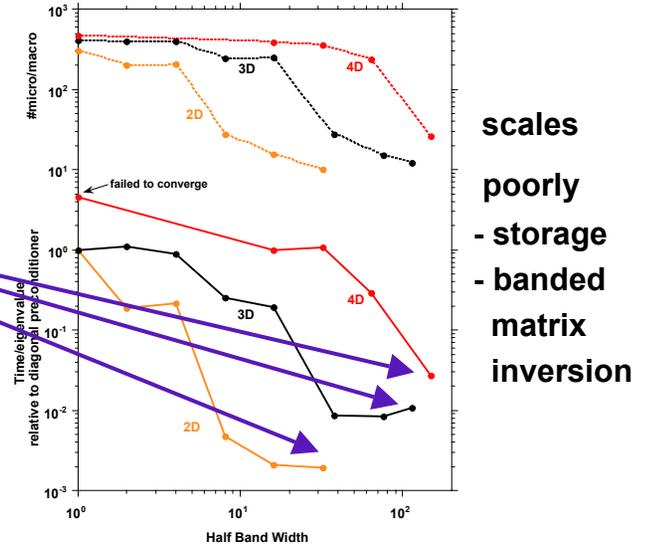
great
performance

SPAM
precond.

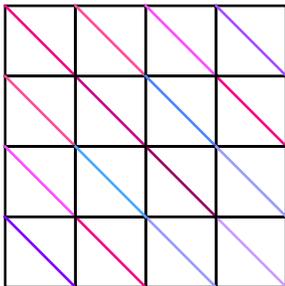


- Sparse optimal similarity transforms (Trifunov)

can SPAM get scalable performance?

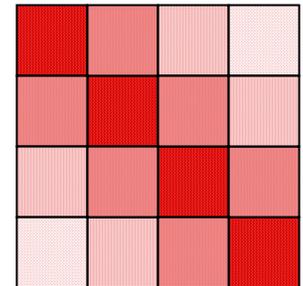


IF Q =



THEN find optimal Q such that QHQT =

optimal block diagonal ->



Parallelization of **C**umulative **R**eaction **P**robabilities Time Dependent Approach

N(E) can be found from time dependent transition state wavepackets (TSWP)
(see Zhang and Light, J. Chem. Phys. 104, 6184 (1996))

$$N(E) = \sum^M N_i(E)$$

where $N_i(E) \propto \text{Im} \langle \phi_i(E) | F \phi_i(E) \rangle$

where **F** = differential flux operator

$$\phi_i(E) \propto \int \exp(iEt) \psi_i(x,t) dt$$

where TSWP $\psi_i(x,t)$ from $i\partial/\partial t \psi_i(x,t) = H \psi_i(x,t)$

where **H** is Schroedinger Eq. Operator

Work

- **M** different TSWPs (each independent of other)
 - each TSWP
 - propagated over time
 - N_t time steps
 - each time step propagation dominated by $H \psi_i$ multiply
- => CPU work = M N_t (work of $H \psi_i$ multiply)**

Parallelization of **C**umulative **R**eaction **P**robabilities Time Dependent Approach

Solution Strategy

- Trivial parallelization over M wavepackets
Nontrivial parallelization for wavepacket propagation
- Real Wavepackets (TS-RWP)
(K. M. Forsythe and S. K. Gray, J. Chem. Phys. 112, 2623 (2000))
 - half the storage, twice as fast relative to complex wavepackets
 - Chebyshev iteration for propagation
 - $H\psi_i$ work \rightarrow action of second order differential operators

Parallelization of Cumulative Reaction Probabilities

Time Dependent Approach

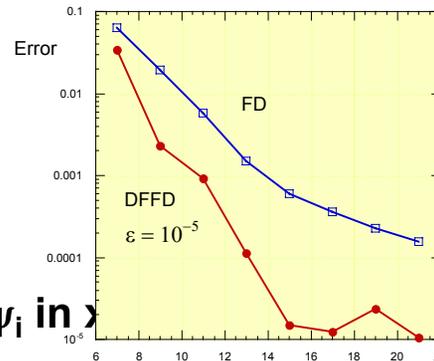
Solution strategy (more)

- Dispersion Fitted Finite Difference (DFFD)

(S. K. Gray and E.M. Goldfield, J. Chem. Phys. 115, 8331 (2001))

- finite difference evaluation of action of differential operators
- optimized constants to reproduce dispersion relation (dispersion related momentum to kinetic energy)
- different optimized constants for selected propagation error ε

- □ x.error for 3D H+H2
- Reaction Probability vs.
- order of finite difference



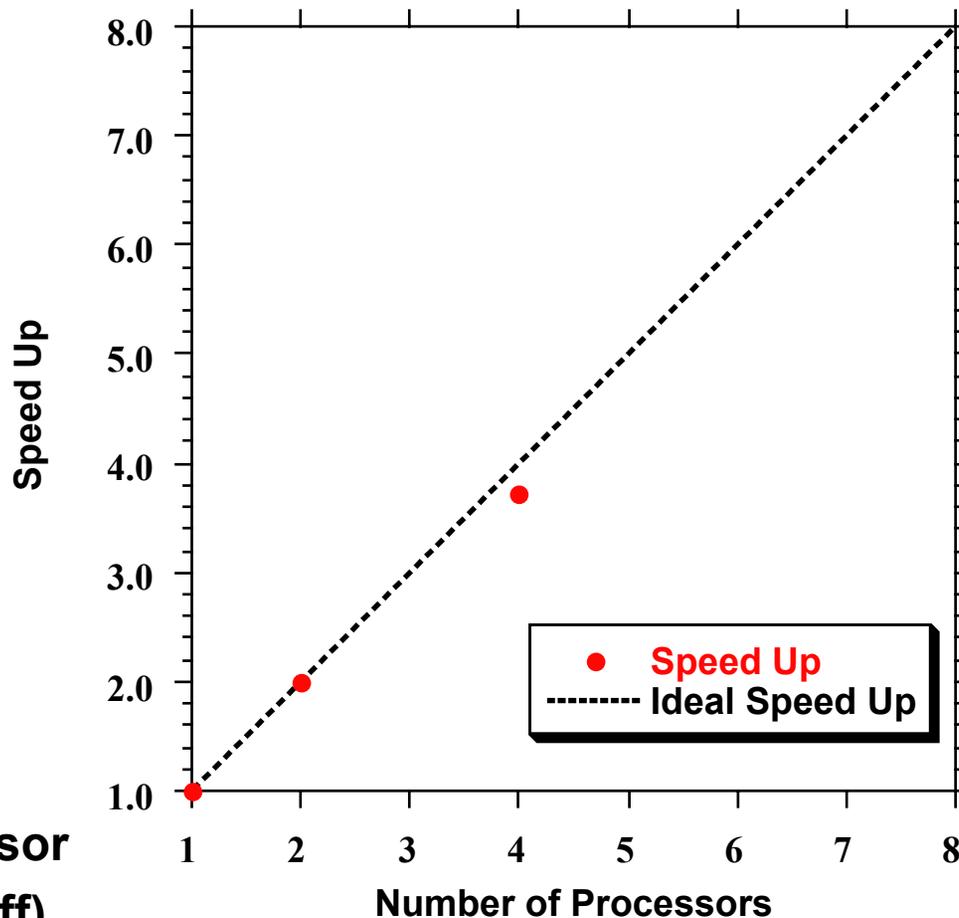
- parallelize via decomposition of ψ_i in x
- DFFD => less edge effects inducing processor communications

Parallelization of Cumulative Reaction Probabilities

Time Dependent Approach

Preliminary Results

- OH+H₂ reaction
 - 6 dimensions
 - zero total ang. mom.
- Wavepacket propagated reaction probability
- RWP + DFFD propagation technique
- up to 4 WinterHawk processor (MPI with shared memory off)



Subspace Projected Approximate Matrix: SPAM

Ron Shepard and Mike Minkoff (Argonne National Laboratory)

- **New iterative method to solving general matrix equations**
 - Eigenvalue
 - Linear
 - Non linear
- **Method**
 - Based on subspace reduction, projection operators, decomposition, sequence of one or more approximate matrices
- **Extensions**
 - Demonstrated for symmetric real eigensolves
 - Demonstrations on linear and non-linear equations planned
- **Applications**
 - Applicable to problems with convergent sequences of physical or numerical approximations
 - Parallelizable, multi-level library implementations via TOPS

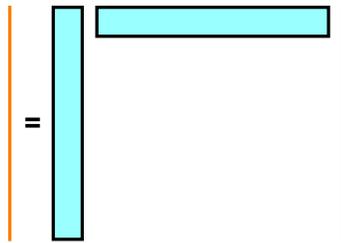
Subspace Projected Approximate Matrix: **SPAM** Method

- Subspace iterative solution to eigenvalue, linear, and nonlinear problems
e.g. eigenvalue problem $(H - \lambda_j)v_j = 0$
- Subspace iterative solutions have form $v_j = X^n c_j$
where: $X^n = \{x^1, x^2, \dots, x^n\}$
- c_j is solved in a subspace: $H^n c_j = \lambda_j^n c_j$
where: $H^n = (W^n)^T X^n$
where: $W^n = H X^n$ <---for $N \gg n$, where all the work is
- New x^{n+1} vector from residual: $r^{n+1} = (W^n - \lambda_j^n X^n)c_j$
- SPAM gives more accurate or faster converging way to get x^{n+1} in 3 steps

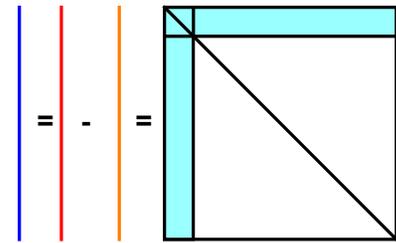
Subspace Projected Approximate Matrix: SPAM Method

Step 1: Assemble and apply Projections Operators on current vector

$$P^n x^{n+1} (= X^n [X^n]^T x^{n+1})$$

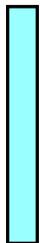


$$Q^n x^{n+1} (= x^{n+1} - P^n x^{n+1})$$



where

n trial vectors
(already processed)
 (X^n)



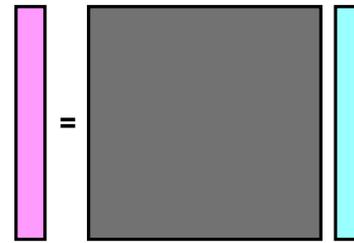
n+1 trial vector
 x^{n+1}



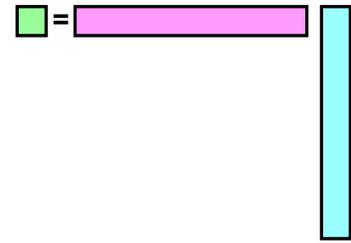
exact
matrix



matrix-vector
product



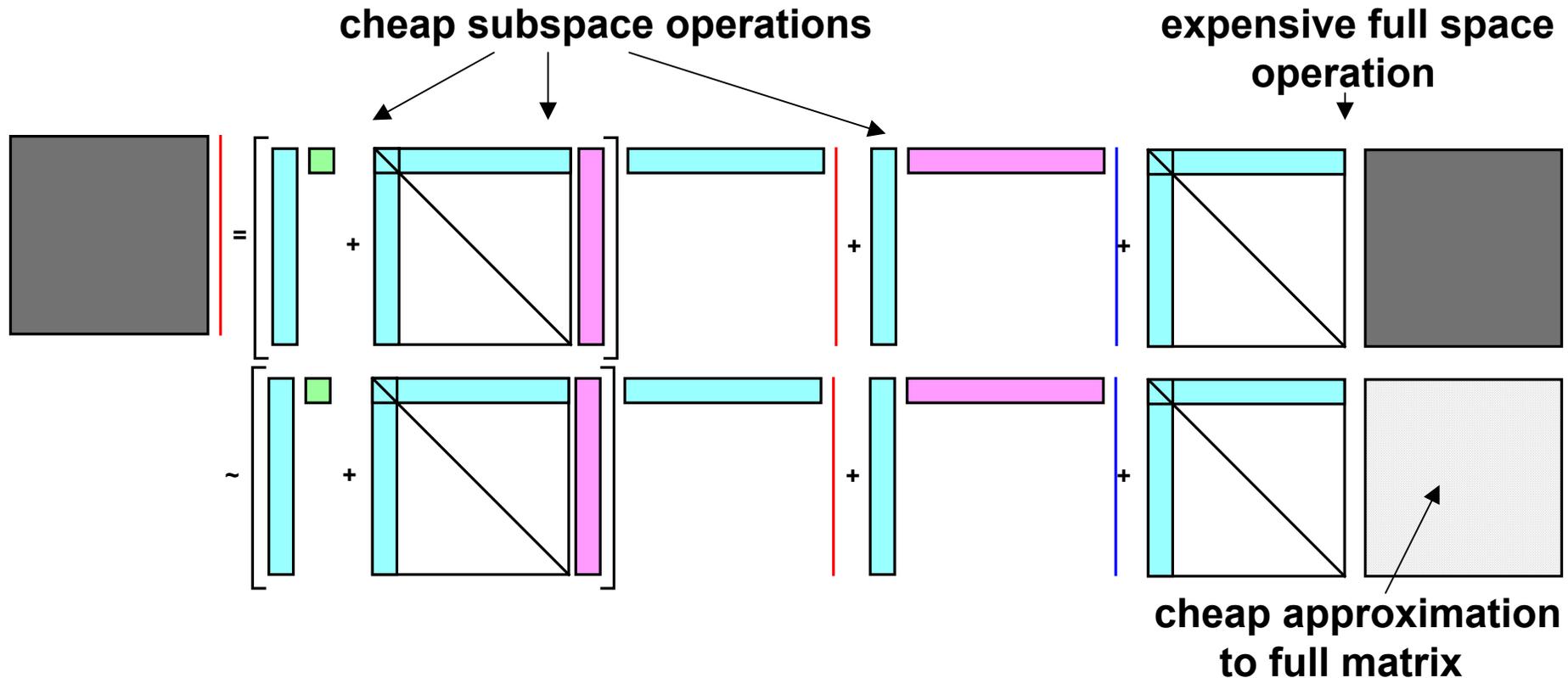
subspace
matrix



Subspace Projected Approximate Matrix: SPAM Method

Step 2: Decomposition and Approximation of H^{n+1}

$$H x^{n+1} = (P^{n+1} + Q^n) H (P^{n+1} + Q^n) x^{n+1}$$



Step 3: Solve approximate subspace problem
- solution is x^{n+1}

Subspace **P**rojected **A**pproximate **M**atrix: **SPAM** Method

SPAM properties:

- projection operators => convergence from any approx. matrix
- multi-level SPAM with dynamic tolerances
 - $\mathbf{Q}^n \mathbf{H} \mathbf{Q}^n$ approximated by $\mathbf{Q}^{(1)n} \mathbf{H}^{(1)} \mathbf{Q}^{(1)n}$
 - $\mathbf{Q}^{(1)n} \mathbf{H}^{(1)} \mathbf{Q}^{(1)n}$ approximated by $\mathbf{Q}^{(2)n} \mathbf{H}^{(2)} \mathbf{Q}^{(2)n}$
 - $\mathbf{Q}^{(2)n} \mathbf{H}^{(2)} \mathbf{Q}^{(2)n}$ approximated by $\mathbf{Q}^{(3)n} \mathbf{H}^{(3)} \mathbf{Q}^{(3)n} \dots$
- tens of lines of code added to existing iterative subspace eigensolvers
- highly parallelizable
- applicable to any subspace problem

Subspace **P**rojected **A**pproximate **M**atrix: **SPAM** Method

SPAM properties (broad view):

- **Relation to other subspace methods (e.g., Davidson)**
 - More flexible (sequence of approx. matrices - no sequence => SPAM= Davidson)
 - If iteration tolerances are correct, always no worse than Davidson
- **Relation to multigrid methods**
 - SPAM sequences of approx. matrices ~ multigrid sequences of approx. grids
 - Subspace method => solution vector composed of multiple vectors
Multigrid methods => single solution vector that is updated
- **Relation to preconditioned conjugate gradient (PCG) methods**
 - SPAM has multiple vectors and approximations always improved by projection
PCG has a fixed single preconditioner and single vector improved by projection
- **Deep injection of physical insight into numerics**
 - Application experts can design physical approximation sequences
 - SPAM maps approximation sequences onto numerics sequences
 - Projection operators continually improve the approximations
=> coarse approximations can still be numerically useful

Subspace **P**rojected **A**pproximate **M**atrix: **SPAM** Extensions

Mathematical Extensions

- **Eigensolves**
 - **Symmetric real**
 - **Done with many applications**
(<http://chemistry.anl.gov/chem-dyn/Section-C-RonShepard.htm>)
 - **Code available**
(<ftp://ftp.tcg.anl.gov/pub/spam/{README,spam.tar.Z}>)
 - **Generalized symmetric planned**
 - **Generalized complex hermitian planned**
 - **General complex non-hermitian planned**
- **Linear solves planned**
- **Nonlinear solves planned**
- **Formal connection to multigrid and conjugate gradient methods in progress**

Subspace Projected Approximate Matrix: SPAM

Applications

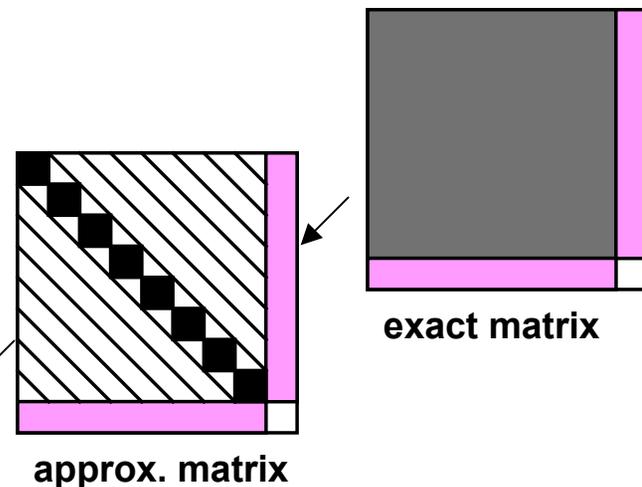
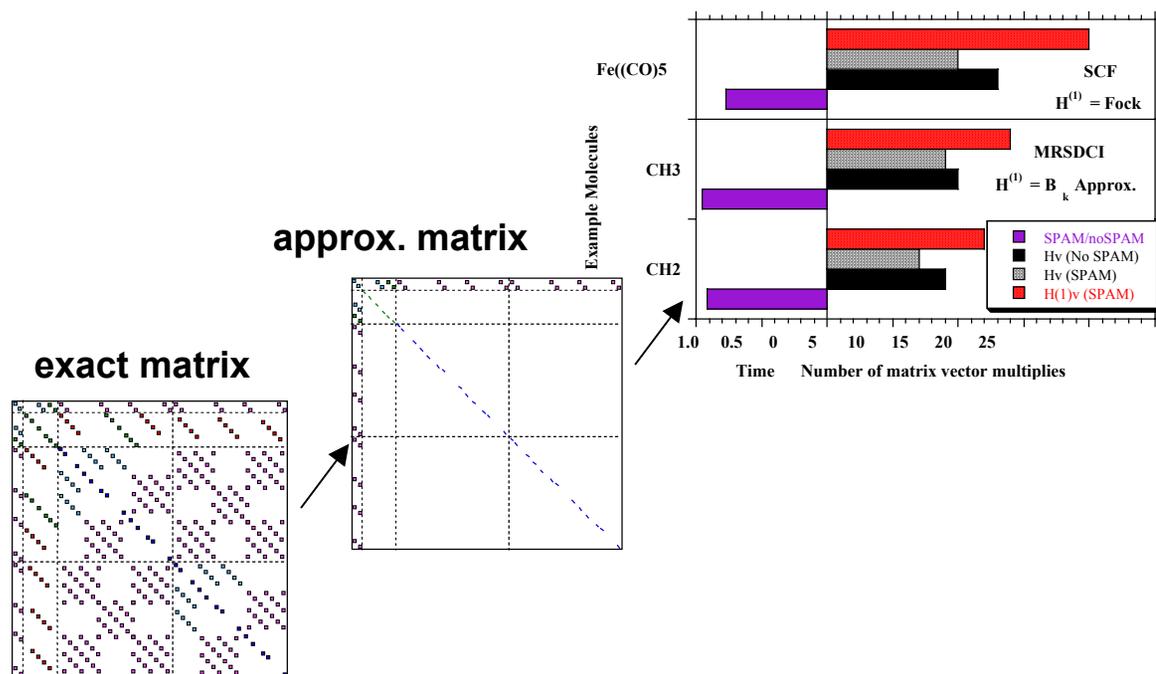
broad view:

- Any iterative problem solved in a subspace with a user-supplied cheap approximate matrix (TOPS connection)
- What is a cheap approximate matrix?
 - Sparser
 - Smaller underlying basis
 - Lower-order expansion of matrix elements
 - Coarser underlying grid
 - Lower-order difference equation
 - Tensor-product approximation
 - Operator approximation
 - More highly parallelized approximation
- Terascale Optimal PDE Simulations (TOPS) connection
 - Basic parallelized multi-level code with user-supplied approx. matrix
 - Template approximate matrices stored in library

Subspace Projected Approximate Matrix: SPAM Applications

Two Chemistry Applications:

- Cumulative Reaction Probability (other poster)
- Electronic structure:



Non Chemistry Tensor Product Model

- 4x4 tensor products + tridiagonal perturbation
- Approx matrix is 4x4 tensor

