

Large-scale electronic structure calculations

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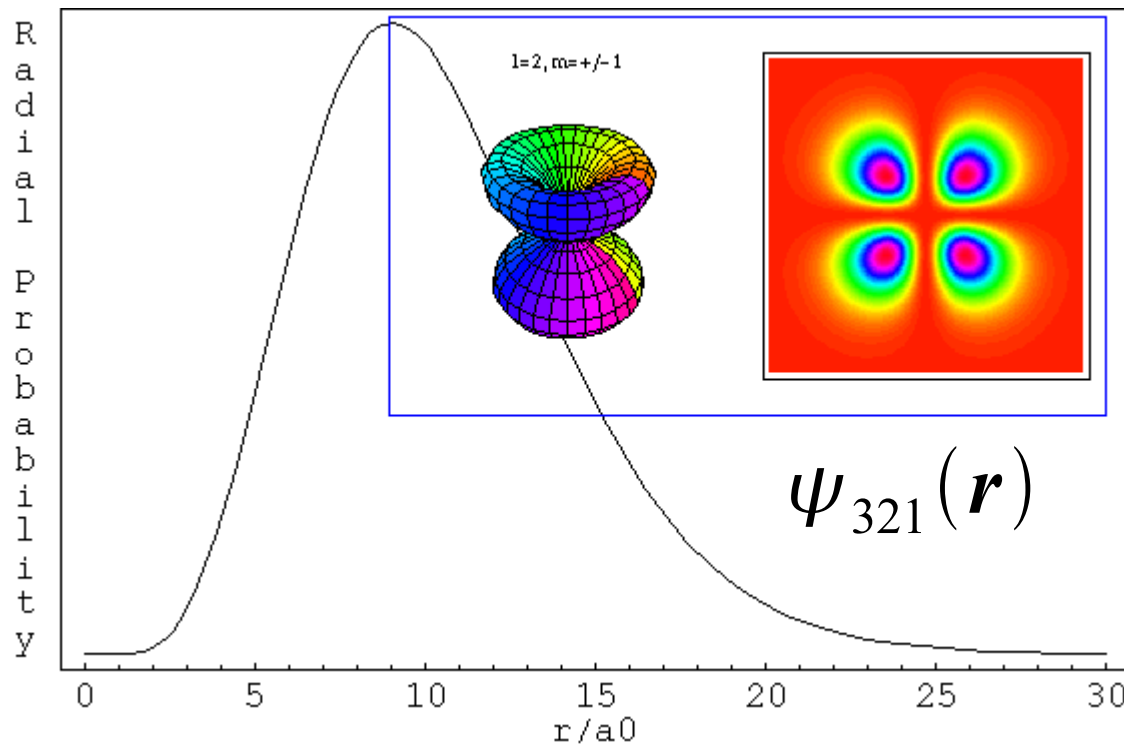
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Electronic Structure of Hydrogen



Problem

$$H \psi_{nlm}(\mathbf{r}) = E_n \psi_{nlm}(\mathbf{r})$$

$$H = -\nabla^2 + V(r)$$

Solution

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

$$E_n = \frac{-13.6}{n^2}$$

Density Functional Theory

The *other* DFT

Key idea

$$\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \rightarrow \rho(\mathbf{r})$$

$$E[\rho] = T[\rho] + V_{ext}[\rho] + V_{hxc}[\rho]$$

- Walter Kohn (Nobel Prize, 1998)

New Problem

Minimize

$$\frac{\partial E}{\partial \rho(\mathbf{r})}$$

$$\rightarrow H \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$$

$$H = -\nabla^2 + V_{ext}[\rho] + V_{hxc}[\rho]$$

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_n^{occ} \overline{\psi}_n(\mathbf{r}) \psi_n(\mathbf{r})$$

Boundary Conditions

Twisted boundary conditions: $\psi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{nk}(\mathbf{r})$
 (i.e., Bloch's theorem)

$$H_k[\rho] u_{nk}(\mathbf{r}) = \epsilon_{nk} u_{nk}(\mathbf{r})$$

$$H_k[\rho] = -\nabla^2 - 2i\mathbf{k}\cdot\nabla + k^2 + V_{ext}[\rho] + V_{hxc}[\rho]$$

$$u_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r} + \mathbf{R})$$

$$\mathbf{n}\cdot\nabla u_{nk}(\mathbf{r}) = \mathbf{n}\cdot\nabla u_{nk}(\mathbf{r} + \mathbf{R}) \quad \mathbf{r} \in \Omega$$

Computational Problem

Rayleigh-Ritz (Variational) Procedure

$$u_n(\mathbf{r}) = \sum_{i=1}^N x_{ni} \phi_i(\mathbf{r})$$



$$H_{ij} = \langle \phi_i | H | \phi_j \rangle$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

$$\mathbf{H} \mathbf{x}_n = \epsilon_n \mathbf{S} \mathbf{x}_n \quad (\rightarrow \mathbf{A} \mathbf{x} = \lambda \mathbf{B} \mathbf{x})$$

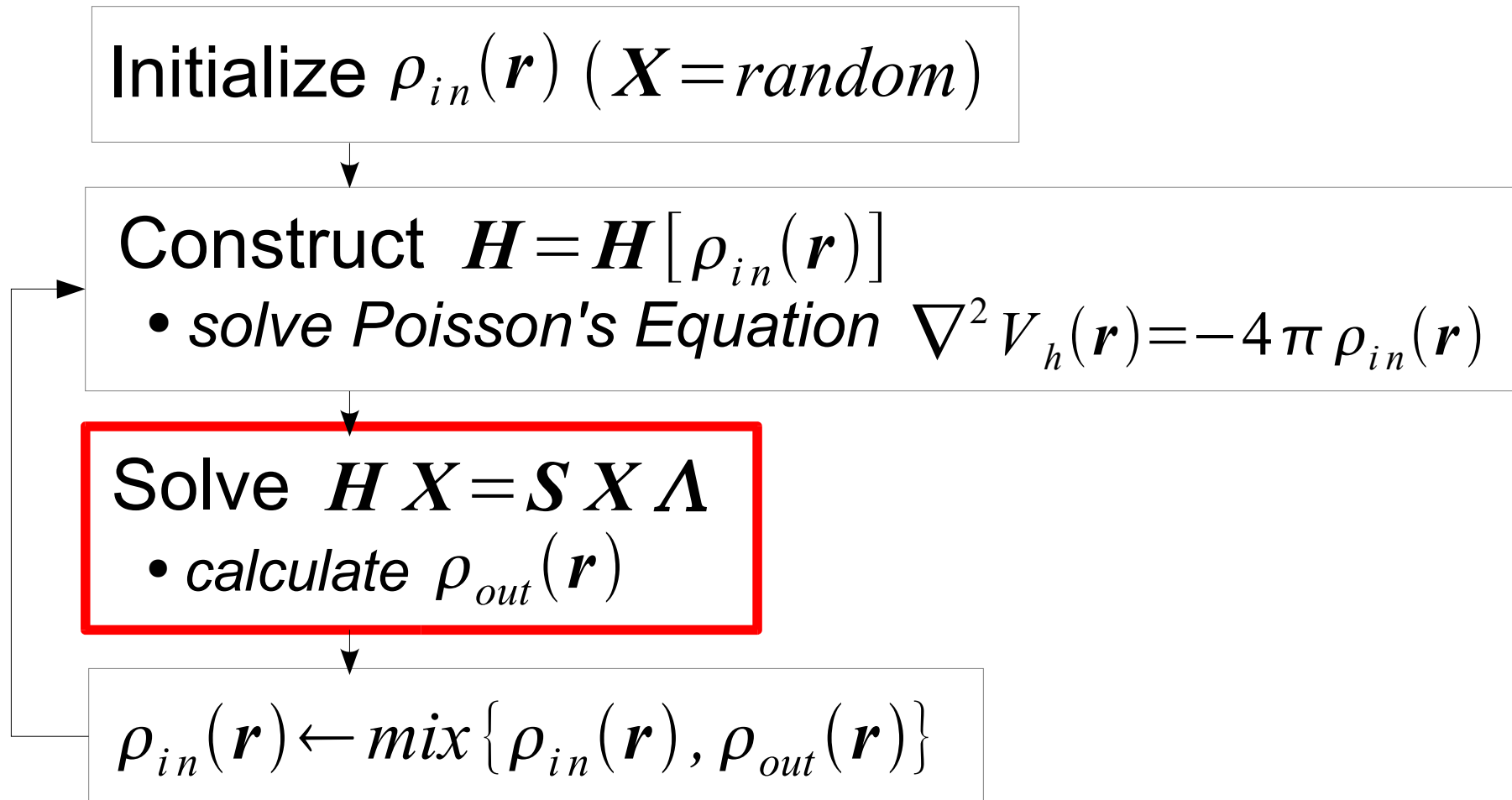
$$\mathbf{H} \in \mathbb{C}^{N \times N}$$

$$\mathbf{S} \in \mathbb{R}^{N \times N}$$

... remember $\mathbf{H} = \mathbf{H}[\rho(\mathbf{r})]$

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_n^{\text{occ}} \sum_{ij} \bar{x}_{ni} x_{nj} \bar{\phi}_i(\mathbf{r}) \phi_j(\mathbf{r})$$

Self-Consistent Procedure



Eigenvalue Problem: Review

$$A \mathbf{x} = \lambda B \mathbf{x}$$

$A \in \mathbb{C}^{N \times N}$ hermitian positive definite

$B \in \mathbb{R}^{N \times N}$ symmetric positive definite

- $N \sim 10^5 - 10^6$
- **Goal:** Find the $M \sim 10^3 - 10^4$ lowest eigenpairs
- Use initial guesses
- Matrix free method desired
 - matrix-vector operations are cheap

Locally-optimal Minimization

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \alpha_k \mathbf{p}_k$$

$$\mathbf{p}_k = \mathbf{r}(\mathbf{x}_k) + \beta_k \mathbf{p}_{k-1}$$

Standard Minimization

- β_k determined using Bradbury-Fletcher or Polak formulas
- α_k determines using line minimization

Locally-optimal Minimization

- Determine α_k, β_k using the Rayleigh-Ritz procedure on the subspace

$$[\mathbf{x}_k, \mathbf{r}(\mathbf{x}_k), \mathbf{p}_k]$$

Implementation Issues

- Block matrices $[X, H, P]$
- Deflation (soft-locking, hard-locking)
- Eigenvector buffer
- Index gymnastics to use initial guess

- **Robustness: does it work?**
- **Performance: preconditioning operator?**

Test Problem

- System: Lithium (local pseudopotential)
- Fixed matrix: non-SCF calculation
- $N \approx 20,000$ (nnz = 0.2%)
- $M = 1000$ (block size = 100)
- $\epsilon_{\text{TOL}} = 10^{-9}$
- Preconditioner: $K \approx A^{-1}$

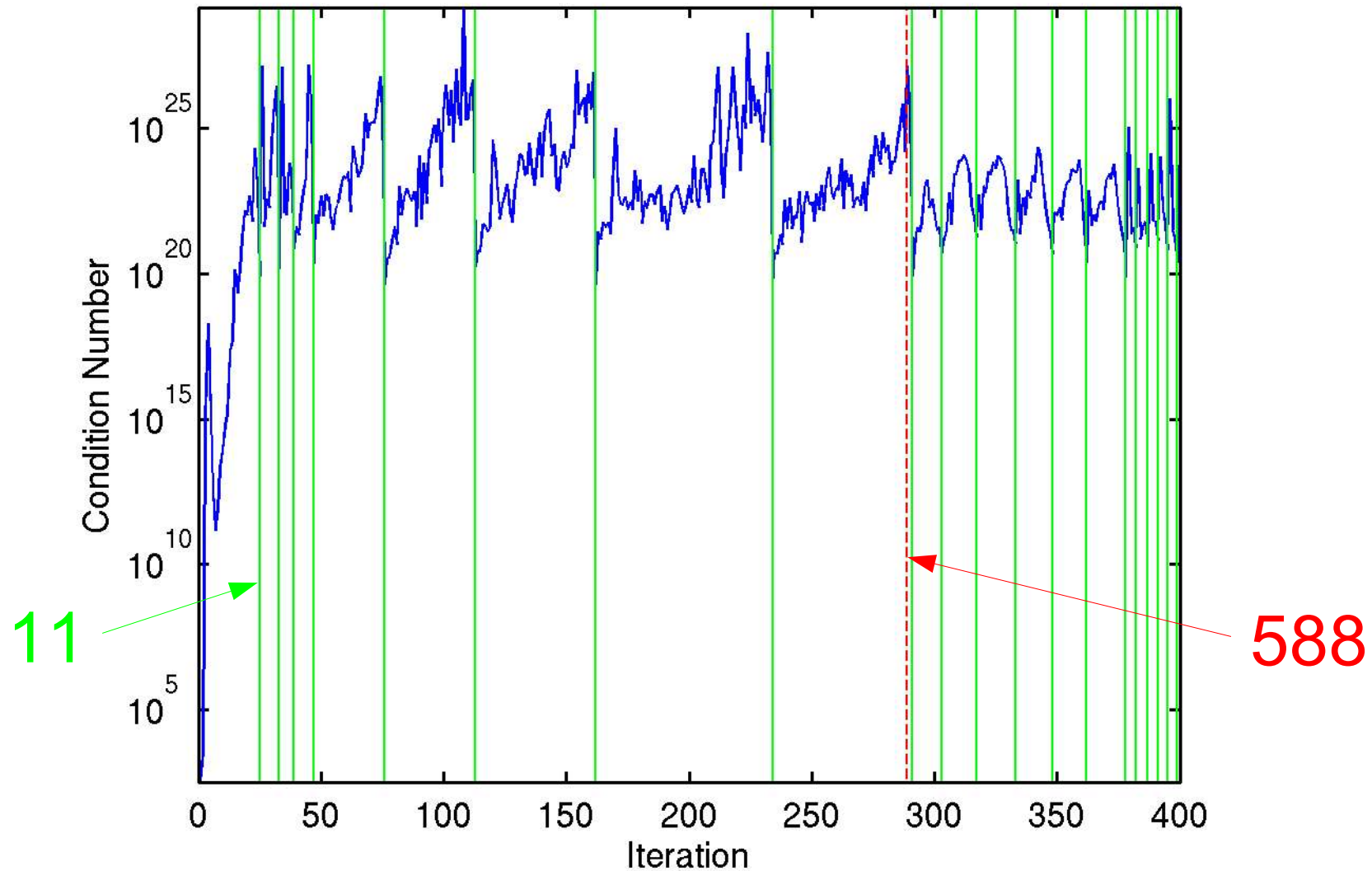
$$\epsilon = \frac{\|\mathbf{r}\|_2}{\|\mathbf{A}\mathbf{x}\|_2}$$

Linear dependence? $\bar{\mathbf{B}} = [\mathbf{X} \mathbf{H} \mathbf{P}]^\dagger \mathbf{B} [\mathbf{X} \mathbf{H} \mathbf{P}]$

- quantify using $\text{cond}(\bar{\mathbf{B}})$

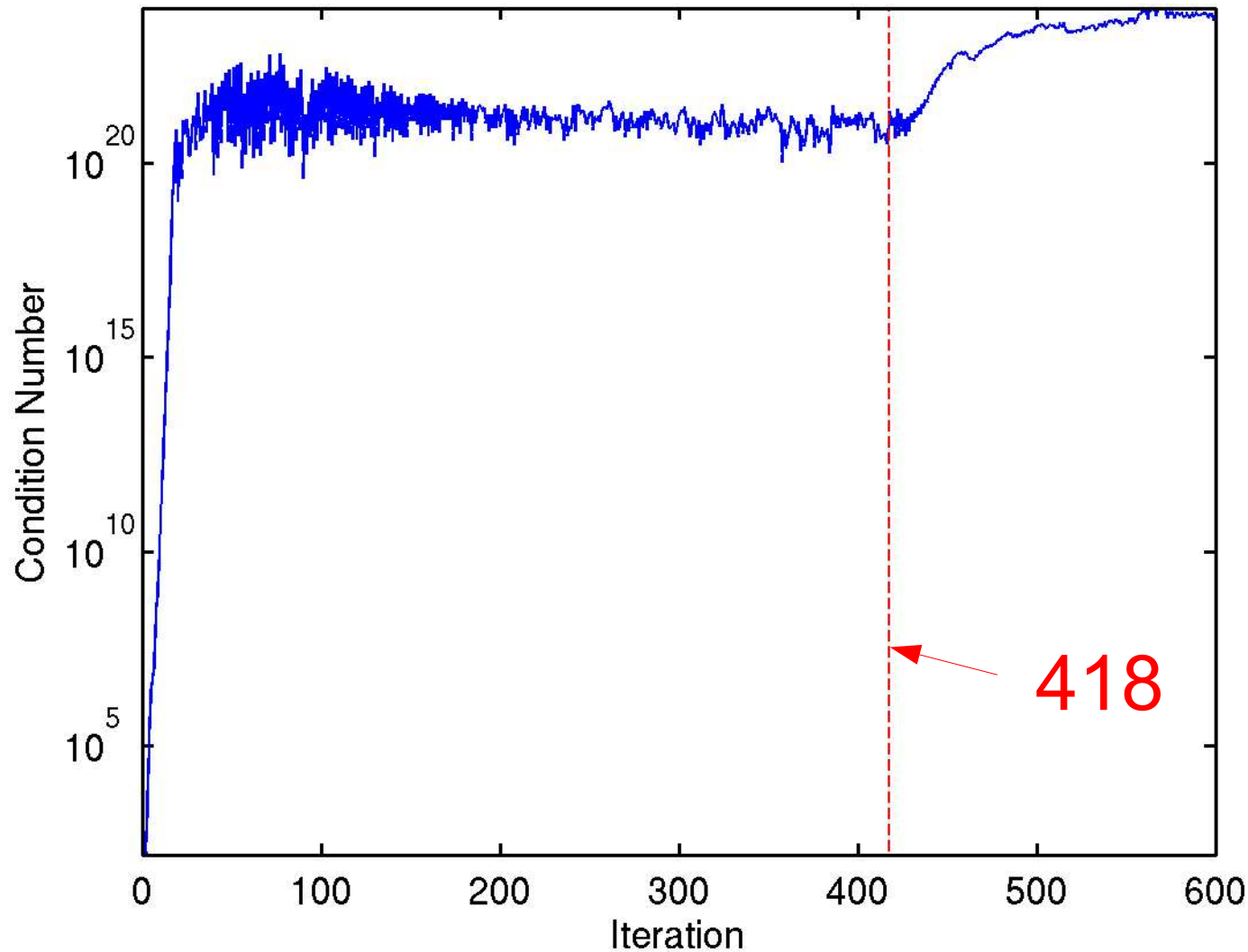
Robustness

Conjugate Gradient and Linear Dependence



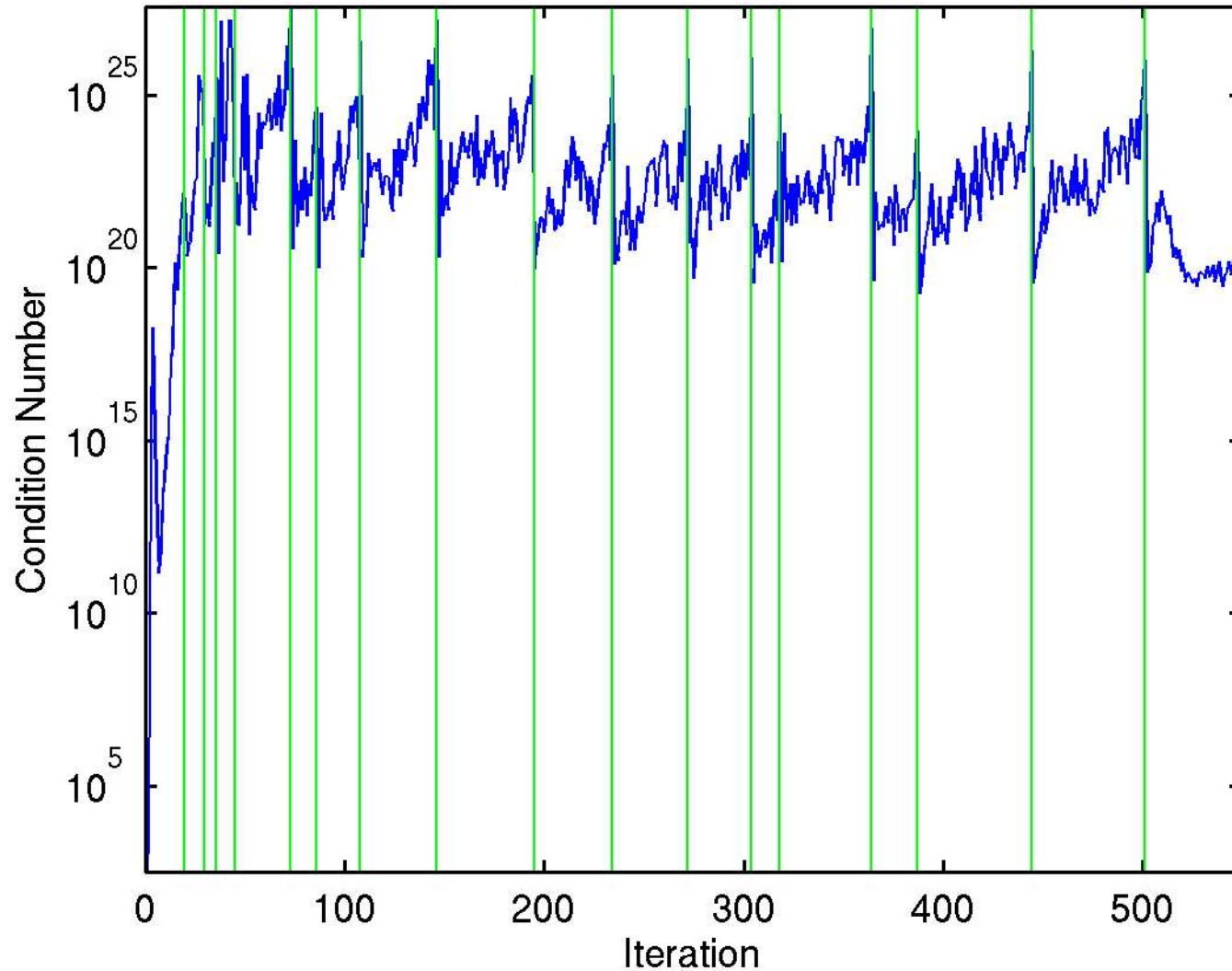
Robustness

Steepest descent, deflation, and 1000 eigenpairs



Robustness

Subspace diagonalization



Realistic Calculation

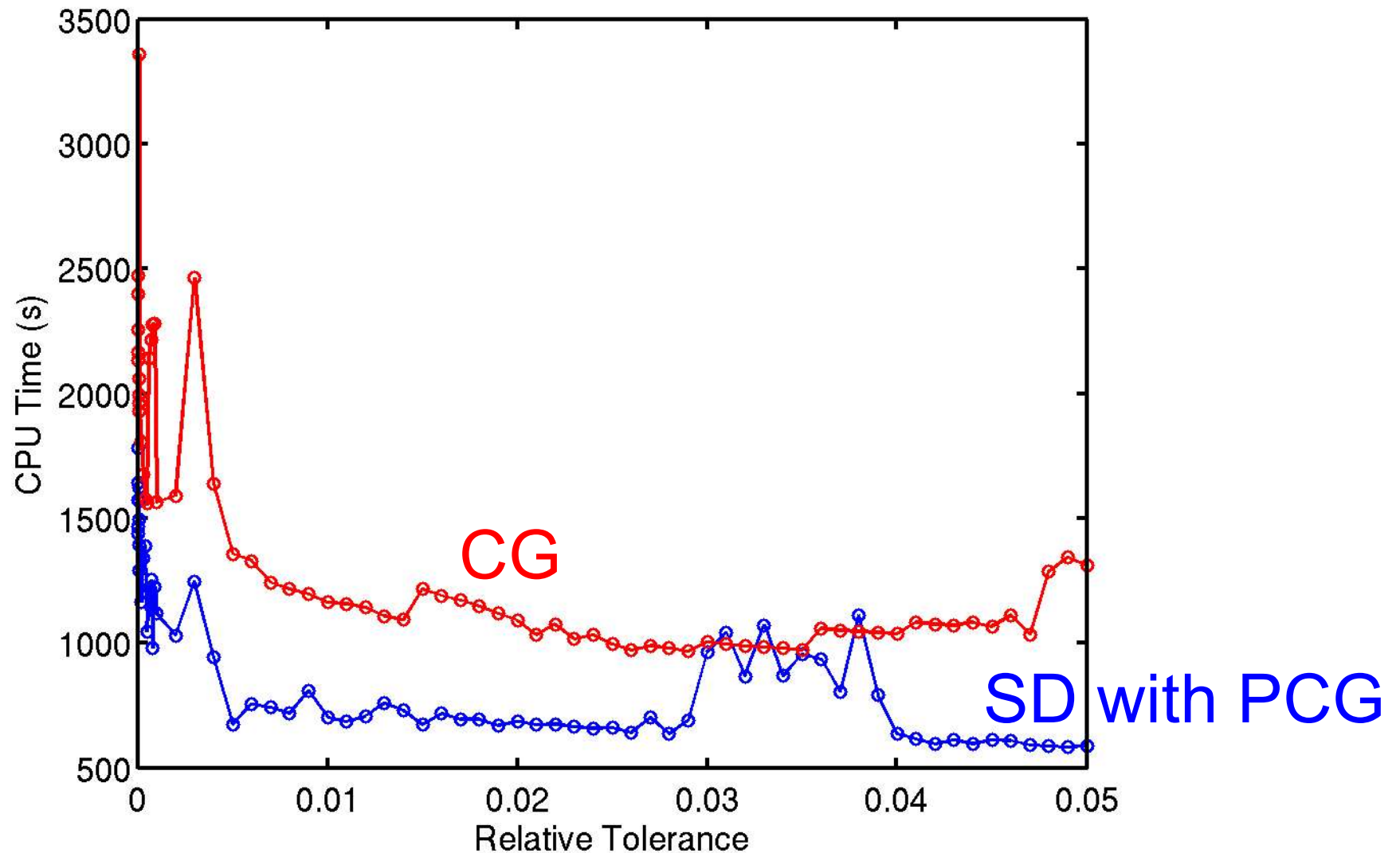
- System: Silicon (conventional cell)
- SCF calculation
- $N \approx 12,000$ (nnz = 0.3%)
- $M = 16$ (block size = 26)
- $\epsilon_{\text{TOL}} = 10^{-6}$
- Physically relevant finite-element mesh

$$\epsilon = \frac{|r|}{|Ax|}$$

Preconditioning Operators

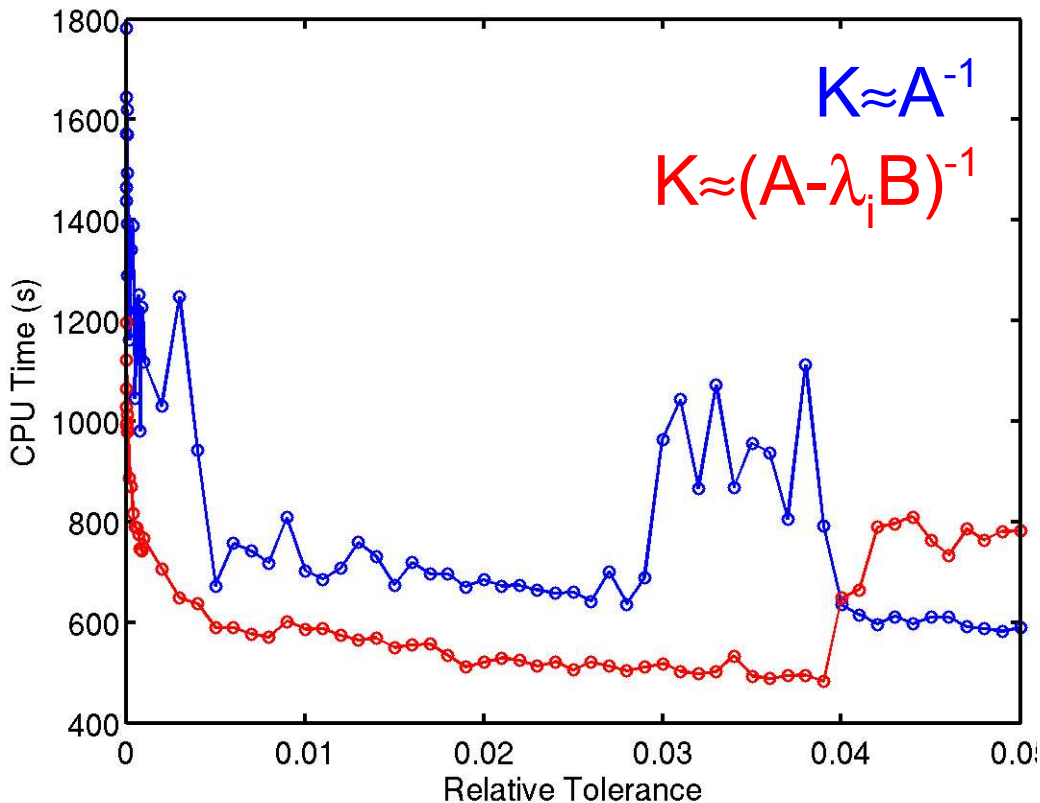
- $K \approx A^{-1}$
 - $K \approx (A - \lambda_i B)^{-1}$
- using *PCG linear solver* approximations

Steepest Descent: Preconditioning

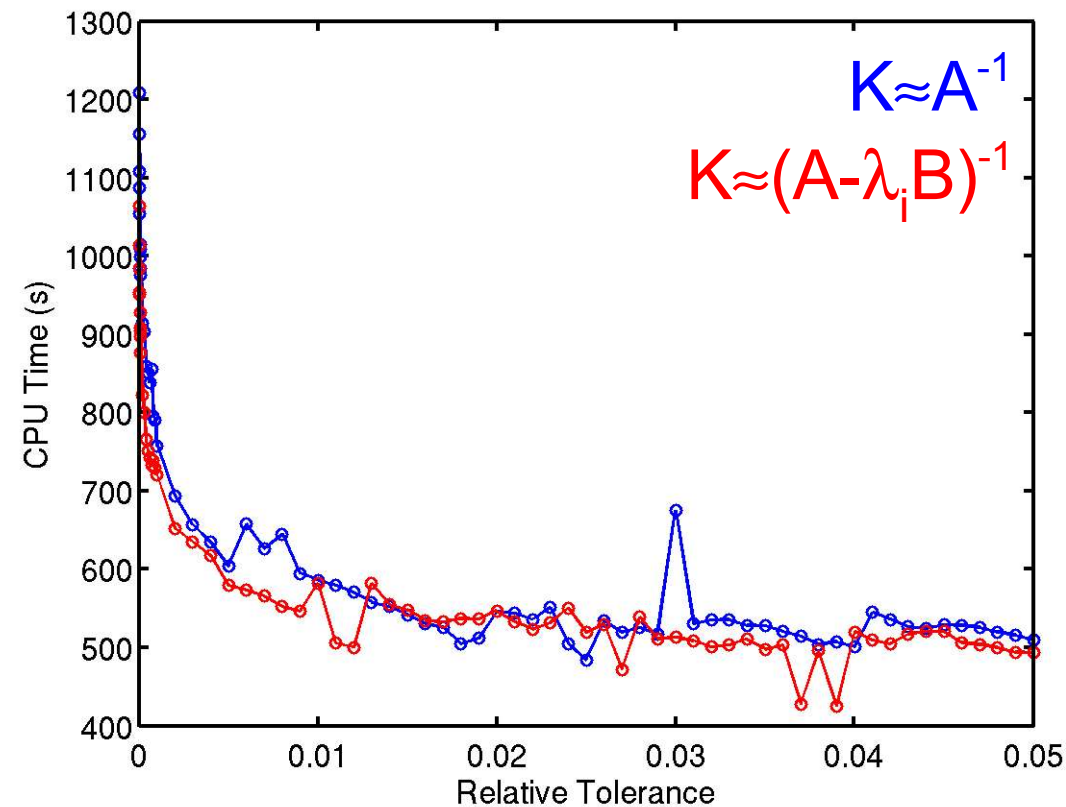


Targeted Preconditioning

Steepest Descent

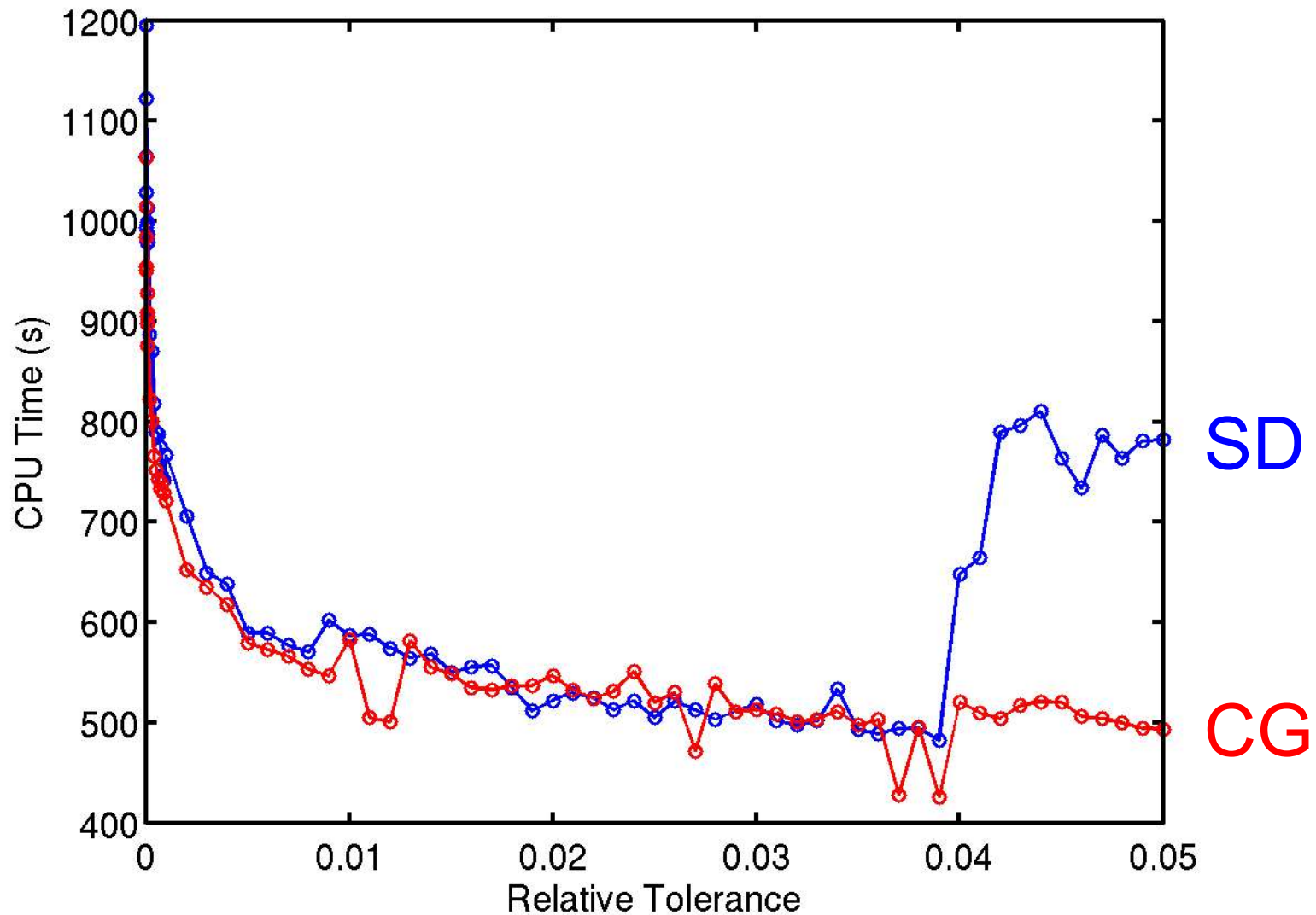


Conjugate Gradient



SD vs CG

Too close to call



Conclusion

- Locally-optimal methods show promise in electronic structure calculations
- “Targeted” preconditioning operator is preferred
- Steepest descent is (surprisingly) competitive

Future Work

- Better preconditioning (operators + implementation)
- Comparisons to other methods!

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