Linear-expansion Shooting Technique (LIST) for Accelerating SCF Convergence

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Outline

- SCF acceleration techiques
- Linear-expansion Shooting Technique (LIST)
- Performance
- Summary

Kohn-Sham DFT

$$\left(-\tfrac{1}{2}\boldsymbol{\nabla}^2 + v_{\mathrm{eff}}^{\mathrm{KS}}[\rho](\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$\left\{-\tfrac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}[\rho^{\mathrm{in}}](\mathbf{r}) + v_{\mathrm{xc}}[\rho^{\mathrm{in}}](\mathbf{r})\right\}\psi_i^{\mathrm{out}} = \varepsilon_i^{\mathrm{out}}\psi_i^{\mathrm{out}}$$

$$E^{\mathrm{HKS}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = \sum_i^{\mathrm{occ}} f_i^{\mathrm{out}}\varepsilon_i^{\mathrm{out}} + E_{\mathrm{H}}[\rho^{\mathrm{out}}] + E_{\mathrm{xc}}[\rho^{\mathrm{out}}] - \langle\rho^{\mathrm{out}}(\mathbf{r})\{v_{\mathrm{H}}[\rho^{\mathrm{in}}](\mathbf{r}) + v_{\mathrm{xc}}[\rho^{\mathrm{in}}](\mathbf{r})\}\rangle$$

$$E^{\mathrm{KS}}[\rho^{\mathrm{KS}}] = \sum_i^{\mathrm{occ}} f_i^{\mathrm{KS}}\varepsilon_i^{\mathrm{KS}} - E_{\mathrm{H}}[\rho^{\mathrm{KS}}] + E_{\mathrm{xc}}[\rho^{\mathrm{KS}}] - \langle\rho^{\mathrm{KS}}(\mathbf{r})v_{\mathrm{xc}}[\rho^{\mathrm{KS}}](\mathbf{r})\rangle$$

W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965)

Accelerating SCF Convergence
Direct Inversion in the Iterative Subspace (DIIS)

Construct a new vector from previous ones

$$\mathbf{p}_{m+1} = \sum_i^m c_i \mathbf{p}_i. \qquad \sum_i^m c_i = 1.$$

Accordingly, the corresponding error vector:

$$\mathbf{e}_{m+1} = \sum_i^m c_i \mathbf{e}_i.$$

Minimize the Lagrangian with constraint

$$L = ||e_{m+1}||^2 - \lambda \left(\sum_i c_i - 1 \right),$$

$$= \sum_{ij} c_j B_{ji} c_i - \lambda \left(\sum_i c_i - 1 \right), \text{ where } B_{ij} = \langle \mathbf{e}_j | \mathbf{e}_i \rangle.$$

P. Pulay, *Chem. Phys. Lett.* **73**, 393 (1980)

Matrix Equation of DIIS

$$\begin{bmatrix} 0 & -1 & -1 & \cdots & -1 \\ -1 & B_{11} & B_{12} & \cdots & B_{1m} \\ -1 & B_{21} & B_{22} & \cdots & B_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & B_{m1} & B_{m2} & \cdots & B_{mm} \end{bmatrix} \begin{bmatrix} \lambda \\ c_1 \\ c_2 \\ \vdots \\ c_m \end{bmatrix} = \begin{bmatrix} -1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix},$$

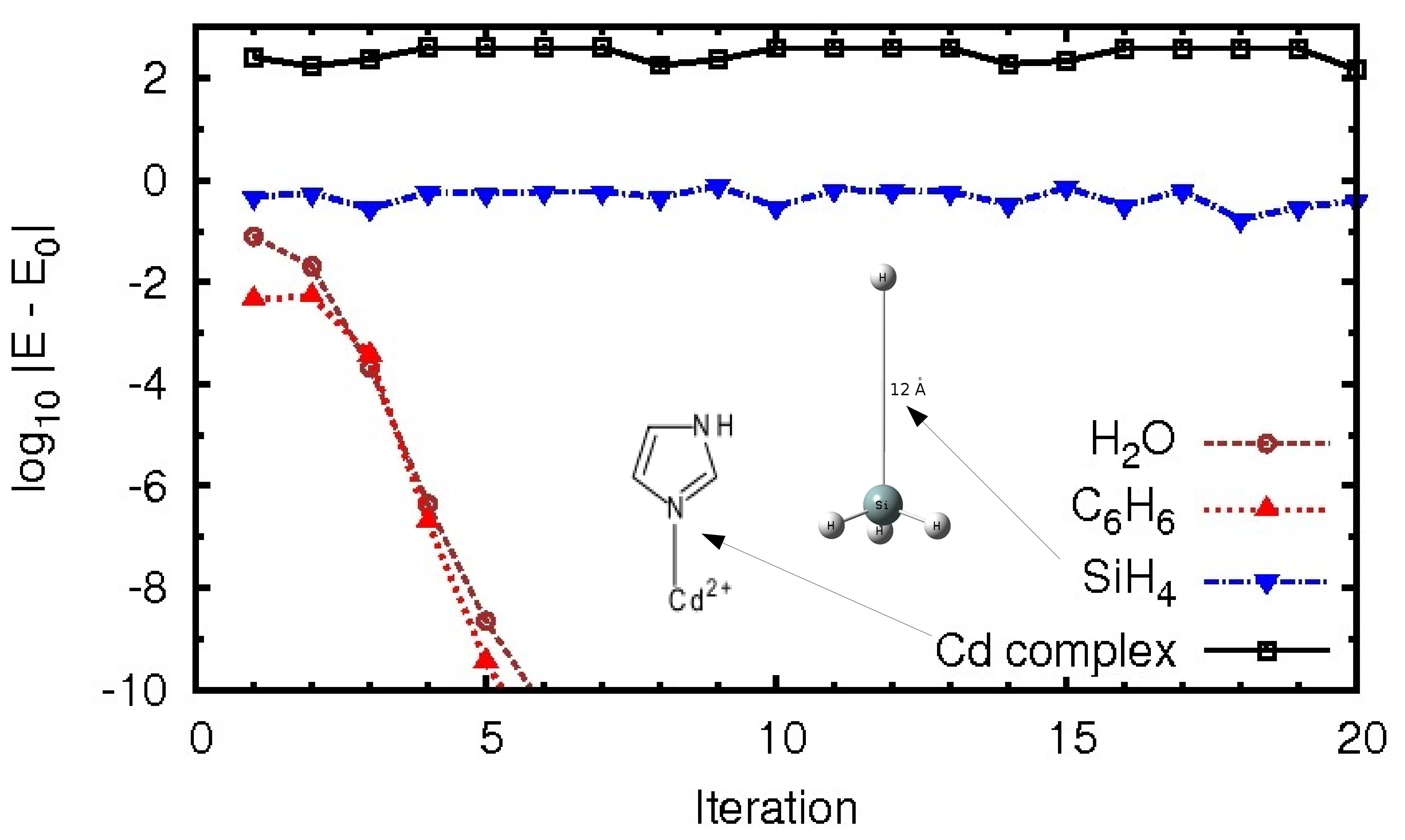
$$\text{where } B_{ij} = \langle e_i | e_j \rangle$$

$$f^{DIIS}(c_1, \ldots, c_n) = || \textstyle\sum_{i=1}^{n} c_i [F_i, D_i] ||^2$$

$$\min \left\{ f^{\text{DIIS}}, \sum_{i=1}^{n} c_i = 1 \right\}$$

P. Pulay, *J. Comput. Chem.* **3**, 556 (1982)

Performance of DIIS



Accelerating SCF: EDIIS
(energy-DIIS)

$$f^{\mathrm{EDIIS}}(c_1, \ldots, c_n) = \sum_{i=1}^{n} c_i E(\mathbf{D}_i) - \boxed{\sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j \langle \mathbf{D}_i - \mathbf{D}_j | \mathbf{F}_i - \mathbf{F}_j \rangle}$$

measure of error

$$\min \left\{ f^{\mathrm{EDIIS}}, \sum_{i=1}^{n} c_i = 1, \boxed{c_i \geq 0} \right\}$$

convex constraint

E. Cancès and C. Le Bris, *Int. J. Quant. Chem.* **79**, 82 (2000)

K. N. Kudin, G. E. Scuseria and E. Cancès, *J. Chem. Phys.* **116**, 8255 (2002)

Accelerating SCF: ADIIS

Augmented Roothaan-Hall energy function:

$$E(\mathbf{D}) \approx E(\mathbf{D}_n) + 2\langle \mathbf{D} - \mathbf{D}_n | \mathbf{F}(\mathbf{D}_n) \rangle + \langle \mathbf{D} - \mathbf{D}_n | \; [\mathbf{F}(\mathbf{D}) - \mathbf{F}(\mathbf{D}_n)] \rangle$$

$$f^{\mathrm{ADIIS}}(c_1, \ldots, c_n) = E(\mathbf{D}_n) + 2\sum_{i=1}^{n} c_i \langle \mathbf{D}_i - \mathbf{D}_n | \mathbf{F}(\mathbf{D}_n) \rangle + \sum_{i=1}^{n}\sum_{j=1}^{n} c_i c_j \langle \mathbf{D}_i - \mathbf{D}_n | [\mathbf{F}(\mathbf{D}_j) - \mathbf{F}(\mathbf{D}_n)] \rangle .$$

measure of error

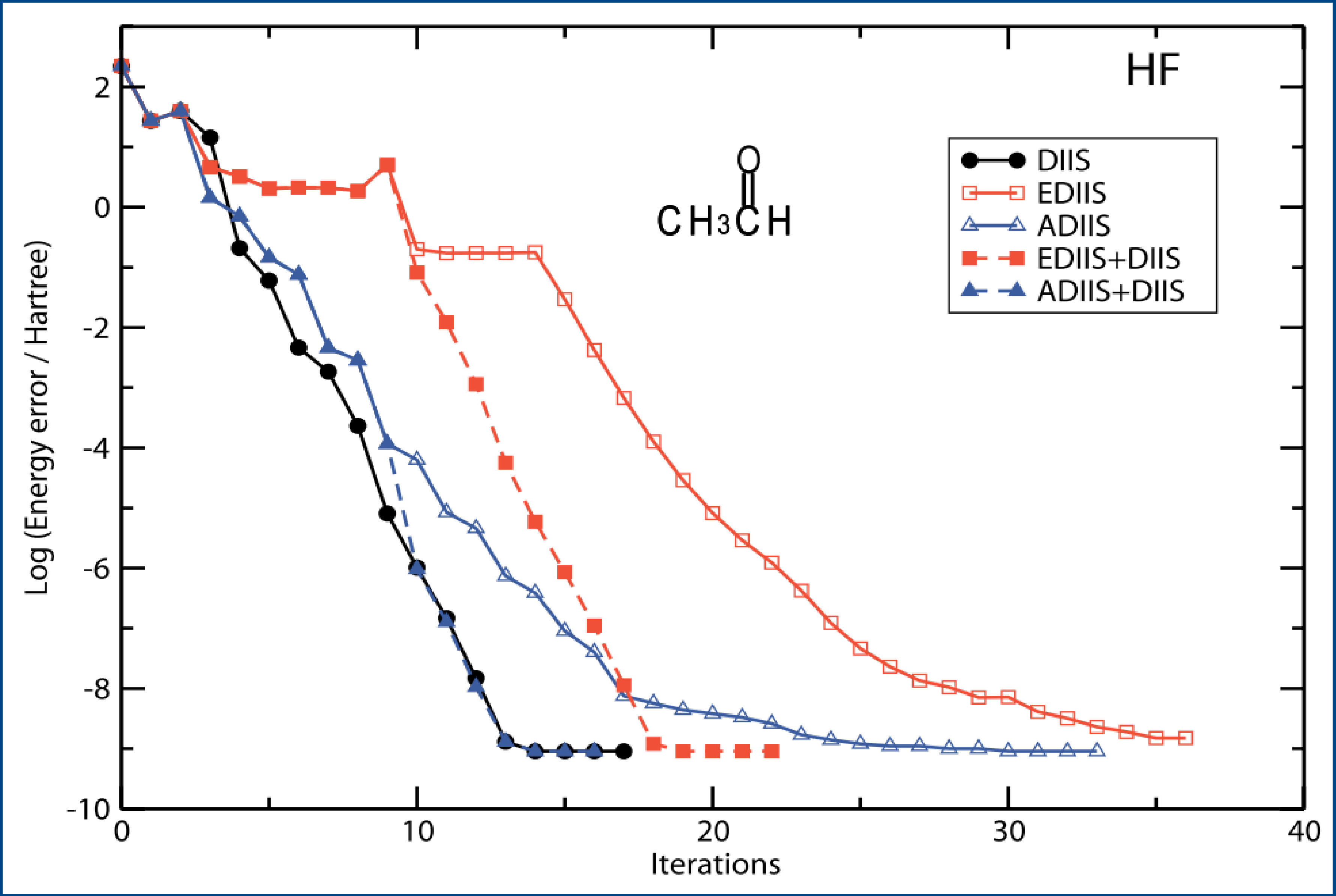
$$\min\left\{ f^{\mathrm{ADIIS}}, \sum_{i=1}^{n} c_i = 1, c_i \geq 0 \right\}$$

convex constraint

S. Høst *et al.*, *J. Chem. Phys.* **129**, 124106 (2008)

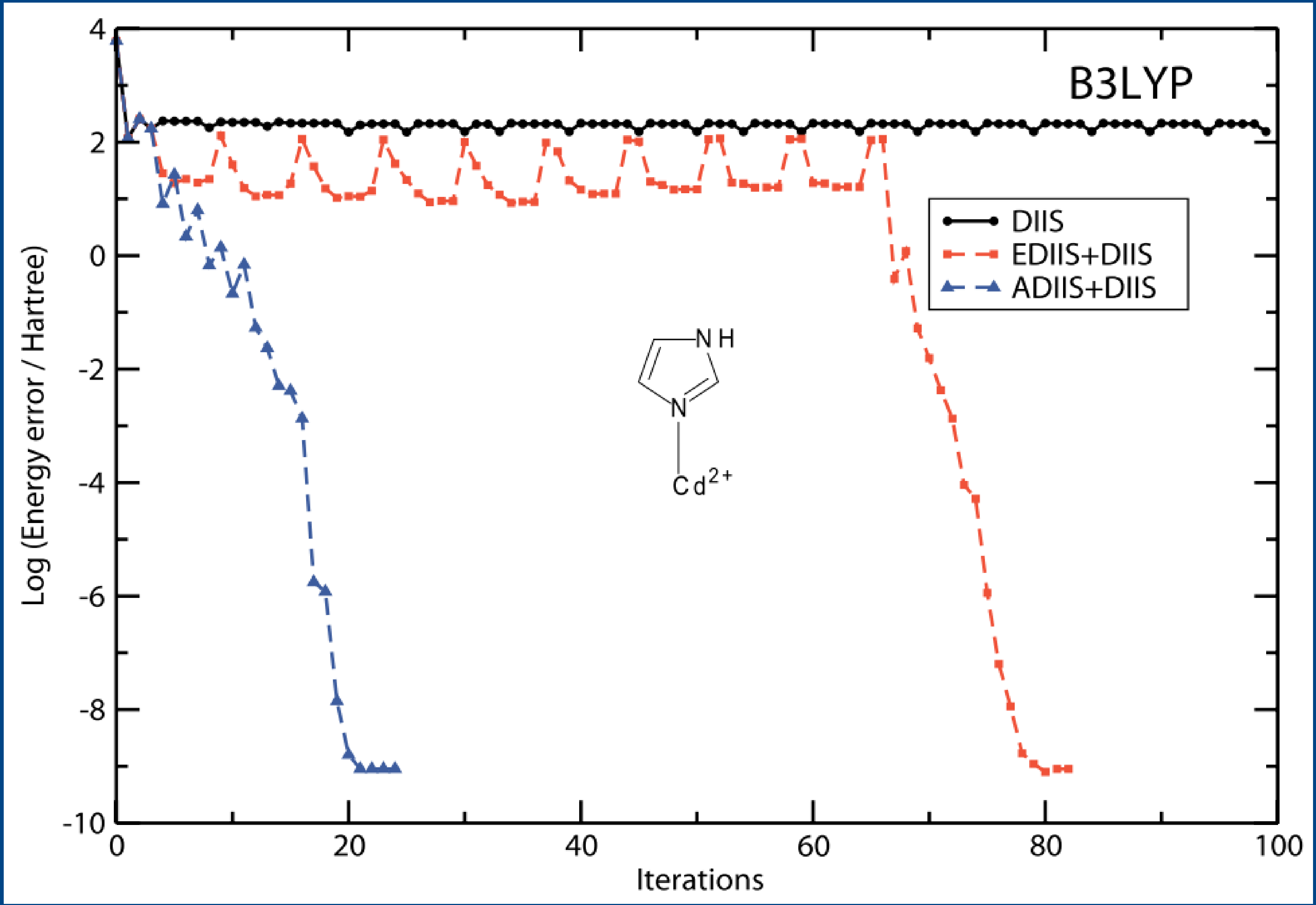
X. Hu and W. Yang, *J. Chem. Phys.* **132**, 054109 (2010)

DIIS/EDIIS/ADIIS Performance



X. Hu and W. Yang, *J. Chem. Phys.* **132**, 054109 (2010)

DIIS/EDIIS/ADIIS Performance



X. Hu and W. Yang, *J. Chem. Phys.* **132**, 054109 (2010)

Accelerating Energy Convergence by Perturbative Expansion without Altering SCF Path

B. Zhou and Y. A. Wang, *J. Chem. Phys.* **124**, 081107 (2006)

B. Zhou and Y. A. Wang, *Int. J. Quantum Chem.* **107**, 2995 (2007)

B. Zhou and Y. A. Wang, *J. Chem. Phys.* **127**, 064101 (2007)

B. Zhou and Y. A. Wang, *J. Chem. Phys.* **128**, 084101 (2008)

Y. A. Zhang and Y. A. Wang, *J. Chem. Phys.* **130**, 144116 (2009)

Energy Evaluation for Any Interation

$$E^{\mathrm{HKS}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = \sum_{i}^{\mathrm{occ}} f_i^{\mathrm{out}}\varepsilon_i^{\mathrm{out}} + E_{\mathrm{H}}[\rho^{\mathrm{out}}] + E_{\mathrm{xc}}[\rho^{\mathrm{out}}] - \langle \rho^{\mathrm{out}}(\mathbf{r})\{v_{\mathrm{H}}[\rho^{\mathrm{in}}](\mathbf{r}) + v_{\mathrm{xc}}[\rho^{\mathrm{in}}](\mathbf{r})\}\rangle$$

$$E^{\mathrm{Harris}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = \sum_{i}^{\mathrm{occ}} f_i^{\mathrm{out}}\varepsilon_i^{\mathrm{out}} - E_{\mathrm{H}}[\rho^{\mathrm{in}}] + E_{\mathrm{xc}}[\rho^{\mathrm{in}}] - \langle \rho^{\mathrm{in}}(\mathbf{r}) v_{\mathrm{xc}}[\rho^{\mathrm{in}}](\mathbf{r})\rangle$$

J. Harris, *Phys. Rev. B* **31**, 1770 (1985)

Energy Perturbative Expansions (exact to 2nd order)

Exact to 2nd order:

$$E^{\mathrm{HKS}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = E^{\mathrm{KS}}[\rho^{\mathrm{KS}}] + \langle\{\rho^{\mathrm{out}}(\mathbf{r}_1)-\rho^{\mathrm{in}}(\mathbf{r}_1)\}C(\mathbf{r}_1,\mathbf{r}_2)\{\rho^{\mathrm{out}}(\mathbf{r}_2)-\rho^{\mathrm{KS}}(\mathbf{r}_2)\}\rangle$$

$$E^{\mathrm{Harris}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = E^{\mathrm{KS}}[\rho^{\mathrm{KS}}] + \langle\{\rho^{\mathrm{out}}(\mathbf{r}_1)-\rho^{\mathrm{in}}(\mathbf{r}_1)\}C(\mathbf{r}_1,\mathbf{r}_2)\{\rho^{\mathrm{in}}(\mathbf{r}_2)-\rho^{\mathrm{KS}}(\mathbf{r}_2)\}\rangle$$

$$C(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + \left.\frac{\delta v_{\mathrm{xc}}[\rho(\mathbf{r}_1)]}{\delta\rho(\mathbf{r}_2)}\right|_{\rho^{\mathrm{in}}} \right)$$

linear response kernel, hard to evaluate, difficult to implement

M. W. Finnis, *J. Phys: Condens. Matter* **2**, 331 (1990)

B. Zhou and Y. A. Wang, *J. Chem. Phys.* **128**, 084101 (2008)

Corrected Energy Functionals
(exact to 2nd order)

$$E^{\mathrm{cHKS}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = E^{\mathrm{HKS}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] + \langle\{\rho^{\mathrm{out}}(\mathbf{r}_1)-\rho^{\mathrm{in}}(\mathbf{r}_1)\}C(\mathbf{r}_1,\mathbf{r}_2)\{\rho^{b}(\mathbf{r}_2)-\rho^{\mathrm{out}}(\mathbf{r}_2)\}\rangle,$$

$$E^{\mathrm{cHarris}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = E^{\mathrm{Harris}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] + \langle\{\rho^{\mathrm{out}}(\mathbf{r}_1)-\rho^{\mathrm{in}}(\mathbf{r}_1)\}C(\mathbf{r}_1,\mathbf{r}_2)\{\rho^{b}(\mathbf{r}_2)-\rho^{\mathrm{in}}(\mathbf{r}_2)\}\rangle$$

Finite difference approximation:

$$\left\langle \{\rho^{\mathrm{out}}(\mathbf{r}_1)-\rho^{\mathrm{in}}(\mathbf{r}_1)\}\left(\left.\frac{\delta v_{\mathrm{xc}}[\rho(\mathbf{r}_2)]}{\delta\rho(\mathbf{r}_1)}\right|_{\rho^{\mathrm{in}}}\right)\right\rangle_{\mathbf{r}_1} \approx v_{\mathrm{xc}}[\rho^{\mathrm{out}}(\mathbf{r}_2)] - v_{\mathrm{xc}}[\rho^{\mathrm{in}}(\mathbf{r}_2)]$$

$$E^{\mathrm{cHKS}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = E^{\mathrm{HKS}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] + \tfrac{1}{2}\langle(\rho^{b}-\rho^{\mathrm{out}})(v_{\mathrm{eff}}^{\mathrm{out}}-v_{\mathrm{eff}}^{\mathrm{in}})\rangle_{\mathbf{r}_1,\mathbf{r}_2}$$

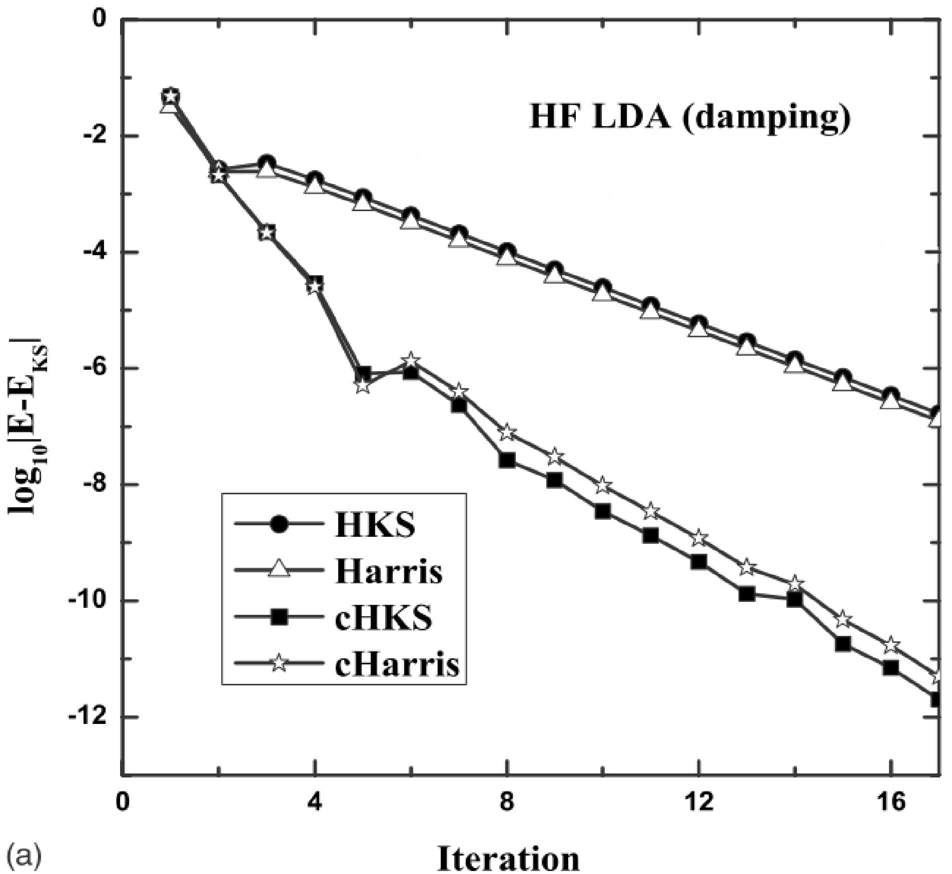
$$E^{\mathrm{cHarris}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] = E^{\mathrm{Harris}}[\rho^{\mathrm{in}},\rho^{\mathrm{out}}] + \tfrac{1}{2}\langle(\rho^{b}-\rho^{\mathrm{in}})(v_{\mathrm{eff}}^{\mathrm{out}}-v_{\mathrm{eff}}^{\mathrm{in}})\rangle_{\mathbf{r}_1,\mathbf{r}_2}$$

B. Zhou and Y. A. Wang, *J. Chem. Phys.* **127**, 064101 (2007)

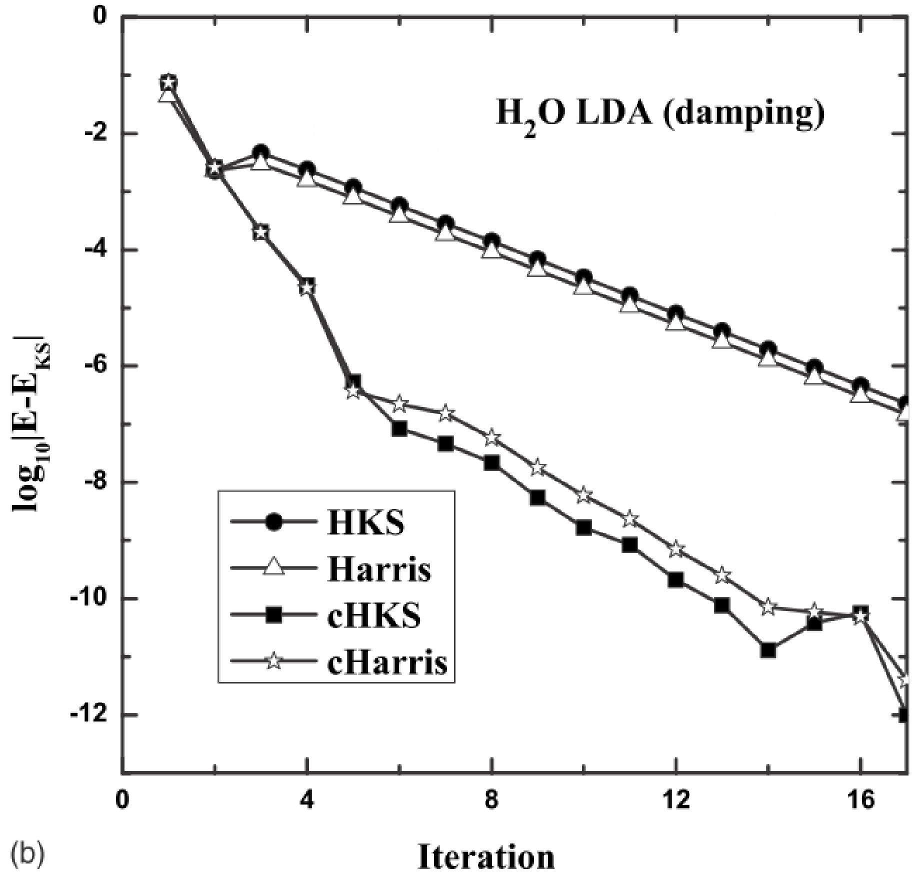
B. Zhou and Y. A. Wang, *J. Chem. Phys.* **128**, 084101 (2008)

Y. A. Zhang and Y. A. Wang, *J. Chem. Phys.* **130**, 144116 (2009)

Performance of Energy Functionals



(a)



(b)

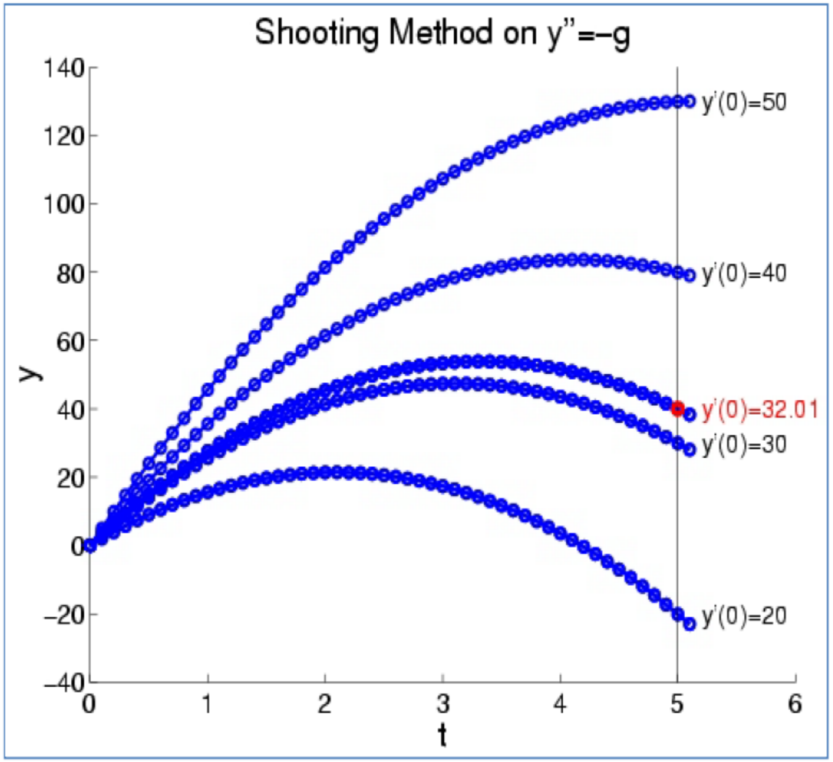
variational path unaltered!

Y. A. Zhang and Y. A. Wang, *J. Chem. Phys.* **130**, 144116 (2009)

Accelerating SCF Convergence via Linear-expansion Shooting Technique (LIST)

for both energy and wave function (density and/or density matrix)

Shooting Method



Wisdom from any "Shooting" act:

- Pick the target, aim, and shoot!
- Estimate the error, adjust the aim, shoot again!
- Reassess the result, shoot till hitting the goal.

The shooting method is a method in numerical analysis for solving a boundary value problem by reducing it to the solution of an initial value problem.

A boundary value problem is a differential equation together with a set of additional restraints (boundary conditions).

Using iterative process to achieve self-consistent field (SCF) in solving the Schrödinger equation *is* a shooting method. Hereafter, the spirit of shooting will be strictly observed as religiously as possible.

An initial value problem is a differential equation together with specified value (the initial condition) of the unknown function at a given point in the domain of the solution.

Essence of LIST

$$E_{KS} = E_{HKS}^{(i)} + \langle (\rho_{KS} - \rho_{out}^{(i)})\, \Delta v_i \rangle + O(\Delta^3)$$

$$E_{cHKS}^{(i)} = E_{HKS}^{(i)} + \langle (\rho_b - \rho_{out}^{(i)})\, \Delta v_i \rangle$$

Finite difference: $\Delta v_i = \frac{1}{2}(v_{out}^{(i)} - v_{in}^{(i)})$

Linear expansion: $\rho_b = \sum_i c_i \rho_i$

B. Zhou and Y. A. Wang, *J. Chem. Phys.* **128**, 084101 (2008)

Direct LIST: LISTd

Shooting at the same energy:

$$E_{cHKS}^{(k)} = E_{HKS}^{(k)} + \langle(\rho_b - \rho_{out}^{(k)})\,\Delta v_k\rangle = E$$

$$E_{cHKS}^{(i)} = E_{cHKS}^{(j)} = E$$

Linear expansion of ρ_b with the constraint:

$$\rho_b = \sum_i c_i \rho_i,\ \sum_i c_i = 1$$

Then, the LIST equation:

$$\sum c_i (E_{HKS}^{(k)} + \langle(\rho_i - \rho_{out}^{(k)}|\Delta v_k\rangle - E) = 0$$

Matrix Equation of LISTd

$$\begin{bmatrix} 0 & -1 & -1 & \cdots & -1 \\ -1 & A_{11} & A_{12} & \cdots & A_{1m} \\ -1 & A_{21} & A_{22} & \cdots & A_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & A_{m1} & A_{m2} & \cdots & A_{mm} \end{bmatrix} \begin{bmatrix} E \\ c_1 \\ c_2 \\ \vdots \\ c_m \end{bmatrix} = \begin{bmatrix} -1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix},$$

where $A_{ij} = E_{HKS}^{(i)} + \langle \rho_j \Delta v_i \rangle - \langle \rho_{out}^{(i)} \Delta v_i \rangle$, and $\Delta v_i = \frac{1}{2}(v_{out}^{(i)} - v_{in}^{(i)})$.

Simplest LIST: LISTs

$$i\text{th iteration: } E_{cHKS}^{(i)} = E_{HKS}^{(i)} + \langle (\rho_b - \rho_{out}^{(i)})\, \Delta v_i \rangle$$

$$j\text{th iteration: } E_{cHKS}^{(j)} = E_{HKS}^{(j)} + \langle (\rho_b - \rho_{out}^{(j)})\, \Delta v_j \rangle$$

$$k\text{th iteration: } \rho_b = \rho^{(k)} = \rho_\lambda^{(k)} = (1-\lambda_k)\rho_{out}^{(k)} + \lambda_k \rho_{in}^{(k)}$$

⇓

$$\lambda_k = \frac{(E^i - E^j) + \langle \rho_{out}^{(k)} \{\Delta v_i - \Delta v_j\}\rangle - (\langle \rho_{out}^{(i)} \Delta v_i \rangle - \langle \rho_{out}^{(j)} \Delta v_j \rangle)}{\langle \{\rho_{out}^{(k)} - \rho_{in}^{(k)}\}\{\Delta v_j - \Delta v_i\}\rangle}$$

$$\{i, j, k\} = \{k-1, k, k\}$$

the latest interation as the simplest choice

Indirect LIST: LISTi

Input-ρ expansion: $\rho_b^{in} = \sum_i \tilde{c}_i \rho_{in}^{(i)} \Rightarrow E[\rho_b^{in}]$

Output-ρ expansion: $\rho_b^{out} = \sum_i c_i \rho_{out}^{(i)} \Rightarrow E[\rho_b^{out}]$

Near convergence

$$\rho_{in}^{(i)} \approx \rho_{out}^{(i)}$$

$$c_i \doteq \tilde{c}_i$$

$$E[\rho_b^{in}] \doteq E[\rho_b^{out}]$$

Then, impose

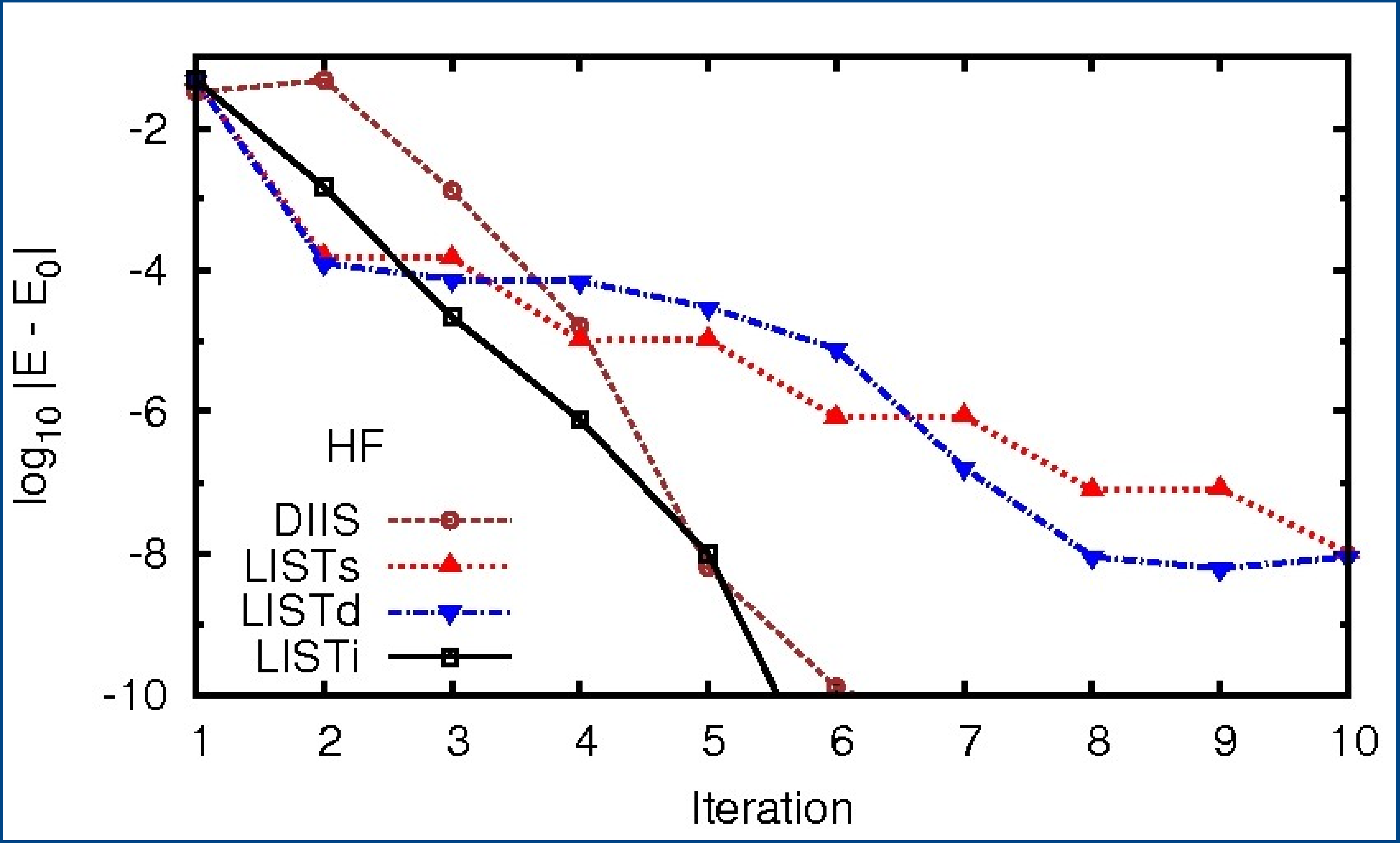
$$\left.\begin{aligned} c_i &= \tilde{c}_i \\ E[\rho_b^{in}] &= E[\rho_b^{out}] \end{aligned}\right\} \Rightarrow \sum_i c_i \langle \Delta\rho_i \Delta v_j \rangle = 0$$

Matrix Equation of LISTi

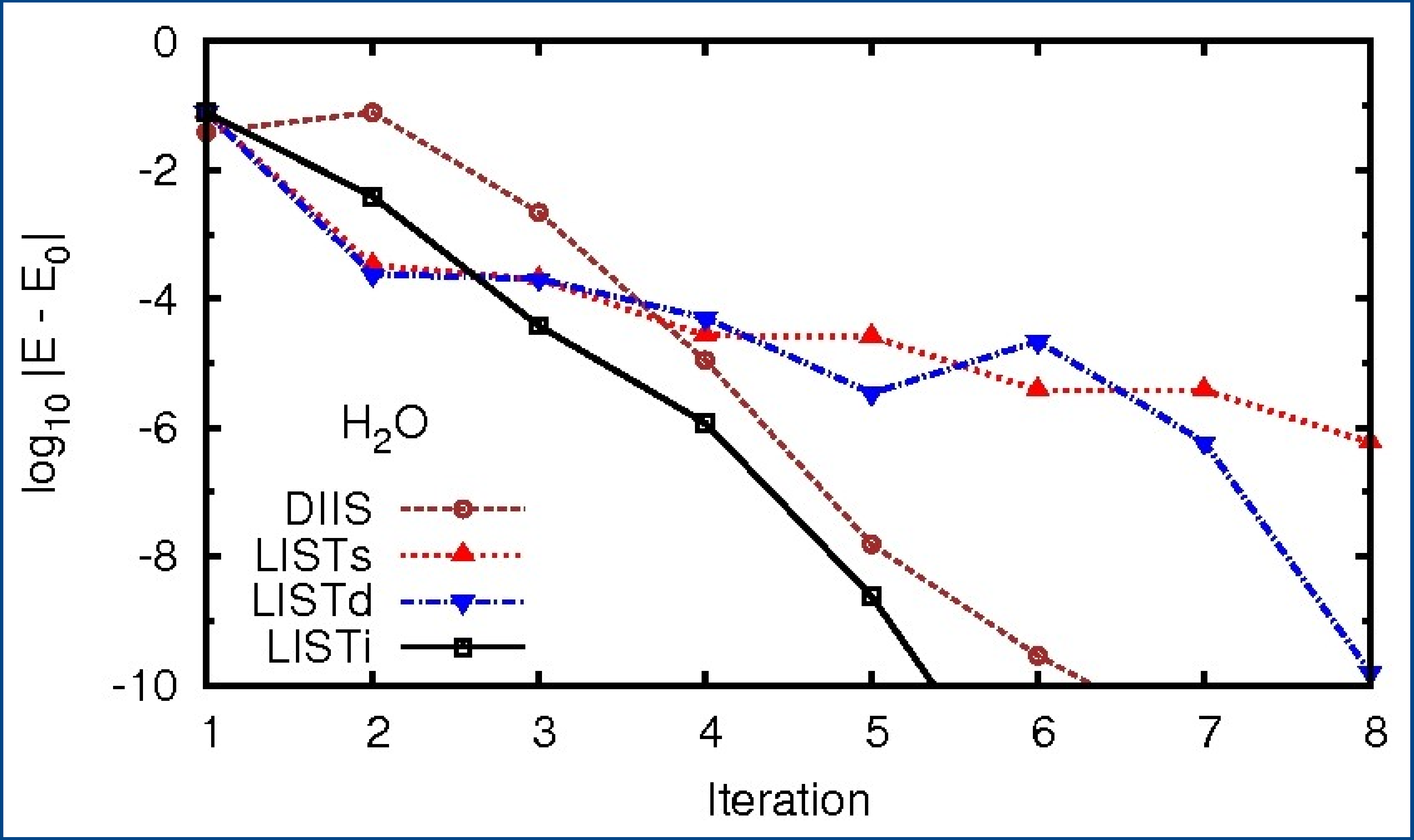
$$\begin{bmatrix} 0 & -1 & -1 & \cdots & -1 \\ -1 & D_{11} & D_{12} & \cdots & D_{1m} \\ -1 & D_{21} & D_{22} & \cdots & D_{2m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & D_{m1} & D_{m2} & \cdots & D_{mm} \end{bmatrix} \begin{bmatrix} \Lambda \\ c_1 \\ c_2 \\ \vdots \\ c_m \end{bmatrix} = \begin{bmatrix} -1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix},$$

where $D_{ij} = \langle (\rho_{out}^{(i)} - \rho_{in}^{(i)})\, \Delta v_j \rangle$, and $\Delta v_j = \frac{1}{2}(v_{out}^{(j)} - v_{in}^{(j)})$.

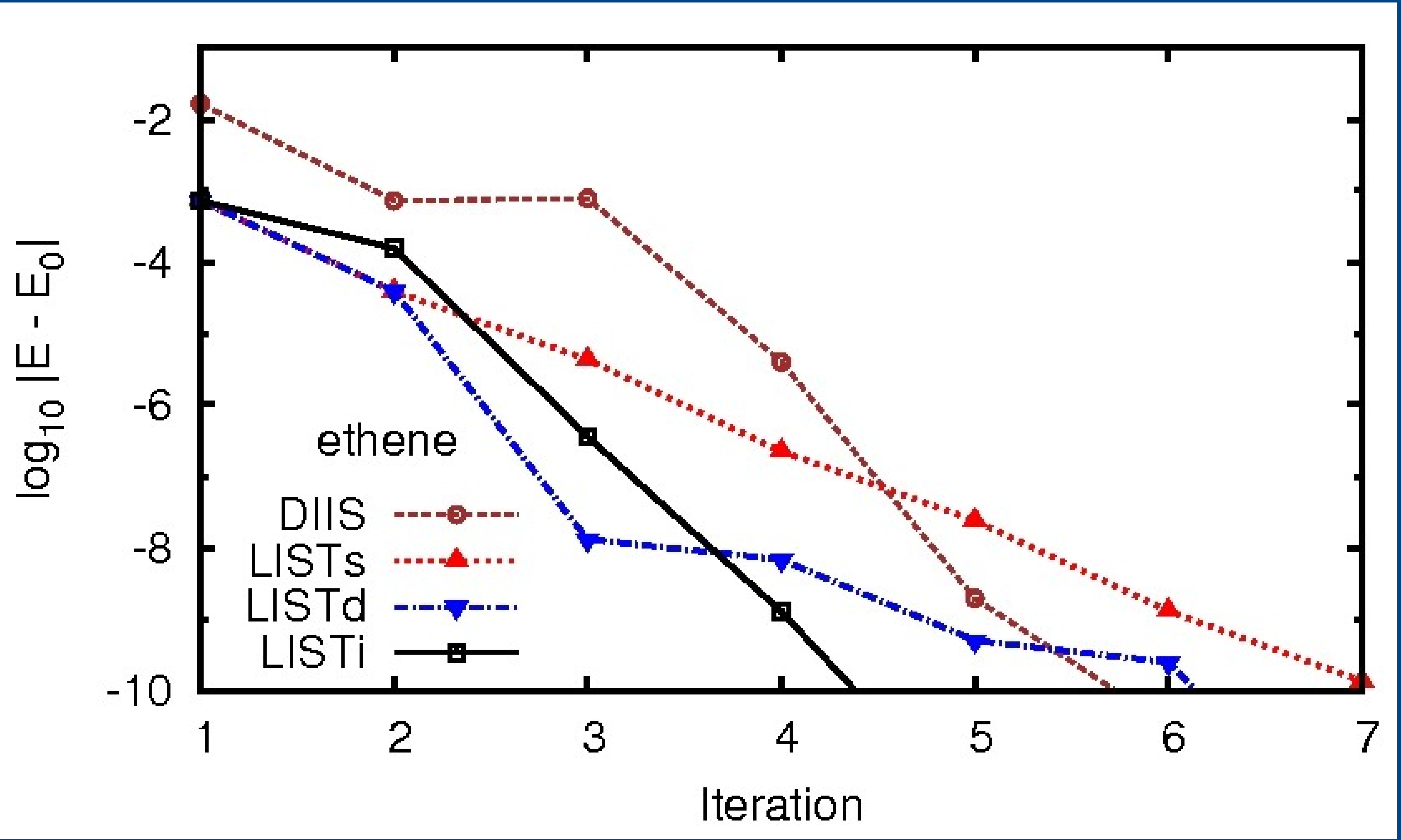
SCF Convergence: HF Molecule



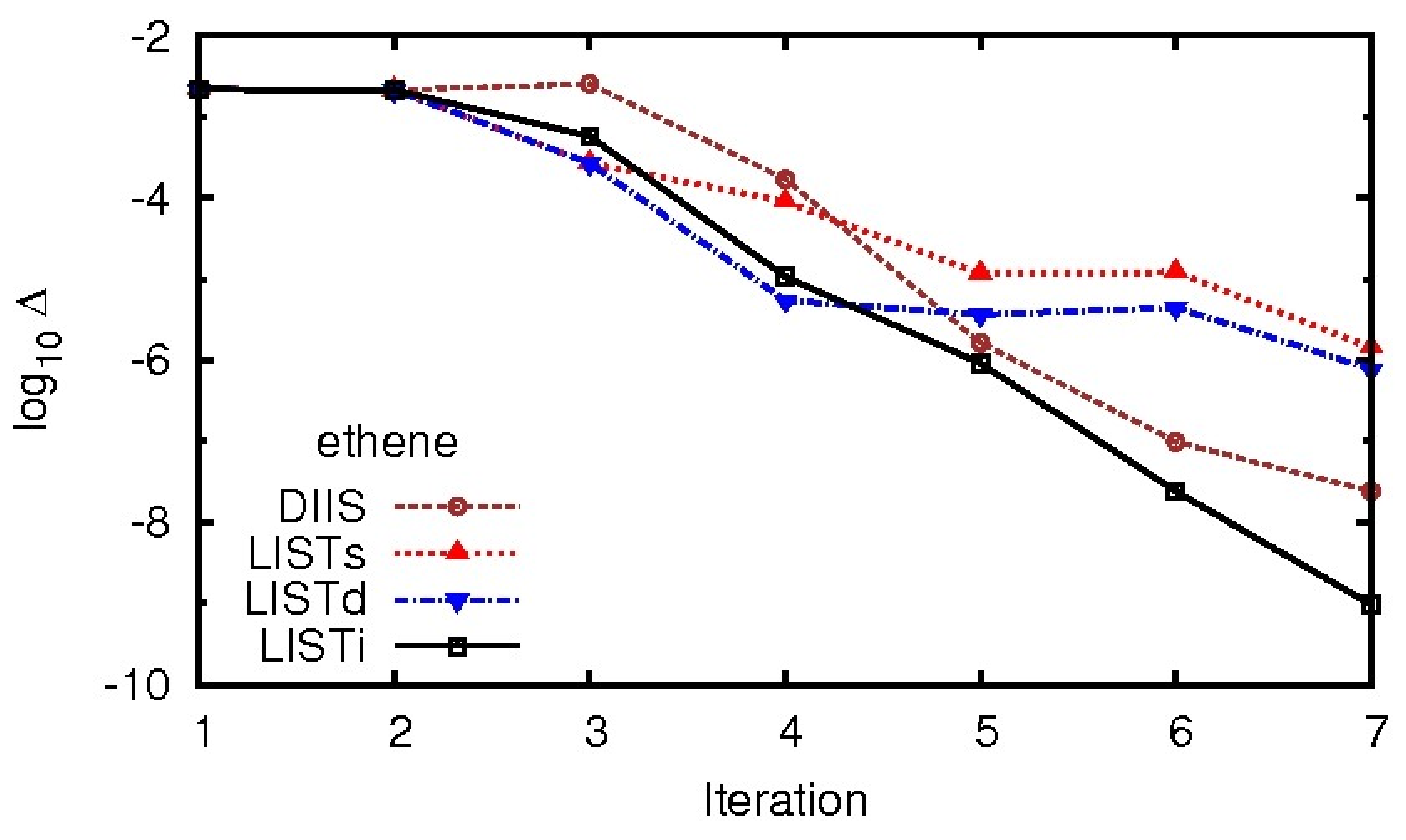
SCF Convergence: Water



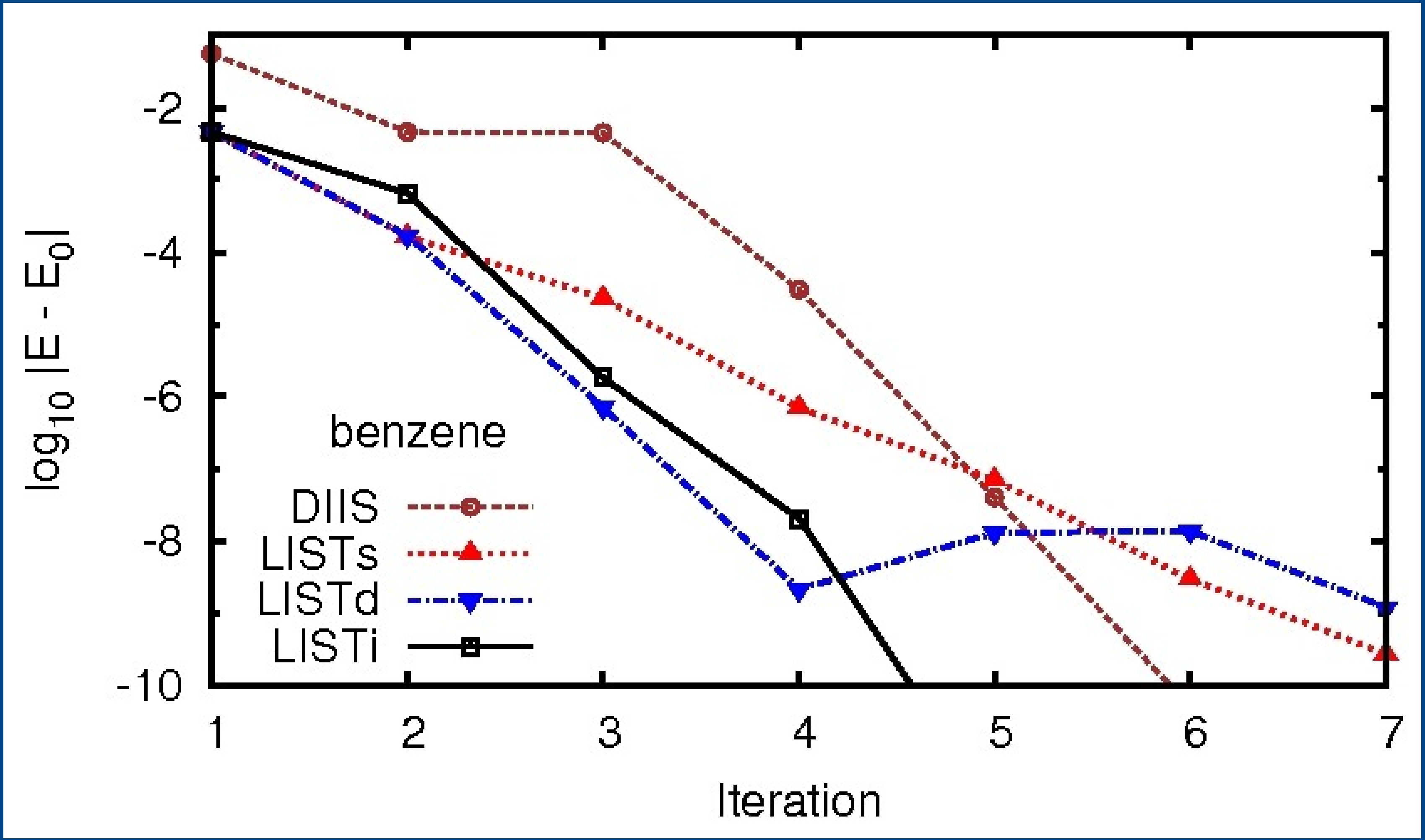
SCF Convergence: Ethylene



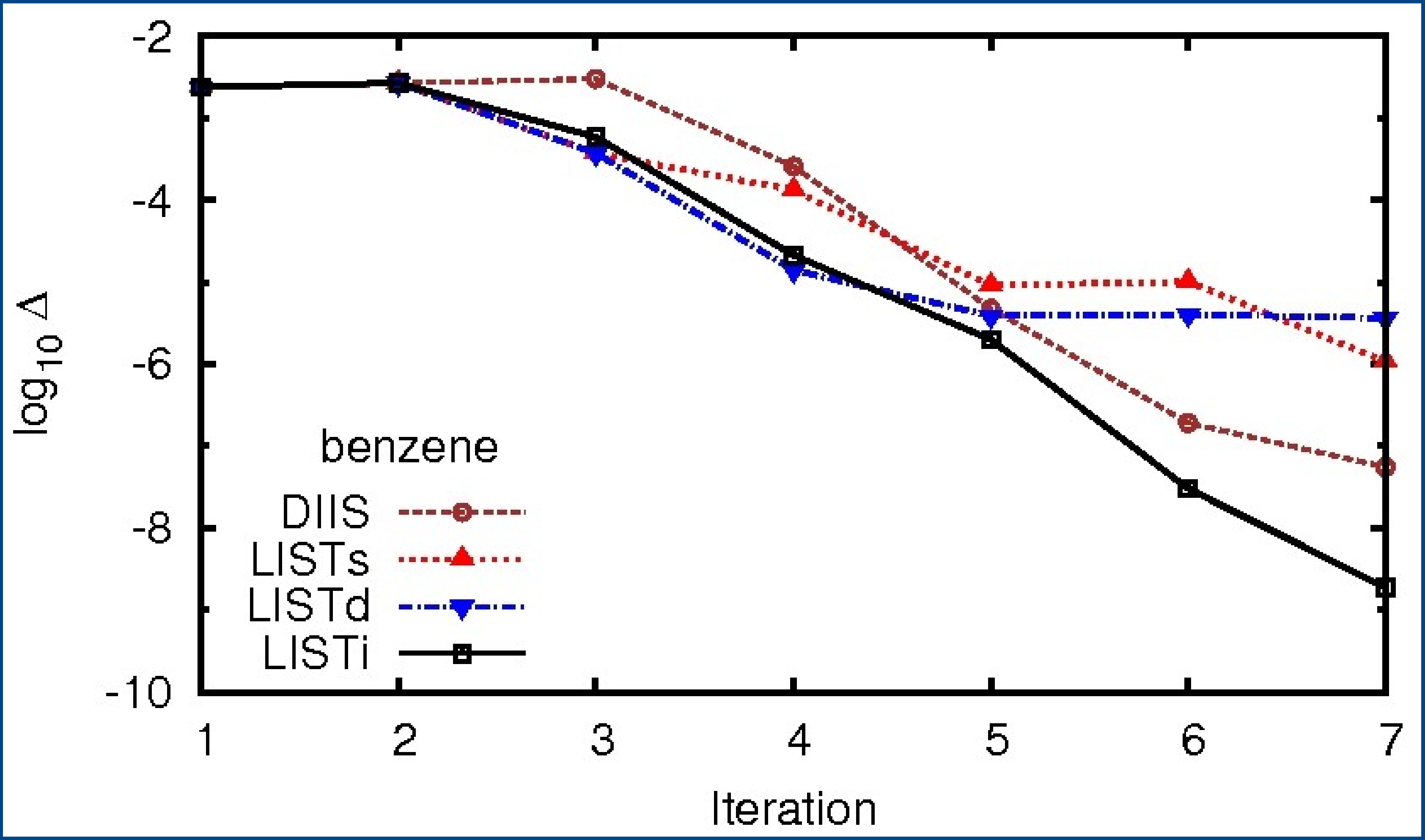
Density Convergence: Ethylene



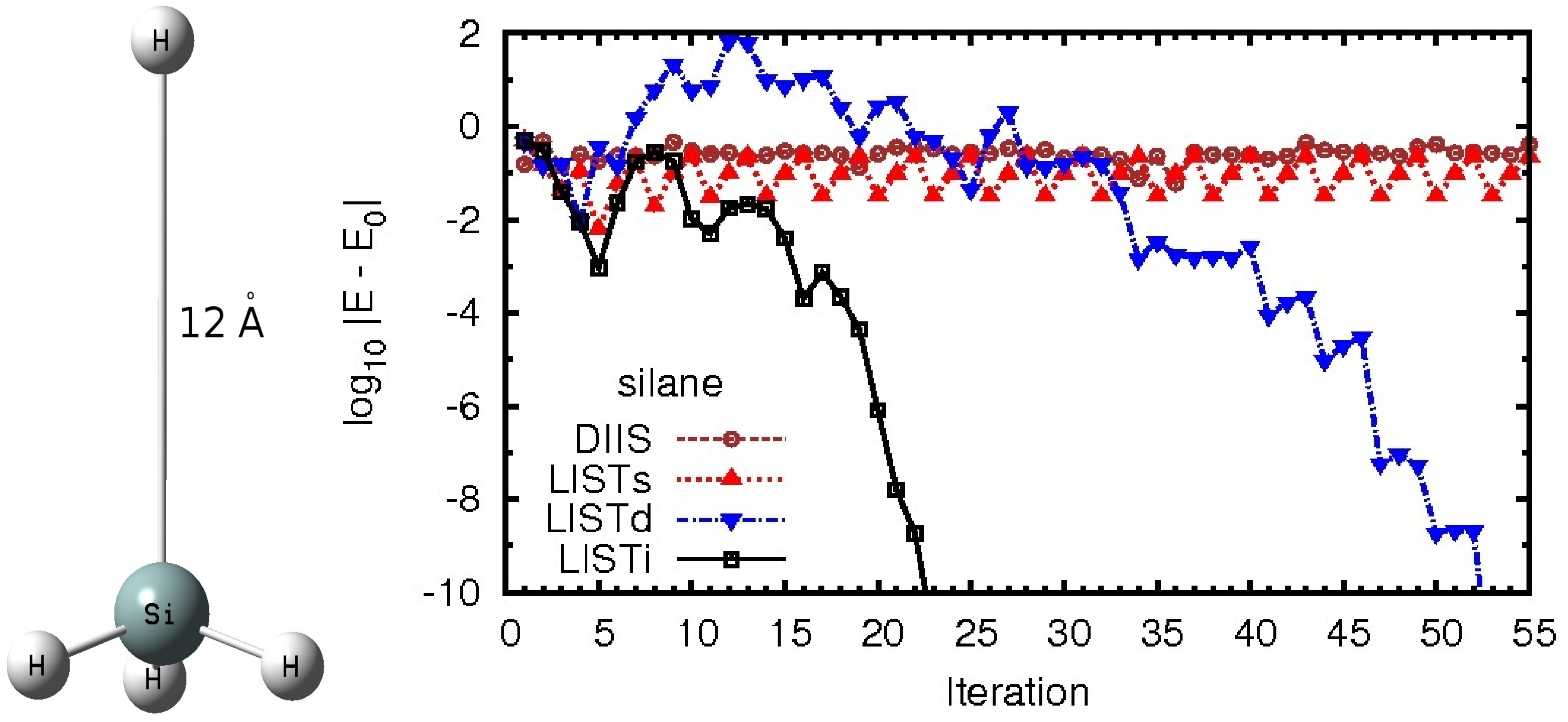
SCF Convergence: Benzene



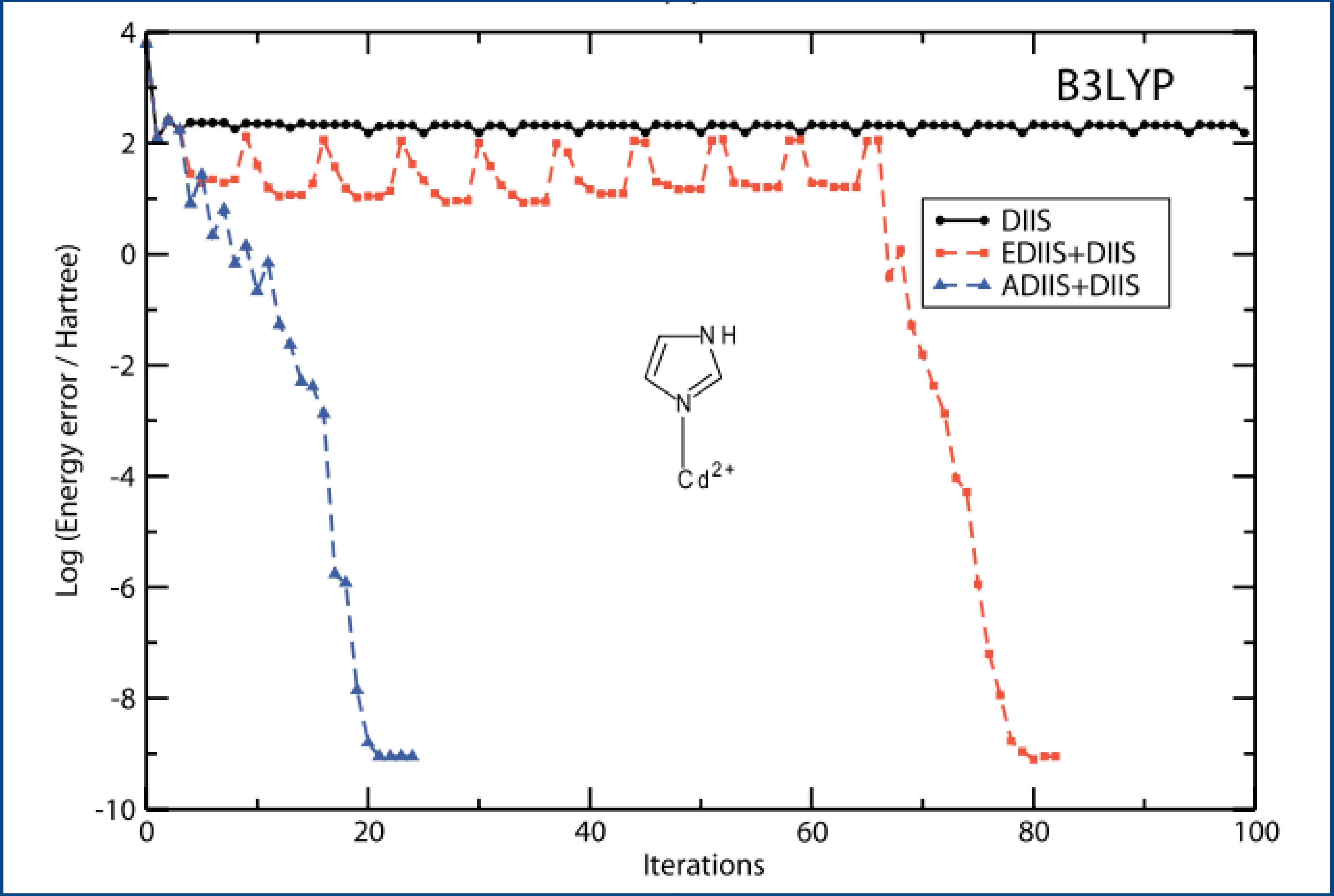
Density Convergence: Benzene



SCF Convergence: Silane



A Chanllenging System



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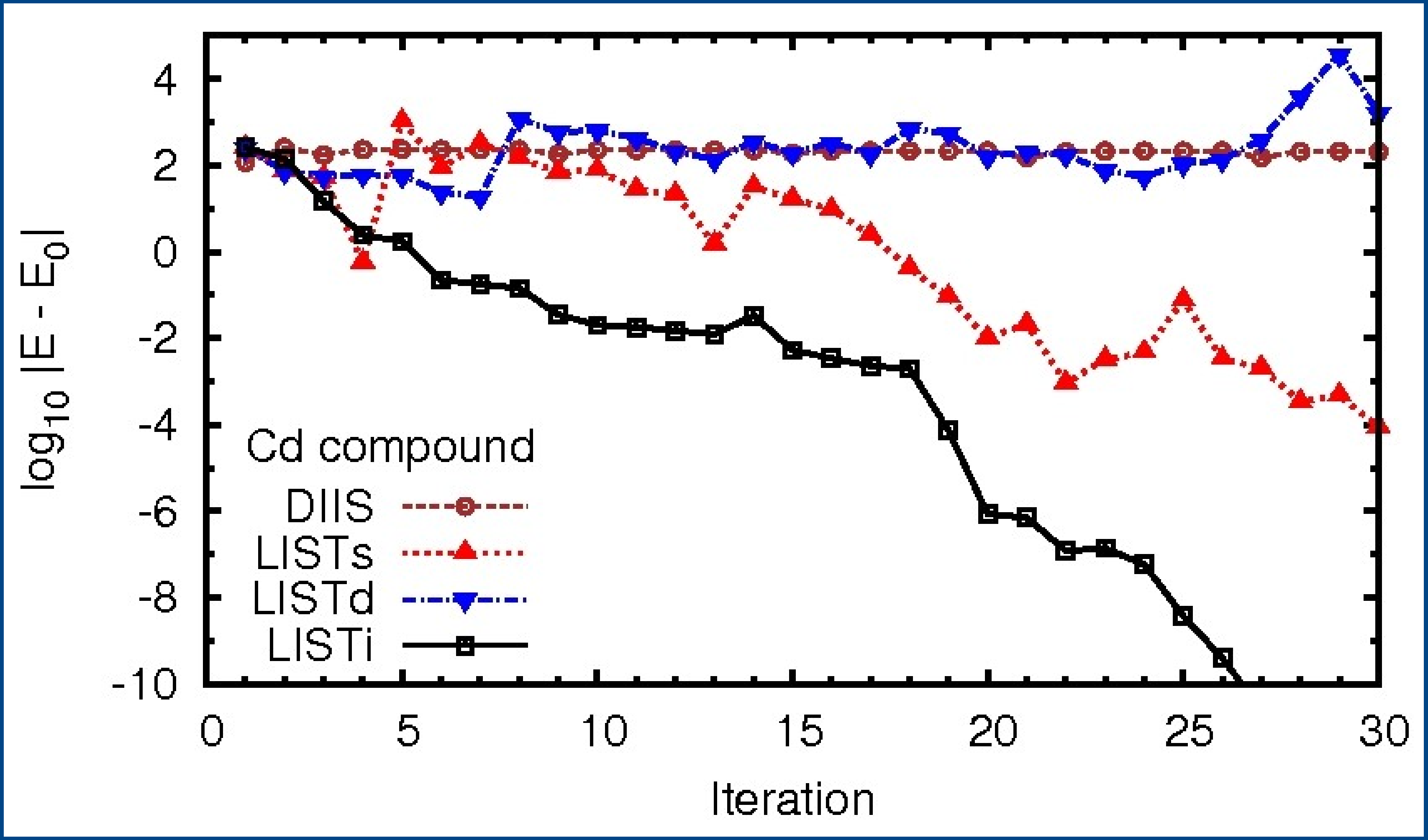
SCF Convergence: Cd Compound



Summary of LIST Methods

- LISTi ourperforms other LIST methods and DIIS/EDIIS/ADIIS in almost all cases.
- The computational cost of LISTi is less than DIIS/EDIIS/ADIIS.
- LISTs and LISTd are better in the early stage of SCF procedure.
- LISTi is a stand-alone method.

Acknowledgement

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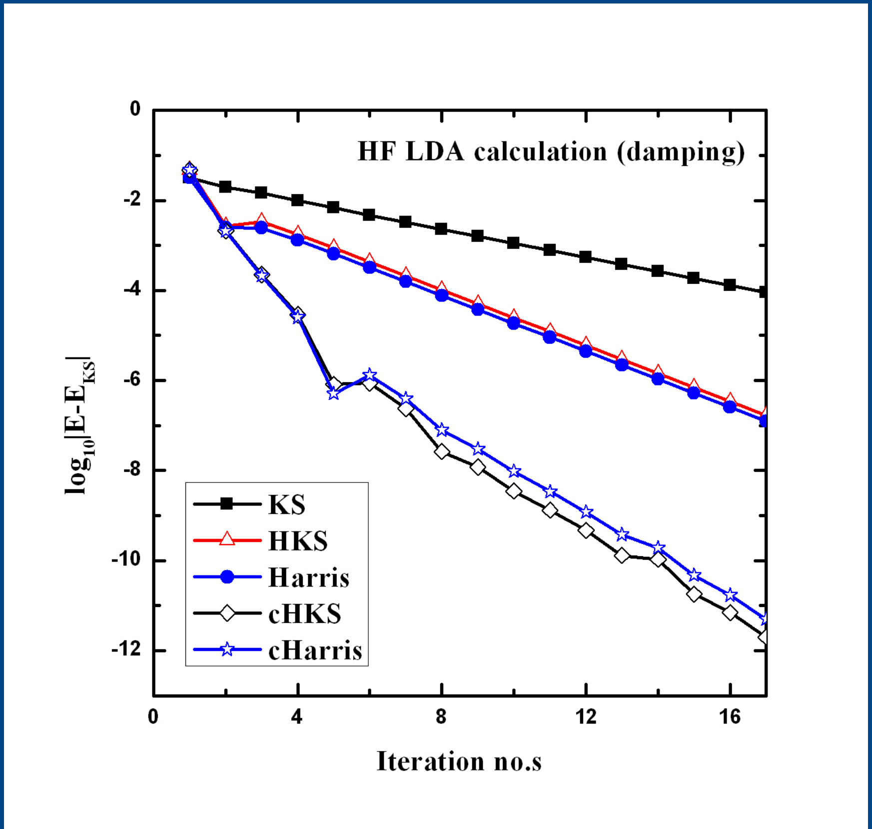
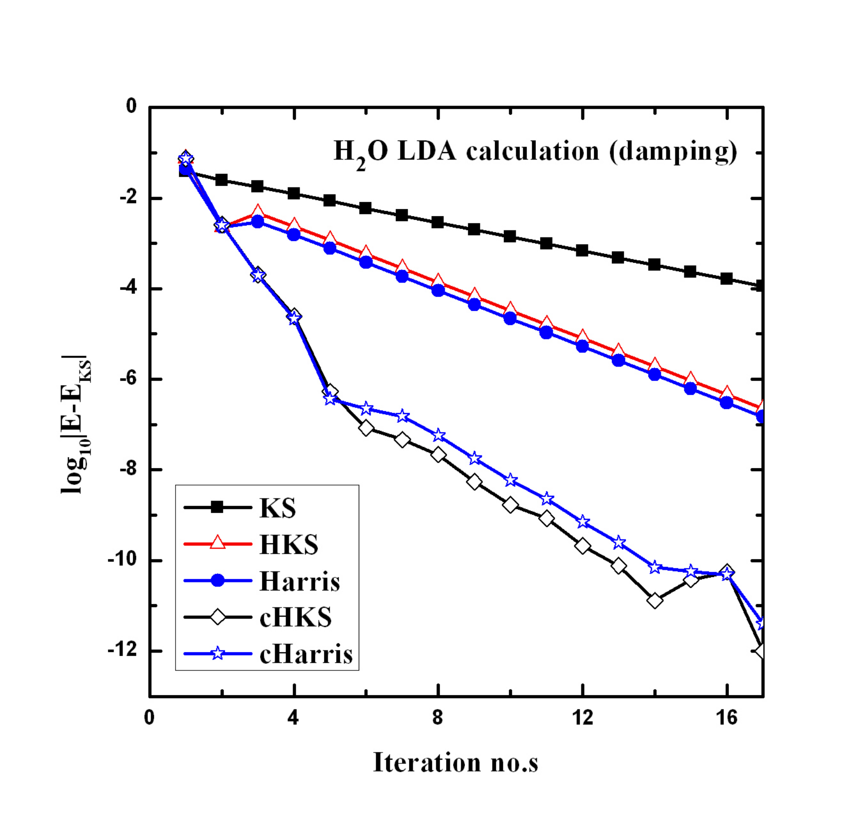
- $$: NSERC

Test on HF and H_2O (with damping)





Zhang & Wang, *J. Chem. Phys.* **130**, 144116 (2009).