CHEM 445A

Implementation of LIST SCF Convergence Methods and MESA in Psi4

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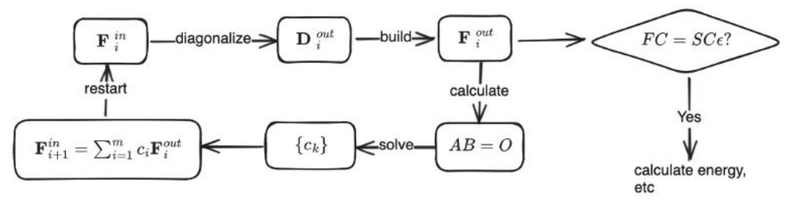
Abstract

The self-consistent field procedure (SCF) is used to solve Hartree-Fock and Density Functional Theory equations. SCF convergence methods try to accelerate the search for a molecule's stable energetic minimum by extrapolating unknown parameters. Unfortunately, a method that reliably achieves convergence for all molecules has yet to be discovered. Thus, to combat this issue, the Wang group has developed a set of linear expansion shooting techniques (LIST) and a minimal error sampling algorithm (MESA), which selects the extrapolated value with the least error from all methods. This project was the implementation of the LIST methods and MESA in Psi4, an open-source quantum chemistry library. Four SCF convergence methods (LISTr, LISTb, LISTf, FDIIS) and MESA were added. Initial tests on molecular systems from the literature that struggle to converge to a stable wavefunction show convergence using these newly implemented techniques, out-competing existing SCF acceleration methods in Psi4.

$$\mathcal{H}\Psi(x,t) = \mathcal{E}\Psi(x,t)$$

$$\downarrow$$

$$\mathbf{F}(\mathbf{P})\mathbf{C} = \mathbf{SC}\epsilon$$



LIST Methods

The LIST methods are based on the shooting technique in numerical analysis. LIST "shoots" for the solution by optimally mixing together previous Fock matrices. Each LIST method solves the matrix problem below with a slightly different A matrix to produce the next input Fock matrix.

$$\mathbf{AB} = \begin{pmatrix} 0 & -1 & -1 & \dots & -1 \\ -1 & a_{11} & a_{12} & \dots & a_{1m} \\ -1 & a_{11} & a_{12} & \dots & a_{1m} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & a_{m1} & a_{m2} & \dots & a_{mm} \end{pmatrix} \begin{pmatrix} \Lambda \\ c_1 \\ c_2 \\ \vdots \\ c_m \end{pmatrix} = \begin{pmatrix} -1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \mathbf{O}$$

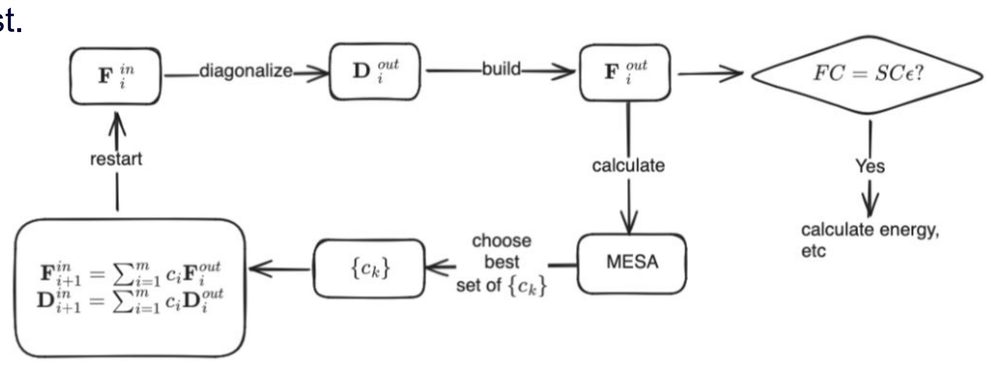
$$\mathbf{F}_{m+1}^{in} = \sum_{i=1}^{m} c_i \mathbf{F}_i^{out}$$

$$\begin{aligned} &\text{LISTr: } a_{ij} = \langle \mathbf{e}_i^{\mathbf{D}} | \mathbf{e}_j^{\mathbf{H}} \rangle \\ &\text{FDIIS: } a_{ij} = \langle \mathbf{e}_i^{\mathbf{F}} | \mathbf{e}_j^{\mathbf{F}} \rangle \\ &\text{LISTb: } a_{ij} = \langle \mathbf{D}_i^{\text{out}} | \mathbf{e}_j^{\mathbf{F}} \rangle \\ &\text{LISTf: } a_{ij} = \langle \mathbf{F}_i^{\text{in}} | \mathbf{e}_j^{\mathbf{F}} \rangle \end{aligned}$$

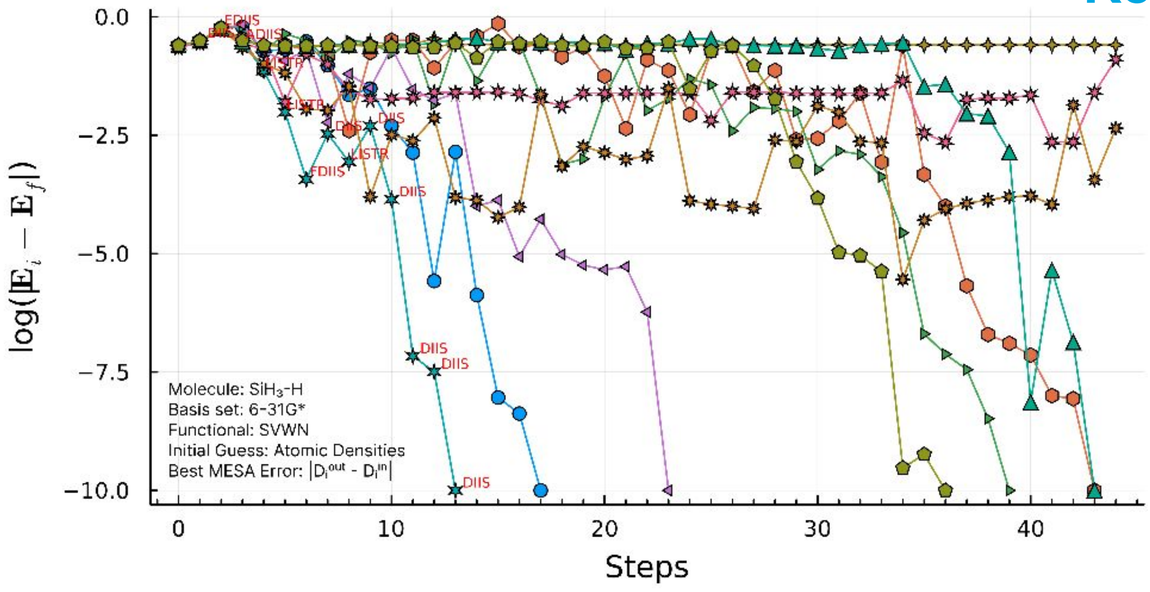
$$\begin{aligned} \mathbf{e}_i^{\mathbf{D}} &= \mathbf{D}_i^{\text{out}} - \mathbf{D}_i^{\text{in}} \\ \mathbf{e}_i^{\mathbf{F}} &= \mathbf{F}_i^{\text{out}} - \mathbf{F}_i^{\text{in}} \\ \mathbf{e}_i^{\mathbf{H}} &= \mathbf{J}_i^{\text{out}} - \mathbf{J}_i^{\text{in}} \end{aligned}$$

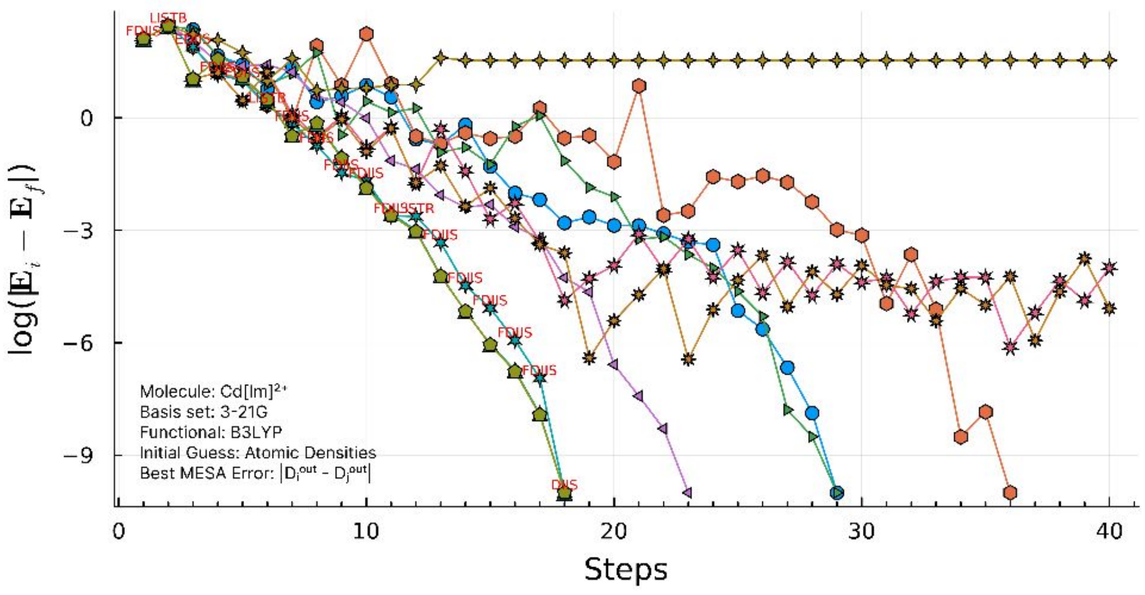
MESA

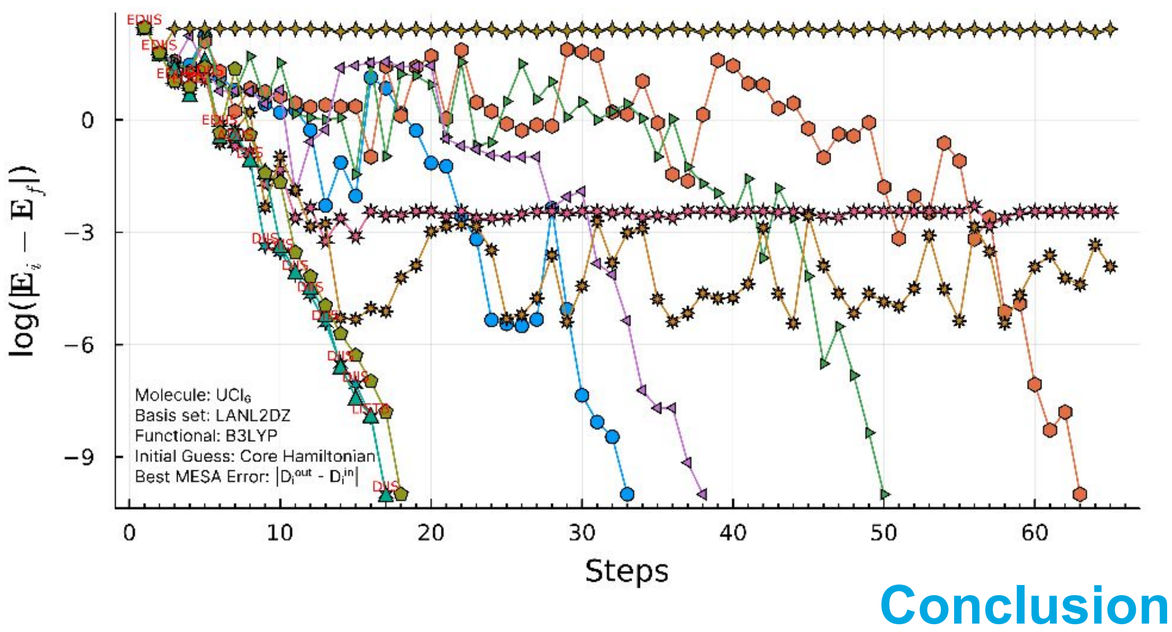
At the MESA stage, the input Fock matrix is given to all SCF convergence methods to see which method best extrapolates. MESA chooses the method with the smallest error, and it's Fock matrix is used in the next iteration. MESA sampled from DIIS, ADIIS, EDIIS, LISTb, LISTr, LISTf and FDIIS. Different measures of error were tried, with the minimum difference between density matrices performing the best.

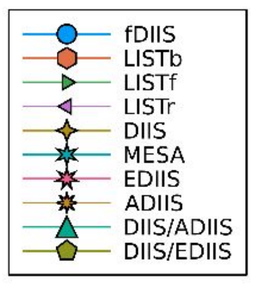


Results









Molecule	SCF Method	Steps	Energy (Ha)	Time (ms/step)
SiH_3-H	fDIIS	17	-290.809760	49.41
	MESA	13	-290.809760	63.08
UCl_6	DIIS/ADIIS	17	-141.412647	308.24
	MESA	17	-141.412647	312.94
$Cd[Im]^{2+}$	DIIS/ADIIS	18	-5667.11605	302.78
	MESA	18	-5667.116052	314.44

Conclusion and Future

The LIST SCF convergence methods and MESA were added to Psi4 with the goal of providing more SCF acceleration methods for molecules that Psi4's existing SCF convergence methods struggled. It was demonstrated that MESA, LISTr, LISTf, LISTb and FDIIS all converge on molecular systems that were reported in literature. Furthermore, these methods can match or outperform the DIIS/EDIIS/ADIIS combination of SCF accelerating methods. Thus, four new SCF convergence methods were successfully added to Psi4, with the additional capability to use MESA to utilize the strengths of all SCF convergence methods at every SCF iteration. Further benchmarking of these new methods will allow for a better understanding of their strengths.

References

1. Smith, D. G. A.; Burns, L. A.; Simmonett, A. C.; Parrish, R. M.; Schieber, M. C.; Galvelis, R.; Kraus, P.; Kruse, H.; Di Remigio, R.; Alenaizan, A.; James, A. M.; Lehtola, S.; Misiewicz, J. P.; Scheurer, M.; Shaw, R. A.; Schriber, J. B.; Xie, Y.; Glick, Z. L.; Sirianni, D. A.; O'Brien, J. S.; Waldrop, J. M.; Kumar, A.; Hohenstein, E. G.; Pritchard, B. P.; Brooks, B. R.; Schaefer, H. F.; Sokolov, A. Yu.; Patkowski, K.; DePrince, A. E.; Bozkaya, U.; King, R. A.; Evangelista, F. A.; Turney, J. M.; Crawford, T. D.; Sherrill, C. D. P SI4 1.4: Open-Source Software for High-Throughput Quantum Chemistry. The Journal of Chemical Physics 2020, 152 (18), 184108. https://doi.org/10.1063/5.0006002.
2. Garcia-Chavez, M. A.; Yakovlev, A.; Chen, Y. K.; Wang, Y. A. General Linear-Expansion Shooting Techniques Based on Minimization of Intra- Iteration Errors. In Advances in Methods and Applications of Quantum Systems in Chemistry, Physics, and Biology; Grabowski, I., Słowik, K., Maruani, J., Brändas, E. J., Eds.; Springer Nature Switzerland: Cham, 2024; Vol. 34, pp 47–66. https://doi.org/10.1007/978-3-031-52078-5_4.
3. HF: Hartree–Fock Theory. https://psicode.org/psi4manual/master/scf.html#convergence- stabilization (accessed 2024-11-21).
4. Szabo, A.; Ostlund, N. S. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory; Macmillan: New York, N.Y, 1982.
5. Baseden, K. A.; Tye, J. W. Introduction to Density Functional Theory: Calculations by Hand on the Helium Atom. J. Chem. Educ. 2014, 91 (12), 2116–2123. https://doi.org/10.1021/ed5004788.
6. Roothaan, C. C. J. New Developments in Molecular Orbital Theory. Rev. Mod. Phys. 1951, 23 (2), 69–89. https://doi.org/10.1103/RevModPhys.23.69.
7. The DIIS Method. http://vergil.chemistry.gatech.edu/notes/diis/diis.html (accessed 2024-11-21).
7. Hu, L.; Sarwono, Y. P.; Ding, Y.; He, F.; Zhang, R.-Q. An Improved DIIS Method Using a Versatile Residual Matrix to Accelerate SCF Starting from a Crude Guess. Journal of Computational Chemistry 2024, 45 (30), 2539–2546. https://doi.org/10.1002/jcc.27463.
8. Install v1.9.1+ | Installs. https://psicode.org/installs/v191/ (accessed 2024-12-11).
9. Shooting Methods. http://homepages.math.uic.edu/~jan/mcs471/shooting.pdf (accessed 2024-12-11).
10. Wang, Y. A.; Yam, C. Y.; Chen, Y. K.; Chen, G. Communication: Linear- Expansion Shooting Techniques for Accelerating Self-Consistent Field Convergence. The Journal of Chemical Physics 2011, 134 (24), 241103. https://doi.org/10.1063/1.3609242. 16
11. Zhang, Y. A.; Wang, Y. A. Perturbative Total Energy Evalua- tion in Self-Consistent Field Iterations: Tests on Molecular Systems. The Journal of Chemical Physics 2009, 130 (14), 144116. https://doi.org/10.1063/1.3104662.
12. Kudin, K. N.; Scuseria, G. E.; Cancès, E. A Black-Box Self-Consistent Field Convergence Algorithm: One Step Closer. The Journal of Chemical Physics 2002, 116 (19), 8255–8261. https://doi.org/10.1063/1.1470195.
13. Hu, X.; Yang, W. Accelerating Self-Consistent Field Convergence with the Augmented Roothaan–Hall Energy Function. The Journal of Chemical Physics 2010, 132 (5), 054109. https://doi.org/10.1063/1.3304922.
14. ACCDB: A collection of chemistry databases for broad computational purposes - Morgante - 2019 - Journal of Computational Chemistry - Wiley Online Library. https://onlinelibrary.wiley.com/doi/abs/10.1002/jcc.25761 (accessed 2024-12-11).
15. Lucy Hao. (2025). psi4-confidential. GitHub. https://github.com/UBCC3/psi4-confidential