A Least-squares Commutator In Iterative Subspace (LCIIS) method for accelerating self-consistent field convergence

Haichen Li and David J. Yaron*

Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213

E-mail: yaron@cmu.edu

Abstract

A Least-squares Commutator In Iterative Subspace (LCIIS) approach is explored for accelerating self-consistent field (SCF) calculations. LCIIS is similar to direct inversion in iterative subspace (DIIS) methods in that the next iterate of the density matrix is obtained as a linear combination of past iterates. However, whereas DIIS methods find the linear combination by minimizing a sum of error vectors, LCIIS minimizes the Frobenius norm of the commutator between the density matrix and the Fock matrix. This minimization leads to a quartic problem that can be solved iteratively through constrained Newton's method. The relationship between LCIIS and CDIIS, the DIIS method that is based on the commutator between the Fock and density matrix, is discussed. Numerical experiments suggest that LCIIS converges more reliably than CDIIS on difficult cases, while maintaining CDIIS's efficiency in regular cases. Trials on a data set of transition metal complexes suggest LCIIS leads to both faster and more robust convergence than CDIIS and Energy-DIIS+CDIIS. The computational cost involved in solving the quartic minimization problem is small compared to the typical cost of SCF iterations and the approach is easily integrated into existing codes.