A Nonlinear Eigensolver-Based Alternative to Traditional SCF Methods

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Problem

Solving the Kohn-Sham Equations

$$H[n]x_i = \lambda_i S x_i \ , \qquad n = \sum_i |x_i|^2$$

Where H[n] is the typical Kohn-Sham Hamiltonian with (for our work here) spinless LDA approximation, x_i, λ_i are eigenvector/eigenvalue pairs, n is the electron density, and S is the mass matrix resulting from a finite elements discretization.

Traditional SCF

The Kohn-Sham equations are traditionally solved using self-consistent field methods that follow the general procedure:

1. Find good initial guess n_1 (e.g. with Thomas-Fermi model)
2. Get $n' = f(n_i)$, where $f(n_i)$ is the procedure consisting of:
   (a) Forming the Kohn-Sham hamiltonian H[n_i] by solving poisson's equation, calculating the exchange-correlation operator, etc.
   (b) Solving the eigenvalue problem $H[n_i]x_i = \lambda_i S x_i$
   (c) Calculating the new density from the occupied states x_i
3. Form n_{i+1} from some function of n' and n_i. If $\|n_{i+1} - f(n_{i+1})\| < \epsilon$ then stop; otherwise GOTO step 2.

Simple Mixing:

$$n_{i+1} = \alpha n_i + (1-\alpha)n' \ , \qquad 0 \le \alpha \le 1$$

The value of α is determined heuristically. Typical $\alpha = 0.1$. Convergence is usually very slow.

DIIS:

A list of m densities is first produced using some other procedure (e.g. simple mixing), and then subsequent n_{i+1} are given by[2]:

$$n_{i+1} = \sum_{j=1}^{m} c_j n_{i-j} + c_j r_{i-j} \ , \quad r_i = n_i - f(n_i)$$

where c_j are the coefficients that minimize $\|\sum c_j r_j\|$ such that $\sum c_j = 1$. Convergence is known to be super linear.

Nonlinear Eigensolver

Our method is based on the FEAST algorithm[1], a method for solving linear eigenvalue problems. The nonlinear Kohn-Sham equations are solved in an approximate subspace Q, which is updated at each iteration:

1. Get initial guess for X, the matrix whose columns are the eigenvectors of interest x_i, and n, either or both of which can be completely random
2. Get density matrix ρ via numerical complex contour integration:

   $$\rho = \oint_C (zS - H[n])^{-1} dz, \quad z \in \mathbb{C}$$

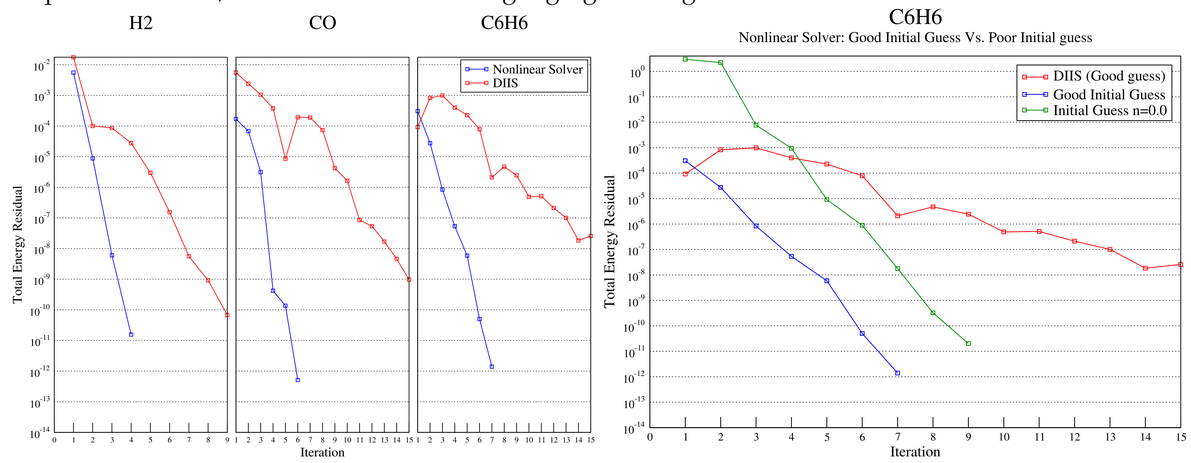
   where C is a contour around the part of the real axis where the eigenvalues of the occupied states are expected to be found.
3. Form the subspace $Q = \rho S X$
4. Solve the projected, reduced nonlinear eigenvector problem

   $$Q^T H[n] Q x_q = \lambda_q Q^T S Q x_q$$

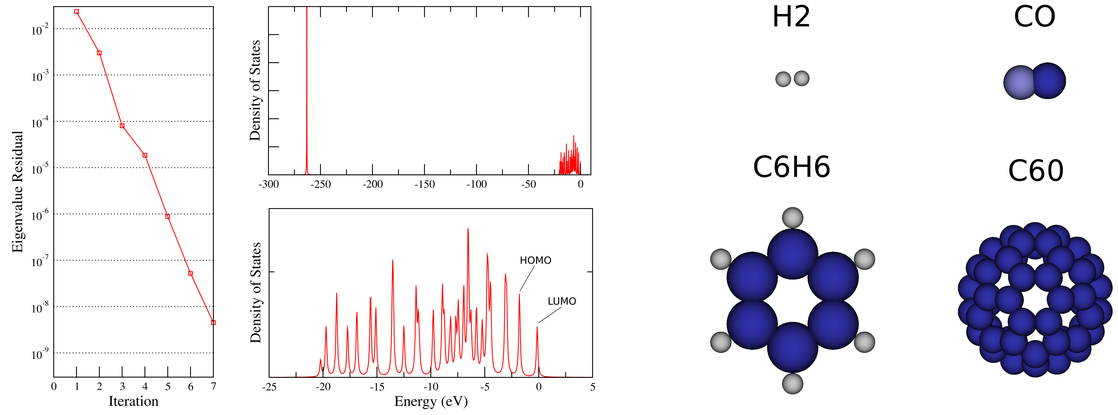
   by iterating over the density n. This procecure is computationally inexpensive compared to performing the full SCF iteration.
5. Calculate $x_i = Q x_q$, $\lambda_i = \lambda_q$, and the new density. If $\sum \lambda_i$ has converged, exit. Otherwise, GOTO step 2.

Results

The following is the result of testing done with LDA all-electron DFT using a third order finite elements discretization. The total energy residual, the relative difference between the calculated total energy at subsequent iterations, is used as the means of gauging convergence.



C60 (Buckminsterfullerine):



Advantages

Computational efficiency: The primary computational costs of our method are mat-vec multiplication and boundary condition assignment in solving Poisson's equation, both of which can easily be parallelized.

No Initial Guess: Our method converges on the correct result for arbitrary initial guess of density and subspace

High Convergence rate: Our method converges significantly faster than DIIS, and the convergence rate remains high regardless of system size.

Future Work

- Parallelize the solution of the subspace problem $Q^T H[n] Q x_q = \lambda_q Q^T S Q x_q$. This will become the primary bottleneck for much larger systems.
- Update the FEAST package to provide a black-box interface for the algorithm described above. FEAST 2.0 currently provides black-box fuctionality for steps 2 and 3 described in "Nonlinear Eigensolver.

  http://www.ecs.umass.edu/~polizzi/feast/

References

[1] E. Polizzi, "Density-matrix-based algorithm for solving eigenvalue problems," Phys. Rev. B., vol 79 115112, Mar. 2009.

[2] T. Rohwedder, R. Schneider, "An analysis for the DIIS acceleration method used in quantum chemistry calculations," J. Math Chem.,Volume 49, Issue 9, pp 1889-1914, Oct2011.