Inexact Restoration Methods for Electronic Structure Calculations

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Outline

1. Presentation of the problem and Challenges.
2. Usual approaches.
3. Inexact Restoration.
4. Characteristics of the problem that favor the application of IR.
5. Implementation.
6. Numerical Results.
7. Conclusions.

"Closed Shell" Electronic Structure Models

Number of Electrons: $2N$

Schrödinger Equation: Provides N waves from which the electronic densities follow. (Unknowns: N functions $\mathbb{R}^3 \to \mathbb{R}$.)

Approximations: Each wave is a Slater-determinant combination of functions that may be expressed as linear combinations of an AO (atomic orbital) basis.

$C \in \mathbb{R}^{K \times N}$: Each column represents the coefficients of each function on the chosen basis.

Density matrix $X = CC^T \in \mathbb{R}^{K \times K}$.

Optimization problem

$S \in \mathbb{R}^{K \times K}$: the symmetric positive definite overlap matrix associated with the basis.

Minimize $f(X)$ subject to $XSX = X, X = X^T, \text{Trace}(XS) = N.$

Taking:

$$\text{new } X = S^{1/2} X S^{1/2} \quad \textit{or} \quad \text{new } X = L^T X L.$$

the problem reduces to:

$$\text{Minimize } f(X) \text{ subject to } X = X^T, X^2 = X, \text{Trace}(X) = N. \quad (1)$$

Feasible points of Problem 1

- The feasible points (matrices) of Problem 1 are Euclidean projection $K \times K$ matrices on subspaces of dimension N.
- Every feasible X may be written $X = CC^T$, where C has K rows and N orthonormal columns (basis of subspace).
- Every feasible X satisfies $\|X\|_F^2 = N$.
- The feasible set of Problem 2 is, in general, smaller than the set of symmetric matrices that satisfy $\|X\|_F^2 = N$ and Trace $(X) = N$. Example: take $K = 3, N = 2$,

$$X = \begin{pmatrix} 1 & 1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1/2 \end{pmatrix}, \; XX = \begin{pmatrix} 1.25 & 0.75 & 0 \\ 0.75 & 1/2 & 0 \\ 0 & 0 & 0.25 \end{pmatrix} \neq X.$$

SCF fixed point iteration

Given X_k feasible, take X_{k+1} as a solution of

$$\text{Minimize } \langle \nabla f(X_k), X - X_k \rangle \quad \text{s.t.} \quad X = X^T, X^2 = X, \ \text{Trace}(X) = N. \tag{2}$$

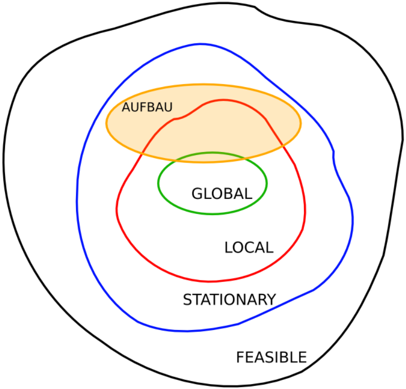
If X_k is a solution of (2) we say that X_k is "aufbau".

Computing the Fixed-Point iteration

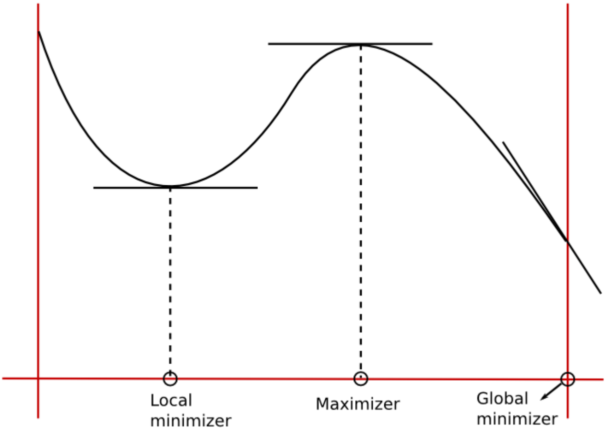
Theorem

Assume that the columns of $C \in \mathbb{R}^{K \times N}$ form an orthonormal basis of the subspace generated the eigenvectors associated to N smallest eigenvalues of $\nabla f(X_k)$. Then, $X_{k+1} = CC^T$ is a solution of (2).

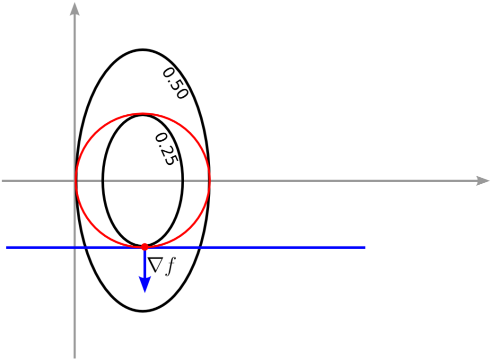
Minimizers, Stationary points and Aufbau points



Aufbaus in a one-dimensional minimization problem



Global minimizers may not be Aufbau



In this example, the global minimizer is a strict global maximizer (!) of the linear approximation.

$$\text{Minimize } 2(x-0.5)^2 + y^2 \text{ subject to } (x-0.5)^2 + y^2 = 0.25.$$

Global minimizers may not be Aufbau

In Problem (1) (Minimize $f(X)$ subject to $X = X^T$, Trace$(X) = N$, $X^2 = X$):
Let $K = 2$, $N = 1$.

$$f(X) = 2(x_{11} - 1/2)^2 + [(x_{12} + x_{21})/2]^2.$$

$$\text{Global Minimizer is } \bar{X} = \begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix}.$$

Now:

$$\nabla f(\bar{X}) = \begin{pmatrix} 0 & -1/2 \\ -1/2 & 0 \end{pmatrix}.$$

The eigenvalues of $\nabla f(\bar{X})$ are $\lambda_{min} = -1/2$ and $\lambda_{max} = 1/2$, corresponding to the eigenvectors $v_{min} = (1/\sqrt{2}, 1/\sqrt{2})^T$ and $v_{max} = (1/\sqrt{2}, -1/\sqrt{2})^T$ respectively.
But:

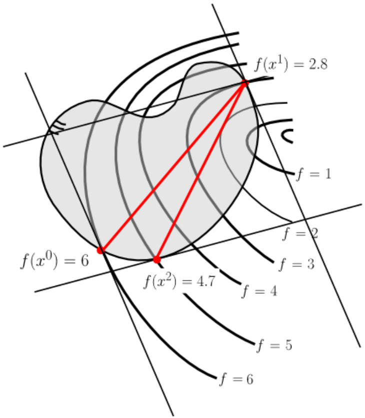
$$v_{min} v_{min}^T = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix} \neq \bar{X}.$$

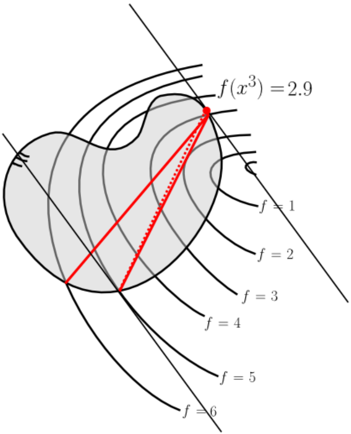
In fact:

$$v_{max} v_{max}^T = \begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix} = \bar{X}.$$

Therefore, $\bar{X}$ is not an Aufbau point. (In fact, is "anti-Aufbau", being equal to $v_{max} v_{max}^T$, where v_{max} is eigenvector corresponding to the biggest eigenvalue, and not the smallest.)

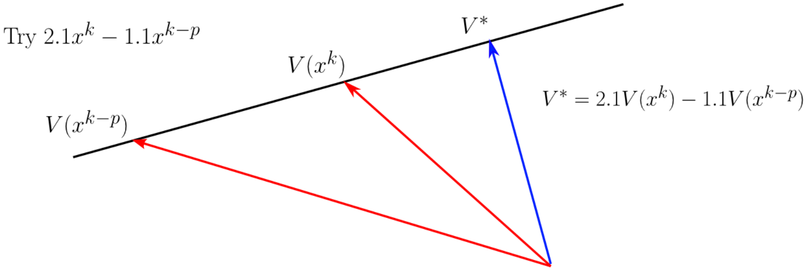
Fixed-Point (SCF-like) Iteration





DIIS acceleration

Step 1. Minimize, with respect to $w_k, \ldots, w_{k-p}$ the function $\|w_k V(x^k) + \ldots + w_{k-p} V(x^{k-p})\|$ (with $\sum_{j=k-p}^{k} w_j = 1$) where V is such that $\|V(x)\|$ is minimal at a desired solution.
Step 2. Try the acceleration $w_k x^k + \ldots + w_{k-p} x^{k-p}$.



Levenberg-Marquardt globally convergent method

At each iteration, given the feasible point X_k and starting with $\mu = 0$, solve:

$$\text{Minimize } \langle \nabla f(X_k), X - X_k \rangle + \mu \|X - X_k\|_F^2 \qquad (3)$$

subject to

$$X = X^T, X^2 = X, \text{Trace } X = N. \qquad (4)$$

If, at the "trial point", the "actual reduction" is not sufficient, increase μ and solve a new subproblem (3-4). Otherwise, accept $X_{k+1} =$ the trial point.

Problem (3-4) may be solved: Take $X_{trial} = CC^T$ where the columns of C are orthonormal eigenvectors corresponding to N smallest eigenvalues of $\nabla f(X_k) - \mu X_k$.

J. B. Francisco, J. M. Martínez, L. Martínez (2004, 2006).

Challenge

Large-scale problems: $N \approx 5000$, $K \approx 10N$.
$n = K^2 \approx 2500000000 = 2.5 \times 10^9$.
Develop "Eigen-free" methods.
Good convergence properties.
Sparsity preserving (with respect to $X \in \mathbb{R}^{K \times K}$ and $\nabla f(X) \in \mathbb{R}^{K \times K}$).
The objective of this contribution is to show how Inexact Restoration can help.

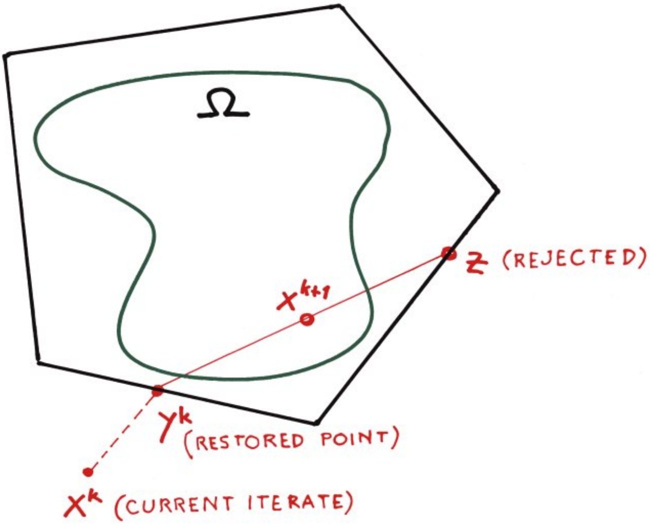
Inexact Restoration

Nonlinear Programming problem

$$\text{Minimize } f(x) \text{ subject to } x \in \Omega \subset \mathbb{R}^n. \quad (5)$$

Inexact Restoration Method

- Restoration Phase: Obtain $y^k \in \mathbb{R}^n$ "sufficiently" more feasible than the current point x^k.
- Minimization Phase: Define $T(y^k) \subset \mathbb{R}^n$, a "tangent approximation" to Ω and minimize, approximately, the Lagrangian on the (non-empty) set $T(y^k, \Omega)$, obtaining z_{trial}.
- Compare z_{trial} with x^k with respect to feasibility and optimality. If z_{trial} is "better" than x^k (merit function, filters) define $x^{k+1} = z_{trial}$. Else, try a different z_{trial} "closer" to y^k (trust regions, line searches) and repeat the comparison.


Ω
Z (REJECTED)
X^k+1
Y^k
(RESTORED POINT)
X^k (CURRENT ITERATE)

Characterization of the Tangent Set

Tangent Characterization Lemma

Let Y be feasible, $T(Y)$ = tangent affine subspace, $S(Y)$ = parallel subspace. Then:

$$S(Y) = \{E \in \mathbb{R}^{K\times K} \mid E = E^T \text{ and } YE + EY - E = 0\}$$

and

$$T(Y)$$
$$= \{Z \in \mathbb{R}^{K\times K} \mid Z = Z^T \text{ and } Y(Z-Y)+(Z-Y)Y-(Z-Y) = 0\}.$$

The dimension of $S(Y)$ is $N(K-N)$.

Projection on the tangent set

Tangent Projection Lemma

Let Y be feasible. Let A be a symmetric $K \times K$ matrix. Then, the Euclidean (Frobenius) projection of A onto $S(Y)$ is given by:

$$P_{S(Y)}(A) = YA + AY - 2YAY.$$

Consequently, the projection of a symmetric matrix $B \in \mathbb{R}^{K \times K}$ onto $T(Y)$ is given by:

$$P_{T(Y)}(B) = Y + Y(B - Y) + (B - Y)Y - 2Y(B - Y)Y.$$

Eigenvalues in the Tangent Set

Tangent Eigenvalues Lemma

Let Y be feasible, $B \in T(Y)$. Then, B has N eigenvalues greater than or equal to 1 and $K - N$ eigenvalues less than or equal to 0 (counting multiplicities).

Local minimizer implies KKT

Optimality Theorem

Let Y_* be a local minimizer of the optimization problem (1) then Y_* satisfies the KKT conditions.

Equivalences with KKT

KKT Theorem

Let Y_* be feasible, $Y_* = C_* C_*^T$, where $C_* \in \mathbb{R}^{K \times N}$ has orthonormal columns. The following statements are equivalent:

1. Y_* satisfies the KKT conditions of the optimization problem (1).
2. $Y_* \nabla f(Y_*) + \nabla f(Y_*) Y_* - 2 Y_* \nabla f(Y_*) Y_* = 0$.
3. $Y_* \nabla f(Y_*) = Y_* \nabla f(Y_*) Y_*$.
4. $\nabla f(Y_*) Y_* = Y_* \nabla f(Y_*) Y_*$.
5. $Y_* \nabla f(Y_*) - \nabla f(Y_*) Y_* = 0$.
6. $\nabla f(Y_*) C_* = C_* H$ for some $H \in \mathbb{R}^{N \times N}$.
7. C_* satisfies the KKT conditions of the problem
   Minimize $f(CC^T)$ subject to $C^T C = I$.
8. $Y_* \nabla f(Y_*)$ is symmetric.

Restoration without Diagonalization I

Given X_{k+1} in the tangent affine subspace $T(Y_k)$, the closest feasible point to X may be computed using its eigenvalue decomposition.
Here we describe an eigen-free procedure with the same result.
Take $Y^0 = X_{k+1}$ and iterate according to:

$$Y^{j+1} = Y^j - (2Y^j - I)^{-1}[(Y^j)^2 - Y^j]. \tag{6}$$

Restoration Theorem

The process (6) converges quadratically to the closest feasible point to Y^0.
Proof: Use the eigenvalue structure of the tangent point Y^0.

We hope that the iterates preserve the sparsity pattern of Y^0 as much as possible.

Restoration without diagonalization II

The iteration (6) “is Newton”. A modified Newton iteration that preserves local superlinear convergence is:

$$Y^{j+1} = 3(Y^j)^2 - 2(Y^j)^3. \tag{7}$$

The iteration (7) converges to the projection matrix that is closest to Y_0 if N eigenvalues of Y_0 are in $(0.5, 1.366)$ and $K - N$ eigenvalues of Y_0 are in $(-0.366, 0.5)$.

Estimation of Lagrange Multipliers

In the Optimality Phase of the Inexact Restoration iteration one minimizes the Lagrangian function. We need approximations of the Lagrange multipliers $\Lambda_k \in \mathbb{R}^{K \times K}$.
A standard argument relating the gradient $\nabla f(Y^k)$ with the first-order approximation of the constraints leads to the approximation:

$$\Lambda_k = -\frac{(2Y_k - I)^{-1}\nabla f(Y_k) + [(2Y_k - I)^{-1}\nabla f(Y_k)]^T}{2},$$

Moreover, if $Y^2 = Y$ we have that $(2Y - I)^{-1} = 2Y - I$. This identity suggests that we can also use the approximation

$$\Lambda_k = -[(2Y_k - I)\nabla f(Y_k) + [(2Y_k - I)\nabla f(Y_k)]^T]/2.$$

Implementing the Optimality Phase I

We need to minimize the Lagrangian $L(Z, \Lambda_k) \equiv f(Z) + \langle Z^2 - Z, \Lambda^k \rangle$ on the tangent affine subspace given by:

$$T(Y_k)$$

$$= \{Z \in \mathbb{R}^{K \times K} \mid Z = Z^T \text{ and } Y_k(Z - Y_k) + (Z - Y_k)Y_k - (Z - Y_k) = 0\}.$$

Computing a basis of the parallel subspace to $T(Y_k)$ is not possible and direct methods based on the KKT system of this subproblems are out of question. However, we know how to compute the projection of $\nabla L(Z, \Lambda_k)$ on the parallel subspace $S(Y_k)$. Using this tool we may implement a reduced-basis conjugate-gradient method for solving the optimality phase without matrix manipulations.

Implementing the Optimality Phase II

The Conjugate Gradient process in the tangent space finishes when

- An iterate Z^j is found such that the projection of $\nabla L(Z^j, \Lambda_k)$ is suitably small.
- K iterations were completed without convergence.
- After the first iteration, we find a negative-curvature direction.

If a negative-curvature direction E is found at the first iteration the trial step corresponds to a line search along E with a maximal step size that ensures that $\|X_{k+1} - Y_k\|_F \leq 3N$.

Globalization

We know how to restore and how to optimize on the tangent space without eigenvalue calculations. With these tools we essentially have a locally quadratically convergent Inexact Restoration method (Birgin-Martínez 2005, Karas-Gonzaga-Ribeiro 2009).
For obtaining global convergence (cluster points are KKT) we need to adopt a merit function approach (Martínez-Pilotta 2000, Martínez 2001, Fischer-Friedlander 2009) or a filter approach(Gonzaga-Karas-Vanti 2003, Karas-Oenig-Ribeiro 2007) in order to accept or reject the trial point.
If the trial point is rejected, a new trial point "closer to the restored point Y_k" on the tangent affine subspace may be computed using trust regions or line searches along the segment $[Y_k, Z_{trial}]$.
Trust regions are difficult to implement in this very large scale problem, so we rely in the line-search approach of Fischer and Friedlander (2009).

Hartree-Fock Model

In the Hartree-Fock model:

$$f(Z) \equiv E_{SCF}(Z) = \text{Trace}\Big[2HZ + G(Z)Z\Big],$$

where Z is the one-electron density matrix in the atomic-orbital (AO) basis, H is the one-electron Hamiltonian matrix, $G(Z)$ is given by

$$G_{ij}(Z) = \sum_{k=1}^{K}\sum_{\ell=1}^{K}(2g_{ijk\ell} - g_{i\ell kj})Z_{\ell k},$$

$g_{ijk\ell}$ is a two-electron integral in the AO basis, K is the number of functions in the basis and $2N$ is the number of electrons. For all $i, j, k, \ell = 1, \ldots, K$ one has the symmetries:

$$g_{ijk\ell} = g_{jik\ell} = g_{ij\ell k} = g_{k\ell ij}.$$

The matrix $F(Z)$ given by $F(Z) = H + G(Z)$ is known as Fock matrix and we have:

$$\nabla E_{SCF}(Z) = 2F(Z).$$

Since $G(Z)$ is linear, the objective function $E_{SCF}(Z)$ is quadratic.

Example $K = 200, N = 20$

Number of variables $n = K^2 = 40,000$.
Dimension of Tangent Subspaces: $3,600$.
Global IR:
Convergence in 83 iterations.
Computer Time: $\approx$ 95 seconds.
At the first 70 IR-iterations CG finished detecting "negative curvature direction" using ≈ 7 CG-iterations.
At the last 13 IR-iterations CG converged using ≈ 150 CG-iterations (58 CG-iterations at the last one).
KKT $(Y_k \nabla f(Y_k) - (Y_k \nabla f(Y_k))^T)$ at the final iterates:
$1.5 \times 10^{-3}, 5.4 \times 10^{-5}, 1.5 \times 10^{-7}, 2.0 \times 10^{-9}$.
Final $f = -0.274$.

Example $K = 200$, $N = 20$: Other methods

Local IR: Convergence in 273 iterations (130 seconds).
SCF+DIIS: Non-convergence (oscillation) in 1800 iterations (5 minutes). Final $f = 14.$. Final KKT: 0.15.
Levenberg-Marquardt: Non-convergence in 3590 iterations (5 minutes). However, Final $f = -0.274$, Final KKT: 3.5×10^{-7}.
In 2888 iterations LM got the same objective function value with $\text{KKT} = 7.5 \times 10^{-6}$.

Example $K = 700, N = 70$

Global IR:

Number of variables $n = K^2 = 490,000$.

Dimension of Tangent Subspaces: $44,100$.

Convergence in 142 iterations.

Computer Time: $\approx$ 3 hours.

At the first 131 IR-iterations CG finished detecting "negative curvature direction" using $\approx$ 100 CG-iterations.

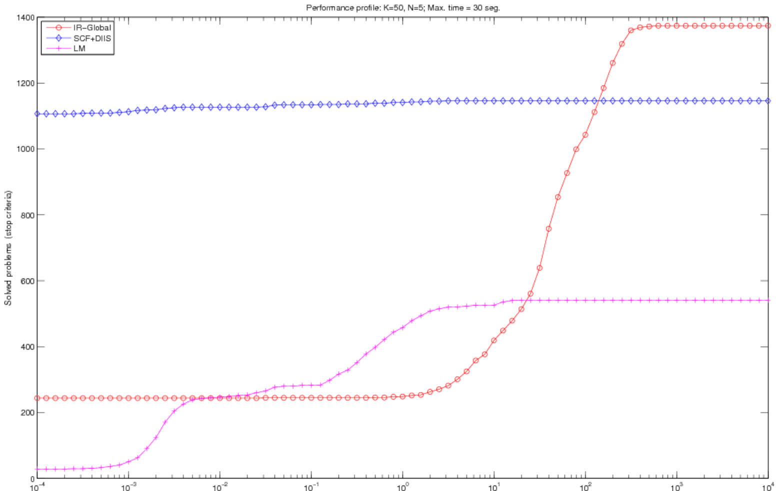
At the last 11 IR-iterations CG converged using $\approx$ 240 CG-iterations (163 CG-iterations at the last one).

KKT at the final iterates:

$4.0 \times 10^{-4}, 4.0 \times 10^{-4}, 4.0 \times 10^{-6}, 1.2 \times 10^{-9}$.

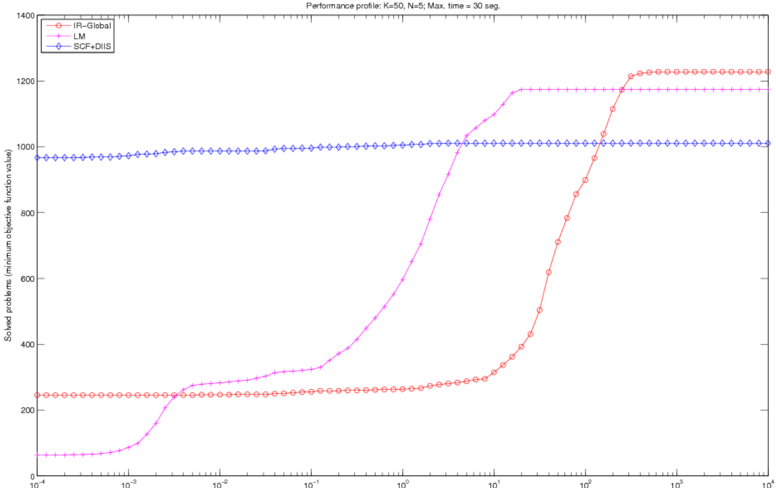
Performance Profiles I

1540 problems with $K = 50, N = 5$.
"Solved" means: Satisfied KKT $\leq 10^{-8}$.

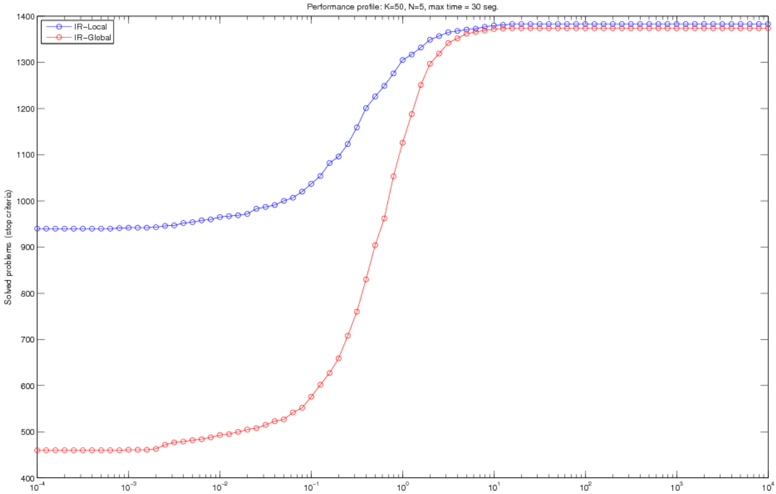


Performance Profiles II

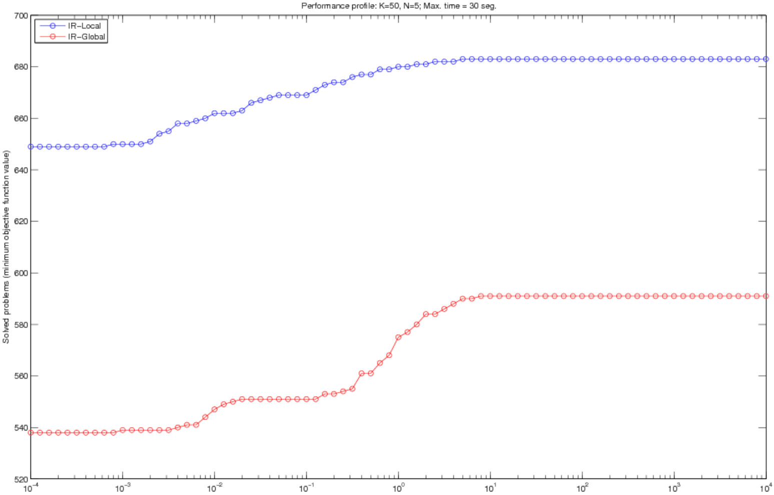
1540 problems with $K = 50, N = 5$.
"Solved" means: Satisfied "Best $f \leq f_{min} + 10^{-6} f_{min}$" .



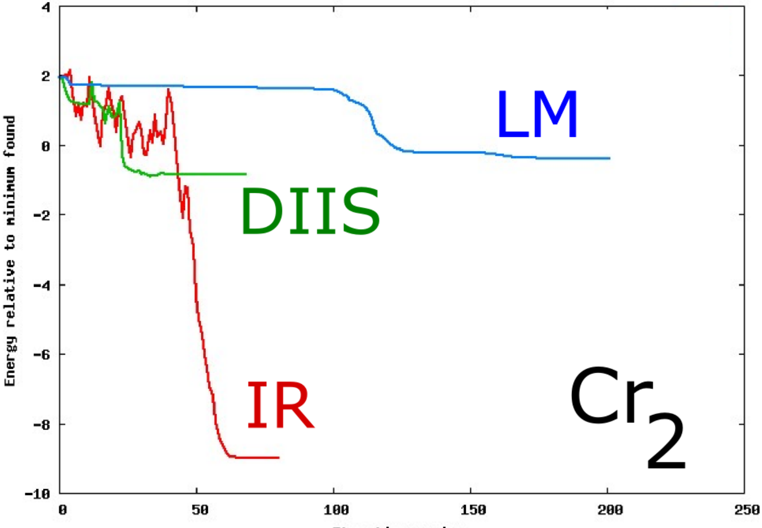
Performance Profiles III



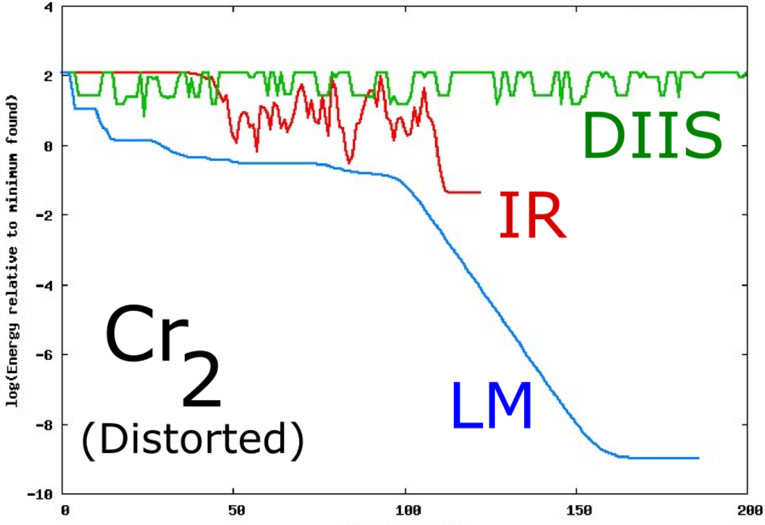
Performance Profiles IV



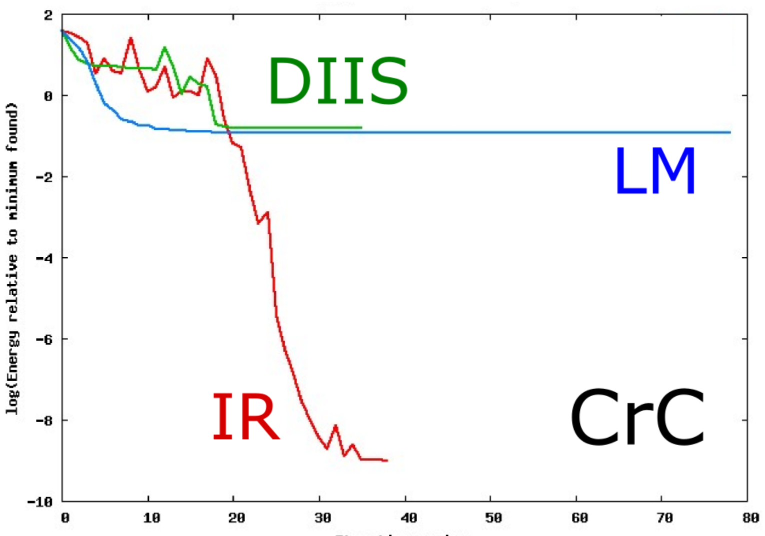
Chemical Example 1



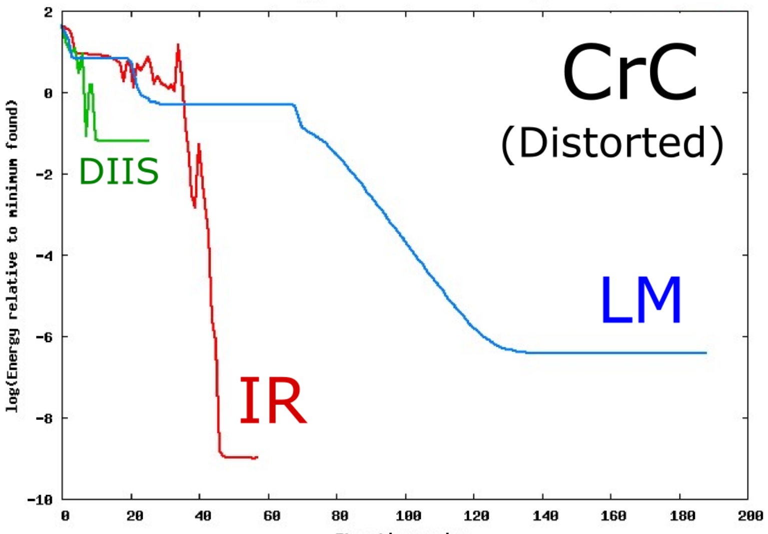
Chemical Example 2



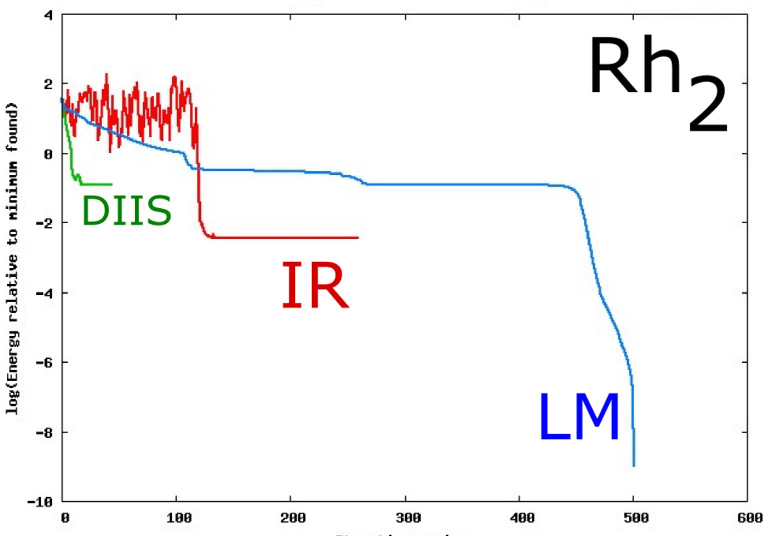
Chemical Example 3



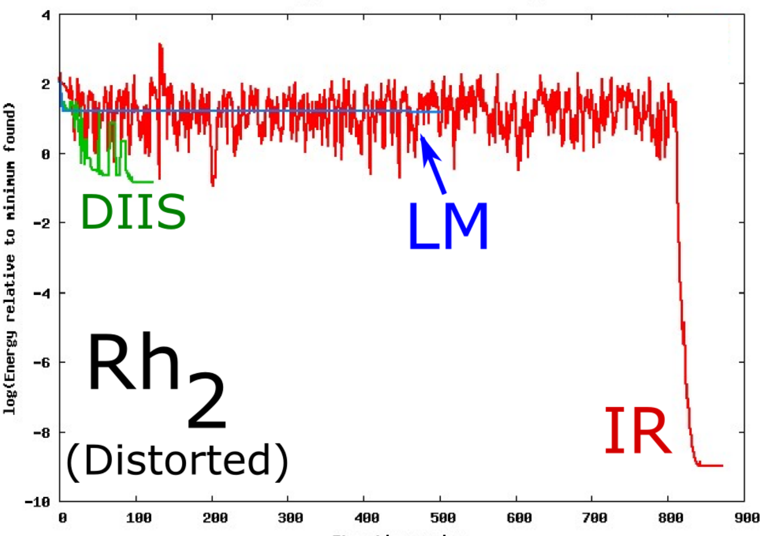
Chemical Example 4



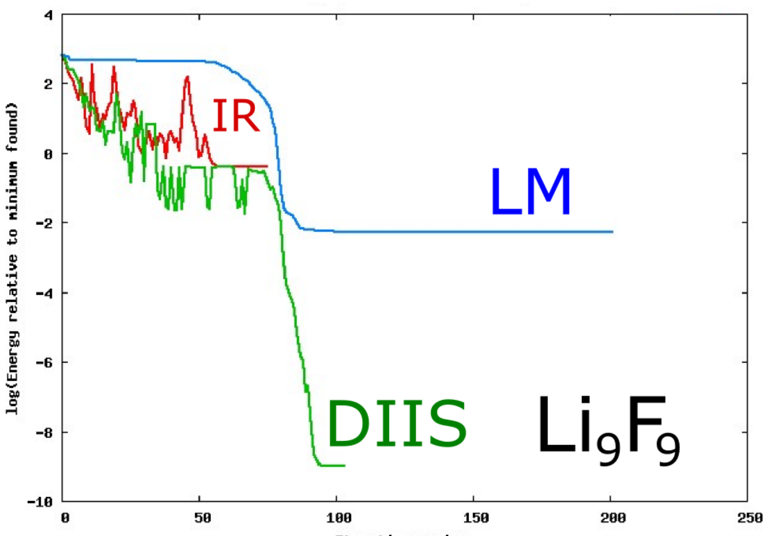
Chemical Example 5



Chemical Example 6



Chemical Example 7



Conclusions

1. The Inexact Restoration approach provides a (globally, quadratically) convergent method for the Closed Shell electronic calculation problem that does not need eigenvalue calculations. IR takes full advantage of the problem structure.
2. Moderate number of CG iterations in the optimality phase, in spite of the large dimension of the tangent space.
3. Eigen-free globally convergent Newton restoration.
4. Its behavior in moderate-size problems is good, when compared with popular alternatives.
5. These facts encourage the implementation for the huge-scale case.