Self-consistent field and direct minimization algorithms for electronic structure

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Introduction

Numerous algorithms exist to solve the Hartree-Fock / Kohn-Sham / Gross-Pitaevskii equations of electronic structure. They are either based on the direct minimization of the energy under constraints or based on fixed point iterations to solve a self-consistent formulation of the problem. It is not clearly understood which class of algorithms is more efficient and robust in which situation.

Objectives

- Prove convergence of both approaches;
- compare algorithms in different situations.

Mathematical framework

We consider a system of N electrons. Given a non-linear discrete energy $E(D) := \mathrm{Tr}(H_0 D) + E_{\mathrm{nl}}(D)$ depending on the model, we have two approaches to the problem:

- using density matrices:

$$\inf_{D \in \mathcal{M}_N} E(D) = \mathrm{Tr}(H_0 D) + E_{\mathrm{nl}}(D),$$

$$\mathcal{M}_N := \left\{ D \in \mathbb{C}^{N_b \times N_b},\ D = D^*,\ \mathrm{Tr}(D) = N,\ D^2 = D \right\}.$$

- using molecular orbitals:

$$\begin{cases} (H_0 + \nabla E_{\mathrm{nl}}(D))\phi_i = \varepsilon_i \phi_i,\ \varepsilon_1 \leqslant \dots \leqslant \varepsilon_N \\ \phi_i^* \phi_j = \delta_{ij}, \\ D = \displaystyle\sum_{i=1}^N \phi_i \phi_i^*. \end{cases}$$

Mathematical setting:

- $F(D) = H_0 + \nabla E_{\mathrm{nl}}(D) = \nabla E(D)$ is the Fock matrix;
- Π_D is the orthogonal projection on the tangent plane $\mathcal{T}_D \mathcal{M}_N$

$$\mathcal{T}_D \mathcal{M}_N := \left\{ h = \begin{pmatrix} 0 & h_{ia} \\ h_{ai} & 0 \end{pmatrix} \right\};$$

- R is a retraction onto $\mathcal{M}_N$ s.t. $R(D + \delta D) = D + \Pi_D \delta D + O(\delta D^2)$ for $D \in \mathcal{M}_N$.

Projected gradient descent

Iteration:

$$\nabla_{\mathcal{M}} E(D^k) := \Pi_D(\nabla E(D^k))$$

$$D^{k+1} := R\left(D^k - \beta_k \nabla_{\mathcal{M}} E(D^k)\right)$$

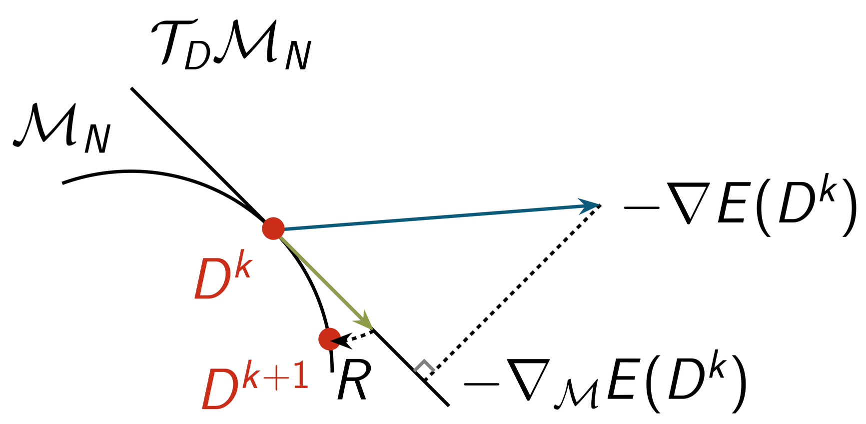

Figure 1: Projected gradient.

Damped SCF

Iteration:

$$\begin{cases} F(D^k)\phi_i^k = \varepsilon_i^k \phi_i^k,\ \varepsilon_1^k \leqslant \dots \leqslant \varepsilon_N^k < \varepsilon_{N+1}^k \\ (\phi_i^k)^* \phi_j^k = \delta_{ij}, \end{cases}$$

$$\mathcal{A}(D^k) := \sum_{i=1}^N \phi_i^k \left(\phi_i^k\right)^*$$

$$D^{k+1} := R\left(D^k + \beta_k \left(\mathcal{A}(D^k) - D^k\right)\right)$$

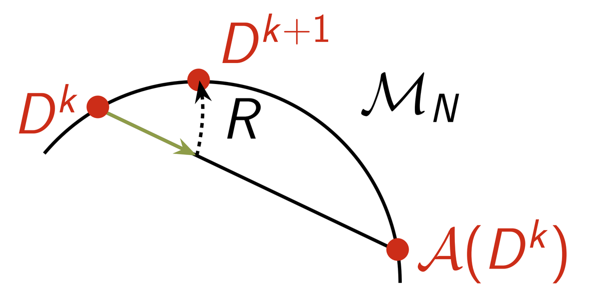

Figure 2: Damped SCF.

Convergence of projected gradient

Assume that the problem $\min_{D \in \mathcal{M}_N} E(D)$ has a non-degenerate minimum: $\forall\ D \in \mathcal{M}_N$ close to $D_{\min}$

$$E(D) \geq E(D_{\min}) + \eta D - D_{\min}{}^2, \quad \eta > 0.$$

Then, if D^0 is close enough to $D_{\min}$, the iteration

$$D^{k+1} := R\left(D^k - \beta \nabla_{\mathcal{M}} E(D^k)\right)$$

converges to $D_{\min}$ for $\beta > 0$ small enough.

Sketch of proof: Banach fixed point theorem on $f : D \mapsto R(D - \beta \Pi_D(\nabla E(D)))$ and show that $J_f(D_{\min})|_{\mathcal{T}_{D_{\min}}\mathcal{M}_N} < 1$:

1. second order condition on the Lagrangian:

$$\nabla^2_{\mathcal{M}} E(D_{\min}) = \nabla^2 E(D_{\min}) + \mathcal{O} \geq \eta > 0$$

where $\mathcal{O} : \mathcal{T}_{D_{\min}}\mathcal{M}_N \to \mathcal{T}_{D_{\min}}\mathcal{M}_N$ multiplies both h_{ia} and h_{ai} by $\varepsilon_a - \varepsilon_i$ and represents the influence of the curvature on the Hessian;

2. the Jacobian at $D_{\min}$ on the tangent plane $\mathcal{T}_{D_{\min}}\mathcal{M}_N$ is $\mathrm{Id} - \beta\left(\nabla^2 E + \mathcal{O}\right)$ and is smaller than 1 for $\beta > 0$ small enough.

Convergence of damped SCF

Assume that the problem $\min_{D \in \mathcal{M}_N} E(D)$ has a non-degenerate minimum: $\forall\ D \in \mathcal{M}_N$ close to $D_{\min}$

$$E(D) \geq E(D_{\min}) + \eta D - D_{\min}{}^2, \quad \eta > 0,$$

and that $F(D_{\min})$ has a gap $\varepsilon_N < \varepsilon_{N+1}$. Then, if D^0 is close enough to $D_{\min}$, the iteration

$$D^{k+1} := R\left(D^k + \beta\left(\mathcal{A}(D^k) - D^k\right)\right)$$

is well defined and converges to D_{min} for $\beta > 0$ small enough.

Sketch of proof: Banach fixed point theorem on $f : D \mapsto R(D + \beta(\mathcal{A}(D) - D))$ and show that J_f on the tangent plane has a spectral radius $r\left(J_f(D_{\min})|_{\mathcal{T}_{D_{\min}}\mathcal{M}}\right) < 1$:

1. compute the Jacobian of $\mathcal{A}$ *on* $\mathcal{T}_{D_{\min}}\mathcal{M}_N$ with a perturbation method:

$$J_{\mathcal{A}}(D_{\min}) = -\mathcal{O}^{-1}\nabla^2 E(D_{\min})$$

where $\mathcal{O}$ is the same as before $\Rightarrow J_{\mathcal{A}}$ has eigenvalues < 1;

2. the Jacobian at $D_{\min}$ on the tangent plane $\mathcal{T}_{D_{\min}}\mathcal{M}_N$ is $\mathrm{Id} - \beta(\mathrm{Id} + \mathcal{O}^{-1}\nabla^2 E)$ which has spectral radius smaller than 1 for $\beta > 0$ small enough.

Comparison of both approaches

Both algorithms have Jacobian of the form $\mathrm{Id} - \beta J \to$ we want the eigenvalues of J to be as close to 1 as possible. In both cases:

- Gradient descent: $J = \nabla^2 E + \mathcal{O}$
- SCF: $J = \mathrm{Id} + \mathcal{O}^{-1}\nabla^2 E$

→ Small gap will make SCF difficult to converge, but it doesn't mean that the gradient is bad in this situation!

→ The SCF can be seen as a matrix splitting method for the first algorithm.

References

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[2] E. Cancès and C. Le Bris. On the convergence of SCF algorithms for the Hartree-Fock equations. *ESAIM: Mathematical Modelling and Numerical Analysis*, 34(4):749–774, July 2000.