Exploiting the Hessian for a better convergence of the SCF RDMFT procedure

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One-body reduced density matrix functional theory (1RDMFT) provides an alternative to Density Functional Theory, able to accurately treat static correlation[1] while keeping a relatively low computation scaling. However, this method is still not widely applied by the community because of its disadvantageous cost, which comes mainly from a slow convergence of the self-consistent energy minimization.[2] To improve on that problem, we propose to use the Hessian of the energy.[3] We include in that Hessian, the coupling term between natural orbitals and natural occupations, the variables optimized by the SCF RDMFT procedure. We show that using the exact Hessian is very effective in improving the convergence. However, since its computation would be too expensive to use in practice, we retain on affordable part of this exact Hessian. We then derive and test different variants of the BFGS update to approximate the remaining part of the Hessian.

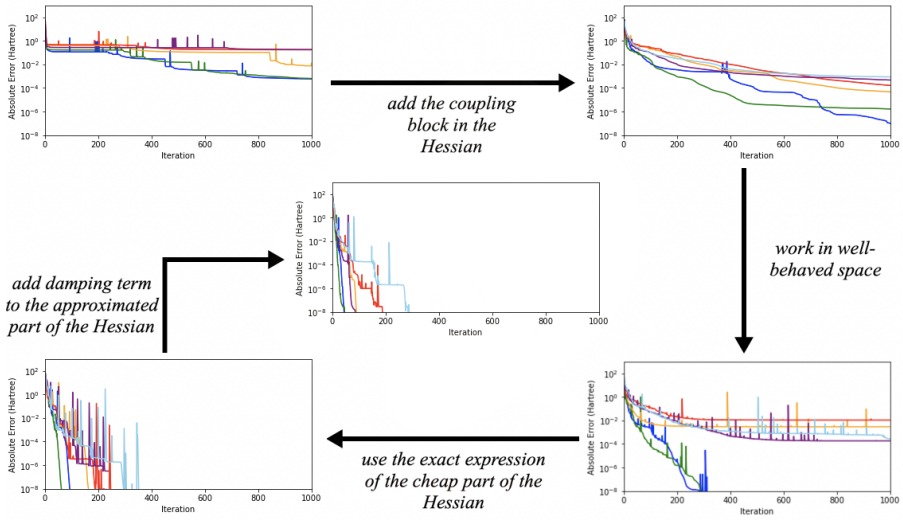

Figure 1. Energy convergence (absolute error with respect to the iterations) for increasingly efficient SCF algorithms in RDMFT, starting from a 'naive' algorithm. The different colors correspond to the convergence of different molecules (dark blue for H_2O, green for CH_4, orange for CH_3OH, red for C_2H_6, purple for HF and light blue for N_2).

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References

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