Diagonalization-free Energy Calculations: Hartree-Fock and Beyond

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In the development of linear scaling algorithms to find the Hartree-Fock solution, special attention has been paid to avoid large eigenproblems. One branch of the proposed schemes apply a direct iteration procedure for the one-electron density matrix P for which preservation of the N-representability conditions should be ensured. Recently, we have proposed a new type of iteration procedure for P, which can be programmed in a linear-scaling fashion using sparse matrix technology, and which preserves the idempotency and the trace of the initial density matrix, while the converged results are shown to be Hermitian. The algorithm has been implemented both at the tight-binding and ab initio Hartree-Fock or Kohn-Sham levels, and its linear scaling feature has been numerically demonstrated.

While the algorithm is very effective in many cases (it can e.g. treat 40 000 basis functions on a PC, if P is sufficiently sparse), convergence difficulties can sometimes occur. To understand these, stability analysis has been carried out at the fixpoints, and the Ljapunov exponents have been determined. These lead to practical considerations on how to avoid chaotic behaviour of the iteration procedure.

Having obtained an idempotent one matrix P, the question of estimating the correlation energy is addressed. One possibility is to use some kind of density functional theory, where, at least in the Kohn-Sham scheme, the one matrix is kept idempotent. Another possibility is to use many-body perturbation theory. Very recently we have shown that the n-th order energy in the Moller-Plesset partitioning can be written as a functional of the Hartree-Fock P matrix, and for the MP2 energy this functional has been explicitly constructed. This means that it is possible to evaluate the MPn energy even in the absence of MO coefficients and canonical orbital energies.

References:

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