Variational optimization of second order density matrices: the past, the present and the future

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The exponential growth of the dimension of the exact wavefunction with the size of a chemical system makes it impossible to compute chemical properties of large chemical systems exactly. A myriad of ab initio methods that use simpler mathematical objects to describe the system have thrived on this realization, among which the variational second order density matrix method [1]. This talk will give an overview of the major theoretical and computational challenges for this method for applications in chemistry.

The main theoretical challenge is to overcome the method's inability to describe ensembles with fractional electron number or spin[1,2] under approximate N- and S-representability conditions[3]. This leads to a problematic description of, for instance, molecular dissociation, transition states and spin degeneracy. Additionally, approximate N-representability conditions make the method size-inconsistent. We have derived subspace energy constraints that fix these problems, albeit in an ad-hoc manner.

The main computational challenge is to find an efficient implementation for the variational optmization subject to semidefinite constraints for N-representability. We have implemented and compared several optimization algorithms. Even though our implementations exploited the specific structure of the problem, their slow speed remains prohibitive. All of the methods that we have tried performed quite similar, which suggests that the underlying problem responsible for their slow convergence, ill-conditioning due to singularity of the optimal second order density matrix, manifests itself in all of these algorithms.

References:

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