

## 密度行列の直接決定法: 簡単なハミルトニアンなのに全く 相関エネルギーが出ない例

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In the ground state calculations of electronic systems, we only need the second-order reduced density matrices (2RDMs) for the energies and other important physical properties, since it only involves one- and two- body interactions. There are some advantages with this method: (i) 2RDMs have only four variables regardless of the number of electrons in the system whereas the wave function has  $N$  variables; (ii) for ground state, we need to minimize a linear functional. Thus there is a hope that we can construct more efficient method than traditional wavefunction methods. The 2RDM is characterized by so-called  $N$ -representability condition [1], which corresponds to the Pauli principle, and the condition is the major obstacle for this scheme.

Unfortunately,  $N$ -representability condition is shown to be NP-hard [2], thus we need a good approximation. Well-known necessary conditions P, Q [1] and G [3] are all of positive semidefinite type involving the 2RDM, and preliminary studies in 1960s showed promising results but somehow faded away. The reasons might be (i) there was no systematic way to do the calculations, and (ii) lack of computational resources.

In 2001 M. Nakata *et al.* [4] showed the result of variational calculation over well-known approximate  $N$ -representable conditions: P, Q and G using the well established semidefinite programming solver and applied to various realistic molecules, atoms, and potential energy surfaces as well [5]. The results were very promising as correctly reproduced the dissociation limit, but usually slightly worse than the chemical accuracy.

Then, in 2004, Z. Zhao *et al.*, implemented other positive semidefinite type conditions called T1 and T2 [6], which were hidden in Erdahl's work in 1978 [7]. The accuracy of approximations are improved considerably; almost the same with CCSD(T), thus this method archived the spectroscopic accuracy.

In this study [8], however, we found that with some simple Hamiltonians

without electron-electron correlation, this method failed drastically with P, Q, G, T1 and T2 conditions. Motivation is following.

1. Using one-particle Hamiltonian as test case, so that the solution is known.
2. Obtain excited states for this Hamiltonian by MacDonald's variational principle, then the problem becomes the eigenvalue problem of two-particle Hamiltonian.
3. We expect P, Q, G, T1 and T2 are strong; typical accuracy is comparable to CCSD(T).

The results show that in some cases, P, Q, G conditions calculated spurious excited states, in some cases, even adding T2 conditions, the results didn't improve at all. We conjecture that obtaining the excited states via variational calculations of 4-RDMs with P, Q, G, T1, T2 like conditions might not work; also continuous excited states as well.

- [1] A. J. Coleman, Rev. Mod. Phys. **35**, 668(1963).
- [2] Y. Liu, M. Christandl, and F. Verstraete, Phys. Rev. Lett **98**, 110503 (2007).
- [3] C. Garrod, J.K. Percus, J. Math. Phys., **5**, 1756 (1964).
- [4] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, K. Fujisawa, J. Chem. Phys. **114**, 8282(2001).
- [5] M. Nakata, M. Ehara, H. Nakatsuji, J. Chem. Phys. **116**, 5432(2002).
- [6] Z. Zhao, B.J. Braams, M. Fukuda, M. Overton, J.K. Percus. J. Chem. Phys. **120**, 2095(2004).
- [7] R. M. Erdahl: Representability. Int. J. Quantum Chem. **13**, 697(1978).
- [8] M. Nakata, B.J. Braams, M. Fukuda, J.K. Percus, M. Yamashita, Z. Zhao, J. Chem. Phys. **125**, 244109(2006).