N-representability Condition and Development of Accurate Semidefinte Solver.

M. Nakata[a], B. J. Braams[b], K. Fujisawa[c], M. Fukuda[d], J. K. Percus[e], M. Yamashita[f] and Z. Zhao[g]

RIKEN[a], Emory University[b], Chuo University[c], Tokyo Institute of Technology [d], New York University [e], Kanagawa University [f], Lawrence Berkeley National Laboratory [g]

email: maho@riken.jp

Also visit : **PP 060 Mituhiro Fukuda** *et al.* : "Using a Black-Box Optimization Software to Determine the Second-Order Reduced Density Matrices of Atoms and Molecules by N-representability conditions"

Abstract

The RDM method has been applied to various small atoms and molecular systems. We used $PQGT1$ along with newly formulated $T2'$ as the best approximation to the N-representability conditions, and solved accrately, within theoretical criteria. Also we show some results of the one-dimensional Hubbard model of high correlation limit using multiple precision arithmetic version of solver [1]. See also PP060: M. Fukuda's poster for details.

Introduction

For the ground state energy and properties of many-particle fermion systems within two-particle interactions, the Hamiltonian of the system can be written as:

$$H = \sum_{ij} v^i_j a^\dagger_i a_j + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w^{i_1 i_2}_{j_1 j_2} a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1}$$

where v and w are the 1- and 2-particle operators and a and $a^\dagger$ are annihilation and creation operators, respectively. The total energy E can be expressed by

$$\begin{aligned} E &= \sum_{ij} v^i_j \langle \Psi | a^\dagger_i a_j | \Psi \rangle + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w^{i_1 i_2}_{j_1 j_2} \langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1} | \Psi \rangle \\ &= \sum_{ij} v^i_j \gamma^i_j + \sum_{i_1 i_2 j_1 j_2} w^{i_1 i_2}_{j_1 j_2} \Gamma^{i_1 i_2}_{j_1 j_2} \end{aligned}$$

where $|\Psi\rangle$ is some N-particle state, γ and Γ are the first- and second- reduced density matrices (1,2-RDMs) defined by

$$\gamma^i_j = \langle \Psi | a^\dagger_i a_j | \Psi \rangle,$$

and

$$\Gamma^{i_1 i_2}_{j_1 j_2} = \frac{1}{2!} \langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1} | \Psi \rangle.$$

The knowledge of the second-order reduced density matrix (2-RDM) is known to be sufficient to describe all the physical quantities [2]. Besides, the number of variables in the 2-RDM is always four regardless of the number of particles involved, whereas for the wavefunction this number scales linearly. This fact motivated us to use the 2-RDM as a basic variable, and determine it directly instead of using the wavefunction.

The RDM method

The ground state energy E_g will be obtained by minimizing the Hamiltonian with respect of using 1, 2-RDMs:

$$E_g = \min_{\Gamma, \gamma} \{ \sum_{ij} v^i_j \gamma^i_j + \sum_{i_1 i_2 j_1 j_2} w^{i_1 i_2}_{j_1 j_2} \Gamma^{i_1 i_2}_{j_1 j_2} \}.$$

We call this scheme as "the RDM method". And subsidiary condition called "N-representability condition" [3].

$$\Gamma(12|1'2') \Longrightarrow \Psi(1, 2, \cdots, N)?$$

This condition is very important. Without that, obtained energy becomes too *low* and 2-RDM becomes non-physical.

Known N-representability conditions

The P, Q, G, $T1$ and $T2$ conditions state that P, Q, G, $T1$ and $T2$- matrices defined as below are all positive semidefinite.

$$\begin{aligned} P^{i_1 i_2}_{j_1 j_2} &= \langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1} | \Psi \rangle, \\ Q^{i_1 i_2}_{j_1 j_2} &= \langle \Psi | a_{i_1} a_{i_2} a^\dagger_{j_2} a^\dagger_{j_1} | \Psi \rangle, \\ G^{i_1 i_2}_{j_1 j_2} &= \langle \Psi | a^\dagger_{i_1} a_{i_2} a^\dagger_{j_2} a_{j_1} | \Psi \rangle, \\ (T1)^{i_1 i_2 i_3}_{j_1 j_2 j_3} &= \langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} a^\dagger_{i_3} a_{j_3} a_{j_2} a_{j_1} + a_{i_1} a_{i_2} a_{i_3} a^\dagger_{j_3} a^\dagger_{j_2} a^\dagger_{j_1} | \Psi \rangle, \\ (T2)^{i_1 i_2 i_3}_{j_1 j_2 j_3} &= \langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} a_{i_3} a^\dagger_{j_3} a_{j_2} a_{j_1} + a_{i_1} a_{i_2} a^\dagger_{i_3} a_{j_3} a^\dagger_{j_2} a^\dagger_{j_1} | \Psi \rangle. \end{aligned}$$

Semidefinite programming

In 2001, Nakata *et al.* realized that the RDM method with P, Q, G-conditions can be formulated for the SDPA (general purpose semidefinite programming solver) [5], like following:

$$\begin{cases} \max & \langle C, X \rangle \\ \text{subject to} & \langle A_p, X \rangle = [b]_p, \ (p = 1, 2, \ldots, m) \\ & X \succeq O, \end{cases}$$

and solved for many small atoms and molecules. SDPA has nice features

- The accuracy of the obtained energy and 2-RDM are guaranteed by duality theorem.
- Polynomial order algorithm (lighter than fullCI).
- Relatively good convergence.

Details and variant of this formulation can be found in PP060: M. Fukuda's poster.

N-representability is very difficult...

After a long efforts, the decision problem "Is a 2-RDM N-representable or not?" is shown to be QMA-complete, thus NP-hard [4]. We cannot solve this problem even we use quantum computer! This fact shows us that we must choose physically and/or chemically important approximations.

But, we know chemically/physically good approximations to N-representability!

In 2004, Zhao *et al.* implemented $T1$ and $T2$ N-representability conditions implicitly stated in Eradahl's 1978 paper [6]. This is a second breakthrough! This is sufficient accuracy to do Chemistry: comparable to CCSD(T) at equilibrium geometry as well as ability of describing dissociation limit. The qualities of approximations are summarized as follows:

Method	Correlation	Dissociation limit
PQG	$100 \sim 120\%$	yes
$PQGT1T2$	$100 \sim 101\%$	yes
CCSD(T)	$100 \sim 101\%$	no

NEW $T2'$ N-representability condition

Braaams *et al* [8] and Mazziotti [7] formulated $T2'$ condition as follows:

$$T2' = \begin{pmatrix} T2 & X \\ X^\dagger & \gamma \end{pmatrix}.$$

This matrix has $T2$-matrix and the 1-RDM γ at the diagonal, and X is defined as

$$X^k_{i_1 i_2 i_3} = \Gamma^{i_1 k}_{i_2 i_3}.$$

Results for atoms and molecules

System	State	N	r	ΔE_{GT1T2}	$\Delta E_{GT1T2'}$	$\Delta E_{CCSD(T)}$	ΔE_{HF}	E_{FCI}
C	^3P	6	20	−0.0004	−0.0001	+0.00016	+0.05202	−37.73653
O	^1D	8	20	−0.0013	−0.0012	+0.00279	+0.10878	−74.78733
Ne	^1S	10	20	−0.0002	−0.0001	−0.00005	+0.11645	−128.63881
O_2^+	$^2\Pi_g$	15	20	−0.0022	−0.0020	+0.00325	+0.17074	−148.79339
BH	$^1\Sigma^+$	6	24	−0.0001	−0.0001	+0.00030	+0.07398	−25.18766
CH	$^2\Pi_r$	7	24	−0.0008	−0.0003	+0.00031	+0.07895	−38.33735
NH	$^1\Delta$	8	24	−0.0005	−0.0004	+0.00437	+0.11495	−54.96440
HF	$^1\Sigma^+$	14	24	−0.0003	−0.0003	+0.00032	+0.13834	−100.16031
SiH_4	$^1A_1$	18	26	−0.0002	−0.0002	+0.00018	+0.07311	−290.28490
F^-	^1S	10	26	−0.0003	−0.0003	+0.00067	+0.15427	−99.59712
P	^4S	15	26	−0.0001	−0.0000	+0.00003	+0.01908	−340.70802
H_2O	$^1A_1$	10	28	−0.0004	−0.0004	+0.00055	+0.14645	−76.15576

GT1T2 :the RDM Method ($P, Q, G, T1, T2$ condition)
GT1T2' :the RDM Method ($P, Q, G, T1, T2'$ conditions)
CCSD(T):Coupled cluster singles and doubles with perturbational treatment of triples
HF :Hartree-Fock
FCI :FullCI

Hubbard model and multiple precision arithmetic version of SDPA (SDPA-GMP)

The Hubbard model is fundamental model of the electron correlation (U/t controls the electron correlation).

$$H = -t \sum_{\langle i,j \rangle} \sum_{\sigma=\uparrow,\downarrow} a^\dagger_{i,\sigma} a_{j,\sigma} + U \sum_{j=1}^{L} a^\dagger_{j,\uparrow} a_{j,\uparrow} a^\dagger_{j,\downarrow} a_{j,\downarrow}$$

For the high correlation limit $|U/t| \to \infty$, all states are degenerated, and "double " which has about 16 significant digits

$$1.00000000000000001 \simeq 1$$

cannot handle such problems. Brute force method to workaround this difficulty, we implemented SDPA-GMP [9]. Using the GMP library (GNU Multiple Precision Arithmetic Library), we can calculate in arbitrary precision. We used 60 significant digits for this case:

$$1.000000000000000000000000000000000000000000000000000001 \simeq 1.$$

The ground state energies of 1D Hubbard model

PBC, # of sites :4, # of electrons: 4, spin 0

U/t	SDPA (double)	SDPA-GMP (PQG)	fullCI
10000.0	0	$-1.1999998800000251 \times 10^{-3}$	$-1.199999880 \times 10^{-3}$
1000.0	-1.2×10^{-2}	$-1.1999880002507934 \times 10^{-2}$	$-1.1999880002 \times 10^{-2}$
100.0	-1.1991×10^{-1}	$-1.1988025013717993 \times 10^{-1}$	$-1.19880248946 \times 10^{-1}$
10.0	-1.1000	-1.0999400441222934	-1.099877772750
1.0	-3.3417	-3.3416748070259956	-3.340847617248

PBC, # of sites:6, # of electrons: 6, Spin 0

U/t	SDPA (double)	SDPA-GMP (PQGT1T2)	fullCI
10000.0	0	$-1.7249951195749525 \times 10^{-3}$	$-1.721110121 \times 10^{-3}$
1000.0	-1×10^{-2}	$-1.7255360310431304 \times 10^{-2}$	$-1.7211034713 \times 10^{-2}$
100.0	-1.730×10^{-1}	$-1.7302157140594339 \times 10^{-1}$	$-1.72043338097 \times 10^{-1}$
10.0	-1.6954	-1.6953843276854447	-1.664362733287
1.0	-6.6012	-6.6012042217806286	-6.601158293375

Conclusion

The RDM method with $PQGT1T2'$ were very good for the ground state energies of atoms and molecules and the $T2'$ condition gave improvements in several sub-mHartree. We also implemented the multiple arithmetic version of SDPA, SDPA-GMP, which was used for the one dimensional Hubbard model and obtained extremely accurate energies. In particular, for the Hubbard model with high correlation limit, large $|U/t|$, we obtained at least sixteen significant figures whereas the ordinal method gave only two to four significant figures.

References

[1] M. Nakata, K. Fujisawa, B. J. Braams, M. Fukuda, J. K. Percus, M. Yamashita, and Z. Zhao, J. Chem. Phys. **128**, (2008), 164113.

[2] K. Husimi, Proc. Phys. Math. Soc. Jpn. **22**, (1940) 264, P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955), J. E. Mayer, Phys. Rev. **100**, 1579 (1955), R. H. Tredgold, Phys. Rev. **105**, 1421 (1957).

[3] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).

[4] M. M. Deza, and M. Laurent, *Geometry of Cuts and Metrics*, (Springer-Verlag, Berlin, 1997), Y. Liu, M. Christandl, and F. Verstraete, Phys. Rev. Lett. **98**, 110503 (2007).

[5] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, J. Chem. Phys. **114**, 8282 (2001).

[6] Z. Zhao, B. J. Braams, M. Fukuda, M. L. Overton, and J. K. Percus, J. Chem. Phys. **120**, 209 5 (2004).

[7] D. A. Mazziotti ed., *Reduced-Density-Matrix Mechanics: With Applications to Many-Electron Atoms and Molecules*, Advances in Chemical Physics Vol. 134, (Wiley, New York, 2007).

[8] B. J. Braams, J. K. Percus, and Z. Zhao, in [7], 93.

[9] You can download the latest version of SDPA-GMP : http://sdpa.indsys.chuo-u.ac.jp/sdpa/download.html