The Reduced Density Matrix Method: Applications of the $T2'$ N-Representability Condition and Development of Accurate Semidefinite Solver

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Abstract

We are interested in realizing the variational calculation with the 2-order Reduced Density Matrix (2-RDM) for fermionic systems. The known necessary N-representability conditions P, Q, G, $T1$, and $T2'$ are imposed, resulting in an optimization problem called semidefinite programming (SDP) problem. The ground state energies for various small atoms and molecules were calculated [3]. Additionally, we show some results of the one-dimensional Hubbard model for high correlation limit using multiple precision arithmetic version of the solver [3].

1. The Reduced Density Matrix Method

The Hamiltonian of an N-particle fermionic system in the second quantized form is:

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

Then, the total energy of some N-particle state $|\Psi\rangle$ is given by:

$$\begin{aligned} E &= \langle\Psi|H|\Psi\rangle = \sum_{ij} v^i_j \gamma^i_j + \sum_{i_1 i_2 j_1 j_2} w^{i_1 i_2}_{j_1 j_2} \Gamma^{i_1 i_2}_{j_1 j_2} \\ &= \mathrm{tr}(\boldsymbol{v}\boldsymbol{\gamma}) + \mathrm{tr}(\boldsymbol{w}\boldsymbol{\Gamma}), \end{aligned}$$

where $\boldsymbol{\gamma}$ is the One-particle Reduced Density Matrix (1-RDM):

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

and $\boldsymbol{\Gamma}$ is the Two-particle Reduced Density Matrix (2-RDM):

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

The ground state energy E_g can be obtained by:

$$E_g = \min_{\Psi} \langle\Psi|H|\Psi\rangle = \min_{\boldsymbol{\gamma},\boldsymbol{\Gamma}} \{\mathrm{tr}(\boldsymbol{v}\boldsymbol{\gamma}) + \mathrm{tr}(\boldsymbol{w}\boldsymbol{\Gamma})\},$$

where the wavefunction Ψ must satisfy the antisymmetry condition:

$$\Psi(1,2,\ldots,i,\ldots,j,\ldots,N) = -\Psi(1,2,\ldots,j,\ldots,i,\ldots,N).$$

The notion of the N-representability for the 2-RDM (and 1-RDM) is understood as follows.

> Given an 2-RDM $\boldsymbol{\Gamma}$ (and an 1-RDM $\boldsymbol{\gamma}$), there exists some wavefunction (pure representability) or some von Neumann density matrix (ensemble representability) corresponding to it.

Therefore, in principle, we can determine the ground state energy solving the following variational calculation for the unknowns $\boldsymbol{\gamma}$ and $\boldsymbol{\Gamma}$.

$$\begin{cases} \textbf{minimize} & \mathrm{tr}(\boldsymbol{v}\boldsymbol{\gamma}) + \mathrm{tr}(\boldsymbol{w}\boldsymbol{\Gamma}) \\ \textbf{subject to} & \boldsymbol{\gamma}, \boldsymbol{\Gamma} \in N\text{-representable set} \end{cases}$$

2. Known N-Representability Conditions

The following N-representability conditions of semidefinitiness type are known:

P: $2\Gamma^{i_1 i_2}_{j_1 j_2}$ — Coleman 1963

Q: $(\delta^{i_1}_{j_1}\delta^{i_2}_{j_2} - \delta^{i_1}_{j_2}\delta^{i_2}_{j_1}) - (\delta^{i_1}_{j_1}\gamma^{i_2}_{j_2} + \delta^{i_2}_{j_2}\gamma^{i_1}_{j_1}) + (\delta^{i_1}_{j_2}\gamma^{i_2}_{j_1} + \delta^{i_2}_{j_1}\gamma^{i_1}_{j_2}) + 2\Gamma^{i_1 i_2}_{j_1 j_2}$ — Coleman 1963

G: $\delta^{i_2}_{j_2}\gamma^{i_1}_{j_1} - 2\Gamma^{i_1 j_2}_{j_1 i_2}$ — Garrod-Percus 1964

kth-order approximation: — Erdahl-Jin 2000

$T1$: $\mathcal{A}[i_1,i_2,i_3]\mathcal{A}[j_1,j_2,j_3]\left(\frac{1}{6}\delta^{i_1}_{j_1}\delta^{i_2}_{j_2}\delta^{i_3}_{j_3} - \frac{1}{2}\delta^{i_1}_{j_1}\delta^{i_2}_{j_2}\gamma^{i_3}_{j_3} + \frac{1}{2}\delta^{i_1}_{j_1}\Gamma^{i_2 i_3}_{j_2 j_3}\right)$ — Erdahl 1978, Zhao *et al.* 2004

$T2$: $\mathcal{A}[i_2,i_3]\mathcal{A}[j_2,j_3]\left(\frac{1}{2}\delta^{i_2}_{j_2}\delta^{i_3}_{j_3}\gamma^{i_1}_{j_1} + \frac{1}{2}\delta^{i_1}_{j_1}\Gamma^{j_2 j_3}_{i_2 i_3} - 2\delta^{i_2}_{j_2}\Gamma^{i_1 i_3}_{j_1 i_3}\right)$ — Erdahl 1978, Zhao *et al.* 2004

$T2'$: $\begin{pmatrix} T2 & X \\ X^\dagger & \gamma \end{pmatrix}$ where $X^k_{i_1 i_2 i_3} = \Gamma^{i_1 k}_{i_2 i_3}$ — Erdahl 1978, Braams-Percus-Zhao 2007, Mazziotti 2006,2007

where $\mathcal{A}[i,j,k]f(i,j,k) = f(i,j,k) - f(i,k,j) - f(j,i,k) + f(j,k,i) + f(k,i,j) - f(k,j,i)$ and δ^i_j is the Kronecker's delta.

3. The N-Representability Problem is Extremely Difficult

Unfortunately, it is well-known that determining all the sufficient N-representability conditions is extremely difficult. If we restrict ourselves to determine only the N-representability conditions for the diagonal elements of the 2-RDM, the problem is equivalent to determining all the facets of the cut polytope, which is NP-hard [1]. More recently, it was shown that deciding if a given 2-RDM is N-representable or not is QMA-complete [2], thus NP-hard.

4. Variational Calculation by Semidefinite Programming Problems

If we only impose the necessary N-representability conditions, we can obtain a lower bound for the ground state energy and approximated 1- and 2-RDMs [3].

$$\begin{cases} \textbf{minimize} & \mathrm{tr}(\boldsymbol{v}\boldsymbol{\gamma}) + \mathrm{tr}(\boldsymbol{w}\boldsymbol{\Gamma}) \\ \textbf{subject to} & P, Q, G, T1, T2' \\ & \text{conditions on } \boldsymbol{\gamma} \text{ and } \boldsymbol{\Gamma} \end{cases}$$

5. Semidefinite Programming Problems and Interior-Point Methods

The primal SDP problem is defined as follows:

$$\texttt{Primal} \begin{cases} \textbf{minimize} & \sum_{i=1}^{\ell} \mathrm{tr}(\boldsymbol{C}_i \boldsymbol{X}_i) \\ \textbf{subject to} & \sum_{i=1}^{\ell} \mathrm{tr}(\boldsymbol{A}_{ip} \boldsymbol{X}_i) = b_p, \quad (1 \le p \le m) \\ & \boldsymbol{X}_i \succeq O, \quad (1 \le i \le \ell) \end{cases}$$

and the *equivalent* dual SDP problem as follows:

$$\texttt{Dual} \begin{cases} \textbf{maximize} & \sum_{p=1}^{m} b_p y_p \\ \textbf{subject to} & \sum_{p=1}^{m} \boldsymbol{A}_{ip} y_p + \boldsymbol{S}_i = \boldsymbol{C}_i, \quad (1 \le i \le \ell) \\ & \boldsymbol{S}_i \succeq \boldsymbol{O}, \quad (1 \le i \le \ell) \end{cases}$$

where $\boldsymbol{C}_i, \boldsymbol{A}_{i1}, \cdots, \boldsymbol{A}_{im} \in \mathcal{S}^{n_i}$ $(1 \le i \le \ell)$, $\boldsymbol{b} \in \mathbb{R}^m$ are given data, $\mathcal{S}^n$ is the space of $n \times n$-symmetric matrices, and $\boldsymbol{X} \succeq \boldsymbol{O}$ means that $\boldsymbol{X}$ is symmetric positive.

It is known that SDP problems can be solved very efficiently by primal-dual interior-point methods.

6. Formulation in Dual SDP Formulation

After some inspection, it becomes clear that the most advantageous formulation is to formulate as the dual SDP format [3, 5]. For that, it is necessary to view each coordinate of the variables, that is, 1-RDM $\boldsymbol{\gamma}$ and 2-RDM $\boldsymbol{\Gamma}$, as the coordinates of the dual variable vector $\boldsymbol{y}$.

7. SDP Sizes in Dual SDP Formulation

r	m	s	P,Q,G n_i(max)	$P,Q,G,T1$ n_i(max)	$P,Q,G,T1,T2'$ n_i(max)
8	178	5	32	24	92
10	435	5	50	50	180
12	906	5	72	90	312
14	1687	5	98	147	497
16	2892	5	128	224	744
18	4653	5	162	324	1062
20	7120	5	200	450	1460
22	10461	5	242	605	1947
24	14862	5	288	792	2532
26	20527	5	338	1014	3224
28	27678	5	392	1274	4032
30	36555	5	450	1575	4965

8. Numerical Results

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

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

$GT1T2$:RDM Method ($P,Q,G,T1,T2$ condition)
$GT1T2'$: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

9. Hubbard Model and the Multiple Precision Arithmetic Version of SDPA (SDPA-GMP)

The Hubbard model is a fundamental model for 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. Using the "double" precision which has about 16 significant digits, $1.0000000000000001 \simeq 1$, we cannot handle such problems. We developed the SDPA-GMP [6] which can solve these kind of problems by brute force. Using the GMP library (GNU Multiple Precision Arithmetic Library), we can perform calculations in arbitrary precision. We used 60 significant digits for this case:

$1.000000000000000000000000000000000000000000000000000000001 \simeq 1.$

10. 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 of 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.

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[6] You can download the latest version of SDPA-GMP :

`http://sdpa.indsys.chuo-u.ac.jp/sdpa/download.html`

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