Using a black-box optimization software to determine the second-order reduced density matrices of atoms and molecules by N-representability conditions

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related poster: **PP 089 Maho Nakata** "The Reduced Density Matrix Method: Application of the T2′ N-representability Condition and Development of Accurate Semidefinite Solver"

1. Objective

We are interested in realizing the variational calculation with the 2-order Reduced Density Matrix (2-RDM) for fermionic systems. Some known necessary N-representability conditions are imposed, resulting in an optimization problem called semidefinite programming (SDP) problem. The utilization of exiting software to solve these SDP problems permits one to formulate the problem as a primal SDP problem [6] or as a dual SDP problem [5, 7]. We show here that the dual SDP formulation is advantageous in all computational aspects. This presentation is complemented by the poster presentation PP 089 by Maho Nakata which contains the actual computational results.

2. 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:

$$\begin{aligned} &\Psi(1,2,\ldots,i,\ldots,j,\ldots,N) = \\ &-\Psi(1,2,\ldots,j,\ldots,i,\ldots,N). \end{aligned}$$

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 $\boldsymbol{\Gamma}$.

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

3. 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

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

4. 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 [3], thus NP-hard.

5. 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 [5].

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

6. 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.

The existing software to solve SDP problems are:

- SDPA 7.1.1 (June, 2008)

  K. Fujisawa, M. Fukuda, K. Kobayashi, M. Kojima, K. Nakata, M. Nakata, and M. Yamashita

  http://sdpa.indsys.chuo-u.ac.jp/sdpa/

- SDPARA 1.0.1 (2005)

  K. Fujisawa, M. Kojima, and M. Yamashita

  http://sdpa.indsys.chuo-u.ac.jp/sdpa/

- SeDuMi 1.2 (April, 2008)

  McMaster Group

  http://sedumi.mcmaster.ca/

- SDPT3 4.0β (2006)

  K.-C. Toh, M. J. Todd, and R. H. Tütüncü

  http://www.math.nus.edu.sg/∼mattohkc/sdpt3.html

- CSDP 6.0.1

  B. Borchers

  https://projects.coin-or.org/Csdp/

- PENNON (commercial)

  M. Kocvara, and M. Stingl

  http://www.penopt.com/

7. Primal and Dual SDP Formulations

One of the most important factors to consider when solving these problems using the exiting software is to notice that we can mathematically formulate the SDP problem arising from the RDM Method as a primal SDP formulation [6] or as a dual SDP formulation [5, 7].

8. Example of Primal SDP Formulation for a Fermionic System with N electrons with P and Q conditions on the 2-RDM

Consider the following problem

$$\begin{cases} \textbf{minimize} & \mathrm{tr}(\hat{\boldsymbol{w}}\boldsymbol{\Gamma}) \\ \textbf{subject to} & \mathrm{tr}(\hat{N}\boldsymbol{\Gamma}) = N, \\ & 2\boldsymbol{\Gamma} \succeq \boldsymbol{O}, \quad \boldsymbol{Q} \succeq \boldsymbol{O}, \end{cases}$$

where $\hat{\boldsymbol{w}}$ is the 2-body Hamiltonian, and $\hat{N}$ is the number operator.

We can formulate this problem as a standard SDP formulation using the following simple linear transformations:

$$\begin{cases} \boldsymbol{P} = 2\boldsymbol{\Gamma} \succeq \boldsymbol{O} \\ \boldsymbol{Q} \succeq \boldsymbol{O} \end{cases} \Leftrightarrow \tilde{\boldsymbol{\Gamma}} = \begin{pmatrix} \boldsymbol{\Gamma} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{Q} \end{pmatrix} \succeq \boldsymbol{O}.$$

Let $\tilde{\boldsymbol{w}} = \begin{pmatrix} \hat{\boldsymbol{w}} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{O} \end{pmatrix}$, $\tilde{N} = \begin{pmatrix} \hat{N} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{O} \end{pmatrix}$,

$$\boldsymbol{A}_{i_1 i_2, j_1 j_2} = \begin{pmatrix} \tilde{\boldsymbol{E}}_{i_1 i_2, j_1 j_2} - \boldsymbol{E}_{i_1 i_2, j_1 j_2} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{E}_{i_1 i_2, j_1 j_2} \end{pmatrix},$$

where $\boldsymbol{E}_{i_1 i_2, j_1 j_2} = \begin{cases} 1, & \text{for } (i_1 + (i_2-1)r, i_1 + (i_2-1)r) \\ 1/2, & \text{for } (i_1 + (i_2-1)r, j_1 + (j_2-1)r) \\ 1/2, & \text{for } (j_1 + (j_2-1)r, i_1 + (i_2-1)r), \\ & i_1 < j_1 \end{cases}$

$$\tilde{\boldsymbol{E}}_{i_1 i_2, j_1 j_2} = \frac{\sum_{k=1}^{r} (\delta^{i_1}_{j_1} \boldsymbol{E}_{i_2,k,j_2,k} + \delta^{i_2}_{j_2} \boldsymbol{E}_{i_1 k, j_1 k} - \delta^{i_1}_{j_2} \boldsymbol{E}_{i_2 k, j_1 k} - \delta^{i_2}_{j_1} \boldsymbol{E}_{i_1 k, j_2 k})}{(N-1)},$$

and r is the # of spin orbitals or rank. Then, we have:

$$\begin{cases} \text{minimize} & \mathrm{tr}(\tilde{\boldsymbol{w}}\tilde{\boldsymbol{\Gamma}}) \\ \text{subject to} & \mathrm{tr}(\tilde{N}\tilde{\boldsymbol{\Gamma}}) = N, \\ & \mathrm{tr}(\boldsymbol{A}_{i_1 i_2, j_1 j_2}\tilde{\boldsymbol{\Gamma}}) = \delta^{i_1}_{j_1}\delta^{i_2}_{j_2} - \delta^{i_1}_{j_2}\delta^{i_2}_{j_1}, \ 1 \le i_1 \le j_1 \le r \\ & \qquad\qquad 1 \le i_2 \le j_2 \le r \\ & \tilde{\boldsymbol{\Gamma}} \succeq \boldsymbol{O}. \end{cases}$$

which is in primal SDP formulation.

9. SDP Sizes in Primal SDP Formulation

	dimensions of matrices n_i
P	$(r/2)^2 \times (r/2)^2$ (1 block), $\binom{r/2}{2} \times \binom{r/2}{2}$ (2 blocks)
Q	$(r/2)^2 \times (r/2)^2$ (1 block), $\binom{r/2}{2} \times \binom{r/2}{2}$ (2 blocks)
G	$2(r/2)^2 \times 2(r/2)^2$ (1 block), $(r/2)^2 \times (r/2)^2$ (2 blocks)
	# of constraints m
P,Q,G	$5 + 3\binom{r^2/4+1}{2} + 2\binom{r(r/2-1)/4+1}{2} + \binom{r^2/2+1}{2}$

where $\binom{a}{b} = (a!)/(b!(a-b)!)$, r spin orbitals or rank.

That is:

	P,Q,G		$P,Q,G,T1$		$P,Q,G,T1,T2'$	
r	m	n_i(max)	m	n_i(max)	m	n_i(max)
8	983	32	1603	24	10971	92
10	2365	50	5025	50	40685	180
12	4871	72	13481	90	120449	312
14	8993	98	32009	147	303385	497
16	15313	128	68905	224	677241	744
18	24503	162	136943	324	1377071	1062
20	37325	200	254795	450	2599915	1460
22	54631	242	448651	605	4621479	1947
24	77363	288	754039	792	7814815	2532
26	106553	338	1217845	1014	12671001	3224
28	143323	392	1900533	1274	19821821	4032
30	188885	450	2878565	1575	30064445	4965

10. Formulation in Dual SDP Formulation

After some inspection, it becomes clear that the most advantageous formulation is to formulate as the dual SDP format [2, 7]. 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 $\boldsymbol{y}$.

11. SDP Sizes in Dual SDP Formulation

	dimensions of matrices n_i
P	$(r/2)^2 \times (r/2)^2$ (1 block), $\binom{r/2}{2} \times \binom{r/2}{2}$ (2 blocks)
Q	$(r/2)^2 \times (r/2)^2$ (1 block), $\binom{r/2}{2} \times \binom{r/2}{2}$ (2 blocks)
G	$2(r/2)^2 \times 2(r/2)^2$ (1 block), $(r/2)^2 \times (r/2)^2$ (2 blocks)
	# of constraints m
any	$\binom{r^2/4+1}{2} + 2\binom{r(r/2-1)/4+1}{2}$ and 5

That is,

		P,Q,G	$P,Q,G,T1$	$P,Q,G,T1,T2'$
r	m s	n_i(max)	n_i(max)	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

12. Floating-Point Operations and Memory Usage by PDIPM [5, 6] and RRSDP[4]

N-representability conditions		P, Q, G		
formulation	algorithm	FLOPI	# iterations	memory
primal SDP	PDIPM	r^{12}	$r \ln \varepsilon^{-1}$	r^8
formulation	RRSDP	r^6	?	r^4
dual SDP	PDIPM	r^{12}	$r \ln \varepsilon^{-1}$	r^8
formulation	RRSDP	r^6	?	r^4
N-representability conditions		P, Q, G, $T1$ or P, Q, G, $T1$, $T2'$		
formulation	algorithm	FLOPI	# iterations	memory
primal SDP	PDIPM	r^{18}	$r^{3/2} \ln \varepsilon^{-1}$	r^{12}
formulation	RRSDP	r^9	?	r^6
dual SDP	PDIPM	r^{12}	$r^{3/2} \ln \varepsilon^{-1}$	r^8
formulation	RRSDP	r^9	?	r^6

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Appendix: Incomplete List on the 2-RDM Computation

1940	Husimi	1955 Löwdin	1955 Mayer	RDM
1960	Coulson			2-RDM
1963	Coleman			N-representability conditions
1964	Garrod-Percus			G condition
1960's-1970's	Kijewski, Garrod-Mihailović-Rosina, Garrod-Fusco Erdahl			1st computations
1975	Mihailović-Rosina			nucleon systems
2001	Nakata-Nakatsuji-Ehara-Fukuda-Nakata-Fujisawa (JCP **114** 8282)			complete computations
2002	Nakata-Ehara-Nakatsuji (JCP **116** 5432)			potential energy surface
2002	Mazziotti (PRA **65** 062511)			
2004	Zhao-Braams-Fukuda-Overton-Percus (JCP **120** 2095)			$T1, T2$
2004	Mazziotti (PRL **93** 213001)			RRSDP
2006	Cancès-Stoltz-Lewin (JCP **125** 064101)			dual
2007	Braams-Percus-Zhao (ACP vol. **134**)			$T2'$ condition
2006,2007	Mazziotti (PRA **74** 32501, ACP vol. **134**)			$\bar{T}2$ condition
2008	Nakata-Braams-Fujisawa-Fukuda-Percus-Yamashita-Zhao (JCP **128** 164113)			$T2'$ condition

Acknowledgment : MEXT's program "Promotion of Environmental Improvement for Independence of Young Researchers"
Supporting : Global COE "Computationism as a Foundation for the Sciences" Program (http://compview.titech.ac.jp/)