The Reduced Density Matrix Method: Current status and open problems

中田真秀(NAKATA, Maho) maho@riken.jp

理化学研究所 (RIKEN), Advanced Center for Computing and Communication

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Collaborators (current and past)

- Fukuda Mituhiro
- Bastiaan J. Braams
- Jerome K. Percus
- Fujisawa Katsuki
- Yamashita Makoto
- Michael Overton
- Zhengji Zhao
- Nakata Kazuhide
- Ehara Masahiro
- Nakatsuji Hiroshi



Motivation

- Introduction of the RDM method
- Review of results.
- Some open problems (negative results).

Prediction of chemical reaction, if and only if possible

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from the first principle

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Motivation: Construct a faster, simpler method for Chemistry.

Candidate: the RDM method

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The RDM method: 2-RDM as basic variable

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$\Gamma(12|1'2')$

Hamiltonian H

$$H = \sum_{j=1}^{N} \left(-\frac{\hbar^2}{2m_e} \nabla_j^2 - \sum_{A}^{K} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Aj}} \right) + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

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 $H\Psi(1,2,\cdots N) = E\Psi(1,2,\cdots N)$

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Schrödinger equation

$$H\Psi(1,2,\cdots N)=E\Psi(1,2,\cdots N)$$

Pauli principle

$$\Psi(\dots, i, \dots, j, \dots) = -\Psi(\dots, j, \dots, i, \dots)$$

Solving Schrödinger equation is difficult

We know the basic equation but...

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We know the basic equation but...



The general theory of quantum mechanics is now almost complete. ... the whole of chemistry are thus *completely known*, and the difficultly is only that the exact application of these laws leads to equations much too complected to be soluble.

He has never think about computational complexity and it's NP-hard :-)

[Dirac 1929]

"Quantum Mechanics of Many-Electron Systems."

A simpler quantum mechanical method

A simpler quantum mechanical method

A success story: "The Density Functional Theory"

[Hoheberg-Kohn 1964] [Kohn-Sham 1965][Kohn 1998; Nobel Prize]

Ground state electronic density $\rho(r)$ \downarrow external potential v(r) \downarrow Hamiltonian H \downarrow Schrödinger equation

Very difficult functional $F[\rho(r)]$. Practically this is semi-empirical theory.

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The second-order reduced density matrix:

[Husimi 1940], [Löwdin 1954], [Mayer 1955], [Coulson 1960], [Nakatsuji 1976]

$$\Gamma(12|1'2') = \binom{N}{2} \int \Psi^*(123\cdots N)\Psi(1'2'3\cdots N)d\mu_{3\cdots N}$$

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Ψ	N, (r !)	Yes
Γ(12 1'2')	$4, (r^4)$	Yes



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Do not depend on the size of the system Equivalent to Schrödinger eq. (ground state)

Definition of 1,2-RDM

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The Hamiltonian contains only 1 and 2-particle interaction.

$$H = \sum_{ij} v_j^i a_i^{\dagger} a_j + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} a_{i_1}^{\dagger} a_{i_2}^{\dagger} a_{j_2} a_{j_1}$$

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The total energy *E* becomes,

$$E = \sum_{ij} v_{j}^{i} \langle \Psi | a_{i}^{\dagger} a_{j} | \Psi \rangle + \frac{1}{2} \sum_{i_{1} i_{2} j_{1} j_{2}} w_{j_{1} j_{2}}^{i_{1} i_{2}} \langle \Psi | a_{i_{1}}^{\dagger} a_{i_{2}}^{\dagger} a_{j_{2}} a_{j_{1}} | \Psi \rangle$$

$$= \sum_{ij} v_{j}^{i} \gamma_{j}^{i} + \sum_{i_{1} i_{2} j_{1} j_{2}} w_{j_{1} j_{2}}^{i_{1} i_{2}} \Gamma_{j_{1} j_{2}}^{i_{1} i_{2}}.$$
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Here we defined the second-order reduced density matrix $\Gamma^{i_1i_2}_{j_1j_2}$ (2-RDM)

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and the first-order reduced density matrix γ_j^i (1-RDM)

$$\gamma_j^i = \langle \Psi | a_i^{\dagger} a_j | \Psi \rangle.$$

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J

N-representability condition

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N-representability condition [Coleman 1963]

$\Gamma(12|1'2') \rightarrow \Psi(123 \cdots N)$ or full Density Matrix $\gamma(1|1') \rightarrow \Psi(123 \cdots N)$ or full Density Matrix

Complete *N*-representability condition is very difficult

Computational complexity for complete N-representability

- Basically every *N*-rep. condition is linear constraint.
- Optimization over diagonal *N*-representable 2-RDM: NP-hard [Deza, Laurent 1997]
- Decision problem "is this 2-RDM *N*-representable?" QMA-complete, NP-hard [Liu 2007]
- Coleman's algorithm [Beste, et al 2002] [Coleman 2000].

Very difficult and hopeless :-(

[See also "Complexity and Electronic Structure Theory" B.J. Braams 741 PT11 16:40 Monday]

Approximation (necessary) condition : where Physics and Chemistry are

• P, Q-condition, ensemble 1-RDM condition [Coleman 1963]

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- Construction of 2-particle density [Pistol 2004, 2006]

PSD type *N*-representability conditions

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P,Q,G,T1,T2-matrix are all positive semidefinite \leftrightarrow eigenvalues $\lambda_i \ge 0$

$$U^{\dagger} \Gamma U = \begin{bmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ & & \ddots & \\ 0 & & & \lambda_n \end{bmatrix} \ge 0$$

First application to Be atom [Garrod et al 1975, 1976] Calculation methods are not very well studied...

Realization of the RDM method for atoms and molecules

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$E_{g} = \underset{\Gamma \in \mathcal{P}}{\operatorname{Min}} \operatorname{Tr} H\Gamma$ $\mathcal{P} = \{\Gamma : \text{Approx. } N \text{-rep.condition} \}$

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[Nakata-Nakatsuji-Ehara-Fukuda-Nakata-Fujisawa 2001] [Nakata-Nakatsuji-Ehara 2002]

Semidifinite programming

We solved exactly for the first time!

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Small enough "primal dual gap, feasibility" values show that total energies etc are MATHEMATICALLY correct

The ground state energy of atoms and molecules [Nakata et al 2008]

System	1 State	N r	ΔE_{GT1T2}	$\Delta E_{GT1T2'}$	$\Delta E_{CCSD(T)} \Delta E_{HF} \qquad E_{FCI}$
С	³ P	6 20	-0.0004	-0.0001	+0.00016 +0.05202 -37.73653
0	^{1}D	8 20	-0.0013	-0.0012	+0.00279 +0.10878 -74.78733
Ne	¹ S	10 20	-0.0002	-0.0001	-0.00005 +0.11645 -128.63881
0,+	$^{2}\Pi_{g}$	15 20	-0.0022	-0.0020	+0.00325 +0.17074 -148.79339
ВĤ	$^{1}\Sigma^{+}$	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
SiH₄	${}^{1}A_{1}$	18 26	-0.0002	-0.0002	+0.00018 +0.07311 -290.28490
F-	¹ S	10 26	-0.0003	-0.0003	+0.00067 +0.15427 -99.59712
Р	⁴ S	15 26	-0.0001	-0.0000	+0.00003 +0.01908 -340.70802
H_2O	${}^{1}A_{1}$	10 28	-0.0004	-0.0004	+0.00055 +0.14645 -76.15576

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

Application to potential energy curve

 Dissociation curve of N₂ (triple bond) the world first result. [Nakata-Nakatsuji-Ehara 2002]



Summary of typical results

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Typical results						
N-rep.	Correlation energy(%)	dissociation limit				
PQG	100 ~ 130%	yes				
PQGT1T2'	$100 \sim 101\%$	yes				
CCSD(T)	$100 \sim 101\%$	no				

Hopeful

([Nakata-Nakatuji-Ehara-Fukuda-Nakata-Fujisawa 2001] [Nakata et

al.2002][Zhao et al. 2004][Mazziotti et al. 2002,3,4,5,6,7,8,9][Eric et al

2006][Fukuda et al 2007][Nakata et al 2008])

[See also "Variational Detremination of the Two Particle Reduced Density Matrix", B. Verstichel 1319 PTP Tuesday]

Essentials of [Nakata et al. 2001, 2002] with P, Q, G-condition

JCP 114,8282(2001), JCP 116, 5432(2002).

- Exact minimization was performed for the first time. Since mid of 1990, solvers are developed mathematical programming community. Among them the SDPA the fastest, and exact. Everyone is doing SDP without aware of it :)
- G-condition is mandatory for chemistry: related to AGP wf (corr. ene. 100%~130%)
- *P*, *Q* conditions are not sufficient (corr. ene. 200 ~ 800%)
- The 3rd, 4th order approx. are not essential
 - In 2000 Erdahl and Jin:"The poor quality of the second-order estimates is consistent with the work of Mihailovic and Rosina..."
 - In 2001, Mazziotti and Erdahl: Lipkin model. Table IV: correlation energies are 478-5238% with P, Q, G conditions (in 2005 silently corrected by Hammond, Mazziotti and Erdahl(?)).

Importance of [Zhao-Braams-Fukuda-Percus-Overton 2004] with

T1, T2-conditions

JCP 120, 2095(2004).

• Formulation of T1 and T2 conditions

- Total energies became comparable to CCSD(T)
- We can do Chemistry with these conditions!!!
- Not a trivial formulation.
- Dual SDP formulation

Lager calculation is possible

They gave us a hope to realization of the RDM method

How large we can calculate until now?

"size" is how many active orbitals are used

Who	Year	Size	N-rep.	system
Garrod et al.	1976	?	PQG	Be
Erdahl	1979	?	PQG	He ₂
Nakata et al.	2001	8	PQG	H ₃ O ⁺
Nakata et al.	2002	8	PQG	C_2, CO, N_2
Zhao et. al	2004	10	PQGT1T2	H_3O^+
Mazziotti	2004	14-18	PQG	N_2, H_6
Gidofalvi et.al.	2005	14-20(?)	PQG	N_2, C_2
Eric et. al	2006	15	PQG	NH ₃
Hammond et. al	2006	14	PQGT2	Hubbard mode
Fukuda et al.	2007	13	PQGT1T2	CH ₃ N
Nakata et al.	2008	14	PQGT1T2'	H ₂ O
Greenman et al.	2009	8	PQGT2	CAS(Benzene et
Greenman et al.	2009	12-24	PQG	CAS(Pentacyne e

NAKATA, Maho (RIKEN, ACCC)



- How many iterations are needed?
- Size consistency or extensively.
- Degeneracy.
- Diagonal representability and excited states.

How many iterations are needed?

How many iterations are required by

- primal-dual interior-point method (PDIPM) or
- Monteiro-Bruner method (RRSDP) [Mazziotti 2004]

		P, Q, and Q	G	P, Q, G, T1, T2		
algorithm	flops	# iterations	memory	flops	# iterations	memory
PDIPM	<i>r</i> ¹²	$r \ln \varepsilon^{-1}$	r^8	r ¹²	$r^{3/2}\lnarepsilon^{-1}$	r ⁸
RRSDP r^6 none r^4 r^9 none r^6						
Note: when we stop the iteration is a big problem						

Lacking size consistency and/or extensively

• *G*-condition servers as a necessary condition to size consistent and/or extensively [Nakata et al. 2002]

 $\lim_{|1-1'|\to\infty}F(1|1')=\langle n(1)n(1')\rangle-\langle n(1)\rangle\langle n(1')\rangle\geq 0\quad \text{this should be zero}$

- *PQG* are not consistent: C₂, CO 33.3mH, and 5.8mH.
- *PQG* seems to be size-extensive [Mazziotti et al. 2005].
- H₂O, NH₃ and N₂ are size consistent. (if molecules dissociates to H, it seems to be size consistent) [JCP 2002]
- Reduce spin number by adding ghost hydrogen atoms [Hammond Mazziotti 2005].
- See also "Dissociation Curves from ...Density Matrices:..." P.Bultink et al. 1552 PT3 [Bultink et al. PCCP 2009]

NAKATA, Maho (RIKEN, ACCC)

Ensemble *N*-representability problem: zero dipole

 H_3 is a meta stable molecule and have two dipole moments at the ground state.

$\mu_{ m fullCI}$	$\mu_{ m HF}$	μ_{PQG}	μ_{PQGT1}	$\mu_{PQGT1T2'}$
0.85948	0.92110	0	0	0

- SDP solver calculates ensemble average of these two dipole moments.
- Adding small perturbation can remove this.

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[Fukuda et al 2007][Nakata et al. 2008]
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non-N-representability: Spin degeneracy

- Spin degeneracy will be observed when $S \neq 0$.
- E.g., S = 1, then the total energies of three states $S_z = 1, 0, -1$ will degenerate.
- Including *T*1, *T*2' recovers, but not complete.
- This is a source of non-size consistency or size-extensively.

System	State	basis	<i>corrE_{PQG}</i>	$corrE_{T1}$	$corrE_{T1T2'}$
С	${}^{3}P_{1}$	double- ζ	107.5%	105.9%	100.1%
С	${}^{3}P_{0}$	double- ζ	133.4%	126.0%	103.9%
0	${}^{3}P_{1}$	double- ζ	117.4%	109.4%	101.1%
0	${}^{3}P_{0}$	double- ζ	134.4%	127.4%	102.3%

corrE means correlation energy error in percentage

[Nakata et al. 2008]
Properties becomes better like total energy?

• The total energy becomes higher when we add a new *N*-representability conditions:

$E_{PQ} \leq E_{PQG} \leq E_{PQGT1} \leq E_{PQGT1T2} \leq \cdots \leq E_{FCI}$

No such kind of conditions for properties, but we USUALLY have a following sequence: [Nakata et al 2008]

$$|\mu_{PQG} - \mu_{\text{FCI}}| \le |\mu_{PQGT1} - \mu_{\text{FCI}}| \le |\mu_{PQGT2} - \mu_{\text{FCI}}| \le 0$$

 μ is the dipole moment of atoms and molecules. Can be arbitrary operators up to 2-body.

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- double (16 digits) $1 + 0.0000000000000001 \simeq 1$
- GMP (GNU multiple precision) ⇒ necessity of highly accurate solver, using multiple precision arithmetic (SDPA-GMP) http://sdpa.indsys.chuo-u.ac.jp/sdpa/ GNU Public License

SDPA-GMP and Hubbard model

The 1D Hubbard model with high correlation limit $|U/t| \rightarrow \infty$: All states are almost degenerated.

The ground state energies of 1D Hubbard model

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

U/t	SDPA (16 digits)	SDPA-GMP (60 digits)	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 (16 digits)	SDPA-GMP (60 digits)	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			

Excited states systems

- RPA: [Garrod et al 1980] [Mazziotti 2003] → can go beyond?
- McDonald's variational principle [Nakata et al 2006][Erdahl Grudziński 1978][Yasuda 2002] → Excited states of one-particle Hamiltonian: essentially difficult problem. Related to 2-particle density, too.



- Urgent How to recover size extensively and/or consistency
- Urgent Large scale semi-definite programming solver.
- Degeneracy problems.
- Understanding *N*-representability conditions: Physical and Chemical meaning.
- How to find "a good" *N*-representability conditions.



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(WELCOME TO THE JUNGLE!)



I missed many very very interesting areas

- Density equation / contracted Schrödinger equation and its variants.
- 1-RDM functional theories.
- 2-RDM parametrization theories.
- 2-particle density functional theories.

How large these SDP are?

# of constraints					
r	constraints	block			
24	15018	2520x2, 792x4, 288x1,220x2			
26	20709	3211x2, 1014x4, 338x1, 286x2			

Elapsed time using Itanium 2 (1.3GHz) 1 node 4 processors.

System, State, Basis	N-rep.	r	Time	# of nodes
SiH ₄ , ¹ A ₁ , STO-6G	PQGT1T2	26	5.1 days	16
$\mathrm{H}_{2}\mathrm{O},^{1}A_{1},\mathrm{double}$ - ζ	PQG	28	2.2 hours	8
$\mathrm{H}_{2}\mathrm{O},^{1}A_{1},\mathrm{double}$ - ζ	PQGT1T2	28	20 days	8
$\mathrm{H}_{2}\mathrm{O},^{1}A_{1},\mathrm{double}$ - ζ	PQGT1T2'	28	24 days	8