Recent progresses in the variational reduced-density-matrix method

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- **安田耕二** (Yasuda Koji)
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- Jerome K. Percus
- **藤澤克樹** (Fujisawa Katsuki)
- **山下真** (Yamashita Makoto)
- Michael Overton
- Zhengji Zhao
- **中田和秀** (Nakata Kazuhide)
- **江原正博** (Ehara Masahiro)
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Overview

- Introduction of the RDM method.
- Recent results.
- Some open problems.

Part 1

Introduction of the RDM method.

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N-representability condition; the only one approximation

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The ground state energy becomes...

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

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Definition of 1, 2-RDMs

$$\Gamma^{i_1 i_2}_{j_1 j_2} = \frac{1}{2} \langle \Psi | a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1} | \Psi \rangle, \quad \gamma^i_j = \langle \Psi | a^\dagger_i a_j | \Psi \rangle.$$

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N-representability condition [Coleman 1963]

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

$\gamma, \Gamma \in \mathcal{P}$ should satisfy N-representability condition:

$$\Gamma(12|1'2') \rightarrow \Psi(123\cdots N)$$

$$\gamma(1|1') \rightarrow \Psi(123\cdots N).$$

Encodes two-body effects completely. Very compact.

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- $T1$, $T2$, $T2'$, ($\bar{T}2$)-condition [Zhao *et al.* 2004], [Erdahl 1978] [Braams et al 2007] [Mazziotti 2006, 2007]

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- Davidson's inequality [Davidson 1969][Ayers et al. 2006]

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- Davidson's inequality [Davidson 1969][Ayers et al. 2006]
- Construction of 2-particle density [Pistol 2004, 2006]

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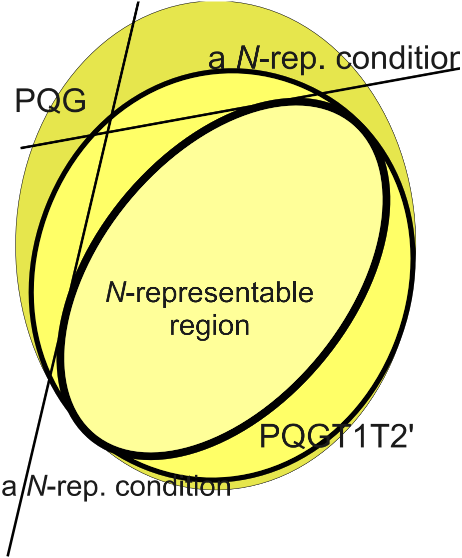

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- Can evaluate total energy exactly via 1 and 2-RDM
- only one approximation is N-representability condition (aka theory of everything)

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Method	# of variable (discritized)	Exact?
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Equivalent to Schrödinger eq. (ground state)

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PSD type N-representability conditions

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

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

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

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[Nakata-Nakatsuji-Ehara-Fukuda-Nakata-Fujisawa 2001]
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Small enough "primal dual gap, feasibility" values show that total energies etc are MATHEMATICALLY correct

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- polynomial algorithm (cf. Hartree-Fock is NP-hard).

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- P, Q and G condition: dissociation limit (sometimes fails).

  [Nakata et al], [Mazziotti], [H. Aggelen et al]

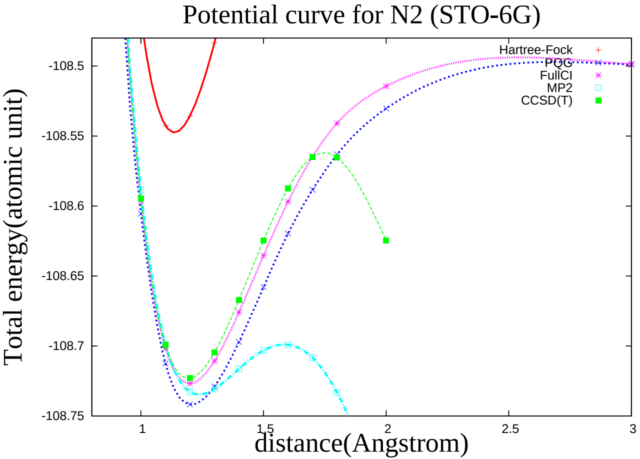
The ground state energy of atoms and molecules [Nakata et al 2008]

System	State	N	r	Δ E$_{GT1T2}$	Δ E$_{GT1T2'}$	Δ E$_{CCSD(T)}$	Δ E$_{HF}$	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 ($P, Q, G, T1$ 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 $\mathbf{N_2}$ (triple bond) the world first result. [Nakata-Nakatsuji-Ehara 2002]



Part 2

Recent results: non-size extensivity

Size-extensivity and consistency

Size extensivity or consistency is very important property for a calculation theory.

$$E(A - -\text{infinity} - -A) = E(A) + E(A)?$$

Size-extensivity and consistency

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- Not size consistnt: [Nakata-Nakatsuji-Ehara 2002] (small deviation), [Aggelen-Bultinck-Verstichel-VanNeck-Ayers 2009] (fractional charge!)

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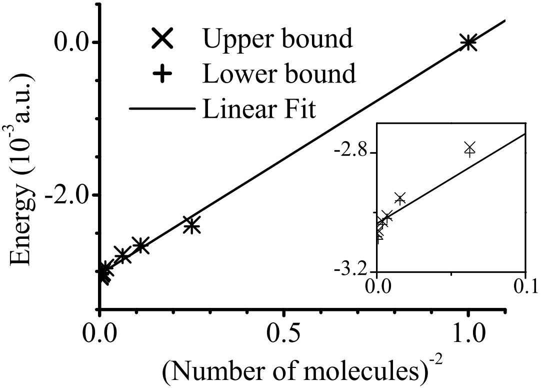
- Not size consistnt: [Nakata-Nakatsuji-Ehara 2002] (small deviation), [Aggelen-Bultinck-Verstichel-VanNeck-Ayers 2009] (fractional charge!)
- Not size extensive: [Nakata-Yasuda 2009] PRA80,042109(2009).
  - $\mathbf{CH_4}$, $\mathbf{N_2}$ non interacting polymers: slightly deviated
  - primal-dual interior point method is mandatory; Monteiro-Bruner [Mazziotti 04] is inaccurate.

Size-extensivity: N_2 polymer

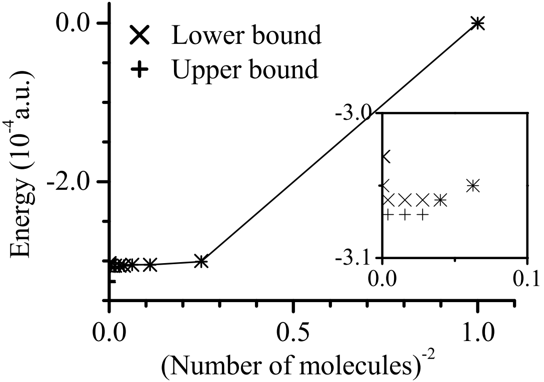
$N_2\ N_2\ N_2 \cdots N_2$ non interacting, N-rep.: PQG



$$E(M) = -108.71553 + 0.00302M^{-2}.\ 3 \times 10^{-4} \text{ au}$$

Size-extensivity: CH_4 polymer

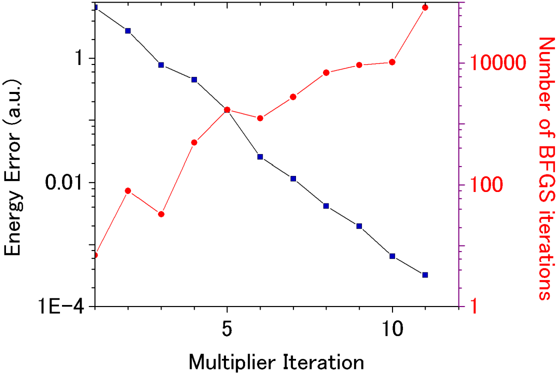
CH_4 CH_4 CH_4 $\cdots$ CH_4 non interacting, N-rep.: PQG



Nither PQG nor $PQGT1T2'$ are size-extensive

Size-extensivity: Inaccurate result by Monteiro-Bruner method

H_2O: solved by Monteiro-Bruner method [Mazziotti 2004]: # of iteration req'ed scale like exponential. Not converged with CO (double-ζ).



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Hopeful and still lot of unknowns!

How many iterations are needed?

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

	P, Q, and G			P, Q, G, $T1$, $T2$		
algorithm	flops	# iterations	memory	flops	# iterations	memory
PDIPM	r^{12}	$r \ln \varepsilon^{-1}$	r^8	r^{12}	$r^{3/2} \ln \varepsilon^{-1}$	r^8
RRSDP	r^6	none	r^4	r^9	none	r^6

Note: *when we stop the iteration is a big problem*

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
$\mathbf{SiH_4}$, $^1A_1$, STO-6G	$PQGT1T2$	26	5.1 days	16
$\mathbf{H_2O}$, $^1A_1$, double-ζ	PQG	28	2.2 hours	8
$\mathbf{H_2O}$, $^1A_1$, double-ζ	$PQGT1T2$	28	20 days	8
$\mathbf{H_2O}$, $^1A_1$, double-ζ	$PQGT1T2'$	28	24 days	8

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SDPA-GMP and Hubbard model

The 1D Hubbard model with high correlation limit
$|U/t| \to \infty$: 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**