

# The Reduced Density Matrix Method: Application Of $T_2'$ $N$ -representability Condition and Development of Highly Accurate Solver

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Odyssey 2008 2008/6/1-6/6

# Overview

- Motivation
- Introduction of the RDM method
- Recent results
- Summary and future direction

# Motivation: theoretical chemistry

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## Goals: prediction and design of chemical reaction

- What happens if we mix substance A and B?
- $\text{CO}_2$  conversion.
- Drug design.

etc...

# Basic equation: Schrödinger equation

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(electronic) Hamiltonian  $H$

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

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Pauli principle: antisymmetric wavefunction is

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

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[Dirac 1929]

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

“Quantum Mechanics of Many-Electron Systems.”

# **Simpler quantum mechanical method**

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A success story: The Density Functional Theory:

[Hoheberg-Kohn 1964] [Kohn-Sham 1965]

Ground state electronic density  $\rho(\mathbf{r})$



external potential  $v(\mathbf{r})$



Hamiltonian  $H$



Schrödinger equation

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

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**The RDM method!**

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The second-order reduced density matrix:

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

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

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Can we construct simpler quantum chemical method using  $\Gamma(\mathbf{12}|\mathbf{1}'\mathbf{2}')$  as a basic variable?

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# Scaling

Method	# of variable (discretized)	Exact?
$\Psi$	$N, (r!)$	Yes
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Good scaling  
Equivalent to Schrödinger eq.

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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,

$$\begin{aligned} E &= \sum_{ij} v_j^i \langle \Psi | a_i^\dagger a_j | \Psi \rangle + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle \\ &= \sum_{ij} v_j^i \gamma_j^i + \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} \Gamma_{j_1 j_2}^{i_1 i_2}. \end{aligned}$$

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Here we defined the second-order reduced density matrix  $\Gamma_{j_1 j_2}^{i_1 i_2}$  (2-RDM)

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and the first-order reduced density matrix  $\gamma_j^i$  (1-RDM)

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



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$$\begin{aligned} E_g &= \min_{\Psi} \langle \Psi | H | \Psi \rangle \\ &= \min_{\gamma, \Gamma} \left\{ \sum_{ij} v_j^i \gamma_j^i + \sum_{i_1 i_2 j_1 j_2} w_{j_1 j_2}^{i_1 i_2} \Gamma_{j_1 j_2}^{i_1 i_2} \right\} \end{aligned}$$

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 **$N$ -representability condition** [Coleman 1963]

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

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  - $G$ -condition [Garrod et al. 1964]
  - $T1$ ,  $T2$ -condition [Zhao et al. 2004], [Erdahl 1978]
  - Quite good for atoms and molecules [Garrod et al. 1975, 1976], [Nakata et al. 2001, 2002], [Zhao et al. 2004] [Mazziotti 2004]

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$P, Q, G, T1, T2$ -matrix are all positive semidefinite  $\leftrightarrow$   
eigenvalues  $\lambda_i$  are non-negative ( $\lambda_i \geq 0$ ).

$$U^\dagger \Gamma U = \begin{bmatrix} \lambda_1 & & & \mathbf{0} \\ & \lambda_2 & & \\ & & \dots & \\ \mathbf{0} & & & \lambda_n \end{bmatrix} \succeq \mathbf{0}$$

First application to Be atom

[Garrod et al 1975, 1976]

Calculation methods are not very well studied...



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[Nakata et al. 2001]

**Semidefinite programming**

**We solved exactly for the first time!**

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$N$ -rep.	Correlation energy(%)	dissociation limit
<i>PQG</i>	<b>100 ~ 120%</b>	yes
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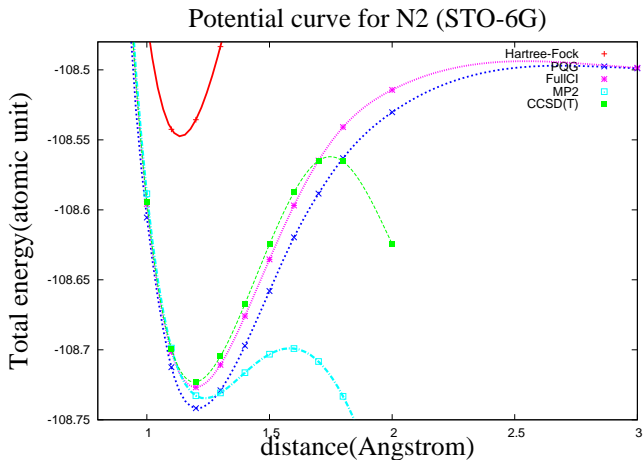
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Details were given in Contributed Talks 13 by Mitsuhiro Fukuda et al., "Exploiting the semidefinite formulation on the variational calculation of second-order reduced density matrix of atoms and molecules."



# Application to potential energy curve

- Dissociation curve of  $\text{N}_2$  (triple bond) [Nakata et al. 2002].



## Recent results

J. Chem. Phys **128**, 164113 (2008),  
“Variational calculation of second-order reduced  
density matrices by strong  $N$ -representability  
conditions and an accurate semidefinite  
programming solver”,

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## Recent results

- Application of recently derived new  $T2'$   $N$ -rep. condition [Braams et al. 2007], [Mazziotti 2006]  $T2' \rightarrow (A + B)^\dagger(A + B) + AA^\dagger$
- The largest system: double- $\zeta$   $\text{H}_2\text{O}$  molecule.
- Development of Multiple precision arithmetic version of SDP solver and application to one dimensional Hubbard model of strong correlation limit  $|U/t| \rightarrow \infty$ .

# The ground state energy of atoms and molecules

System	State	$N$	$r$	$\Delta E_{GT1T2}$	$\Delta E_{GT1T2'}$	$\Delta E_{CCSD(T)}$	$\Delta E_{HF}$	$E_{FCI}$
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 <sub>2</sub> <sup>+</sup>	$^2\Pi_g$	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 <sub>4</sub>	$^1A_1$	18	26	-0.0002	-0.0002	+0.00018	+0.07311	-290.28490
F <sup>-</sup>	$^1S$	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 <sub>2</sub> O	$^1A_1$	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 perturbational treatment of triples

HF : Hartree-Fock

FCI : FullCI

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- double (16 digits)

$$1 + 0.000000000000000001 \simeq 1$$







# 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	$-1.2 \times 10^{-2}$	$-1.1999880002507934 \times 10^{-2}$	$-1.1999880002 \times 10^{-2}$
100.0	$-1.1991 \times 10^{-1}$	$-1.1988025013717993 \times 10^{-1}$	$-1.19880248946 \times 10^{-1}$
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	$-1 \times 10^{-2}$	$-1.7255360310431304 \times 10^{-2}$	$-1.7211034713 \times 10^{-2}$
100.0	$-1.730 \times 10^{-1}$	$-1.7302157140594339 \times 10^{-1}$	$-1.72043338097 \times 10^{-1}$
10.0	-1.6954	-1.6953843276854447	-1.664362733287
1.0	-6.6012	-6.6012042217806286	-6.601158293375

## 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
$\text{SiH}_4$ , $^1A_1$ , STO-6G	<i>PQGT1T2</i>	26	5.1 days	16
$\text{H}_2\text{O}$ , $^1A_1$ , double- $\zeta$	<i>PQG</i>	28	2.2 hours	8
$\text{H}_2\text{O}$ , $^1A_1$ , double- $\zeta$	<i>PQGT1T2</i>	28	20 days	8
$\text{H}_2\text{O}$ , $^1A_1$ , double- $\zeta$	<i>PQGT1T2'</i>	28	24 days	8

## Summary and future direction

- Introduction of the RDM method.
- Semidefinite Programming
- Calculation with *PQGT1T2'*: comparable to CCSD(T)
- Improvement are typically **0.1mHartree** ~ **0.6mHartree** by replacing from *PQGT1T2* to *PQGT1T2'*.
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WIP : Developing a SDP solver suitable for quantum chemistry.