Recent progresses in the variational reduced-density-matrix method

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The 50th Sanibel Symposium (February 24 - March 2, 2010)
Collaborators current and past

- 福田光浩 (Fukuda Mituhiro)
- 安田耕二 (Yasuda Koji)
- Bastiaan J. Braams
- 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)
- 中辻博 (Nakatsuji Hiroshi)
Overview

- Introduction of the RDM method.
- Recent results.
- Some open problems.
Introduction of the RDM method.
What is the RDM method in short?

The RDM method: 2-RDM as basic variable

Equivalent to the Schrödinger equation

Ground state energy: Minimize directly!
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The RDM method: 2-RDM as basic variable

\[ \Gamma^{i_1i_2}_{j_1j_2} = \frac{1}{2} \langle \Psi | a_{i_1}^{\dagger} a_{i_2}^{\dagger} a_{j_2} a_{j_1} | \Psi \rangle \]

Equivalent to the Schrödinger equation

Ground state energy: Minimize directly!

N-representability condition; the only one approximation

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What is the RDM method in short?

The RDM method: 2-RDM as basic variable

\[
\Gamma_{i_1i_2}^{j_1j_2} = \frac{1}{2} \langle \Psi \mid a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} \mid \Psi \rangle
\]

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\( N \)-representability condition; the only one approximation
Our goal: doing chemistry from the first principle, faster calculation and deeper understanding

Our target

- *ab initio*...theoretically and practically good approximation
- faster method ...mathematically simpler
- deeper understanding...electronic structure
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The ground state and energy calculation

[Husimi 1940], [Löwdin 1954], [Mayer 1955], [Coulson 1960], [Rosina 1968]
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\[ H = \sum_{ij} v_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w_{i_1 i_2 j_1 j_2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} \]
The ground state and energy calculation

\[ H = \sum_{ij} v_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{i_1i_2j_1j_2} w_{i_1i_2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} \]

The ground state energy becomes...

\[ E_g = \min \langle \Psi | H | \Psi \rangle \]

\[ = \min \sum_{ij} v_{ij} \langle \Psi | a_i^\dagger a_j | \Psi \rangle + \frac{1}{2} \sum_{i_1i_2j_1j_2} w_{i_1i_2} \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle \]

\[ = \min \{ \sum_{ij} v_{ij} \gamma_{ij} + \sum_{i_1i_2j_1j_2} w_{i_1i_2} \Gamma_{i_1i_2} \} \]
The ground state and energy calculation

[Husimi 1940], [Löwdin 1954], [Mayer 1955], [Coulson 1960], [Rosina 1968]

\[
H = \sum_{ij} v_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w_{i_1 i_2 j_1 j_2} a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}
\]

The ground state energy becomes...

\[
E_g = \min \langle \Psi | H | \Psi \rangle
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\[
= \min \sum_{ij} v_{ij} \langle \Psi | a_i^\dagger a_j | \Psi \rangle + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w_{i_1 i_2 j_1 j_2} \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle
\]

\[
= \min \left\{ \sum_{ij} v_{ij} \gamma^i_j + \sum_{i_1 i_2 j_1 j_2} w_{i_1 i_2 j_1 j_2} \Gamma_{j_1 j_2}^{i_1 i_2} \right\}
\]

Definition of 1, 2-RDMs

\[
\Gamma_{j_1 j_2}^{i_1 i_2} = \frac{1}{2} \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} | \Psi \rangle, \quad \gamma^i_j = \langle \Psi | a_i^\dagger a_j | \Psi \rangle.
\]
$N$-representability condition

\[ E = \min_P \sum_{ij} v_{ij} + \sum_{i_1j_1j_2} w_{i_1j_1i_2j_2} \]

should satisfy $N$-representability condition:

\[ (120_2) \leq (123_N) \]

\[ (1j_1) \leq (123_N) \]
$N$-representability condition

[Mayers 1955], [Tredgold 1957]: *Far lower* than the exact one
$N$-representability condition

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$N$-representability condition [Coleman 1963]

$$E_g = \min_{\rho} \left\{ \sum_{ij} v_{ij} \gamma_{ij} + \sum_{i_1i_2j_1j_2} w_{i_1i_2} \Gamma_{j_1j_2} \right\}$$

$\gamma, \Gamma \in \mathcal{P}$ 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.
Approximate $N$-representability condition

Approximation (necessary) condition: where Physics and Chemistry are
Approximate $N$-representability condition

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- $T_1, T_2, T_2', (\bar{T}2)$-condition [Zhao et al. 2004], [Erdahl 1978] [Braams et al 2007] [Mazziotti 2006, 2007]
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- $T1, T2, T2', (T2)$-condition [Zhao et al. 2004], [Erdahl 1978] [Braams et al. 2007] [Mazziotti 2006, 2007]
- Davidson’s inequality [Davidson 1969][Ayers et al. 2006]
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Approximate $N$-representability condition

$N$-representable region

PQG

a $N$-rep. condition

PQGT1T2'

a $N$-rep. condition
Summary 1: the RDM method is an \textit{ab initio} method
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- Can evaluate total energy exactly via 1 and 2-RDM
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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)
Our goal: doing chemistry from the first principle, faster calculation and deeper understanding

Our target

- *ab initio*...theoretically and practically good approximation
- faster method ...mathematically simpler
- deeper understanding...electronic structure
Mathematically simpler:
number of variables are always four
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<table>
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<tr>
<th>Method</th>
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Do not depend on the size of the system
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Do not depend on the size of the system
Equivalent to Schrödinger eq. (ground state)
Mathematically simpler: minimization of linear functional

\[ E = \text{Min} \quad 2P \quad \text{Tr} H \quad P = f \]

Approx. \( N \)-rep.condition

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Mathematically simpler:
minimization of linear functional

\[ E_g = \min_{\Gamma \in \mathcal{P}} \text{Tr} \, H \Gamma \]

\[ \mathcal{P} = \{ \Gamma : \text{Approx. } N\text{-rep.condition}\} \]
PSD type $N$-representability conditions

$P, Q, G, T_1, T_2$-matrix are all positive semidefinite

$U^\dagger U = \begin{pmatrix} 1 & 0 & 2 & \vdots & 0 \\ 0 & 1 & 0 & \vdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \end{pmatrix}$

First application to Be atom

[Garrod et al 1975, 1976]

Calculation methods are not very well studied...
PSD type $N$-representability conditions

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

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

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

$E = \min \sum \tau H \tau P = f$: Approx.


Semidifinite programming

We solved exactly for the first time!

Small enough "primal dual gap, feasibility" values show that total energies etc are MATHEMATICALLY correct
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[Nakata-Nakatsuji-Ehara 2002]

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- HF ref. MP2, Coupled cluster: \( \text{NP-hard} \), post Hartree-Fock part is polynomial
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Summary 2: the RDM method is a simpler (and possibly faster) method

- Number of variables are always four.
- Minimization of linear functional.
- Semidefinite programming solved exactly for the first time M.N.’s major contribution
- Polynomial algorithm (cf. Hartree-Fock is NP-hard).
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Physical and Chemical meaning of approx. $N$-representability condition

Theoretical
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Theoretical

- $P, Q$ condition: electron and hole exist [Coleman].

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

[NAKATA, Maho (RIKEN, ACCC)]

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Sanibel symposium 2010/2/25

21 / 34
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- $P, Q$ and $G$ condition: $100 \sim 130\%$ corr. [Nakata et al], [Mazziotti et al] [Eric et al]
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- **\(P, Q\)** and **\(G\)** condition: \(100 \sim 130\%\) corr. [Nakata et al], [Mazziotti et al] [Eric et al]
- **\(P, Q, G, T1, T2'\)** condition: \(100 \sim 101\%\) corr. [Zhao et al], [Nakata et al]
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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]

<table>
<thead>
<tr>
<th>System</th>
<th>State</th>
<th>N</th>
<th>r</th>
<th>$\Delta E_{GT1T2}$</th>
<th>$\Delta E_{GT1T2'}$</th>
<th>$\Delta E_{CCSD(T)}$</th>
<th>$\Delta E_{HF}$</th>
<th>$E_{FCI}$</th>
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<tr>
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<tr>
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<td>-0.0002</td>
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<td>H$_2$O</td>
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<td>-0.0004</td>
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<td>+0.14645</td>
<td>-76.15576</td>
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$GT1T2$ : 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 $\text{N}_2$ (triple bond) the world first result. [Nakata-Nakatsuji-Ehara 2002]

![Potential curve for N2 (STO-6G)](image)
Recent results: non-size extensivity
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


CH$_4$, N$_2$ non interacting polymers: slightly deviated

primal-dual interior point method is mandatory; Monteiro-Bruner [Mazziotti 04] is inaccurate.
Not size consistent: [Nakata-Nakatsuji-Ehara 2002] (small deviation),
[Aggelen-Bultinck-Verstichel-VanNeck-Ayers 2009] (fractional charge!)


- $\text{CH}_4$, $\text{N}_2$ 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: CH₄ polymer**

CH₄ CH₄ CH₄ ⋯ CH₄ non interacting, \( N \)-rep.: \( PQG \)

Neither \( PQG \) nor \( PQGT1T2' \) are size-extensive
Size-extensivity: Inaccurate result by Monteiro-Bruner method

$\text{H}_2\text{O}$: solved by Monteiro-Bruner method [Mazziotti 2004]: # of iteration req’ed scale like exponential. Not converged with CO (double-$\zeta$).
The RDM method: 2-RDM as basic variable

Equivalent to the Schrödinger equation

Ground state: minimize directly via semidef. prog.!

[Nakata et al 2001]

N-rep: PQGT

[Zhao et al 2004]

Polynomial method but takes very long time: H2O double...

Hopeful and still lot of unknowns!

NAKATA, Maho (RIKEN, ACCC) Recent progresses in the variational reduced-de Sanibel symposium 2010/2/25 30 / 34
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How many iterations are required by

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

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>Flops $P, Q, G$</th>
<th># Iterations $P, Q, G, T1, T2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDIPM</td>
<td>$r^{12}$</td>
<td>$r \ln \varepsilon^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$r^{6}$</td>
<td>$r^8$</td>
</tr>
<tr>
<td>RRSDP</td>
<td>$r^6$</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>$r^4$</td>
<td>$r^{8/3}$</td>
</tr>
</tbody>
</table>

Note: when we stop the iteration is a big problem
How large these SDP are?

<table>
<thead>
<tr>
<th>$r$</th>
<th>constraints</th>
<th>block</th>
<th>System, State, Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>15018</td>
<td>2520x2, 792x4, 288x1, 220x2</td>
<td>SiH$_4$, $^1A_1$, STO-6G, $PQGT1T2$</td>
</tr>
<tr>
<td>26</td>
<td>20709</td>
<td>3211x2, 1014x4, 338x1, 286x2</td>
<td>H$_2$O, $^1A_1$, double-$\zeta$, $PQG$</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>System, State, Basis</th>
<th>$N$-rep.</th>
<th>$r$</th>
<th>Time</th>
<th># of nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_4$, $^1A_1$, STO-6G</td>
<td>$PQGT1T2$</td>
<td>26</td>
<td>5.1 days</td>
<td>16</td>
</tr>
<tr>
<td>H$_2$O, $^1A_1$, double-$\zeta$</td>
<td>$PQG$</td>
<td>28</td>
<td>2.2 hours</td>
<td>8</td>
</tr>
<tr>
<td>H$_2$O, $^1A_1$, double-$\zeta$</td>
<td>$PQGT1T2$</td>
<td>28</td>
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<td>H$_2$O, $^1A_1$, double-$\zeta$</td>
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Necessity of highly accurate solver

- SDP results are usually not accurate; typically 8 digits or so.
- When the ground state is degenerated, the SDP becomes more difficult when approaching to the exact optimal.
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- GMP (GNU multiple precision) \( \Rightarrow \) necessity of highly accurate solver, using multiple precision arithmetic (SDPA-GMP) http://sdpa.indsys.chuo-u.ac.jp/sdpa/ GNU Public License
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

<table>
<thead>
<tr>
<th>U/t</th>
<th>SDPA (16 digits)</th>
<th>SDPA-GMP (60 digits)</th>
<th>fullCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000.0</td>
<td>0</td>
<td>$-1.1999998800000251 \times 10^{-3}$</td>
<td>$-1.1999998800 \times 10^{-3}$</td>
</tr>
<tr>
<td>1000.0</td>
<td>$-1.2 \times 10^{-2}$</td>
<td>$-1.1999880002507934 \times 10^{-2}$</td>
<td>$-1.1999880002 \times 10^{-2}$</td>
</tr>
<tr>
<td>100.0</td>
<td>$-1.1991 \times 10^{-1}$</td>
<td>$-1.1988025013717993 \times 10^{-1}$</td>
<td>$-1.19880248946 \times 10^{-1}$</td>
</tr>
<tr>
<td>10.0</td>
<td>$-1.1000$</td>
<td>$-1.0999400441222934$</td>
<td>$-1.099877772750$</td>
</tr>
<tr>
<td>1.0</td>
<td>$-3.3417$</td>
<td>$-3.3416748070259956$</td>
<td>$-3.340847617248$</td>
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<tr>
<td>10000.0</td>
<td>0</td>
<td>$-1.7249951195749525 \times 10^{-3}$</td>
<td>$-1.721110121 \times 10^{-3}$</td>
</tr>
<tr>
<td>1000.0</td>
<td>$-1 \times 10^{-2}$</td>
<td>$-1.7255360310431304 \times 10^{-2}$</td>
<td>$-1.7211034713 \times 10^{-2}$</td>
</tr>
<tr>
<td>100.0</td>
<td>$-1.730 \times 10^{-1}$</td>
<td>$-1.7302157140594339 \times 10^{-1}$</td>
<td>$-1.72043338097 \times 10^{-1}$</td>
</tr>
<tr>
<td>10.0</td>
<td>$-1.6954$</td>
<td>$-1.6953843276854447$</td>
<td>$-1.664362733287$</td>
</tr>
<tr>
<td>1.0</td>
<td>$-6.6012$</td>
<td>$-6.6012042217806286$</td>
<td>$-6.601158293375$</td>
</tr>
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