The Reduced Density Matrix Method: Current status and open problems

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Overview

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

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Prediction of chemical reaction, if and only if possible

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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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$$\boldsymbol{\Gamma(12|1'2')}$$

Basic equation: Schrödinger equation

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Hamiltonian $\boldsymbol{H}$

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

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

Pauli principle

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

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 RDM method!

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The second-order reduced density matrix:

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

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

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Comparison

Method	# of variable (discritized)	Exact?
$\boldsymbol{\Psi}$	$\boldsymbol{N}$, $(\boldsymbol{r!})$	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.

$$H = \sum_{ij} v^i_j a^\dagger_i a_j + \frac{1}{2} \sum_{i_1 i_2 j_1 j_2} w^{i_1 i_2}_{j_1 j_2} a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1}$$

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The total energy E becomes,

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

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

$$\Gamma^{i_1 i_2}_{j_1 j_2} = \frac{1}{2}\langle \Psi | a^{\dagger}_{i_1} a^{\dagger}_{i_2} a_{j_2} a_{j_1} | \Psi \rangle,$$

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and the first-order reduced density matrix γ^{i}_{j} (1-RDM)

$$\gamma^{i}_{j} = \langle \Psi | a^{\dagger}_{i} a_{j} | \Psi \rangle.$$

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$$
\begin{aligned}
E_g &= \min_{\Psi} \langle \Psi | H | \Psi \rangle \\
&= \min_{\gamma,\Gamma} \left\{ \sum_{ij} v^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} \right\}
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$\boxed{N\text{-representability condition}}$

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$\boldsymbol{\gamma(1|1') \rightarrow \Psi(123\cdots N)}$ 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]

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- $\boldsymbol{G}$-condition [Garrod et al. 1964]

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

PSD type N-representability conditions

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$\boldsymbol{P}, \boldsymbol{Q}, \boldsymbol{G}, \boldsymbol{T1}, \boldsymbol{T2}$-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...

Realization of the RDM method for atoms and molecules

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[Nakata-Nakatsuji-Ehara-Fukuda-Nakata-Fujisawa 2001]
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Semidifinite programming

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

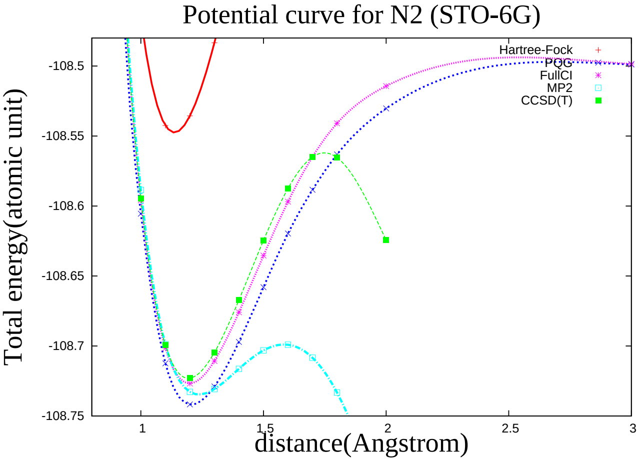
The ground state energy of atoms and molecules [Nakata et al 2008]

System	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]



Summary of typical results

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Typical results

N-rep.	Correlation energy(%)	dissociation limit
PQG	$\mathbf{100 \sim 130\%}$	yes
$PQGT1T2'$	$\mathbf{100 \sim 101\%}$	yes
CCSD(T)	$\mathbf{100 \sim 101\%}$	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.* $200 \sim 800$*%)*
- *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	$\mathbf{He_2}$
Nakata et al.	2001	8	PQG	$\mathbf{H_3O^+}$
Nakata et al.	2002	8	PQG	$\mathbf{C_2, CO, N_2}$
Zhao et. al	2004	10	$PQGT1T2$	$\mathbf{H_3O^+}$
Mazziotti	2004	14-18	PQG	$\mathbf{N_2, H_6}$
Gidofalvi et.al.	2005	14-20(?)	PQG	$\mathbf{N_2, C_2}$
Eric et. al	2006	15	PQG	$\mathbf{NH_3}$
Hammond et. al	2006	14	$PQGT2$	Hubbard mode
Fukuda et al.	2007	13	$PQGT1T2$	$\mathbf{CH_3N}$
Nakata et al.	2008	14	$PQGT1T2'$	$\mathbf{H_2O}$
Greenman et al.	2009	8	$PQGT2$	CAS(Benzene et
Greenman et al.	2009	12-24	PQG	CAS(Pentacyne e

Open problems

- 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 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*

Lacking size consistency and/or extensively

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

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

- PQG are not consistent: $\mathbf{C_2}$, $\mathbf{CO}$ 33.3mH, and 5.8mH.
- PQG seems to be size-extensive [Mazziotti et al. 2005].
- $\mathbf{H_2O}$, $\mathbf{NH_3}$ and $\mathbf{N_2}$ are size consistent. (if molecules dissociates to $\mathbf{H}$, 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]

Ensemble N-representability problem: zero dipole

$\mathbf{H_3}$ is a meta stable molecule and have two dipole moments at the ground state.

μ_{fullCI}	μ_{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.

[Fukuda et al 2007][Nakata et al. 2008]

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 $T1$, $T2'$ recovers, but not complete.
- This is a source of non-size consistency or size-extensively.

System	State	basis	$corrE_{PQG}$	$corrE_{T1}$	$corrE_{T1T2'}$
C	$^3P_1$	double-ζ	107.5%	105.9%	100.1%
C	$^3P_0$	double-ζ	133.4%	126.0%	103.9%
O	$^3P_1$	double-ζ	117.4%	109.4%	101.1%
O	$^3P_0$	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:

  $$E_{PQ} \le E_{PQG} \le E_{PQGT1} \le E_{PQGT1T2} \le \cdots \le E_{\mathrm{FCI}}$$

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

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

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

Necessity of highly accurate solver

- SDP results are usually not accurate; typically 8 digits or so.
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- GMP (60 digits; can be arbitrary)
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  $\mathbf{1 + 0.000000000000000000000000000000000000000000000000000000000001 \simeq 1}$
- GMP (GNU multiple precision)

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.
- WE NEED MORE DIGITS, FOR EXAMPLE 60 DIGITS!

- double (16 digits) $\mathbf{1 + 0.0000000000000001 \simeq 1}$
- GMP (60 digits; can be arbitrary)
  $\mathbf{1 + 0.000000000000000000000000000000000000000000000000000000000001 \simeq 1}$
- 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 $|U/t| \to \infty$: 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

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.

Open problems

- 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!

Missing topics

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
$\mathbf{SiH_4}$, $^1A_1$, 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