The Reduced Density Matrix Method: Application Of $T2'$ N-representability Condition and Development of Highly Accurate Solver

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

Pauli principle: antisymmetric wavefunctionis
$$\Psi(\cdots, i, \cdots, j, \cdots) = -\Psi(\cdots, j, \cdots, i, \cdots)$$

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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.

[Dirac 1929]   "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 $\rho(r)$

$\Downarrow$

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]

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

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Scaling

Method	# of variable (discritized)	Exact?
Ψ	N, ($r!$)	Yes
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Equivalent to Schrödinger eq.

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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,

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

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Here we defined the second-order reduced density matrix $\Gamma^{i_1 i_2}_{j_1 j_2}$ (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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N-representability condition [Coleman 1963]

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

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

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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*,*T*1,*T*2**-matrix are all positive semidefinite ↔ eigenvalues λ_i are non-negative ($\lambda_i \geq 0$)

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

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

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[Nakata et al. 2001]

Semidifinite programming

We solved exactly for the first time!

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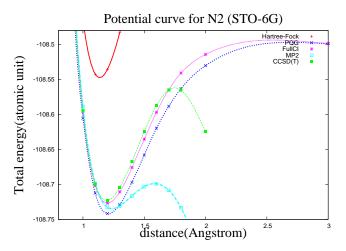
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Details were given in Contributed Talks 13 by
Mituhiro Fukuda et al.,"Exploiting the semidefinite
formulation on the variational calculation of second-order
reduced density matrix of atoms and molecules."

Application to potential energy curve

- Dissociation curve of N_2 (triple bond) [Nakata et al. 2002].

Potential curve for N2 (STO-6G)

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",

Maho Nakata, Bastiaan J. Braams, Katsuki Fujisawa,
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Recent results

- Application of recently derived new $T2'$ N-rep. condition [Braams et al. 2007], [Mazziotti 2006] $T2' \rightarrow (A + \textcolor{red}{B})^{\dagger}(A + \textcolor{red}{B}) + AA^{\dagger}$

- The largest system: double-ζ H_2O molecule.

- Development of Multiple precision arithmetic version of SDP solver and application to one dimentional Hubbard model of strong correlation limit $|U/t| \rightarrow \infty$.

The ground state energy of atoms and molecules

System	State	N	r	ΔE_{GT1T2}	$\Delta E_{GT1T2'}$	$\Delta E_{CCSD(T)}$	ΔE_{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 perturbational treatment of triples
HF	:	Hartree-Fock
FCI	:	FullCI

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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

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

Summary and future direction

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- Semidefinite Programming
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- Improvement are typically 0.1mHartree $\sim$ 0.6mHartree by replacing from $PQGT1T2$ to $PQGT1T2'$.
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WIP : Developing a SDP solver suitable for quantum chemistry.