Large Scale Semidefinite Programming Arising from Chemistry

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Overview

- Motivation
- The Shördinger equation: fundamental equation of Chemistry
- The RDM method; a candidate to a simple quantum chemical theory
- Some recent results
- Summary

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Ultimate goals are...
Prediction and design of chemical reaction.

- What happens if we mix substance A and B?
- CO_2 conversion.
- Drug design ...

etc..

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Electrons
Nuclei (protons and neutrons)

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H: Hamiltonian: the information of the system,
Ψ: wavefunction: complete information of the molecule or atom.
E: energy of the molecule or atom.

We can predict everything from Ψ and E.

The Schrödinger equation

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The Hamiltonian H of the molecular system is:

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

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$$H\Psi(1, 2, \cdots N) = E_{min}\Psi(1, 2, \cdots N)$$

The Pauli principle:
wavefunction is antisymmetric

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

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The general theory of quantum mechanics is now almost complete. $\cdots$ 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.”

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

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Approach	# of variables (discritized)	Exact?
$\boldsymbol{\Psi}$	N, $(\boldsymbol{r}!)$	Yes
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Equivalent to the Schrödinger equation

The RDM Method

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Hamiltonian $\boldsymbol{H}$:

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where

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Then, the total energy E becomes

$$E = \int v_1 \gamma(1|1') d\mu_1 + \int w_{12} \Gamma(12|1'2') d\mu_1 d\mu_2$$

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The first order reduced density matrix (1-RDM) $\gamma(1|1')$

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

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N-representability condition [Coleman:1963]

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

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    - $\boldsymbol{P}$, $\boldsymbol{Q}$-condition [Coleman 1963]
    - $\boldsymbol{G}$-condition [Garrod et al. 1964]
    - $\boldsymbol{T1}$, $\boldsymbol{T2}$-condition [Zhao et al. 2004], [Erdahl 1978]

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  - $T1$, $T2$-condition [Zhao et al. 2004], [Erdahl 1978]
  - Very 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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  - Known “good” approximations are usually semidifinite relaxation.

Semidefinite relaxation to the N-representability condition

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Well known N-representability conditions are usually non-negativity of 2-RDM and linearly transformed 2-RDM.

$$\Gamma(12|1'2') \succeq 0$$

$$-\Gamma(11'|22') + \delta(2-1')\gamma(1|2') \succeq 0$$

etc.

Semidefinite relaxation to the *N*-representability condition

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etc.

Semidefinite programming. [Nakata et al 2001, 2002]

Results for atoms and molecules

[Nakata, Braams, Fujisawa, Fukuda, Percus, Yamashita, Zhao, J. Chem. Phys. 2008]

The ground state energies of atoms and molecules by various methods.

System	State	N	r	Δ E$_{GT1T2'}$	Δ E$_{CCSD(T)}$	Δ E$_{HF}$	E$_{FCI}$
C	^3P	6	20	−0.0001	+0.00016	+0.05202	−37.73653
O	^1D	8	20	−0.0012	+0.00279	+0.10878	−74.78733
Ne	^1S	10	20	−0.0001	−0.00005	+0.11645	−128.63881
O_2^+	$^2\Pi_g$	15	20	−0.0020	+0.00325	+0.17074	−148.79339
BH	$^1\Sigma^+$	6	24	−0.0001	+0.00030	+0.07398	−25.18766
CH	$^2\Pi_r$	7	24	−0.0003	+0.00031	+0.07895	−38.33735
NH	$^1\Delta$	8	24	−0.0004	+0.00437	+0.11495	−54.96440
HF	$^1\Sigma^+$	14	24	−0.0003	+0.00032	+0.13834	−100.16031
F^-	^1S	10	26	−0.0003	+0.00067	+0.15427	−99.59712
H_2O	$^1A_1$	10	28	−0.0004	+0.00055	+0.14645	−76.15576

GT1T2 : the RDM method with $P, Q, G, T1, T2'$ condition
CCSD(T) : Coupled cluster singles and doubles with perturbational treatment of triples
HF : Hartree-Fock (mean field approximation)
FCI : FullCI(the exact value with given basis)

How large SDPS are they?

Number of constraints, blocks (stnadard dual type SDP)

r	# of constraints	blocks
24	15018	2520x2, 792x4, 288x1,220x2
26	20709	3211x2, 1014x4, 338x1, 286x2

Timing using Itanium 2 (1.3GHz) four processors per node.

System, State, Basis	r	Solver	Time	Proc.
$\mathbf{SiH_4}$, $^1A_1$, STO-6G	26	SDPARA	5.1 days	16
$\mathbf{H_2O}$, $^1A_1$, double-ζ	28	SDPARA	2.2 hours	8
$\mathbf{H_2O}$, $^1A_1$, double-ζ	28	SDPARA	20 days	8
$\mathbf{H_2O}$, $^1A_1$, double-ζ	28	SDPARA	24 days	8

Ultra highly accurate SDP solver

At the strong correlation limit($|U/t| \to \infty$), the ground state of the Hubbard model becomes degenerated, thus we need multiple arithmetic version of SDP solver (SDPA-GMP)

The ground state energies of 1D Hubbard model

PBC, Sites:4, Electrons: 4, Spin: 0

U/t	SDPA (double)	SDPA-GMP (PQG)	fullCI
10000.0	$\mathbf{0}$	$\mathbf{-1.1999998800000251 \times 10^{-3}}$	$\mathbf{-1.199999880 \times 10^{-3}}$
1000.0	$\mathbf{-1.2 \times 10^{-2}}$	$\mathbf{-1.1999880002507934 \times 10^{-2}}$	$\mathbf{-1.1999880002 \times 10^{-2}}$
100.0	$\mathbf{-1.1991 \times 10^{-1}}$	$\mathbf{-1.1988025013717993 \times 10^{-1}}$	$\mathbf{-1.19880248946 \times 10^{-1}}$
10.0	$\mathbf{-1.1000}$	$\mathbf{-1.0999400441222934}$	$\mathbf{-1.099877772750}$
1.0	$\mathbf{-3.3417}$	$\mathbf{-3.3416748070259956}$	$\mathbf{-3.340847617248}$

PBC, Sites:6, Electrons: 6, Spin: 0

U/t	SDPA (double)	SDPA-GMP (PQGT1T2)	fullCI
10000.0	0	$\mathbf{-1.7249951195749525 \times 10^{-3}}$	$\mathbf{-1.721110121 \times 10^{-3}}$
1000.0	$\mathbf{-1 \times 10^{-2}}$	$\mathbf{-1.7255360310431304 \times 10^{-2}}$	$\mathbf{-1.7211034713 \times 10^{-2}}$
100.0	$\mathbf{-1.730 \times 10^{-1}}$	$\mathbf{-1.7302157140594339 \times 10^{-1}}$	$\mathbf{-1.72043338097 \times 10^{-1}}$
10.0	$\mathbf{-1.6954}$	$\mathbf{-1.6953843276854447}$	$\mathbf{-1.664362733287}$
1.0	$\mathbf{-6.6012}$	$\mathbf{-6.6012042217806286}$	$\mathbf{-6.601158293375}$

Current problems

- Usually the size of problems becomes extremly large in SDP.
- Moreover, still we cannot solve midium sized molecules with the RDM method where the traditional methods can solve in seconds; too large SDP!
- Chemist intersted in large/huge systems like protein, DNA...

Summary

- The RDM method is a promising candidate to a simpler and exact method of chemistry.
- N-representability condition is the major obstacle, and can be cast as semidefinite programming.
- Semidefintite relaxation works very nicely; almost comparable to the exact results.
- Development and application of SDPA-GMP (multiple pricision arithmetic version of SDP solver) for degenerated systems.
- Future direction: development of SDP for quantum chemistry.