Large Scale Semidefinite Programming Arising from Chemistry

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2008/5/10

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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$$H\Psi = E\Psi$$

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 $\boldsymbol{H}$ of the molecular system is:

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

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

The Pauli principle:
wavefunction is antisymmetric

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

Problems ...

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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 difficultly is only that the exact application of these laws leads to equations much too complected to be soluble.

"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?
Ψ	N, $(r!)$	Yes
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Equivalent to the Schrödinger equation

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Hamiltonian 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) $\boldsymbol{\gamma(1|1')}$

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

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N-representability condition [Coleman:1963]

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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.

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

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

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

etc.

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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	$\Delta E_{GT1T2'}$	$\Delta E_{CCSD(T)}$	ΔE_{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	**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	**−1.1000**	**−1.0999400441222934**	**−1.099877772750**
1.0	**−3.3417**	**−3.3416748070259956**	**−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	**−1.6954**	**−1.6953843276854447**	**−1.664362733287**
1.0	**−6.6012**	**−6.6012042217806286**	**−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.