“New Development Of Numerical Simulations in Low-Dimensional Quantum Systems:
From Density Matrix Renormalization Group to Tensor Network Formulations”,
Kyoto University, 27-29 Oct. 2010

Optimizing Hartree-Fock Orbitals by the Density Matrix Renormalization Group

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H.-G. Luo, M.-P. Qin, T. Xiang, PRB **81**, 235129 (2010); arXiv:1002.1287

Also see poster session

Fundamental issue in quantum chemistry calculation

How to solve the Schrodinger equation of molecules **accurately** and **efficiently** ?

The Schrodinger Equation:

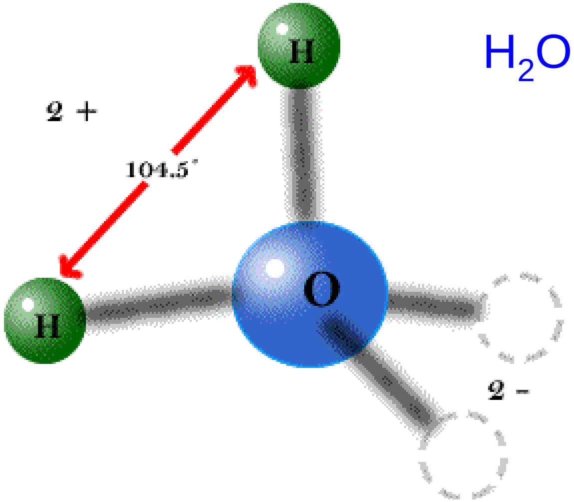
$$i\hbar\frac{\partial}{\partial t}\psi(r,R)=\left[-\sum_i\frac{\hbar^2}{2m_e}\nabla_i^2+V(r,R)\right]\psi(r,R)$$

$$V(r,R)=-\sum_{il}\frac{Z_l e^2}{|r_i-R_l|}+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i-r_j|}$$

The basic difficulty to solve the equation is **the exponential wall problem.**

For example, for a water molecule, which has 10 electrons, if N molecule orbitals are used, the total number of basis states is

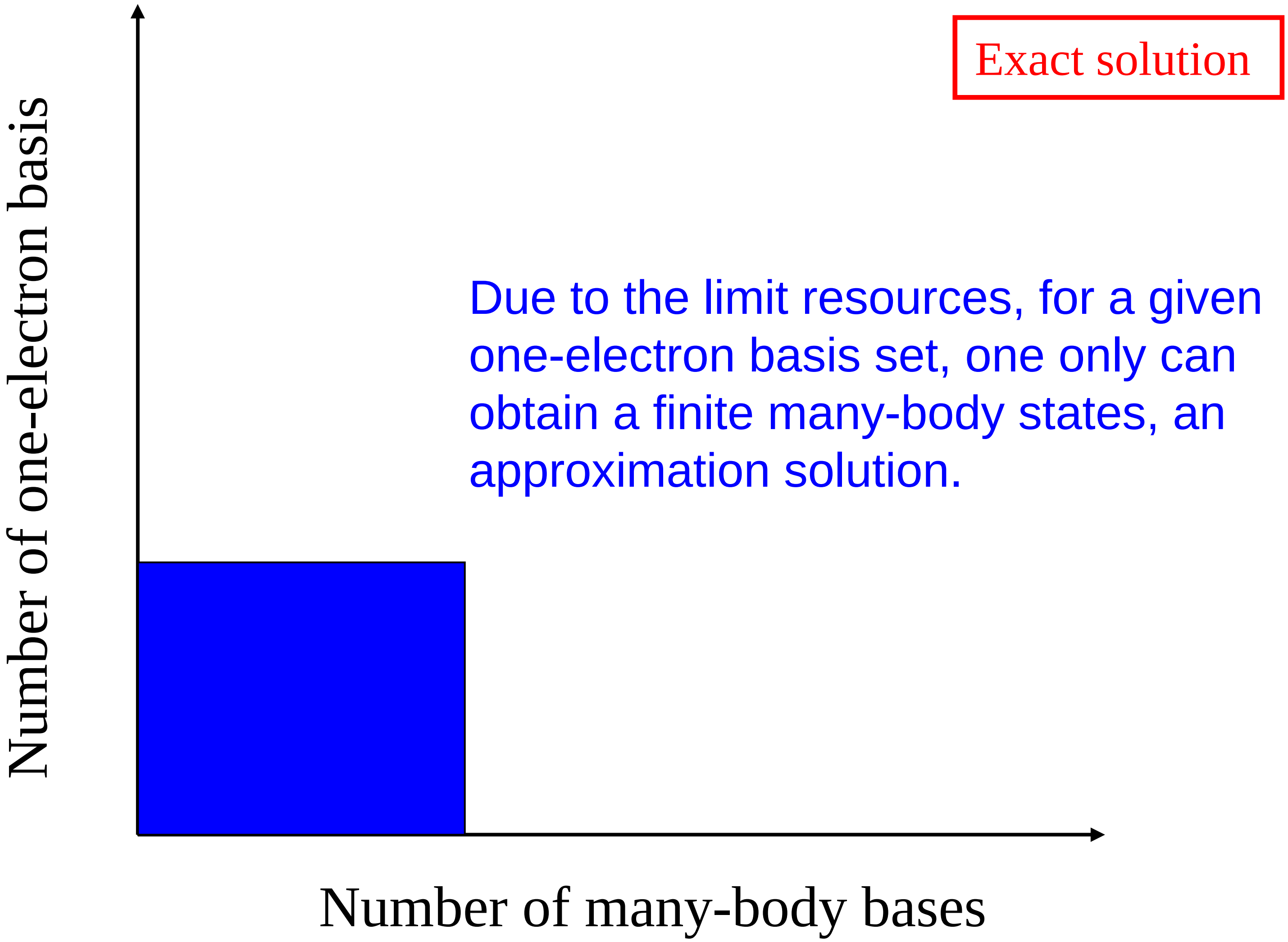
$$C_N^5 C_N^5 \sim N^{10}$$



H_2O

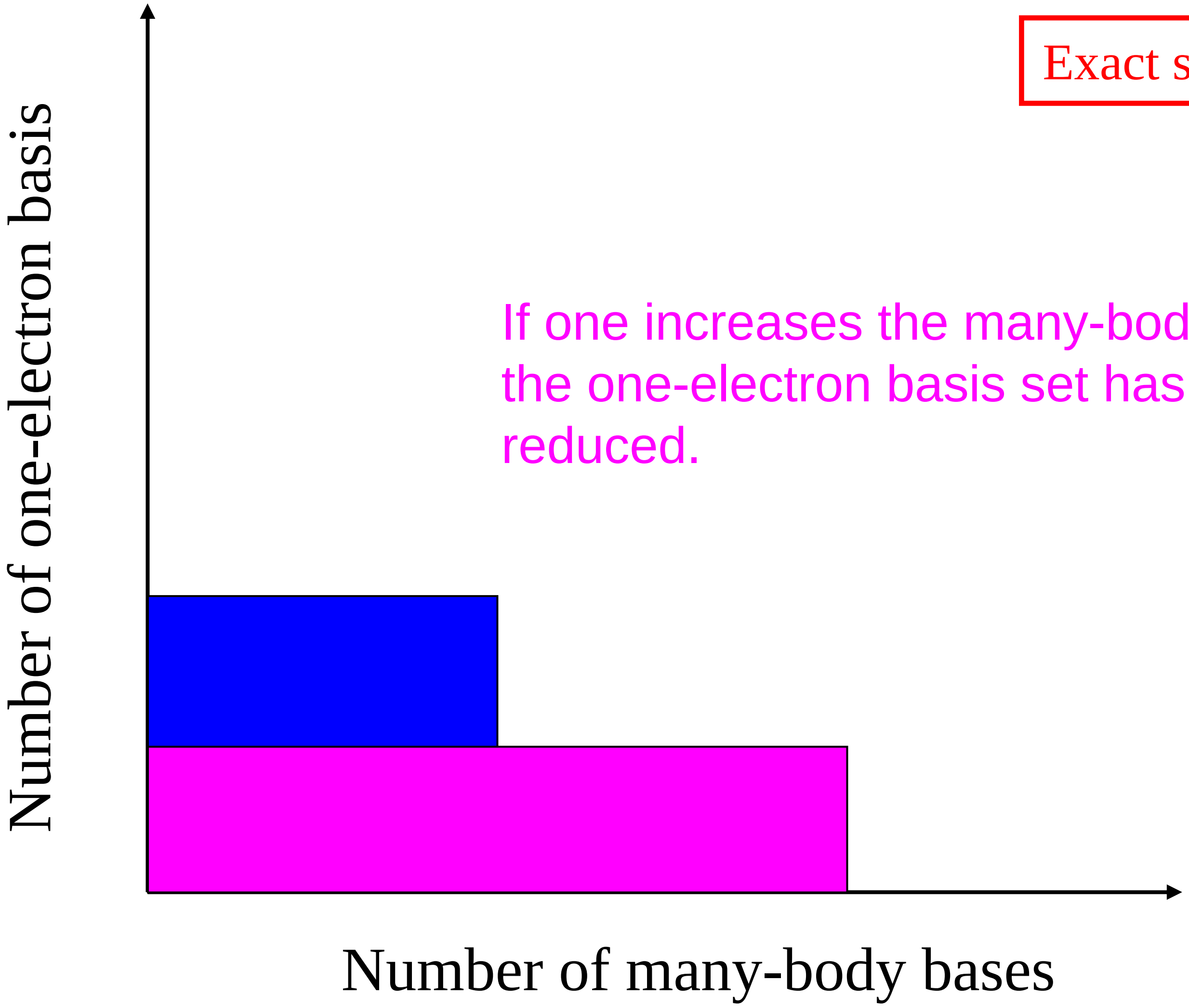
The total degree of freedom increases exponentially with the number of electrons!

In practical calculation, some truncation approximations are made, as show in the cartoon.



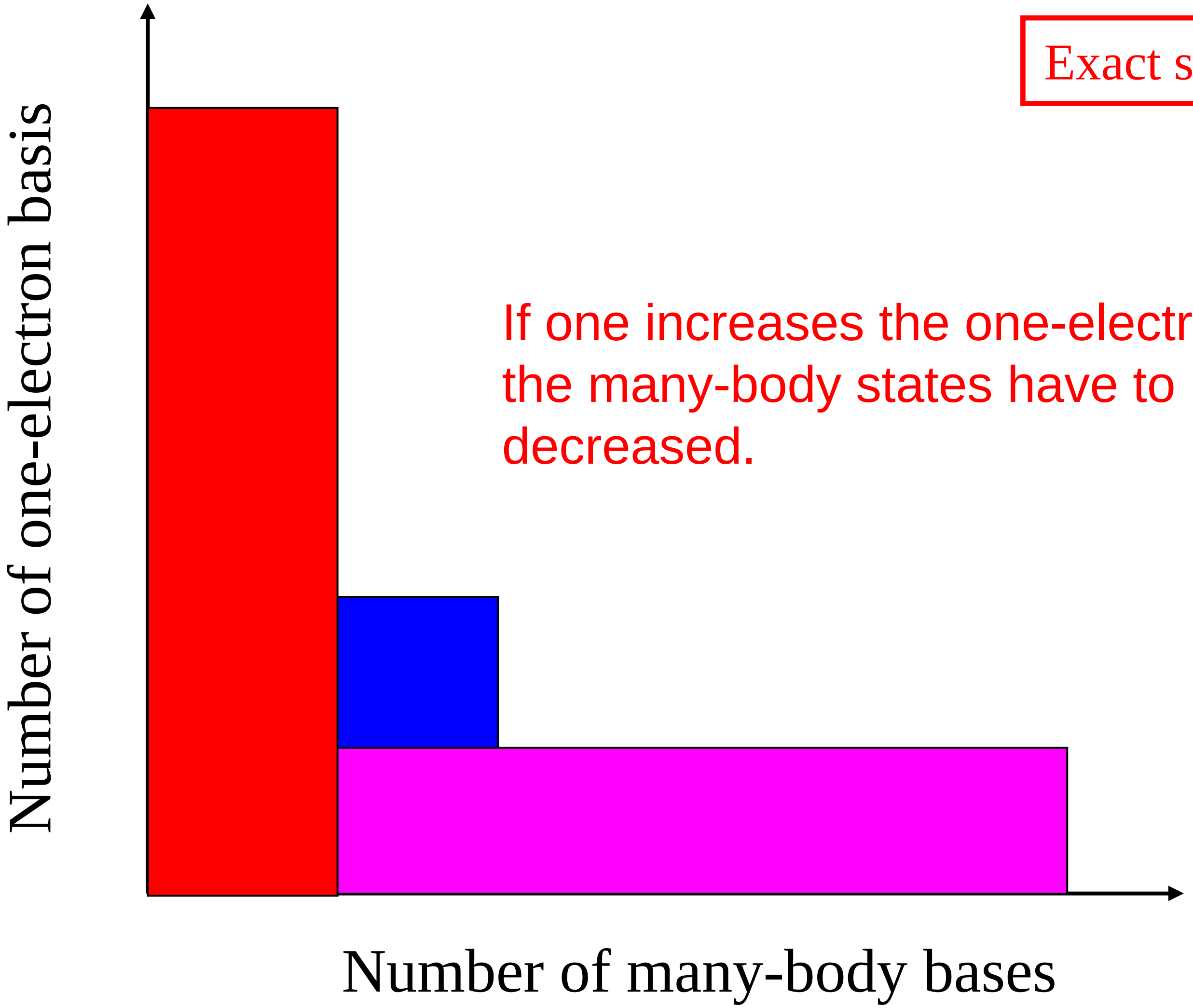
Due to the limit resources, for a given one-electron basis set, one only can obtain a finite many-body states, an approximation solution.

Exact solution

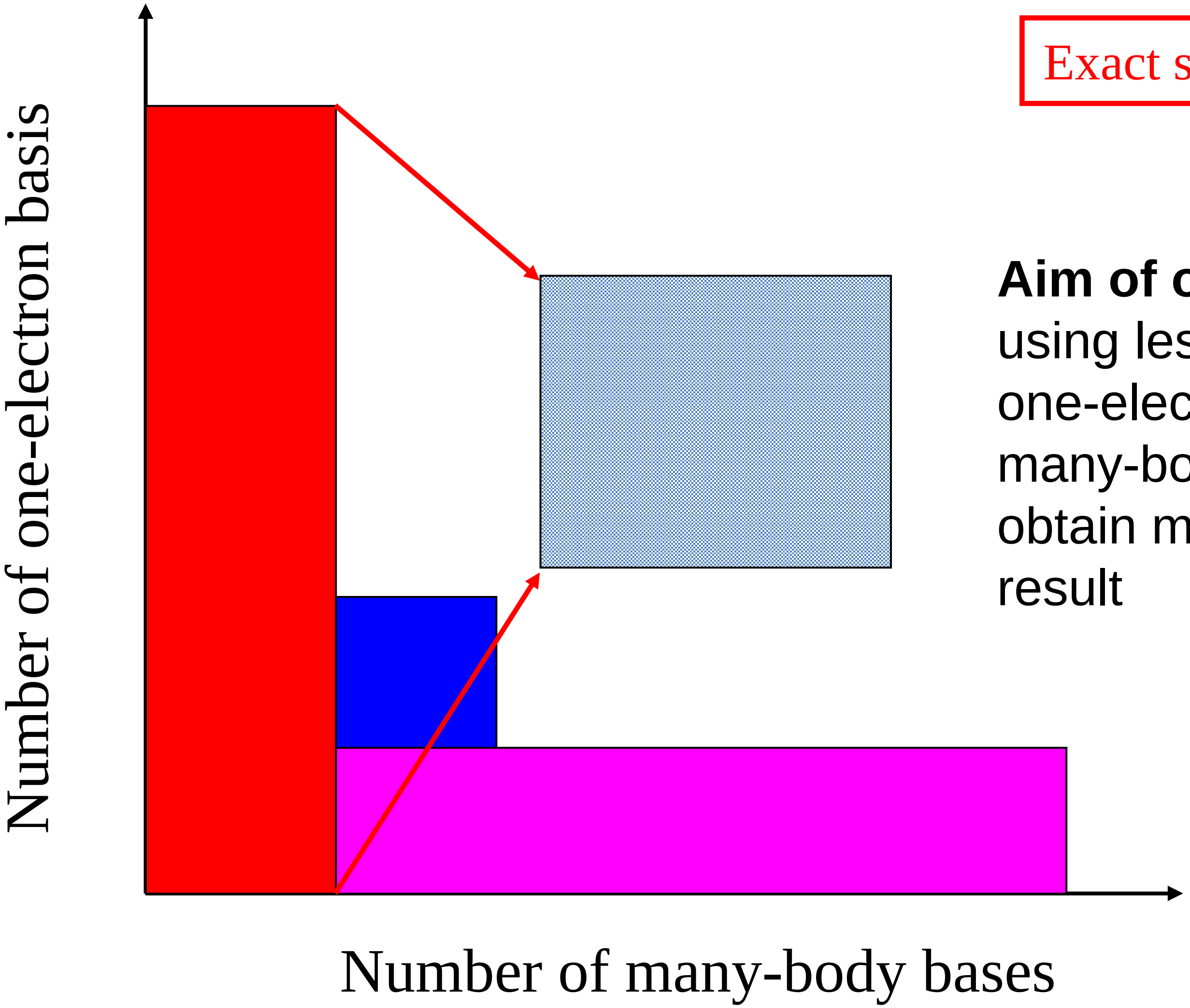


If one increases the many-body states, the one-electron basis set has to be reduced.

Exact solution



If one increases the one-electron basis, the many-body states have to be decreased.



Exact solution

Aim of our work :
using less optimized one-electron basis and many-body states to obtain much accurate result

How to apply DMRG to quantum chemistry

The starting point is to represent the Hamiltonian in the second quantized form by using a set of HF orbitals

$$H=\sum_{ij\sigma}^{N} t_{ij} c_{i\sigma}^{+} c_{j\sigma}+\tfrac{1}{2}\sum_{ijrt,\sigma\sigma'}^{N} V_{ijrt} c_{i\sigma}^{+} c_{j\sigma'}^{+} c_{t\sigma'} c_{r\sigma}$$

$$t_{ij}=\int dr\varphi_i^*(r)\left[-\tfrac{1}{2}\Delta-\sum_{k=1}\frac{Z_k e^2}{|r-r_k|}\right]\varphi_j(r)$$

One-electron integral

$$V_{ijrt}=\int\int drdr'\varphi_i^*(r)\varphi_j^*(r')\left[\frac{e^2}{|r_i-r_j|}\right]\varphi_t(r')\varphi_r(r)$$

Two-electron integral

Molecular orbital: HF single particle basis

But, the interaction includes N^4 terms, thus the compute time and storage cost expensive, > $O(N^5)$

$$\hat{H} = \sum_{ij}^{N} t_{ij} c_i^{+} c_j + \frac{1}{2} \sum_{ijkl}^{N} V_{ijkl} c_i^{+} c_j c_k^{+} c_l$$

N^4 terms!

Only a small number of Hartree-Fock orbitals can be used, thus it is impractical in quantum chemistry calculation!

The way to solve this problem is regrouping operators introduced by T. Xiang in 1996, namely, if some orbitals in the same block, the summation can be performed in advance, as a result some complementary operators are introduced.

$$O = \sum_{ijkl\in Sys} V_{ijkl} c_i^+ c_j c_k^+ c_l \quad \Longrightarrow \quad O(N^4) \to O(1)$$

$$O_i = \sum_{jrt\in Sys} V_{ijrt} c_j^+ c_t c_r \quad \Longrightarrow \quad O(N^4) \to O(N)$$

$$O_{ij} = \sum_{rt\in Sys} V_{ijrt} c_t c_r \quad \Longrightarrow \quad O(N^4) \to O(N^2)$$

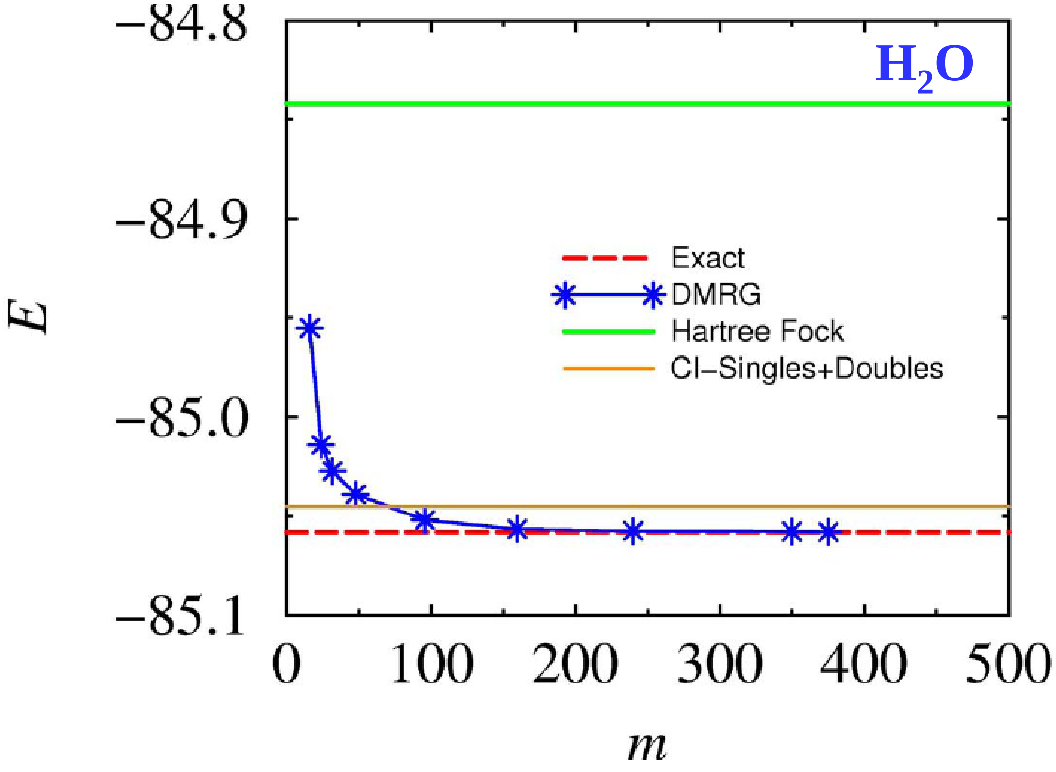
$O(N^4)$ terms → $O(N^2)$ terms

$$\hat{H} = \sum_{ij}^{N} t_{ij} c_i^+ c_j + \frac{1}{2} \sum_{ijkl}^{N} V_{ijkl} c_i^+ c_j c_k^+ c_l$$

~~N^4 terms!~~

T Xiang, Phys Rev B **53**,R10445 (96)

In 1999, White and Martin performed for the first time the *ab initio* DMRG calculation of the ground state energy of a water molecule, in the case of about 300 many-body states kept, the result is almost exact one, *which gives us confidence to apply the DMRG to quantum chemistry calculation.*

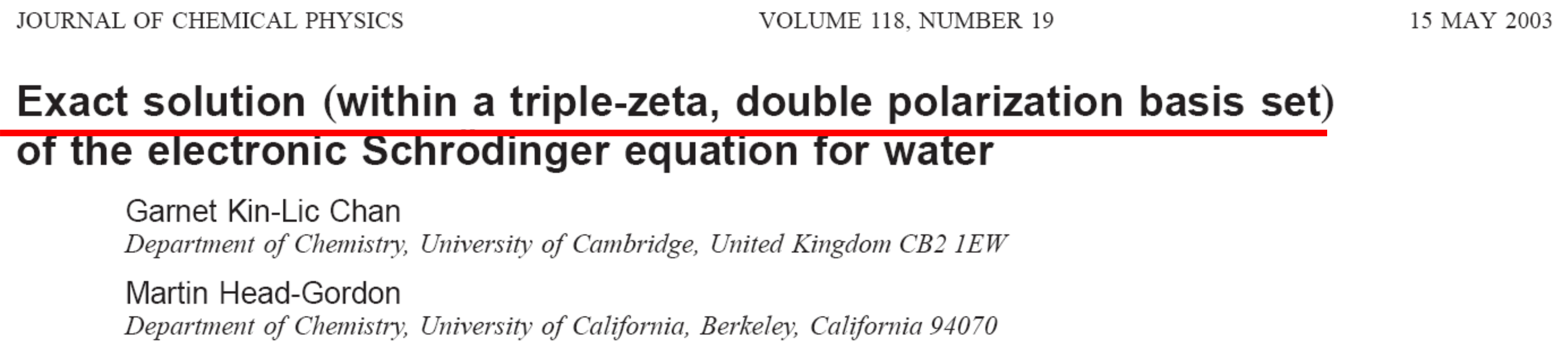


Number of many-body bases

Use 25 H_2O molecular orbitals

DMRG: $1s^2$ of oxygen is frozen

S. R. White and R. Martin, J. Chem. Phys. 110, 4127 (1999)



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Exact solution (within a triple-zeta, double polarization basis set) of the electronic Schrodinger equation for water

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- ✓ In 2003, Chan and Head-Gordon gave a benchmark calculation of the ground state energy of water molecule. This large scale calculation obtained near-exact result for 41 Hartree-Fock orbitals.

Orbital #: *N*	Unrestricted Hartree-Fock	Coupled Cluster (SDT)	DMRG[1]	Quantum Monte Carlo[2]
41	-85.254555	-85.511075	-85.511649 (M=6000)	-85.5132(6)
92	-85.257519	-85.564462		-85.567(1)

[2] Shiwei Zhang et al J. Chem. Phys. 124, 224101 (2006)

Our goal:
One can handle large basis set, for example, 200, even more.

Basis idea:
Optimizing the HF orbitals by the DMRG

See poster session

New result for ground state energy of water molecule (unpublished)

$$E_{gs} = -85.575(\text{a.u.})$$

(N_{tot} =172 orbitals, N = 60 orbitals, M =128, M_{max} = 512)

This is the best result obtained by DMRG for 172 Hartree-Fock orbitals.

Orbital #: *N*	Unrestricted Hartree-Fock	Coupled Cluster (SDT)	DMRG[1]	Quantum Monte Carlo[2]
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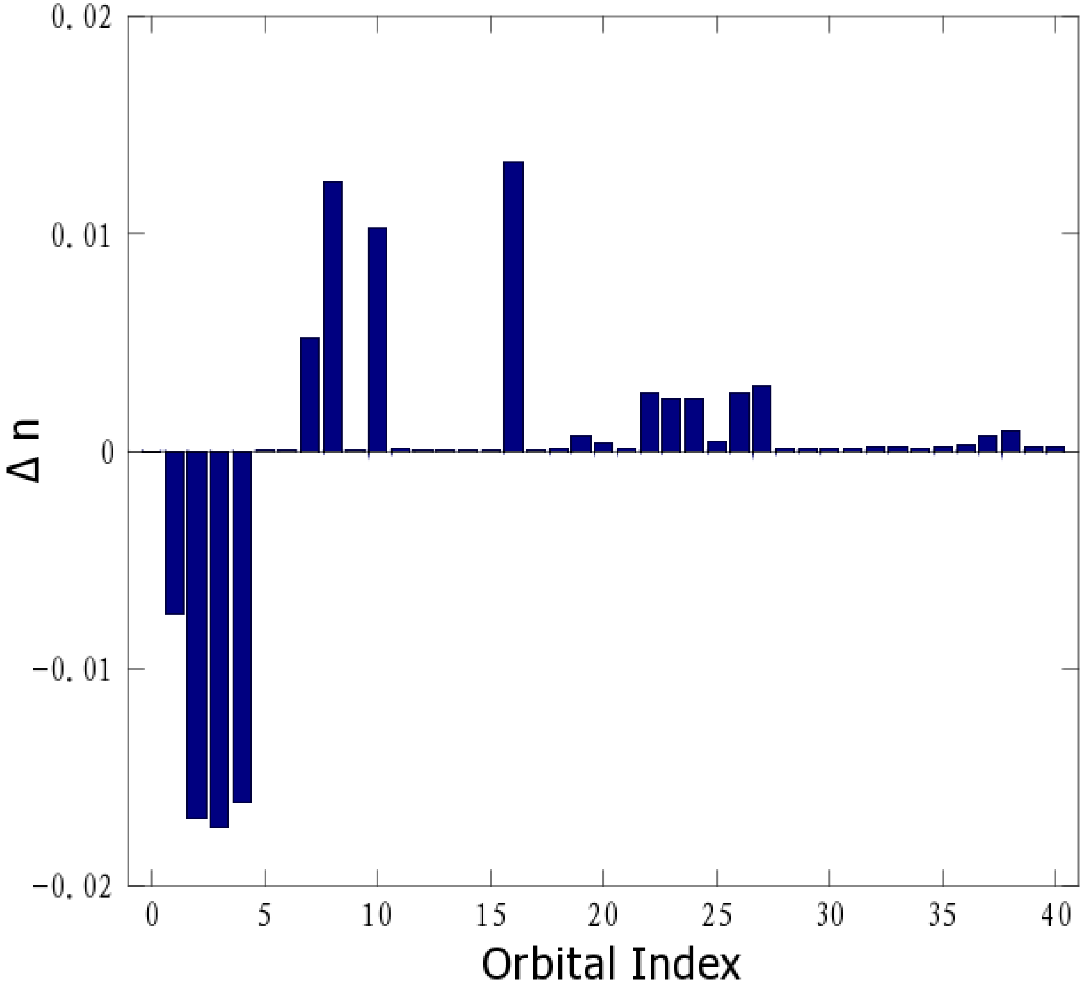
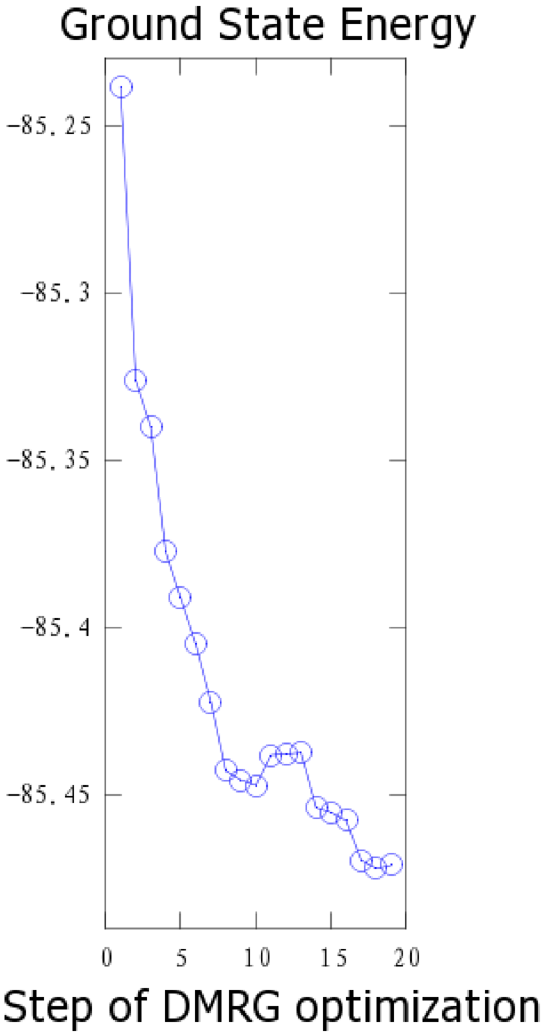
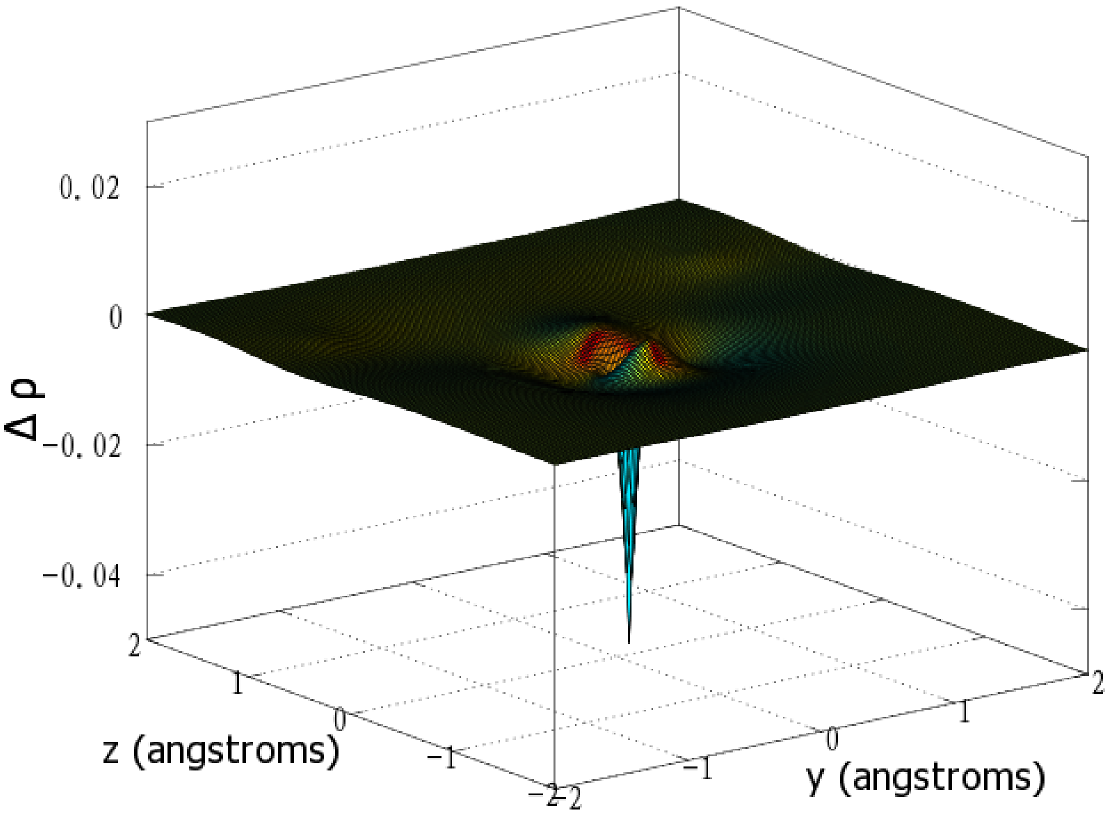
92	-85.257519	-85.564462	?	-85.567(1)

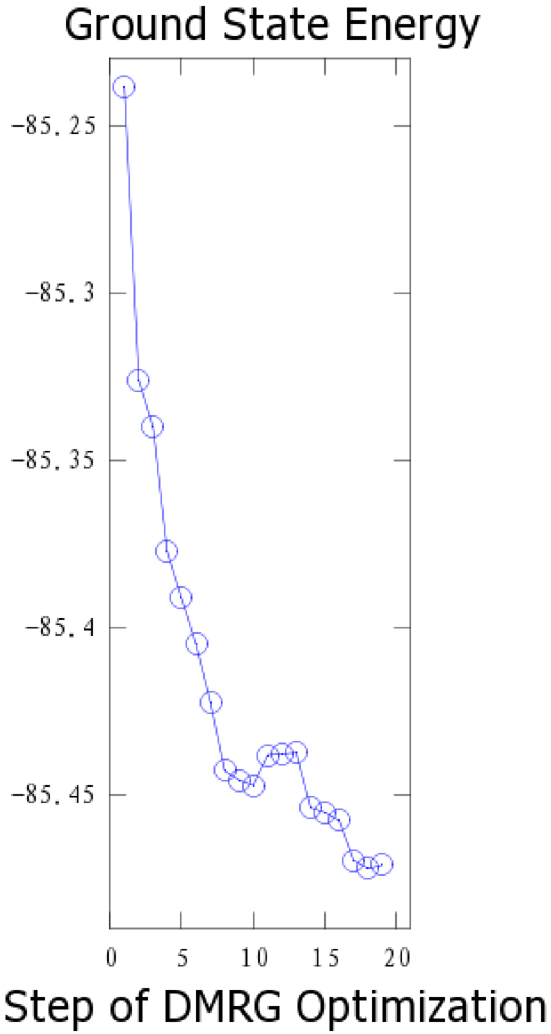
Animation to display the optimizing process of the HF orbitals





Electronic density distribution





Thank you for your attentions !