

# The DMRG in Quantum Chemistry

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1. DMRG and Quantum Chemistry
2. Connected DMRG

## What is Ab-initio Quantum Chemistry?

- ▶ Input molecular geometry, and a basis set (set of real space 1- $e$  functions typically atom-centred Gaussians  $|i\rangle$ )
- ▶ Calculate molecular integrals for Hamiltonian

$$\begin{aligned}t_{ij} &= \langle i | -\frac{1}{2}\nabla^2 + v_{ext} | j \rangle \\v_{ijkl} &= \langle ij | r_{12}^{-1} | ji \rangle \\H &= \sum_{ij} t_{ij} a_i^\dagger a_j + \sum_{ijkl} v_{ijkl} a_i^\dagger a_j^\dagger a_k a_l\end{aligned}$$

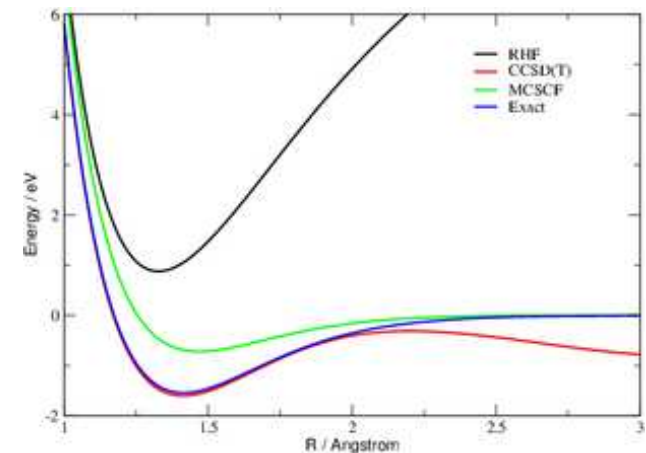
- ▶ Use favourite method to solve for many-particle wavefunction (i.e. not DFT)

## The Two Correlation Problems

We wish to compute

$$E_c = E_0 - E_{HF}$$

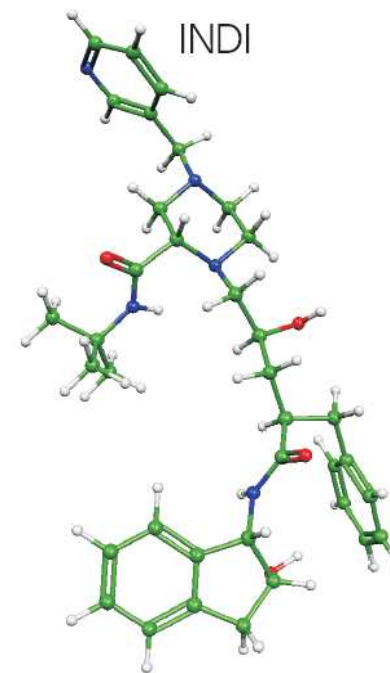
- ▶ Same order as binding energy: e.g.  $\text{H}_2\text{O}$ , atomization en. =  $0.352 E_h$ , corr. en  $\approx -0.3 E_h$ .
- ▶ **Dynamical** (short-range) correlation:  $e - e$  cusp, correlation energy converges
- ▶ **Non-dynamical** (long-range) correlation: near-degeneracies with mean-field reference



## Dynamical Correlation Problems

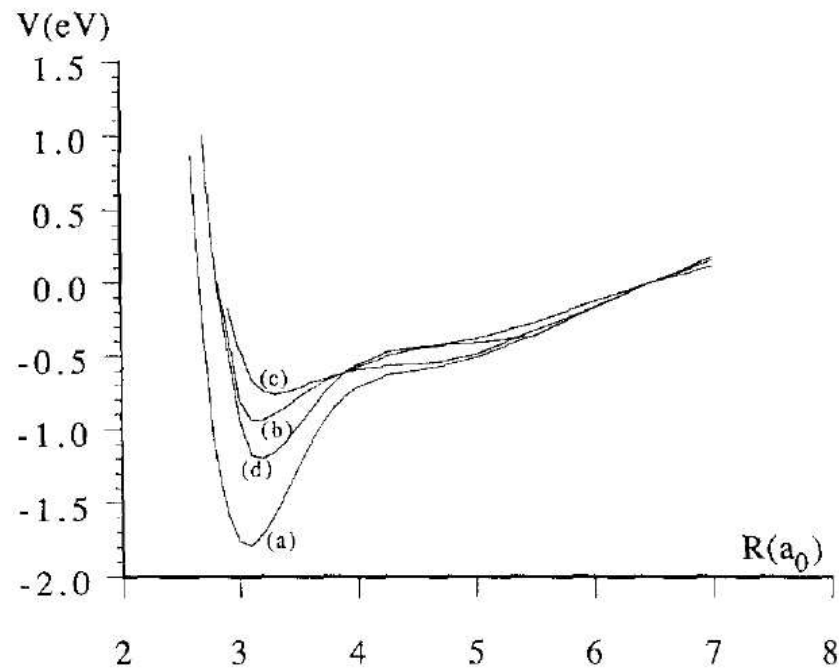
Water vibrational spectrum: Polyansky et al  
Science **299**, 539 (2003)

	Predicted freq ( $cm^{-1}$ )
Obs	1,594.74
6Z	-2.29
CBS + CV	0.48
Rel + QED	-0.75
DBOC + Nonad	-0.27



5846 fns, LCCSD, 1 day:  
Schütz et al PCCP **5**, 3349  
(2003)

## Nondynamical Correlation Problems



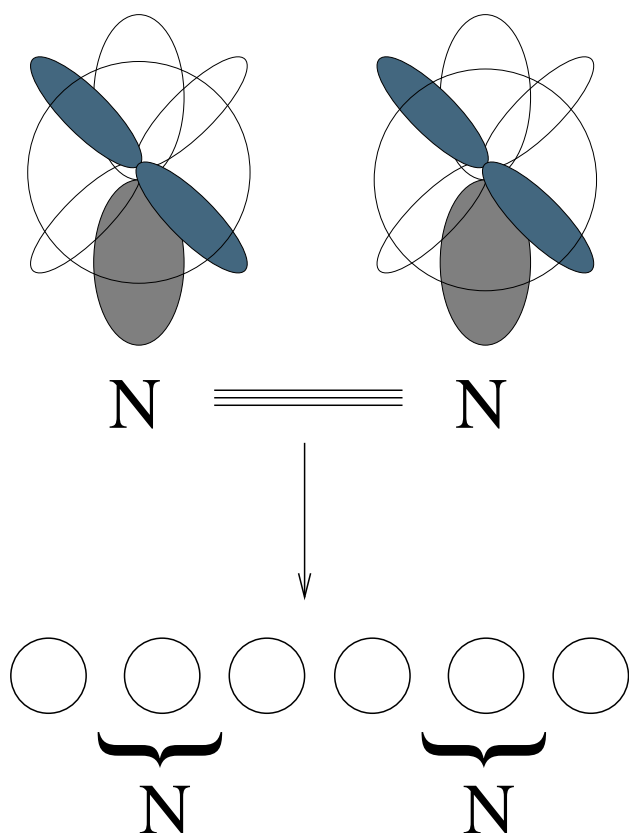
- ▶ Formal *sextuple* bond, shortest diatomic bond 1.6788 Å (Bulk chromium 2.5 Å)
- ▶ Bond is very weak, weaker than singly bonded  $\text{Cu}_2$ !
- ▶ As bond is stretched, bonded singlets unpair
- ▶ Range of energies, lengths: 4s/3d bonding

## DMRG and Quantum Chemistry

$$H = \sum_{ij} t_{ij} a_i^\dagger a_j + \sum_{ijkl} v_{ijkl} a_i^\dagger a_j^\dagger a_k a_l$$

- ▶ White and Martin JCP **110**, 4127 (1999)
  - PPP, Extended Hubbard:
    - Fano, Ortolani, Ziosi JCP **108**, 9246 (1998)
    - Ramasesha et al. JCP **106**, 10230 (1997)
  - Xiang PRB **53**, 10445 (1996)
- ▶ Several efficient implementations now exist:
  - Mitrushenkov et al. JCP **115**, 6815 (2001)
  - GKC et al, JCP **116**, 4462 (2002)
  - Legeza et al. PRB **67**, 125114 (2003)

## The QC picture



- ▶ Orbitals must be ordered.  
(Which ordering?)
- ▶  $H$  is long-ranged
  - Coulomb repulsion
  - ordering
- ▶  $H$  has many interaction terms:  $v_{ijkl}$  i.e.  $n^4$  - need efficient algorithm.

## The DMRG Algorithm

$$A \left\{ \begin{array}{|c|c|} \hline \square & \bigcirc \\ \hline \end{array} \right\} B$$

$$H = H_A + H_B + \Delta_{AB}$$

Main cost is  $v_{ijkl} a_i^\dagger a_j^\dagger a_k a_l$ . Introduce complementary operators

$$P_{ij}^B = \sum_{kl \in B} v_{ijkl} a_k a_l$$

$$Q_{ij}^B = \sum_{kl \in B} x_{ijkl} a_k^\dagger a_l$$

$$R_i^B = \sum_{jkl \in B} w_{ijkl} a_j^\dagger a_k a_l$$

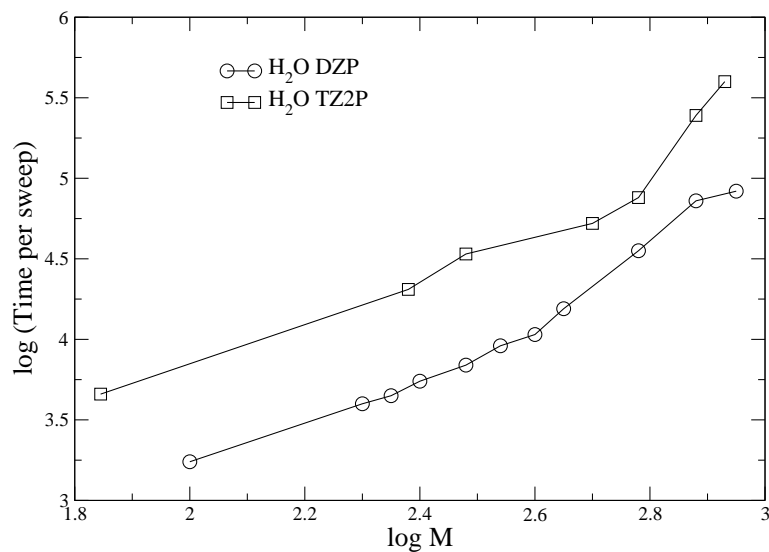
Then we form  $\Delta_{AB}$  like

$$\Delta_{AB} = \sum_{ij \in A} \left( a_i^\dagger a_j^\dagger P_{ij}^B + a_i^\dagger a_j Q_{ij}^B \right) + \sum_{i \in A} a_i^\dagger R_i^B + \dots$$

Operator	Complementary	Disk Storage
$a_i a_j$	$P_{ij} = \sum_{kl} v_{ijkl} a_k^\dagger a_l^\dagger$	$O(M^2 n^3)$
$a_i^\dagger a_j$	$Q_{ij} = \sum_{kl} v_{ijkl} a_l^\dagger a_k$	$O(M^2 n^3)$

$$H = \sum_i a_i^L S_i^R + \sum_{ij} a_i a_j^L P_{ij}^R + a_i^\dagger a_j^L Q_{ij}^R + \dots$$

- ▶ matrix multiply in Davidson step:  $O(M^3 n^3)$
- ▶  $P_{ij}, Q_{ij}$  operators,  $O(M^2 n^4)$  per sweep

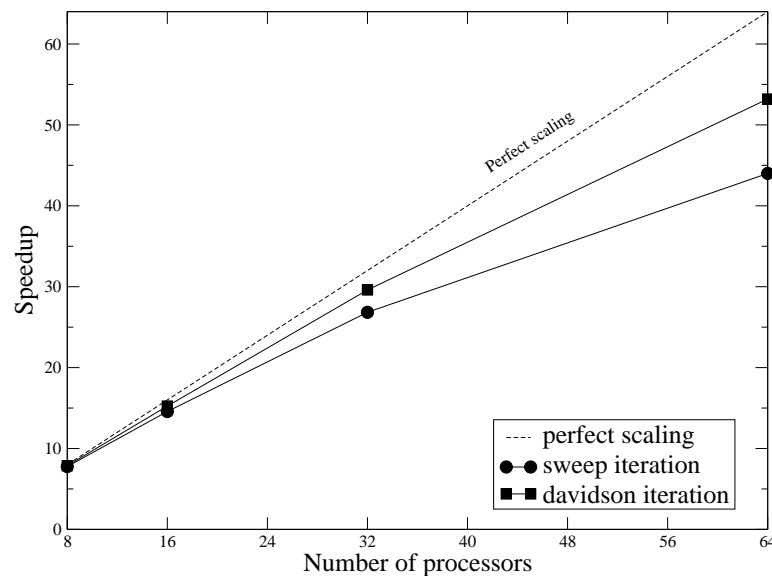


# Parallelisation

DMRG algorithm embarrassing parallel:

- ▶ e.g.  $H_c$  like dot-product e.g.  $\sum_{ij} a_i a_j^L P_{ij}^R$ , operator rotations independent etc.
- ▶ Distributed memory parallelisation:  $\frac{1}{p} O(M^3 n^3) + O(M^2 n^4)$  time,  $\frac{1}{p} O(M^2 k^2)$  memory per processor,  $O(M^2 k \log p)$  communication.

GKC, JCP **120**, 3172 (2004)



$n_{proc}$	$H_c$	DM
1	99.0	0.4
4	98.6	0.8
16	95.2	3.8
64	81.5	15.3

## DMRG with Non-orthogonal Orbitals

GKC and Van Voorhis, to submit JCP (2004)

In QC, sometimes convenient to use NO orbitals, i.e.  $\langle i|j\rangle = S_{ij}$ . Define **biorthogonal** (contravariant, covariant) operators, see e.g. Head-Gordon et al, JCP **108**, 616 (1998)

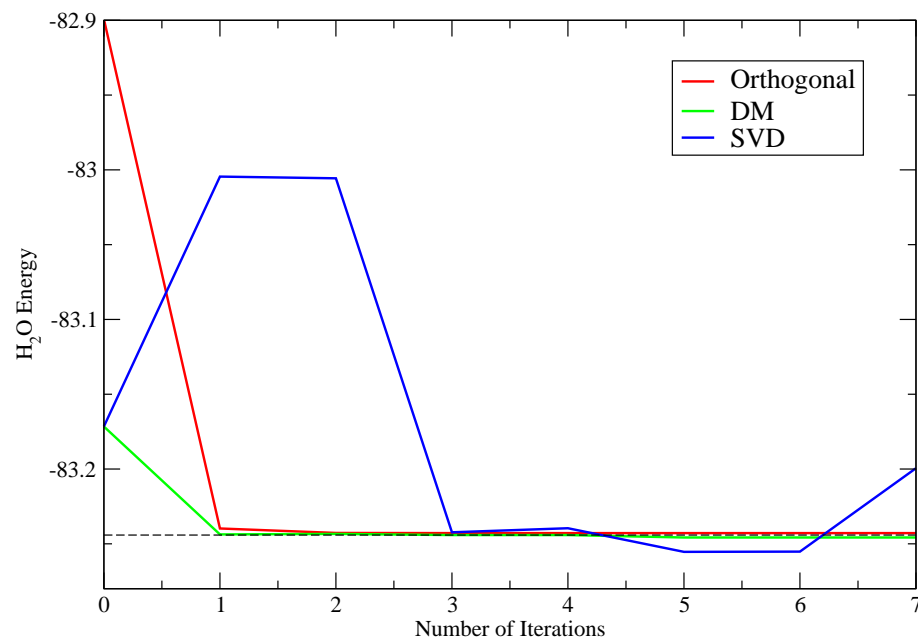
$$\begin{aligned} a^{\dagger i} &= S^{-1} a_i^{\dagger} \\ \{a^{\dagger i}, a_j\} &= \delta_j^i \\ H &= \sum_{ij} t_i^j a^{\dagger i} a_j + \sum_{ijkl} v_{ij}^{kl} a^{\dagger i} a^{\dagger j} a_k a_l \end{aligned}$$

- ▶  $H$  now non-Hermitian
- ▶ Basic DMRG algorithm same same, two sets of operators  $(a^{\dagger i}, a_i)$ , non-symmetric Davidson etc.
- ▶ Must allow **complex** wavefunctions (due to truncation)

**BUT...**

DM and SVD of wavefunction **not** equivalent! Define left, right solutions of  $H, \Psi_l, \Psi_r$ .

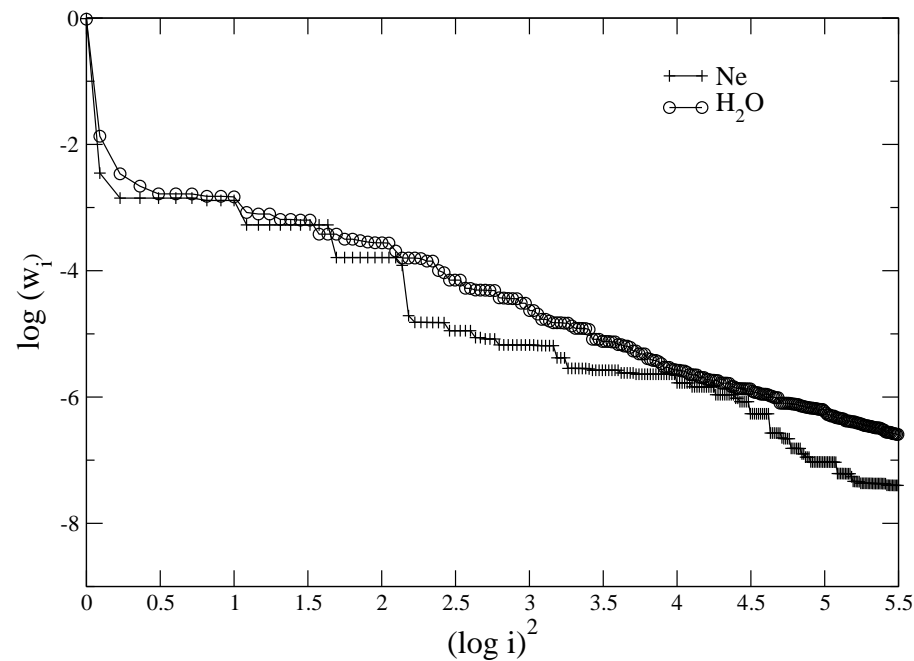
- ▶ *Natural* defn of DM =  $|\Psi_l\rangle\langle\Psi_r|$ : left, right eigenvectors  $\rightarrow$  left, right system states.
- ▶ SVD of  $\Psi_l \rightarrow$  left system states, SVD of  $\Psi_r \rightarrow$  right system states.



DM is correct; use abs. of eigenvalues.

# Convergence

Error in energy  $\sim$  discarded DM weight, rate of decay of eigenvalues *not quite* exponential.



We can argue from weights of grand canonical density matrix:

$$w_i = Z^{-1} \exp(-\beta(E_i - \mu))$$

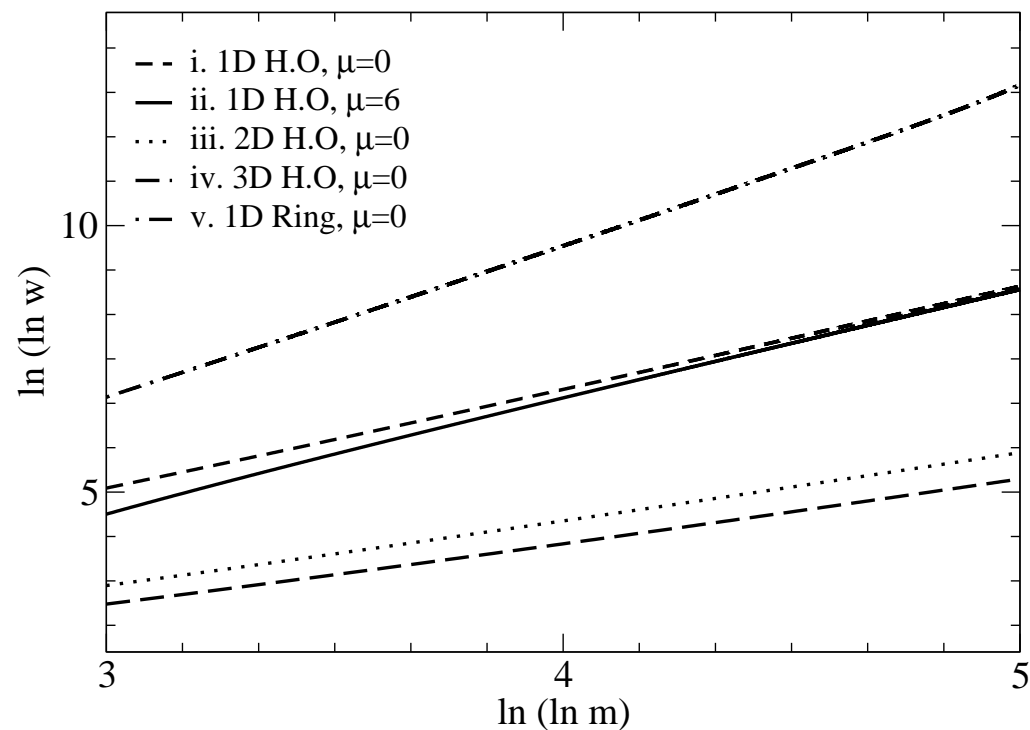
1-D Ising model  $w_i \sim \exp[-\alpha(\log(i))^2]$

Okunishi et al, PRE **59**, R6227, 1999

Any finite weakly interacting quasi-particle system in D dimension

$$w_i \sim \exp[-\rho^{-1}(\log(i))^f(D)]$$

where for Coulombic Hamiltonians  $D = 5/3$ . Chan et al, J Stat Phys **109**, 289 (2002),  
see also works by Zhang and Henley, Chung and Peschel



# Samples of Quantum Chemistry

## Specific studies

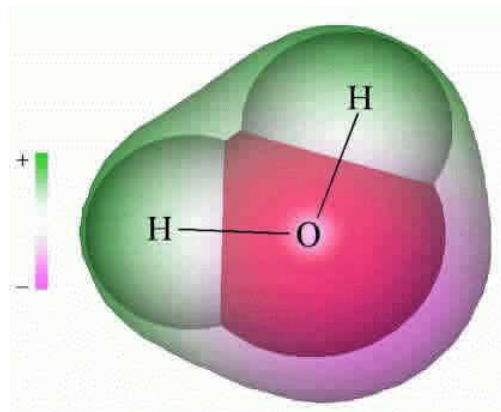
Water 25 fns, 8e. Exact Diagonalisation  $2 \times 10^7$  space

Bauschlicher and Taylor JCP **85**, 2779 (1986)

$M$	$E/H$	$\delta E/mH$
100	-76.2545	2.1
200	-76.2559	0.71
300	-76.25632	0.32
<b>400</b>	<b>-76.256477</b>	<b>0.157</b>
500	-76.256540	0.094
600	-76.256592	0.042
750	-76.256617	0.017
<b>900</b>	<b>-76.256624</b>	<b>0.010</b>
CCSD	-76.252503	4.131
CCSD(T)	-76.255907	0.727

- ▶  $M = 400$  O(hours)
- ▶ CCSD takes  $O(1)$  min
- ▶ Exact Diagonalisation much quicker:  $H$  is very sparse in Slater Determinant space.

## Water, larger basis sets



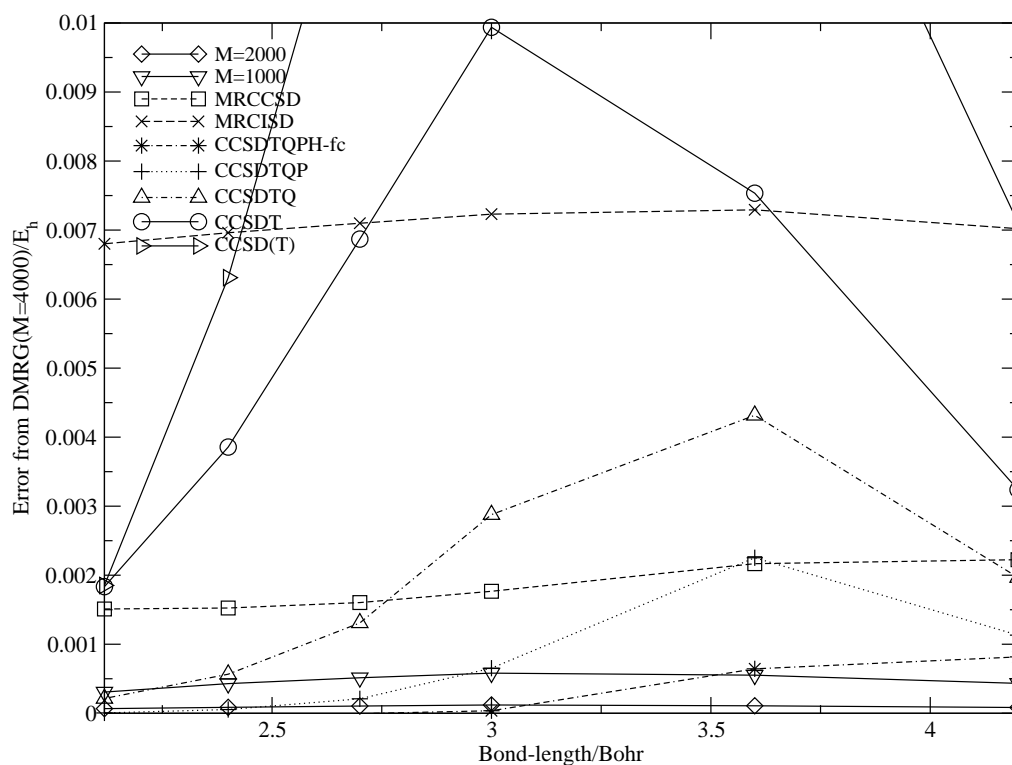
	DMRG (exact)	CCSD	CCSD(T)	CCSDT	CCSDTQ
$r_e$	-76.314715	7.597	0.574	0.421	0.019
$1.5r_e$	-76.131050	15.961	1.608	1.663	0.165

- ▶ At the time, we claimed this was the largest “exact” calculation done ( $10e$ , 41 fns,  $5.6 \times 10^{11}$  Hilbert space)!
- ▶ DMRG calculations used up to  $M = 6000$ .
- ▶ “Exact” non-relativistic energy  $-76.438 E_h$ ; remaining error  $-0.123 E_h$  due to  $1e$  basis.

# Nitrogen Dissociation

Standard  $14e$ , 28 site model for non-dynamical correlation: triple bond dissociation.

GKC et al, JCP (2004) to appear.



- ▶ New benchmark (exact to  $0.03 E_h$ )
- ▶ **Good news:** DMRG gives a well balanced description with small  $M$ .

## Summary

- ▶ DMRG is a promising theory to treat strongly correlated electrons in QC (nondynamic correlation).
- ▶ Cost v. high due to large  $M$  we need to keep (at least 1000).
- ▶ DMRG is good if not too many states per site, **but** predictive (as opposed to model/benchmark) calculations require **dynamical** correlation i.e. 10-100 states per site.

# Connected DMRG

## What is a connected cluster expansion?

We all know it! See also irreducible, cumulant, etc.

Cluster decomposition

$$C(1) = T_1(1)$$

$$C(1, 2) = \frac{1}{2}T_1(1)T_1(2) + T_2(1, 2)$$

$$C(1, 2, 3) = \frac{1}{6}T_1(1)T_1(2)T_1(3) + \frac{1}{2}T_1(1)T_2(2, 3) + T_3(1, 2, 3)$$

We call e.g.  $\frac{1}{2}T_1(1)T_1(2)$  the “disconnected” (reducible) part of  $C(1, 2)$  and  $T_2(1, 2)$  the “connected” (irreducible) part.

## CI and CC Theory

- ▶ CI (Configuration Interaction): Start with reference  $|0\rangle$ .  $E_i^a$  excite particles from  $i$ th orbital to  $a$ th orbital  $i \rightarrow a$ ,  $|0\rangle \rightarrow |i^a\rangle$

$$|\Psi\rangle = (1 + \sum_{ia} c_i^a E_i^a + \sum_{ijab} c_{ij}^{ab} E_{ij}^{ab} + \dots)|0\rangle$$

- ▶ CC (Coupled Cluster Theory)

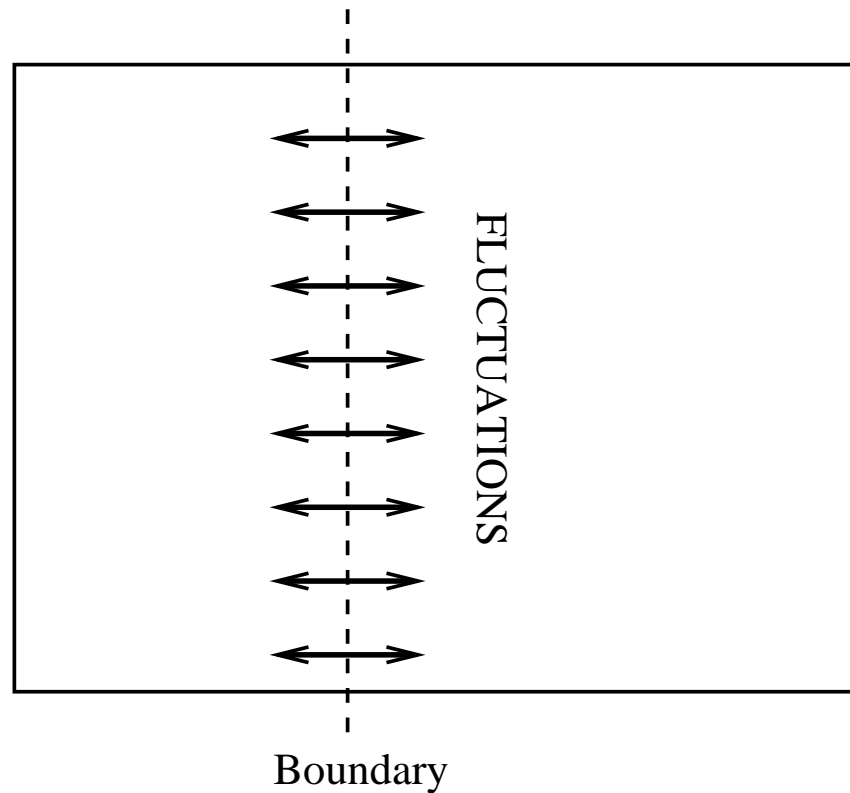
$$|\Psi\rangle = \exp \left[ \sum_{ia} t_i^a E_i^a + \sum_{ijab} t_{ij}^{ab} E_{ij}^{ab} + \dots \right] |0\rangle$$

c.f. BCS. Expanding the exponential, gives a cluster decomposition of CI

$$c_{ij}^{ab} = \frac{1}{2} t_i^a t_j^b + t_{ij}^{ab}$$

CC is a generalised mean-field theory (effective pair theory, effective triple theory etc.)

## DMRG and Connected Fluctuations



- ▶ For 2/3d systems; number of fluctuations grows exponentially with width! DMRG gets worse (but mean field theory gets better!?)
- ▶ DMRG uses **disconnected** representation. Number of **connected** fluctuations is constant with boundary size (by defn. depends only on correlation length). How to fix?

## Canonical (Heisenberg) representation

- ▶ Hermitian operators are diagonalised by unitary transformation. Starting from a repr. in non-interacting fns, then in Heisenberg representation

$$O_d = U^\dagger O U$$

where  $O_d$  is diagonal in basis of non-interacting fns.

- ▶ States are constant, operators evolve. Consider creation operators

$$\bar{a}_i^\dagger = U a_i^\dagger U$$

- ▶ Exact eigenfunctions of  $O_d$  are non-interacting fns

$$\Psi = \bar{a}_i^\dagger \bar{a}_j^\dagger \dots \bar{a}_n^\dagger$$

i.e.  $\bar{a}_i^\dagger$  is the exact quasi-particle creation operator.

## DMRG in the Canonical Representation

$$A \left\{ \boxed{\quad} \bigcirc \quad \bigcirc \boxed{\quad} \right\} B$$

Start with set of noninteracting states  $|A_i B_j\rangle$ . Then

$$|\Psi\rangle = \sum_{ij} c_{ij} |A_i B_j\rangle$$

In DMRG, transform to basis of eigenstates of the DM,

$$\bar{A}_i = U_A^\dagger A_i U_A$$

$$\bar{B}_i = U_B^\dagger B_i U_B$$

$$|\Psi\rangle = \sum_i c_i |\bar{A}_i \bar{B}_i\rangle$$

But,  $\bar{A}_i$  is also a **non-interacting** state, of quasi-particles

$$\bar{A}_i = \bar{a}_1^\dagger \bar{a}_2^\dagger \dots$$

Therefore, DMRG **is a CI** in the basis of DM quasi-particles determined via

$$\bar{a}_i^\dagger = U_A^\dagger U_B^\dagger a_i^\dagger U_B U_A$$

## Connected formulation

Now do CC theory in basis of DM quasiparticles, i.e. rewrite CI expression as

$$\Psi = \exp \left[ \sum_i t_i \hat{A}_i \hat{B}_i + \dots \right] |\bar{0}\rangle$$

where  $A_i, B_i$  are fluctuation operators, e.g.  $A_i = a_1^\dagger a_2^\dagger, B_i = a_5 a_6$  etc.

Since CC ansatz deals with connected correlations, the **unphysical** exponential dependence of DMRG on uncorrelated fluctuations is removed.

More generally, would consider

$$\Psi = \exp \left[ \sum_i t_i \hat{A}_i \hat{B}_i + \dots \right] |ref\rangle$$

where  $|ref\rangle$  is any state in  $\{A_i\} \otimes \{B_i\}$ . Fluctuations are then truncated on the basis of the magnitude of  $t_i$ .

## Connected DMRG algorithm

All steps of DMRG follow through.

- ▶ Blocking (adding one site): Equivalent to blocking during first sweep of DMRG.
  - Instead of storing operator matrices (e.g. for  $H$ ), we store the second-quantised representation.
- ▶ Solving for the wavefunction: Equivalent to solving CC/MRCC equations.
- ▶ Diagonalisation of DM: performed with canonical diagonalisation.
- ▶ Renormalisation transform: Operators (e.g.  $H$ ) transformed to  $U^\dagger H U$ , truncated (e.g. if fluctuation  $a_i a_j$  is removed, remove corresponding terms in operators).

## Acknowledgments

- ▶ S. R. White, I. Peschel, T. Nishino, for many interesting discussions.