Generalized tensor methods and entanglement measurements for electronic structure calculations

Örs Legeza in collaboration with

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- Florian Gebhard, Reinhard M. Noack (Marburg, 2003-)
- Valentin Murg, Frank Verstraete (Wien, 2009-)
- Markus Reiher, Konrad H. Marti, Katharina Boguslawski, Pawel Tecmer, S. Knecht (Zurich, 2010-)
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Mathematical Methods for Ab Initio Quantum Chemistry-2013, Nice, 07.11.2013.

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Topics to be covered

1. Model Hamiltonian, i.e. problem to solve
2. Algorithms in quantum chemistry with polynomial costs:
    - Density matrix renormalization group (DMRG) White,1992
    - Matrix Product State (MPS) Ostlund,1995; Verstraete,2004
    - Tree Tensor Network States (TTNS) Murg,2010; Chan,2013
3. One- and Two-orbital mutual information→Entanglement
    - Optimizing the algorithms Legeza,2003; Rissler,2006
    - Efficient construction of active spaces Legeza,2003
    - Identifying static, dynamic correlations Boguslawski,2012
    - Description of bond formation and breaking procedures Boguslawski,2012
4. Four-Component DMRG (4c-DMRG) Knecht, Reiher, Legeza,2013
5. Modeling: Experimental measurements reproduced for poly-diacetylenes by correlating 102 electrons on 102 orbitals Barcza,2013

Model Hamilton: Real ab initio problem

- The system is described by the Hamiltonian, for example,

$$\mathcal{H} = \sum_{ij\sigma} T_{ij\sigma\sigma'} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{ijkl\sigma\sigma'} V_{ijkl\sigma\sigma'} c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{k\sigma'} c_{l\sigma} , \qquad (1)$$

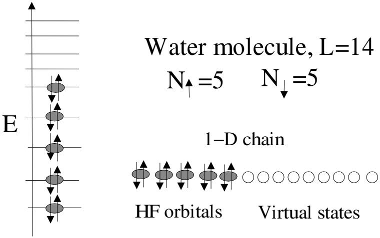
- T_{ij} denotes the one-electron integral comprising the kinetic energy of the electrons and the external electric field of the nuclei.
- V_{ijkl} stands for the two-electron integrals and contains the e-e repulsion operator.

$$V_{ijkl} = \int d^3x_1 d^3x_2 \Phi^*_i(\vec{x}_1)\Phi^*_j(\vec{x}_2)\frac{1}{\vec{x}_1 - \vec{x}_2}\Phi_k(\vec{x}_2)\Phi_l(\vec{x}_1)$$

Quantum Chemistry application (QC-DMRG)

White(1999), Mitrushenkov(2001), Chan(2002), Legeza(2002), Reiher(2005), Zgid(2006), Yanai(2008), ...

1-d chain is built up from the molecular orbitals that were obtained, e.g., in a suitable mean-field or MCSCF calculation (MOLPRO program package). Ex.: H_2O in double-ζ(DZ) basis.



Slater determinants by removing one (S), two (D), three (T) or four (Q) electrons form the HF orb.:

$$\Psi_{CI} = a_0 \Phi_{SCF} + \sum_S a_S \Phi_S + \sum_D a_d \Phi_D + \sum_T a_t \Phi_T + \ldots .$$

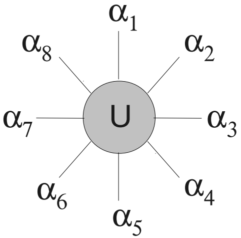
Connection to standard quantum chemistry approaches:

For example using a spin-orbit basis (d=4):

$$|\alpha_i\rangle \equiv |0\rangle, |\downarrow\rangle, |\uparrow\rangle |\downarrow\uparrow\rangle$$

Wavefunction in full tensor form:

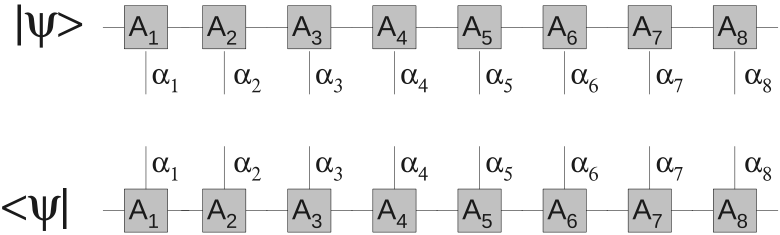
$$|\Psi\rangle = \sum_{\alpha_1,\cdots,\alpha_N} U_{\alpha_1,\cdots,\alpha_N} |\alpha_1, \cdots, \alpha_N\rangle$$



Tensor product approximations:

- Matrix Product State (MPS) representation:

$$|\Psi\rangle = \sum_{\alpha_1,\alpha_2,\ldots,\alpha_N}^{d} A^1_{\alpha_1} A^2_{\alpha_2} \cdots A^N_{\alpha_N} |\alpha_1\rangle|\alpha_2\rangle \cdots |\alpha_N\rangle$$

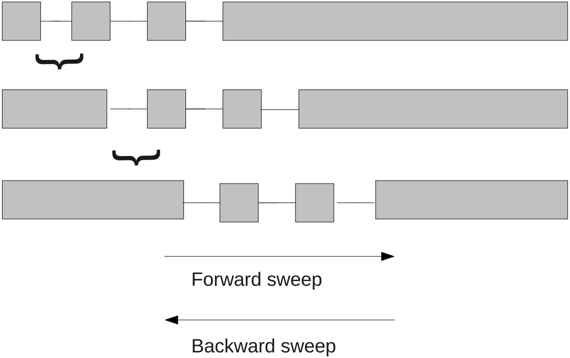


$A_i[m, m]_{d_i}$

- We can call this as a network.
- The Density Matrix Renormalization Group (DMRG) is a special algorithm that provides the optimized set of A_i matrices.

DMRG provides MPS wavefunction:

Density matrix renormalization group wavefunction: White (1992)

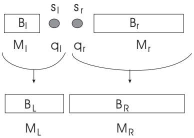


$$|\Psi_{\mathrm{TG}}\rangle = \sum_{\alpha ij\beta} \psi_{\alpha ij\beta} |\phi_{\alpha}^{(l)}\rangle \otimes |\phi_{i}^{s_l}\rangle \otimes |\phi_{j}^{s_r}\rangle \otimes |\phi_{\beta}^{(r)}\rangle$$

where $\psi_{\alpha ij\beta}$ coefficients are determined by the diagonalization of the superblock Hamiltonian.

MPS form: Ostlund, Rommer (1995), Verstraete, Murg, Cirac (2004), Marti, Reiher (2010)

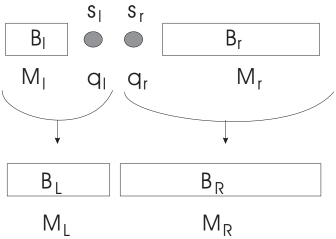
Schmidt-decomposition for bipartite a system



- For a bipartite system: $|\Psi_T\rangle = \sum_{ij} \psi_{ij} |\phi_i^L\rangle |\phi_j^R\rangle$
- Reduced density matrix: $\rho(i,i')^{\mathrm{red}}_{\mathrm{L,R}} = \sum_j \psi_{ij} * \psi^*_{i'j}$
- If $|\Psi\rangle$ pure state then for $|\Psi\rangle \in \Lambda = \Lambda_L \otimes \Lambda_R$

$$|\Psi\rangle = \sum_{i=1}^{r \le \min(M_L, M_R)} \omega_i |e_i\rangle \otimes |f_i\rangle \,.$$

- $|e_i\rangle, |f_i\rangle$ biorthogonal basis, and r is the Schmidt number $\rightarrow$Entanglement: non-local property of quantum mechanics
- Neumann entropy: $s(\rho_i) = -\mathrm{Tr}(\rho_i \ln \rho_i)\,, i \equiv L, R$
- $|\Psi_T\rangle$ pure state $\rightarrow$ $s(\rho_L) = s(\rho_R)$



1. Forming and diagonalizing the superblock Hamilton operator

$$|\Psi_{\mathrm{TG}}\rangle = \sum_{\alpha ij\beta} \psi_{\alpha ij\beta} |\phi^{(l)}_{\alpha}\rangle \otimes |\phi^{s_l}_{i}\rangle \otimes |\phi^{s_r}_{j}\rangle \otimes |\phi^{(r)}_{\beta}\rangle \qquad (1)$$

   where $\psi_{\alpha ij\beta}$ coefficients are determined by the diagonalization of the superblock Hamiltonian.
2. Forming bi-partite representation $|\Psi_{\mathrm{TG}}\rangle = \sum_{ij} \psi_{i,j} |\phi^{(L)}_{i}\rangle |\phi^{(R)}_{j}\rangle$
3. Forming reduced subsystem density matrix $\rho_{i,i'} = \sum_{j} \psi_{i,j} \psi^{\dagger}_{i',j}$
4. Diagonalizing $\rho \rightarrow \omega_{\alpha}$ eigenvalues, $|\phi_{\alpha}\rangle$ eigenstates
5. Forming O matrix using M selected $|\phi_{\alpha}\rangle$ eigenstates corresponding to the M largest ω_{α}
6. Renormalize operators: $c_i = O c_i O^{\dagger}$

Connection to standard quantum chemistry approaches:

Full tensor form: $|\Psi\rangle = \sum_{\alpha_1,\ldots,\alpha_N} U_{\alpha_1\ldots\alpha_N}|\alpha_1,\ldots,\alpha_N\rangle$.

Matrix product state(MPS) / Tensor train (TT): (Ostlund, Rommer (1995), Verstraete, Cirac (2004), Marti, Reiher (2011), Oseledets 2009, Hackbush 2009)

$$|\Psi\rangle = \sum_{\alpha_1,\ldots,\alpha_N}^{d} A^1_{\alpha_1} A^2_{\alpha_2} \ldots A^N_{\alpha_N} |\alpha_1\rangle|\alpha_2\rangle\ldots|\alpha_N\rangle.$$

bi-partite DMRG wavefunction:

$$\Psi^{(s)}(N) = \sum_{ij} \psi^{(s)}_{ij}\, |i\rangle \otimes |j\rangle$$

CI-type wavefunction:

$$\Psi^{(s)}(N) = \sum_{\{\mathbf{n}\}} C^{(s)}_{\{\mathbf{n}\}} \Phi_{\{\mathbf{n}\}},$$

Transfer tensor:

$$|m_l\rangle = \sum_{m_{l-1},n_l} (A_l[n_l])_{m_l;m_{l-1}} |m_{l-1}\rangle \otimes |n_l\rangle,$$

Series of transfer tensors:

$$|m_l\rangle = \sum_{n_1 \dots n_l} (A_l[n_l] \dots A_2[n_2])_{m_l;n_1} \, |n_1 \dots n_l\rangle,$$

DMRG wavefunction in MPS form:

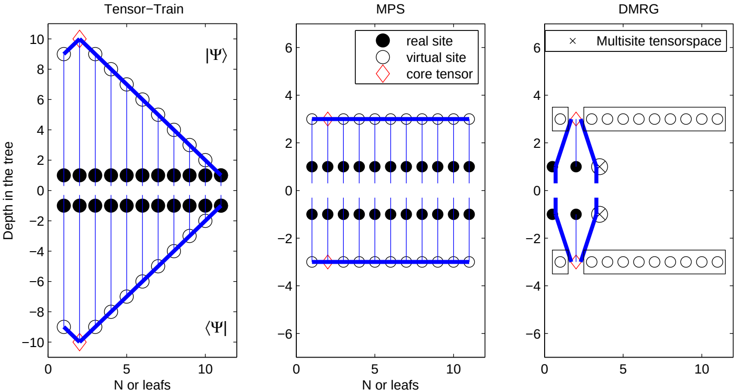
$$\begin{aligned}\Psi^{(s)}(N) = & \sum_{\{\mathbf{n}\}} \sum_{m^S} \sum_{m^E} \psi^{(s)}_{m^S n_{l+1} n_{l+2} m^E} \\ & \times (A_l[n_l] \dots A_2[n_2])_{m^S;n_1} \times (A_{l+3}[n_{l+3}] \dots A_{L-1}[n_{L-1}])_{m^E;n_L} \times |n_1 \dots n_L\rangle\end{aligned}$$

CI-coefficients in MPS form

$$\begin{aligned} C^{(s)}_{\{\mathbf{n}\}} &= \sum_{m^S}^{m} \sum_{m^E}^{m} \psi^{(s)}_{m^S n_{l+1} n_{l+2} m^E} \\ & \quad \times (A_l[n_l] \dots A_2[n_2])_{m^S;n_1} \times (A_{l+3}[n_{l+3}] \dots A_{L-1}[n_{L-1}])_{m^E;n_L} \,. \end{aligned}$$

Pictorial or diagrammatic description

- Component tensors by a dot (or vertex)
- Each index or variable by a single line coming out of the vertex
- Line connection two tensors, corresponds to an index over which one has to sum. We call contraction.
- Simplification of Goldstein, Feynman and related diagrams.



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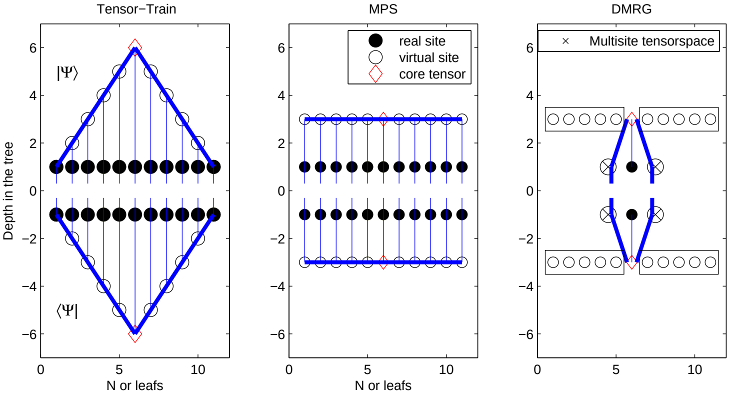

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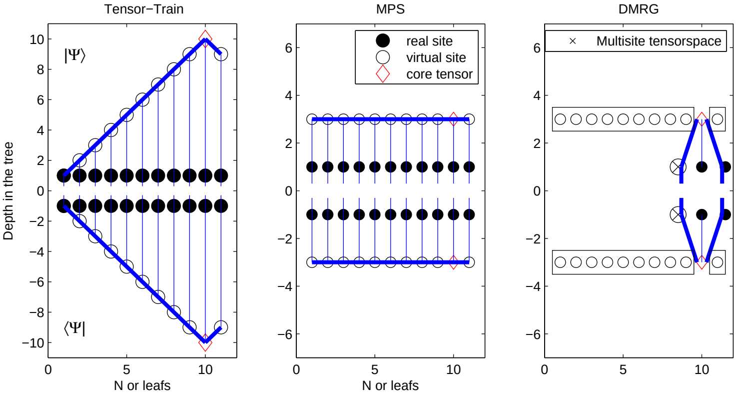


Dynamic Block State Selection (DBSS) procedure

- To control the weight of retained information during the RG procedure:

$$\rho^{(L)} = p_{\mathrm{kept}} \rho^{(L)}_{\mathrm{kept}} + (1 - p_{\mathrm{kept}}) \rho^{(L)}_{\mathrm{lost}} \,, \qquad (2)$$

  where $\rho^{(L)}_{\mathrm{kept}}$ is formed from the M largest eigenvalues of $\rho^{(L)}$ and $\rho^{(L)}_{\mathrm{lost}}$ from the remaining eigenvalues with $\mathrm{Tr}\rho^{(L)}_{\mathrm{kept}} = \mathrm{Tr}\rho^{(L)}_{\mathrm{lost}} = 1$.
- The accessible information for such a binary channel would be less than the Kholevo bound

$$\chi \leq S(\rho) - p_{\mathrm{kept}} S(\rho_{\mathrm{kept}}) - (1 - p_{\mathrm{kept}}) S(\rho_{\mathrm{lost}}) \,, \qquad (3)$$

- In DMRG the atypical subspace is neglected → loss of information.
- truncation scheme: $\chi \equiv S(\rho) - S(\rho_{\mathrm{kept}}) < \epsilon$ fixed in advance → M is chosen accordingly in every step. Legeza, Sólyom, PRB(2004)

Data sparse representation of the wavefunction

Example from 2002: DBSS approach applied on F_2 (D_{2h}) (18/18)

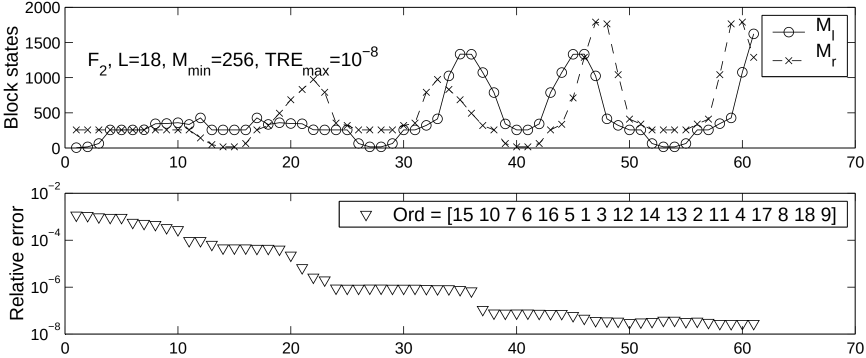
$\Lambda_{\mathrm{FCI}} = (2N)!/[(2N - N_e)!N_e!] = 9075135300$

$\Lambda_{\mathrm{DMRG}} = M_l \times 4 \times 4 \times M_r = 28800000$ ($M_l = 1200, Mr = 1500$)

sparsity$\simeq$ 315

$\Lambda_{\mathrm{DMRG}} = M_l \times 4 \times 4 \times M_r = 7680$ ($M_l = 120, Mr = 4$)

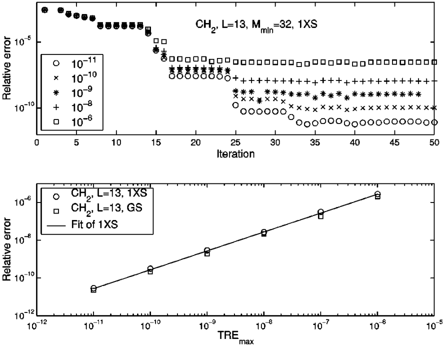
sparsity$\simeq$ 1181658 Legeza, Roder, Hess, Phys Rev B (2002)



A priory defined error margin for ground and excited states

One can define the required accuracy a prior to the calculations

All parameters of the algorithm are adjusted dynamically based on the strength of entanglement encoded in the wavefunction



Legeza, Sólyom, PRB (2003)

- Obtained quantum correlation in one RG step:

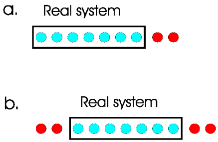
$$I_L(l) = s_L(l+1) - s_L(l) - s_{l+1} \;, 1 \leq l < N-1$$

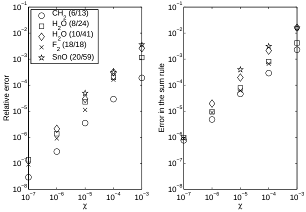
- Sum rule:

$$\sum_{l=1}^{N-1} I_L(l) = -\sum_{l=1}^{N} s_l \,.$$

- In case of truncation:

$$\sum_{l=1}^{N-1} I_L(l) + \sum_{l=1}^{N} s_l < (N-1)\epsilon \,.$$





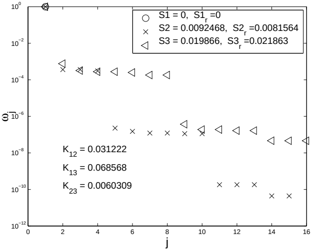
- For $L = N-2 \rightarrow r = ML = MR = 1$, correlation functions can be calculated very quickly

Initialization procedure

- $\rho^{(N)} \neq \rho_{\mathrm{L}} \otimes \rho_{\mathrm{R}}$
- For a pure Ψ_{T}: $s_{\mathrm{L}} = s_{\mathrm{R}}$
- Kullback-Leibler relativ quantum entropy:

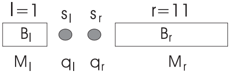
$$K(\rho_{\mathrm{L}}||\sigma_{\mathrm{L}}) \equiv \mathrm{Tr}\left(\rho_{\mathrm{L}} \ln \rho_{\mathrm{L}} - \rho_{\mathrm{L}} \ln \sigma_{\mathrm{L}}\right),$$

  where ρ_{L} and σ_{L} denote reduced density matrices of the left block corresponding to two different right (environment) blocks.
- Optimize environment block based on Kullback-Leibler entropy.



CI-based Dynamically Extended Active Space procedure

$$\Psi_{CI} = a_0\Phi_{SCF} + \sum_S a_S\Phi_S + \sum_D a_d\Phi_D + \sum_T a_t\Phi_T + \ldots .$$

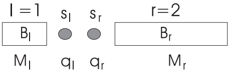


$l+1+1+r = 14$

	4	5	6	7	8	9	10	11	12	13	14	
1	⇅	○	⇅	○	⇅	⇅	○	○	○	⇅	○	HF
2	⇅	○	⇅	○	⇅	○	○	○	○	⇅	○	D
3	⇅	○	⇅	○	↑	⇅	○	○	○	⇅	○	S
4	⇅	○	⇅	○	↓	⇅	○	○	○	⇅	○	S
5	⇅	○	⇅	○	↑	○	○	○	○	⇅	○	T
6	⇅	○	⇅	○	↓	○	○	○	○	⇅	○	T
7	⇅	○	⇅	○	○	⇅	○	○	○	⇅	○	D
M$_r$	⇅	○	⇅	○	○	○	○	○	○	⇅	○	Q
	D	E	D	E	A	A	E	E	E	D	E	

E = Empty sites
D = Doubly filled sites
A = Active sites

→



$l+1+1+r = 5$

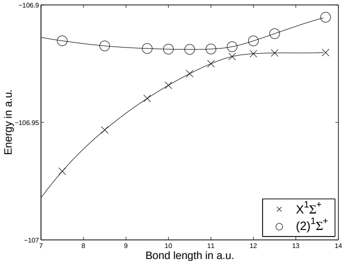
	4	5
1	⇅	⇅
2	⇅	○
3	↑	⇅
4	↓	⇅
5	↑	○
6	↓	○
7	○	⇅
M$_r$	○	○
	A	A

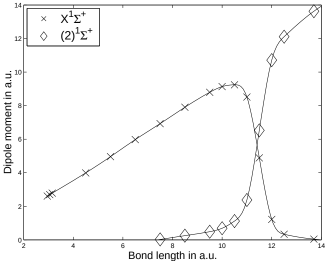
A = Active sites

CAS-vector ≡ ordering sites with descreasing site entropy values.

Exciting benchmark results from 2002-2004

- E_{GS} of F_2 molecule (d2h) (18/18) up to 8 d.p. using an FCI QC program on an Origin Memory Server (Erlangen) took 50-60 hours using 24-30GB of RAM.
  $\Delta E_{\mathrm{GS}} = 10^{-6}$ using QC-DMRG took 20 minutes, 1GB RAM on a PIV-2GHz Notebook. Legeza, Roder, Hess, PRB (2002)
- The ground state energy of H_2O (10/41) with QIT optimized DMRG up to 4 d.p. : 1cpu, (PIV-2GHz Notebook), 1GB RAM, took 4h only. Legeza, Solyom, PRB (2004)
- Example: Ionic–neutral curve crossing of LiF → continuous curves Legeza, Roder, Hess, Mol. Phys. (2002)

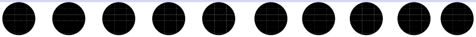




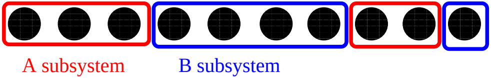
Part III

Properties of strongly correlated systems

Mutual information: entanglement correlation

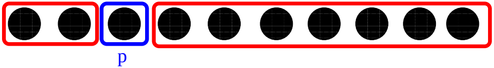


$$\varrho = |\psi\rangle\langle\psi|$$



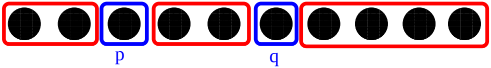
$$\varrho^B = \mathrm{Tr}_\mathrm{A}\,\varrho$$

$$S^B = -\mathrm{Tr}(\varrho^\mathrm{B}\ln\varrho^\mathrm{B})$$



$$\varrho^p \Rightarrow S^p$$

S^p describes the entanglement of site p with the rest of the system.



$$\varrho^{p,q} \Rightarrow S^{p,q}$$

$S^{p,q}$ describes the entanglement of site p and q with the rest of the system.
$I^{p,q}$ describes the mutual information between site p and q

$$I^{p,q} = 1/2(S^p + S^q - S^{p,q})(1 - \delta_{p,q})$$

Legeza, Sólyom, PRB (2003): Quantum Chemistry,
Legeza, Sólyom, PRL (2005): quantum phase transitions (QPT) with $q = p + 1$.

Rissler, White, Noack, ECP (2005): Quantum chemistry, arbitrary p and q.

n-site density matrix and generalized correlation functions

Transitions between states of a q-dimensional local Hilbert space:

$$\mathcal{O}_i^{(m)} = \bigotimes_{j=1}^{i-1} \mathbb{I} \otimes \mathcal{O}^{(m)} \otimes \bigotimes_{j=i+1}^{L} \mathbb{I}.$$

where $(\mathcal{O}^{(m)})_{k,l} = \delta_{(l+q[k-1]),m}$ for $m = 1 \dots q^2$.
Example spin-1/2 boson (qbit):

	⤈	⤉
⤈	$\mathcal{O}_i^{(1)}$	$\mathcal{O}_i^{(2)}$
⤉	$\mathcal{O}_i^{(3)}$	$\mathcal{O}_i^{(4)}$

$\mathcal{O}_i^{(1)}$	$-S_i^z + \frac{1}{2}\mathbb{I}$
$\mathcal{O}_i^{(2)}$	S_i^-
$\mathcal{O}_i^{(3)}$	S_i^+
$\mathcal{O}_i^{(4)}$	$S_i^z + \frac{1}{2}\mathbb{I}$

ρ_{ij}	⤈⤈	⤈⤉	⤉⤈	⤉⤉
⤈⤈	$\mathcal{O}^{(1)}\mathcal{O}^{(1)}$			
⤈⤉		$\mathcal{O}^{(1)}\mathcal{O}^{(4)}$	$\mathcal{O}^{(2)}\mathcal{O}^{(3)}$	
⤉⤈		$\mathcal{O}^{(3)}\mathcal{O}^{(2)}$	$\mathcal{O}^{(4)}\mathcal{O}^{(1)}$	
⤉⤉				$\mathcal{O}^{(4)}\mathcal{O}^{(4)}$

The two-site reduced density matrix for spin-1/2 fermions

	$n=0$, $s_z=0$	$n=1$, $s_z=-\frac{1}{2}$		$n=1$, $s_z=\frac{1}{2}$		$n=2$, $s_z=-1$	$n=2$, $s_z=0$				$n=2$, $s_z=1$	$n=3$, $s_z=-\frac{1}{2}$		$n=3$, $s_z=\frac{1}{2}$		$n=4$, $s_z=0$
$\rho_{i,j}$	−−	−↓	↓−	−↑	↑−	↓↓	−⇅	↓↑	↑↓	⇅−	↑↑	↓⇅	⇅↓	↑⇅	⇅↑	⇅⇅
−−	1/1															
−↓		1/6	2/5													
↓−		5/2	6/1													
−↑				1/11	3/9											
↑−				9/3	1/11											
↓↓						6/6										
−⇅							1/16	2/15	3/14	4/13						
↓↑							5/12	6/11	7/10	8/9						
↑↓							9/8	10/7	11/6	12/5						
⇅−							13/4	14/3	15/2	16/1						
↑↑											11/11					
↓⇅												6/16	8/14			
⇅↓												14/8	16/6			
↑⇅														11/16	15/12	
⇅↑														15/12	16/11	
⇅⇅																16/16

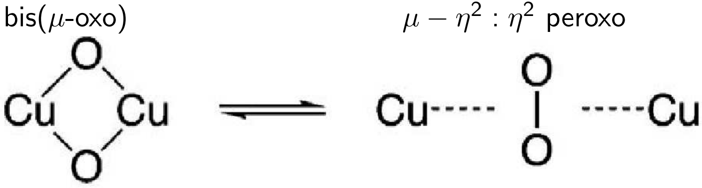
Expressing the two-site reduced density matrix, $\rho_{i,j}$, in terms of single-site operators, $\mathcal{O}_i^{(m)}$ with $m = 1 \cdots 16$. For better readability only the operator number indices, m are shown, thus m/n corresponds to $\langle\Psi| \mathcal{O}_i^{(m)} \mathcal{O}_j^{(n)} |\Psi\rangle$. n and s_z, denote the quantum numbers of two sites.

$\mathcal{O}^{(m)}$ operators in terms of standard site operators

$\mathcal{O}^{(1)}$	$1 - n_\uparrow - n_\downarrow + n_\uparrow n_\downarrow$
$\mathcal{O}^{(2)}$	$c_\downarrow - n_\uparrow c_\downarrow$
$\mathcal{O}^{(3)}$	$c_\uparrow - n_\downarrow c_\uparrow$
$\mathcal{O}^{(4)}$	$c_\downarrow c_\uparrow$
$\mathcal{O}^{(5)}$	$c_\downarrow^\dagger - n_\uparrow c_\downarrow^\dagger$
$\mathcal{O}^{(6)}$	$n_\downarrow - n_\uparrow n_\downarrow$
$\mathcal{O}^{(7)}$	$c_\downarrow^\dagger c_\uparrow$
$\mathcal{O}^{(8)}$	$-n_\downarrow c_\uparrow$
$\mathcal{O}^{(9)}$	$c_\uparrow^\dagger - n_\downarrow c_\uparrow^\dagger$
$\mathcal{O}^{(10)}$	$c_\downarrow c_\uparrow^\dagger$
$\mathcal{O}^{(11)}$	$n_\uparrow - n_\uparrow n_\downarrow$
$\mathcal{O}^{(12)}$	$n_\uparrow c_\downarrow$
$\mathcal{O}^{(13)}$	$c_\downarrow^\dagger c_\uparrow^\dagger$
$\mathcal{O}^{(14)}$	$-n_\downarrow c_\uparrow^\dagger$
$\mathcal{O}^{(15)}$	$n_\uparrow c_\downarrow^\dagger$
$\mathcal{O}^{(16)}$	$n_\uparrow n_\downarrow$

Quantum chemistry (some 40 electrons on 40 orbitals)

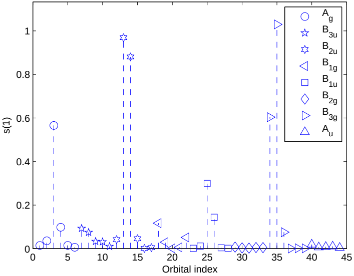
Example: Task to determine the electronic structure of the binuclear oxo-bridged copper clusters

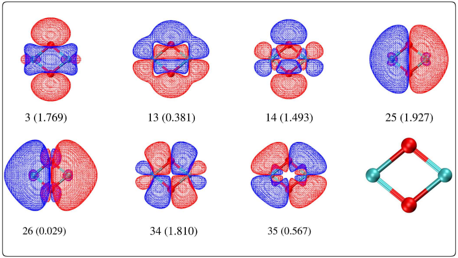


- CASSCF calculations yield a qualitative wrong interpretation of the energy difference between different isomers.
- Too large active space required to get qualitatively correct picture for standard QC methods.
- open d shell problem
- K.H. Marti, I.Malkin Ondik, G. Moritz, and M. Reiher, J. Chem. Phys. **128**, 014104 (2008).
  Y. Kurashige, and T. Yanai, J. Chem. Phys. **130**, 234114 (2009).
  T. Yanai, Y. Kurashige, E. Neuscamman, and G.K.-L. Chan, J.Chem.Phys. **132**, 024105 (2010).
  G. Barcza, Ö. Legeza, K. H. Marti, and M. Reiher, Phys. Rev. A. **83**, 012508 (2011).

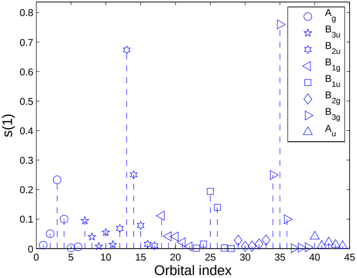
Site entropy profile→ highly entangled orbitals

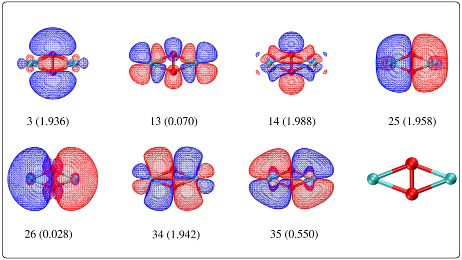
bis(μ-oxo)





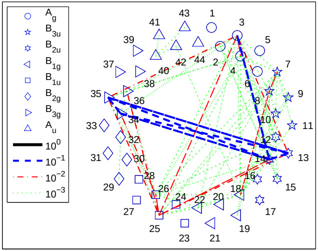
$\mu-\eta^2:\eta^2$ peroxo



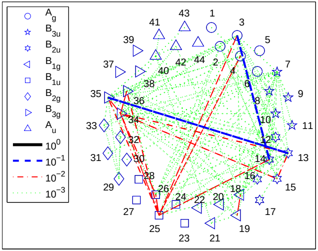


Entanglement picture of the two isomers

bis(μ-oxo)



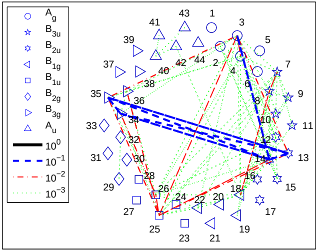
$\mu - \eta^2 : \eta^2$ peroxo



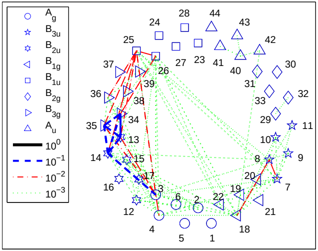
- peroxo: orbital pairs 3–14 and 13–35 are highly entangled
  → bonding and anti-bonding orbitals → the O–O bond is intact
- bis(μ-oxo): all five orbitals 3, 13, 14, 34, and 35 are entangled
  → four equivalent Cu–O bonds
- O–O bond breaking process → transition from the peroxo to the bisoxo isomer
- Mutual information + DMRG → relative energy of the two-isomers

Entanglement localization, example for bis(μ-oxo)

energetical ordering

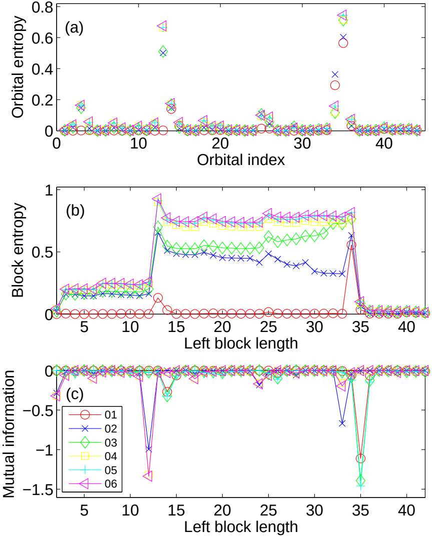


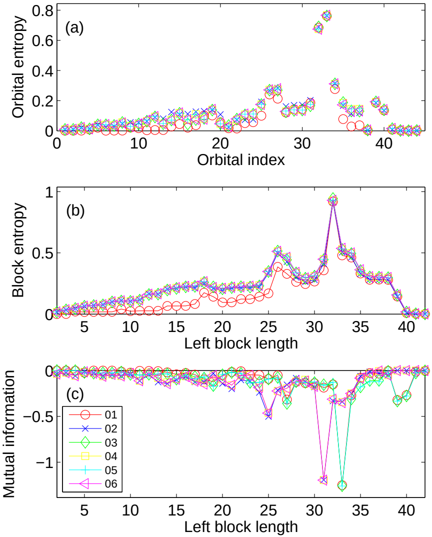
optimized ordering



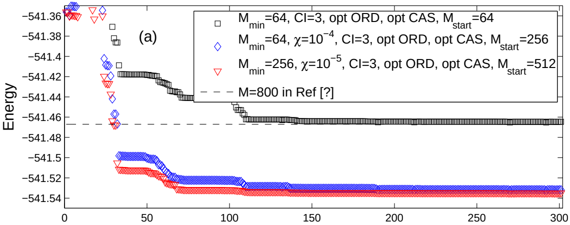
- Reordering orbitals by minimizing the entanglement distance: $\hat{I}_{\mathrm{dist}} = \sum_{i,j} I_{i,j} \times |i-j|^\eta$,
- Apply spectral graph theory: Fiedler vector $x = (x_1, \ldots x_N)$ is the solution that minimizes $F(x) = x^\dagger L x = \sum_{ij} I_{i,j}(x_i - x_j)^2$, with $\sum_i x_i = 0$ and $\sum_i x_i^2 = 1$, and the graph Laplacian is $L = D - I$ with $D_{i,i} = \sum_j I_{i,j}$.
  The second eigenvector of the Laplacian is the Fiedler vector.

Entanglement localization





Relative energy of the isomers: a notebook calculation



<u>Fixed number of block states vs DBSS</u>

Dynamic Block State Selection

$$s_L(l+1) - s_L^{\mathrm{Trunc}}(l+1) < \chi$$

- DBSS guarantees that the number of block states are adjusted according to the entanglement between the DMRG blocks and the a priori defined accuracy can be reached.
- Dynamically Extended Active Space (CI-DEAS)

method	ΔE
Reference energies	
CASSCF(16,14)	1
CASPT2(16,14)	6
bs-B3LYP	221
RASPT2(24,28)	120
Previously published DMRG energies	
[1],DMRG(26,44)[m=800]	78
[2],DMRG(32,62)[m=2400]	149
[3],DMRG(28,32)[m=2048]-SCF	107
[3],DMRG(28,32)[m=2048]SCF/CT	113
DMRG energies from this work	
DMRG(26,44)[64/256/10^{-4}]	111
DMRG(26,44)[256/512/10^{-4}]	115
DMRG(26,44)[256/1024/10^{-4}]	113
DMRG(26,44)[256/512/10^{-5}]	113
DMRG(26,44)[256/1024/10^{-5}]	113

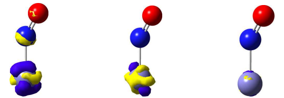
M. Reiher *et al*, J. Chem. Phys. **128**, (2008).
T. Yanai *et al*, J. Chem. Phys. **130**, (2009).
G.K.-L. Chan *et al*, J.Chem.Phys. **132**, (2010).

Ab initio spin densities: $[Fe(NO)]^{2+}$

$$\hat{\delta}^{\text{spin}}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)\hat{s}_{z,i},$$

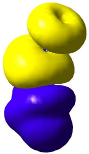
$$\hat{\delta}^{\text{spin}}(\mathbf{r}) = \frac{1}{2}\sum_{p,q} \phi_p^*(\mathbf{r})\phi_q(\mathbf{r}) \left(a_{p\alpha}^\dagger a_{q\alpha} - a_{p\beta}^\dagger a_{q\beta}\right)$$

$$= \sum_{p,q} \phi_p^*(\mathbf{r})\phi_q(\mathbf{r})\hat{T}_{pq},$$



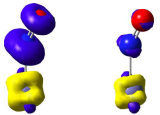
DMRG(7,7)[16] DMRG(7,7)[32] DMRG(7,7)[48]

(a) $d_{\text{pc}} = 1.131$Å



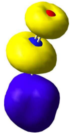
CAS(7,7)SCF

(b) $d_{\text{pc}} = 1.131$Å



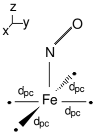
DMRG(7,7)[32] DMRG(7,7)[48]

(c) $d_{\text{pc}} = 0.598$ Å



CAS(7,7)SCF

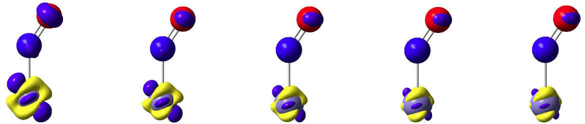
(d) $d_{\text{pc}} = 0.598$ Å



(e) $[\text{FeNO}]^{2+}$

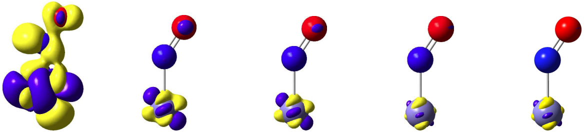
(Boguslawski, Marti, Legeza, Reiher, 2012)

For large active space



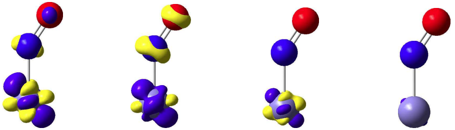
$m = 128$ $m = 256$ $m = 512$ $m = 1024$ $m = 2048$

(a) DMRG(13,20)[m]–DMRG(13,29)[2048] spin density differences



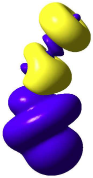
$m = 128$ $m = 256$ $m = 512$ $m = 1024$ $m = 2048$

(b) DMRG(13,24)[m]–DMRG(13,29)[2048] spin density differences



$m = 128$ $m = 256$ $m = 512$ $m = 1024$

(c) DMRG(13,29)[m]–DMRG(13,29)[2048] spin density differences

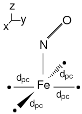


$m = 2048$

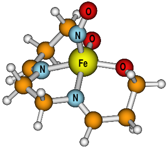
(d) DMRG(13,29)

Entanglement Measures for Single- and Multireference Correlation Effects

Boguslawski, Tecmer, Legeza, Reiher (2012)

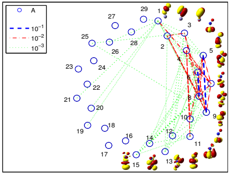


(a) $[Fe(NO)^{2+}]$

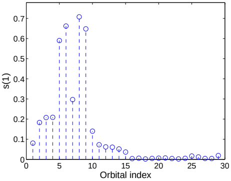


(b) FeL(NO)

$[Fe(NO)^{2+}]$

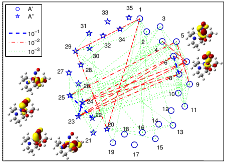


(a) Mutual information

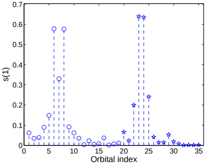


(b) Single orbital entropy

FeLNO

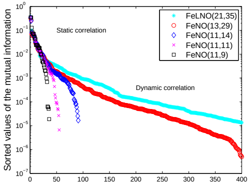


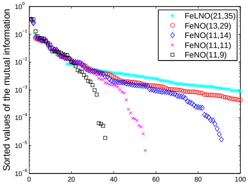
(a) Mutual information

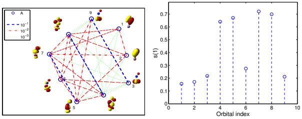


(b) Single orbital entropy

Entanglement effect of the basis (active space)

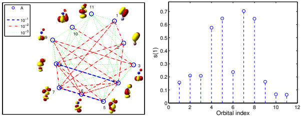






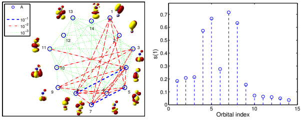
Mutual information Single orbital entropy

(a) CAS(11,9)



Mutual information Single orbital entropy

(b) CAS(11,11)



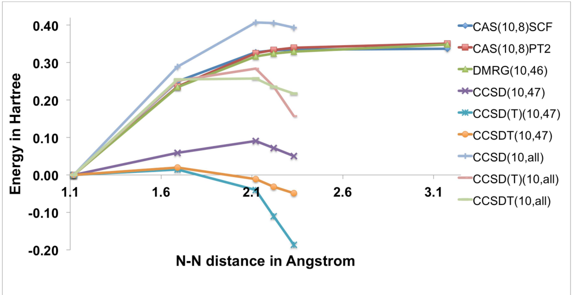
Mutual information Single orbital entropy

(c) CAS(11,14)

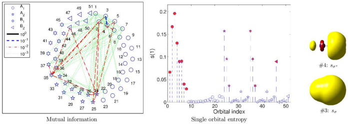
Chemical bond forming: dissociation of N_2

Method	1.12 Å	1.69 Å	2.12 Å	2.22 Å	2.33 Å	3.18 Å
CAS(10,8)SCF	−109.132 549	−108.882 463	−108.804 469	−108.800 108	−108.797 850	−108.795 397
CAS(10,8)PT2	−109.359 217	−109.123 008	−109.034 004	−109.025 152	−109.019 396	−109.008 111
DMRG(10,46)	−109.229 813	−108.995 701	−108.912 849	−108.905 589	−108.900 737	−108.881 603
CCSD(10,47)	−109.000 679	−108.941 650	−108.909 788	−108.928 743	−108.950 482	[a]
CCSD(T)(10,47)	−109.000 713	−108.985 858	−109.041 195	−109.110 778	−109.187 441	[a]
CCSDT(10,47)	−109.006 569	−108.986 784	−108.986 784	−109.038 483	−109.055 259	[a]
CCSD(10,all)	−109.360 160	−109.070 979	−108.953 165	−108.954 475	−108.966 565	[a]
CCSD(T)(10,all)	−109.380 205	−109.128 573	−109.095 725	−109.144 281	−109.222 288	[a]
CCSDT(10,all)	−109.379 815	−109.124 975	−109.122 251	−109.144 221	−109.162 828	[a]

[a] Not computed due to convergence difficulties.



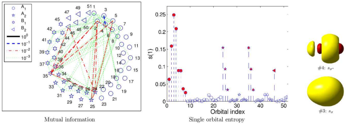
Chemical bond forming and breaking vs Entanglement



Mutual information

Single orbital entropy

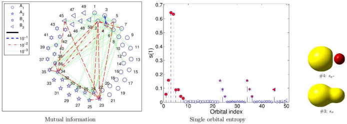
(a) $d_{\mathrm{CsH}} = 2.5\text{Å}$



Mutual information

Single orbital entropy

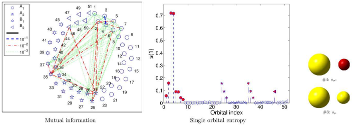
(b) $d_{\mathrm{CsH}} = 3.5\text{Å}$



Mutual information

Single orbital entropy

(c) $d_{\mathrm{CsH}} = 5.5\text{Å}$



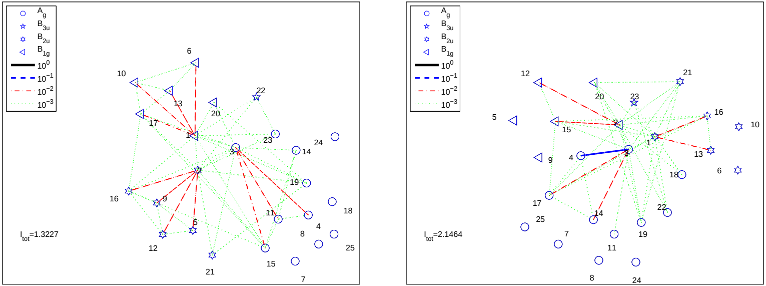
Mutual information

Single orbital entropy

(d) $d_{\mathrm{CsH}} = 7.0\text{Å}$

Part IV
Higher dimensional networks

Entanglement → Multiply connected networks



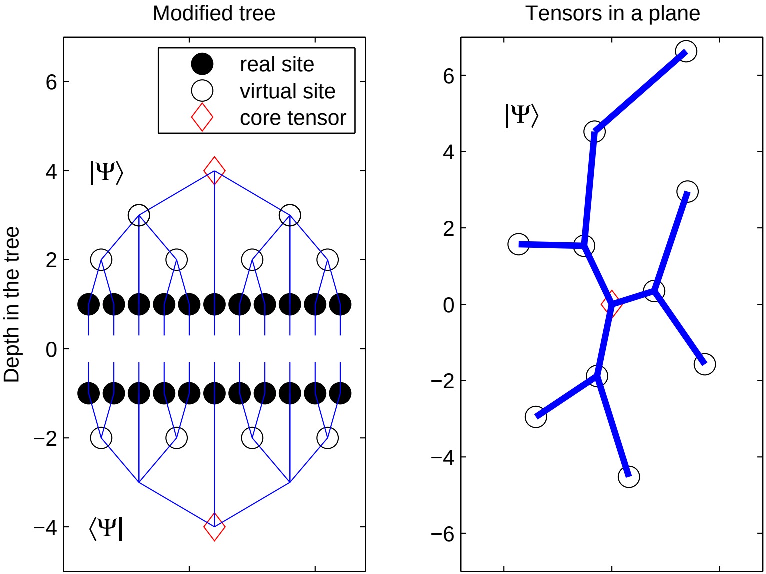
LiF at r=3.05 LiF at r=13.7

Rissler, White, Noack, ECP (2006)

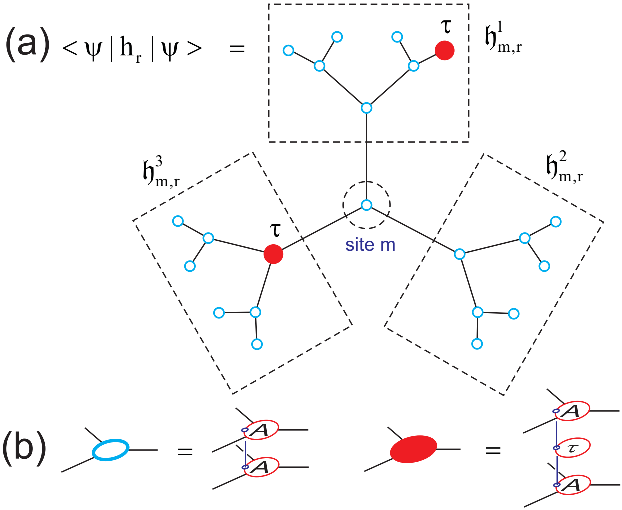
Murg, Verstraete, Schneider, Nagy, Legeza (2013)

- DMRG → Matrix product states, i.e. optimization along one-spatial dimension
- Need for an algorithm that reflects the entanglement topology of the problem → Tensor Network State (TNS) methods
- Use tensors $[A_i]^k_{\alpha_1 \ldots \alpha_z}$ where z is the coordination number

Two dimensional networks



Tree Tensor Network State (TTNS)



Vidal, Corboz (2009); Murg, Verstraete, Legeza, Noack (2010); Nakatani, Chan (2013)

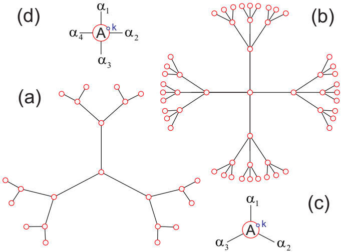
Tensor topology optimization: $\sum_{ij} I_{ij} \times d_{ij}^{\eta}$

I_{ij} is model dependent:

- depends on T_{ij} and V_{ijkl} interaction strengths
- depends on the choice of basis
- major aim: could we optimize basis on-the-fly (different approches are under investigations, Chan, Murg, Verstraete, Legeza, Krumnov, Eisler, Schneider); unsolved problem

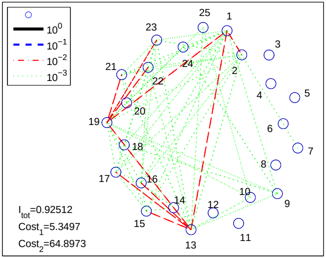
d_{ij} depends on the tensor topology

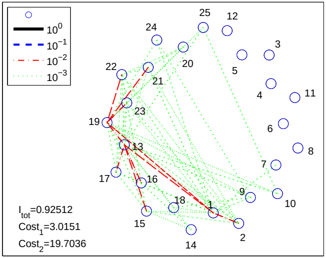
- a possible solution: TTNS with site dependent coordination number z_i.



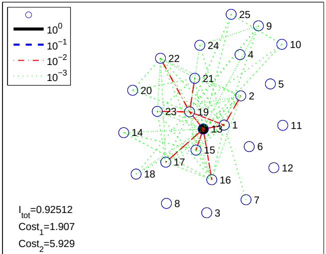
Tensor topology optimization: $\sum_{ij} I_{ij} \times d_{ij}^{\eta}$

Energetical ordering (MPS) $d_{ij} = |i - j|$ Entanglement localization (MPS)

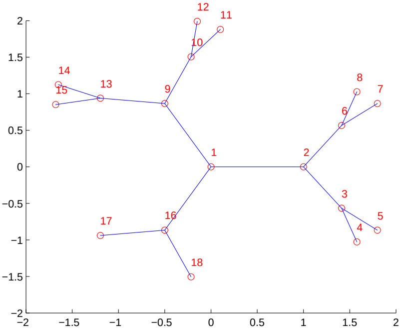


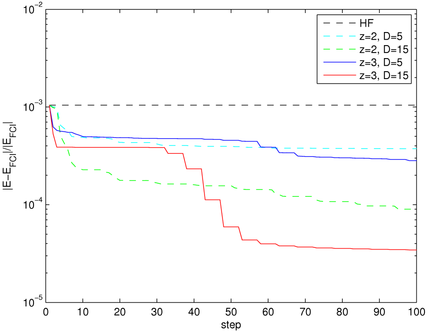


Tree Tensor Network State (TTNS)



TTNS preliminary result on F2(18/18)

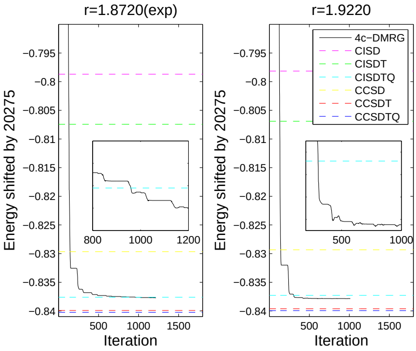


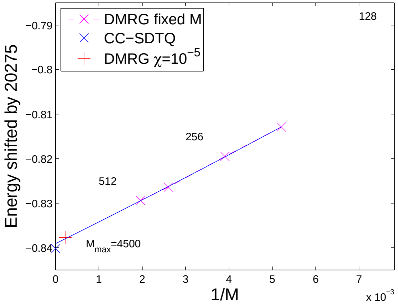


Murg, Verstraete, Legeza, Noack, PRB (2010)
V. Murg, P. Nagy, F. Verstraete, R. Schneider, Ö. Legeza, in progress (2013)
N. Nakatani, G. Chan (2013)

Four-Component Density Matrix Renormalization Group

- TlH with double group C_{2v} symmetry (14 e / 94 spinors),
- DIRAC12(2012), a relativistic ab initio electronic structure program,
- including spin-orbit coupling,
- 4c-DMRG with $\max(M) \simeq 4500 - 5000$, $\chi = 10^{-5}$





S. Knecht, M. Reiher, Ö Legeza (2013)

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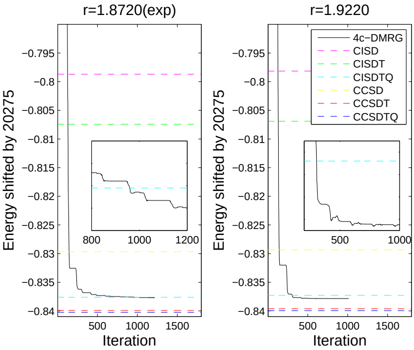
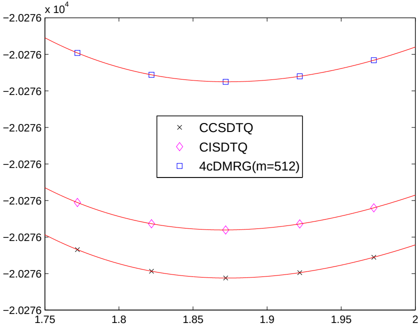




S. Knecht, M. Reiher, Ö Legeza (2013)

Coherent DMRG solution of a long standing problem

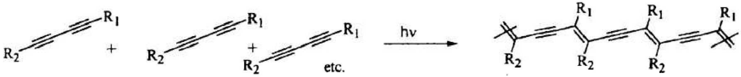
Barcza, Gebhard, Barford, Legeza (PRB 2010, PRB 2013)

Experimentalists fabricate single crystals of diacetylene monomers

Monomer = R-C≡C-C≡C-R

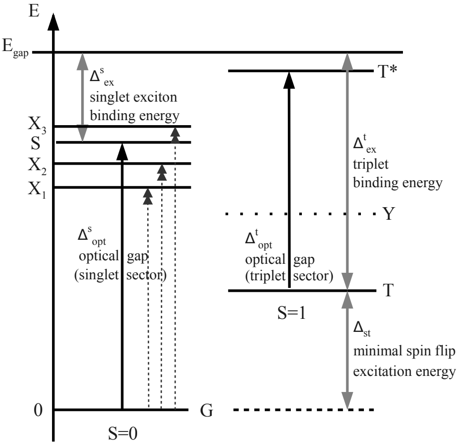
*n*BCMU family: R = $(CH_2)_n$-OCONH-CH_2-COO-$(CH_2)_3CH_3$

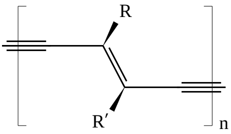
Polymerization induced by temperature or ultraviolet light:



- We have almost perfect chains: several micrometer long
- Disorder plays no role! (like ultracold atoms)
- The exciton state S lies at $E_{\rm S} = 1.8\,{\rm eV}$
- The band edge is located at $E_{\rm gap} = 2.4\,{\rm eV}$.
- The exciton binding energy of $\Delta_{\rm ex}^{\rm s} = 0.6\,{\rm eV}$ is about 25% of the single-particle gap. The Coulomb interaction is substantial and effective→ failure of previous attempts(DFT,LDA).
- For excitation energies $\hbar\omega < 3\,{\rm eV}$, only the π-electron system of the carbon atoms on the chain is relevant.
- There is one p_z electron per C atom, the system is half filled.

Experimental data





$r_t = 1.20$ Å, (1.239)

$r_d = 1.36$ Å, (1.373)

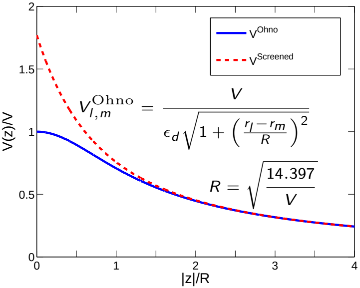
$r_s = 1.43$ Å, (1.425)

Energia/eV	3BCMU	4BCMU
E_{X_1}	*1.5*	*1.4*
E_{X_2}	*1.7*	*1.6*
$E_S = \Delta^s_{opt}$	**1.896**	**1.810**
E_{X_3}	*2.0*	*1.9*
E_{gap}	**2.482**	**2.378**
$\Delta^s_{ex} = E_{gap} - E_S$	**0.586**	**0.568**
$E_T = \Delta_{st}$	*1.0 ± 0.05*	*0.95 ± 0.05*
$E_{T*} = \Delta_{st} + \Delta^t_{opt}$	*2.36 ± 0.05*	*2.30 ± 0.05*
Δ^t_{opt}	**1.360**	**1.345**
$\Delta^t_{ex} = E_{gap} - E_T$	*1.5 ± 0.05*	*1.4 ± 0.05*

directly measured data, *approximated*

- **measured data**: electron absorption/ one-photon absorption
- *approximated data*: two-phonon absorbtion/non-radiative decay processes

Parametrization of PPP: Peierls–Hubbard-Ohno model



$$V^{\mathrm{Ohno}}_{l,m} = \frac{V}{\epsilon_d\sqrt{1+\left(\frac{r_l-r_m}{R}\right)^2}}$$

$$R = \sqrt{\frac{14.397}{V}}$$

$$H = T+V+H_{\mathrm{lattice}}$$

$$T = -\sum_{l;\sigma}(t_0+\delta^{\mathrm{e}}_l/2+\delta_l/2)\left(\hat{c}^{\dagger}_{l,\sigma}\hat{c}_{l+1,\sigma}+h.c.\right)$$

$$V = U\sum_{l=1}^{N}\left(\hat{n}_{l,\uparrow}-\frac{1}{2}\right)\left(\hat{n}_{l,\downarrow}-\frac{1}{2}\right)+\frac{1}{2}\sum_{l\neq m=1}^{N}V^{\mathrm{Ohno}}_{l,m}\left(\hat{n}_l-1\right)\left(\hat{n}_m-1\right)$$

Control parameters

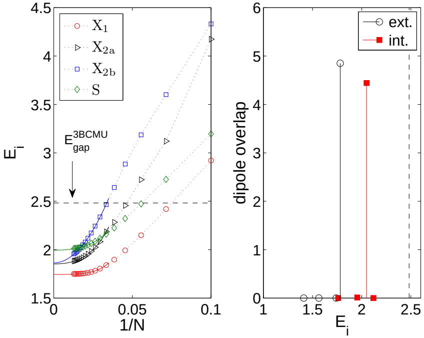
$t_0,\ U,\ V,\ \alpha$

$$H_{\mathrm{lattice}} = \sum_{l=1}^{N-1}\frac{\delta_l^2}{4\pi t_0\lambda_l},\quad \delta r_l = r_l - R_l = -\frac{\delta_l}{2\alpha}$$

Peierls-distrortion

Numerical simulations up to 102 electrons on 102 atoms

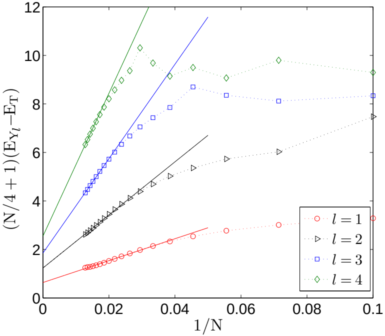
S=0 excitations



Energy/eV	3BCMU	DMRG
E_{X_1}	1.5	1.74 [1.94]
E_{X_2}	1.7	1.85 [1.94]^{a}
$E_S = \Delta^{s}_{opt}$	1.896	2.00 [2.05]
E_{X_3}	2.0	

S=1 excitations

spinflip density waves with q momentum: $\epsilon_{sf}(q) = c_{sf}\, q$



$$\left(\frac{N}{4}+1\right)(E_{Y_l}-E_{T}) = c_{sf}\,\frac{l\pi}{d}+\frac{\alpha_l}{N}+\dots$$

quantized quasi-momentum, $q_l = \pi l/[(N/4+1)d]$

A little advertisement

- Event: Winter school and workshop at Mariapfarr, Austria (February 17.-21.2014)
- Title: New wavefunction methods and entanglement optimizations in quantum chemistry
- Organizers: Alexander Sax and Örs Legeza
- Lecturers: Markus Reiher, Reinhold Schneider, Reinhard M. Noack, and Örs Legeza

- ERA-Chemistry (Legeza, Schneider, Verstraete): All collaborations are welcomed!

- Technical aspects: Tensor Network State algorithms on kilo-processor architectures: A hybrid CPU-GPU implementation of DMRG is under progress: see arxiv