

The density matrix renormalization group for ab initio quantum chemistry

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Quantum chemistry 101

DMRG and matrix product states

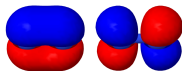
Dealing with the entanglement

Applications

The Hamiltonian for ab initio quantum chemistry

$$\hat{H} = \sum_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + \sum_{ijkl\sigma\tau} v_{ij;kl} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\tau}^\dagger \hat{a}_{l\tau} \hat{a}_{k\sigma}$$

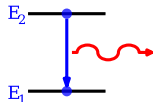
- ▶ $ijkl$: spatial orbitals
- ▶ $\sigma\tau$: electron spin projections (\uparrow, \downarrow)
- ▶ U(1) particle number symmetry
- ▶ SU(2) spin symmetry
- ▶ P point group symmetry:
how the spatial orbitals transform under rotations, inversions & reflections



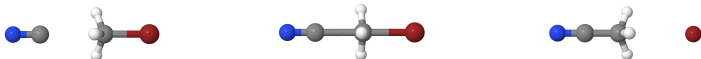
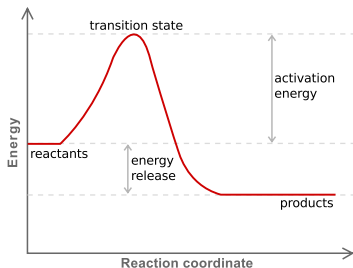
Information in the Hamiltonian & links to experiment

- ▶ Direct link: eigenvalues yield **electronic absorption & emission spectra**

Fe atom



- ▶ Indirect link: prediction of chemical reaction barriers \implies **reaction rates**



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Matrix product states

Suppose we have L spatial orbitals. A wavefunction in occupation number representation

$$|\Psi\rangle = \sum_{\{n_{i\sigma}\}} C^{n_{1\uparrow}n_{1\downarrow}n_{2\uparrow}n_{2\downarrow}n_{3\uparrow}\dots n_{L\uparrow}n_{L\downarrow}} \left(\hat{a}_{1\uparrow}^\dagger\right)^{n_{1\uparrow}} \left(\hat{a}_{1\downarrow}^\dagger\right)^{n_{1\downarrow}} \left(\hat{a}_{2\uparrow}^\dagger\right)^{n_{2\uparrow}} \dots \left(\hat{a}_{L\uparrow}^\dagger\right)^{n_{L\uparrow}} \left(\hat{a}_{L\downarrow}^\dagger\right)^{n_{L\downarrow}} |-\rangle$$

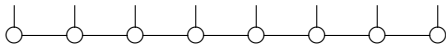
is represented by the C -tensor of size 4^L (exponential in the number of orbitals).

$$\begin{aligned} & C^{n_{1\uparrow}n_{1\downarrow}n_{2\uparrow}n_{2\downarrow}n_{3\uparrow}\dots n_{L\uparrow}n_{L\downarrow}} \\ = & \sum_{\alpha_1, \alpha_2, \dots, \alpha_L} A[1]_{\alpha_1}^{n_{1\uparrow}n_{1\downarrow}} A[2]_{\alpha_1; \alpha_2}^{n_{2\uparrow}n_{2\downarrow}} A[3]_{\alpha_2; \alpha_3}^{n_{3\uparrow}n_{3\downarrow}} \dots A[L-1]_{\alpha_{L-2}; \alpha_{L-1}}^{n_{L-1\uparrow}n_{L-1\downarrow}} A[L]_{\alpha_{L-1}}^{n_{L\uparrow}n_{L\downarrow}} \\ = & \mathbf{A}[1]^{n_{1\uparrow}n_{1\downarrow}} \mathbf{A}[2]^{n_{2\uparrow}n_{2\downarrow}} \mathbf{A}[3]^{n_{3\uparrow}n_{3\downarrow}} \dots \mathbf{A}[L-1]^{n_{L-1\uparrow}n_{L-1\downarrow}} \mathbf{A}[L]^{n_{L\uparrow}n_{L\downarrow}} \end{aligned}$$

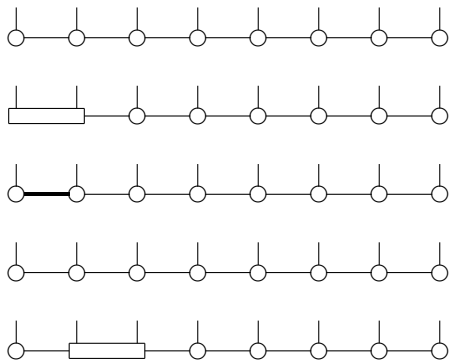
Full Fock space: $\dim(\alpha_i) = \min(4^i, 4^{L-i})$



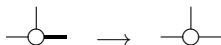
MPS ansatz: $\dim(\alpha_i) = \min(4^i, 4^{L-i}, D) \rightarrow D$ is called the **virtual** or **bond** dimension



The density matrix renormalization group algorithm



- ▶ **Algorithm:** keep D largest singular values from SVD
- ▶ **Quantum information:** D most probable many-body states of Schmidt decomposition
- ▶ **Renormalization group:** augment the many-body basis with an extra orbital & truncate



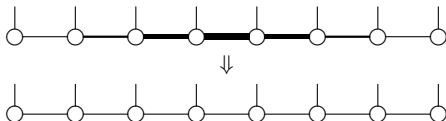
Dimensionality of the Hamiltonian

- ▶ Molecules are compact
- ▶ All orbitals interact \implies Hamiltonian interactions are ∞ -dimensional
- ▶ The Schmidt decomposition of the wavefunction in the total Fock space

$$|\Psi\rangle = \sum_{kl} C^{kl} |A_k\rangle |B_l\rangle = \sum_{kl\alpha} U_{k\alpha} \lambda_\alpha V_{\alpha l}^\dagger |A_k\rangle |B_l\rangle = \sum_{\alpha} \lambda_\alpha |\tilde{A}_\alpha\rangle |\tilde{B}_\alpha\rangle$$

allows to define the von Neumann entropy for the bipartition $A | B$

$$S_{A|B} = - \sum_{\alpha} \lambda_{\alpha}^2 \log(\lambda_{\alpha}^2) \geq 0$$



- ▶ For infinite 1-dimensional non-critical systems $S_{A|B}$ is a constant \implies MPS works well
- ▶ For higher-dimensional finite-size systems an MPS is still useful as a variational ansatz, but $D(L)$ then typically grows with system size.

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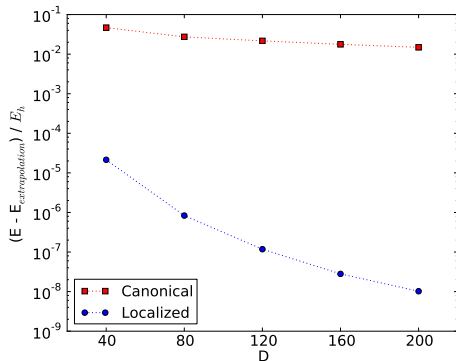
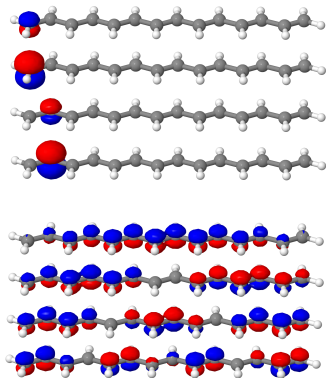
What can we do?

For higher-dimensional finite-size systems an MPS is still useful as a variational ansatz, but $D(L)$ then typically grows with system size.

1. Choose and order orbitals wisely
2. Exploit the symmetry group of \hat{H}
3. More computer power \implies parallelization

1. Choose and order orbitals wisely: extended systems

- ▶ Extended systems: localize and order according to the molecule's topology
- ▶ Polyene



SW and D. Van Neck, *EPJD* 68, 272 (2014)

1. Choose and order orbitals wisely: compact molecules

- ▶ Rules-of-thumb from minimizing the bandwidth of the two-orbital mutual information matrix:

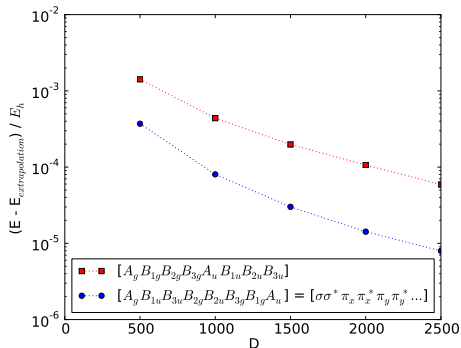
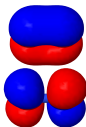
$$I_{ij} = \frac{1}{2} (S_1(i) + S_1(j) - S_2(ij)) (1 - \delta_{ij}) \geq 0$$

- ▶ Compact molecules:

Group orbitals per irrep, and place bonding and anti-bonding irreps adjacent

J. Rissler, R.M. Noack and S.R. White, *Chem. Phys.* **323**, 519 (2006)

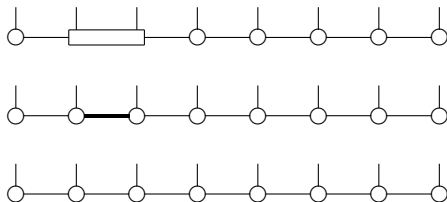
- ▶ Nitrogen dimer



1. Choose and order orbitals wisely: on-the-fly

C. Krumnow, Ö. Legeza and J. Eisert, *arXiv:1504.00042*

- ▶ When performing the SVD decomposition of the just optimized two-orbital block:



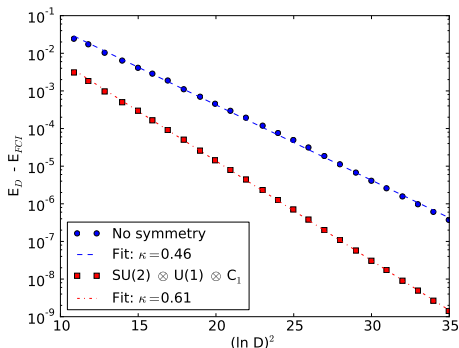
- ▶ Allow for rotations between the current two orbitals, so that the entanglement at the bipartition is minimized
- ▶ Various cost functions are possible
- ▶ Orbitals & their ordering are optimized together with the wavefunction
- ▶ Approach minimizes bandwidth of two-orbital mutual information

2. Exploited Hamiltonian symmetries in CHEMPS2

- ▶ Symmetry group $SU(2) \otimes U(1) \otimes P$ with $P \in \{C_1, C_i, C_2, C_s, D_2, C_{2v}, C_{2h}, D_{2h}\}$

$$\text{---} \bigcirc \text{---} = A_{(j_L j_L^z N_L l_L \alpha_L); (j_R j_R^z N_R l_R \alpha_R)}^{(ss^z NI)} = \langle j_L j_L^z ss^z | j_R j_R^z \rangle \delta_{N_L+N, N_R} \delta_{l_L \otimes l, l_R} T_{(j_L N_L l_L \alpha_L); (j_R N_R l_R \alpha_R)}^{(sNI)}$$

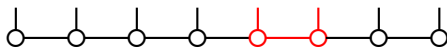
- ▶ **Block-sparsity** whenever a Clebsch-Gordan coefficient is zero
- ▶ **Data compression** for spin multiplets other than singlets
- ▶ Hubbard model OBC $L = 36$, $N = 22$, $S = 0$, $U = 6$



3. Computer power: hybrid MPI & OpenMP parallelization in CHEMPS2

- ▶ OpenMP over $SU(2) \otimes U(1) \otimes P$ symmetry sectors in the virtual bonds
- ▶ MPI over (complementary) operator pairs

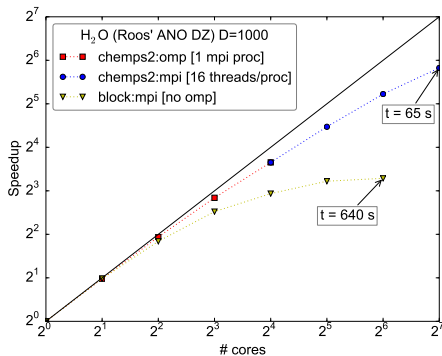
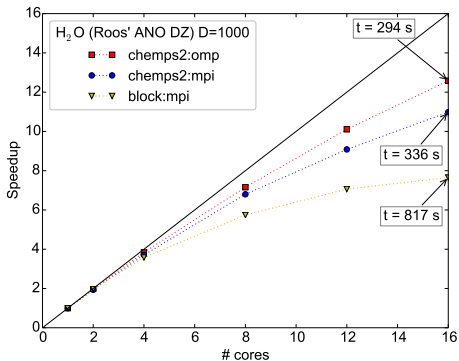
$$\hat{H} = \sum_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + \sum_{ijkl\sigma\tau} v_{ij;kl} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\tau}^\dagger \hat{a}_{l\tau} \hat{a}_{k\sigma}$$



$$\sum_{k,l} (-1)^P v_{ij;kl} \begin{array}{c} \circ \\ | \\ \circ \\ | \\ \circ \\ | \\ \circ \end{array} \begin{array}{c} \circ \\ | \\ \square \hat{a}_{l\tau} \\ | \\ \circ \\ | \\ \circ \end{array} \begin{array}{c} \circ \\ | \\ \square \hat{a}_{i\sigma}^\dagger \\ | \\ \circ \\ | \\ \circ \end{array} \begin{array}{c} \circ \\ | \\ \circ \\ | \\ \circ \\ | \\ \circ \end{array} = \begin{array}{c} \text{---} \\ | \\ \square Q_{j\tau;k\sigma} \\ | \\ \text{---} \end{array} \Rightarrow \sum_{j\tau;k\sigma} \begin{array}{c} \text{---} \\ | \\ \square Q_{j\tau;k\sigma} \\ | \\ \text{---} \end{array} \begin{array}{c} \circ \\ | \\ \circ \end{array} \begin{array}{c} \circ \\ | \\ \square P_{j\tau;k\sigma} \\ | \\ \circ \\ | \\ \circ \end{array}$$

3. Computer power: scaling of the parallelization in CHEMPS2

- ▶ H₂O in Roos' ANO DZ basis ($L = 41$ orbitals)
- ▶ Equilibrium: O @ (0, 0, 0) Å and H @ ($\pm 0.790689766, 0, 0.612217330$) Å
- ▶ Intel Xeon Sandy Bridge (E5-2670): 16 cores per node @ 2.6 GHz
- ▶ Timings: wall times per sweep in seconds



SW, work in progress (2015)

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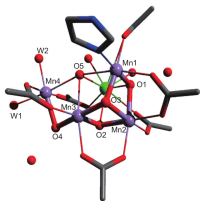
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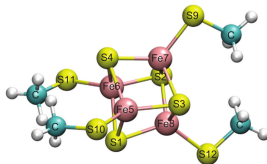
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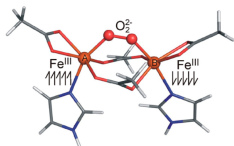
Important catalysts



Mn₄CaO₅ cluster [1]
(oxygen evolving complex in PS2)



iron-sulfur clusters [2]



Δ^9 desaturase [3]
(its binuclear non-Heme iron active site)



oxo-Mn(Salen) [4]
(Jacobsen's catalyst)

1. Y. Kurashige, G.K.-L. Chan and T. Yanai, *Nat. Chem.* **5**, 660 (2013)
2. S. Sharma, K. Sivalingam, F. Neese and G.K.-L. Chan, *Nat. Chem.* **6**, 927 (2014)
3. J. Chalupsky, T. A. Rokob, Y. Kurashige, T. Yanai, E.I. Solomon, L. Rulisek and M. Srnc, *JACS* **136**, 15977 (2014)
4. SW, T. Bogaerts, P. Van Der Voort, V. Van Speybroeck and D. Van Neck, *JCP* **140**, 241103 (2014)

oxo-Mn(Salen)

SW, T. Bogaerts, P. Van Der Voort, V. Van Speybroeck and D. Van Neck, *JCP* **140**, 241103 (2014)

- ▶ Relative stability DMRG-SCF(28e, 22o) with $D=4800$ (extrapolated):

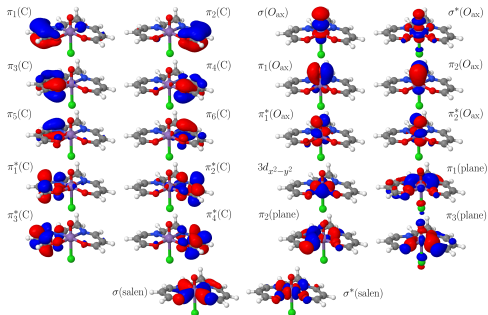
[kcal/mol]	6-31G*	cc-pVDZ	ANO-RCC-VDZP + DKH2
$E(^3A) - E(^1A)$	-5.0	-5.3	-4.0
$E(^5A) - E(^1A)$	14.5	12.1	14.5

- ▶ CASSCF(12e, 11o)/6-31G* : $E(^5A) - E(^1A) = 42.9$ kcal/mol ?









J.S. Sears and C.D. Sherrill, *JCP* **124**, 144314 (2006)

- ▶ Dynamic correlation estimated to shift relative energies by ≈ 5 kcal/mol

D. Ma, G.L. Manni and L. Gagliardi, *JCP* **135**, 044128 (2011)



oxo-Mn(Salen): Mn-O bond order

NOON		DMRG-SCF(28e, 22o)			CASSCF(12e, 11o)
		1A	3A	5A	5A
$\sigma(O_{ax})$		$\uparrow\downarrow$ (1.91)	$\uparrow\downarrow$ (1.90)	$\uparrow\downarrow$ (1.89)	$\uparrow\downarrow$
$\sigma^*(O_{ax})$		- (0.11)	- (0.11)	- (0.12)	-
$\pi_1(O_{ax})$		$\uparrow\downarrow$ (1.86)	$\uparrow\downarrow$ (1.77)	$\uparrow\downarrow$ (1.94)	$\uparrow\downarrow$
$\pi_2(O_{ax})$		$\uparrow\downarrow$ (1.85)	$\uparrow\downarrow$ (1.95)	$\uparrow\downarrow$ (1.94)	\uparrow
$\pi_1^*(O_{ax})$		- (0.17)	\uparrow (1.04)	\uparrow (1.05)	\uparrow
$\pi_2^*(O_{ax})$		- (0.17)	- (0.24)	\uparrow (1.04)	\uparrow
$3d_{x^2-y^2}$		$\uparrow\downarrow$ (1.97)	\uparrow (1.00)	\uparrow (1.00)	\uparrow
$\pi(C)$		$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow (1.01)	$\uparrow\downarrow$ (occ)
Bond order O_{ax}		3	2.5	2	1.5

Acknowledgements



$\he[M][P][S] 2$

- ▶ Symmetry group $SU(2) \otimes U(1) \otimes P$ with $P \in \{C_1, C_i, C_2, C_s, D_2, C_{2v}, C_{2h}, D_{2h}\}$
- ▶ c++ library with python interface
- ▶ GNU GPLv2
- ▶ <https://github.com/sebwouters/chemps2>
- ▶ Part of PSI4 and PYSCF (general purpose quantum chemistry packages)
- ▶ Hybrid MPI & OpenMP parallelization
- ▶ Easy access to correlation functions & two-orbital mutual information

SW, W. Poelmans, P.W. Ayers and D. Van Neck, *Comput. Phys. Commun.* **185**, 1501 (2014)

SW and D. Van Neck, *EPJD* **68**, 272 (2014)