Two Lectures on DMRG in Quantum Chemistry

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1. First-Generation Density Matrix Renormalization Group (DMRG) in Quantum Chemistry
2. Second-Generation DMRG:
   Matrix Product and Tensor Network States
   Matrix Product Operators
3. Some Results of Actual Quantum-Chemical Calculations

Very useful introductory reference:

U. Schollwöck, *The density-matrix renormalization group in the age of matrix product states*, arXiv: 1008.3477v2

Reviews on DMRG in Quantum Chemistry

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2. G. K.-L. Chan, J. J. Dorando, D. Ghosh, J. Hachmann, E. Neuscamman, H. Wang, T. Yanai, An Introduction to the Density Matrix Renormalization Group Ansatz in Quantum Chemistry, Prog. Theor. Chem. and Phys., 18, 49 (2008)
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6. K. H. Marti, M. Reiher, New Electron Correlation Theories for Transition Metal Chemistry, Phys. Chem. Chem. Phys., 13, 6750-6759 (2011)
7. Y. Kurashige, Multireference electron correlation methods with density matrix renormalisation group reference functions, Mol. Phys. 112, 1485-1494 (2014)
8. S. Wouters and D. Van Neck, The density matrix renormalization group for ab initio quantum chemistry, Eur. Phys. J. D 68, 272 (2014)
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10. S. Szalay, M. Pfeffer, V. Murg, G. Barcza, F. Verstraete, R. Schneider, Ö. Legeza, Tensor product methods and entanglement optimization for ab initio quantum chemistry, arXiv:1412.5829 (2015)

Lecture 1

First-Generation DMRG in Quantum Chemistry

1. Standard Configuration Interaction in Explicit Second Quantization
2. Dimension Reduction by Decimation
3. Elements of the DMRG Algorithm

Non-Relativistic Many-Electron Hamiltonian

- many-electron Hamiltonian in position space (Hartree atomic units)

$$H_{el} = \sum_{i}^{N} \left(-\frac{1}{2}\nabla_i^2 - \sum_{I} \frac{Z_I}{r_{iI}} \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{1}$$

with $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ and N being the number of electrons.

- eigenvalue equation: electronic Schrödinger equation

$$H_{el}\ \Psi_{el}^{\{\boldsymbol{R}_I\}}(\{\boldsymbol{r}_i\}) \ = \ E_{el}(\{\boldsymbol{R}_I\})\ \Psi_{el}^{\{\boldsymbol{R}_I\}}(\{\boldsymbol{r}_i\}) \tag{2}$$

- central in electronic structure theory: how to approximate Ψ_{el} ?

Standard Procedure: Construction of Many-Electron Basis

- Construct many-electron (determinantal) basis set $\{\Phi_I\}$ from a given (finite) one-electron (orbital) basis set ϕ_i
- From the solution of the Roothaan–Hall equations, one obtains n orbitals from n one-electron basis functions.
- From the N orbitals with the lowest energy, the Hartree–Fock (HF) Slater determinant is constructed.
- The other determinants (configurations) are obtained by subsequent substitution of orbitals in the HF Slater determinant Φ_0:

$$\{\Phi_I\} \rightarrow \Phi_i^a, \Phi_j^b, \cdots \rightarrow \Phi_{ij}^{ab}, \Phi_{ik}^{ac}, \cdots \rightarrow \Phi_{ijk}^{abc}, \Phi_{ijl}^{abd}, \ldots \tag{3}$$

- Determinants are classified by number of 'excitations' (= substitutions in HF reference determinant).

Standard Full Configuration Interaction (FCI)

- The number of possible determinants is determined by the number of virtual orbitals $n - N$.
- Including all possible excited Slater determinants for a finite or infinite one-electron basis set leads to the so-called **full CI** approach.
- Number of Slater determinants n_{SD} for N spin orbitals chosen from a set of n spin orbitals (slang: N electrons in n spin orbitals):

$$n_{\mathrm{SD}} = \binom{n}{N} = \frac{m!}{N!(n-N)!} \tag{4}$$

  Example: There are $\approx 10^{12}$ different possibilities to distribute 21 electrons in 43 spin orbitals.

- *In physics FCI is called exact diagonalization*.

Truncated CI Wave Functions

Standard recipe to avoid the factorial scaling of the many-electron basis-set size: **truncate basis**! *Note: basis is pre-defined!*

Assumption: Substitution hierarchy is a useful measure to generate a systematically improvable basis set.

CIS: all singly-(S)-excited determinants are included:

$$\Psi_{el}^{\mathrm{CIS}} = C_0\Phi_0 + \sum_{(ai)} C_{(ai)}\Phi_i^a \tag{5}$$

CISD: all singly- and doubly-(D)-excited determinants are included:

$$\Psi_{el}^{\mathrm{CISD}} = C_0\Phi_0 + \sum_{(ai)} C_{(ai)}\Phi_i^a + \sum_{(ai)(bj)} C_{(ai,bj)}\Phi_{ij}^{ab} \tag{6}$$

$$C_0, C_{(ai)}, C_{(ai,bj)} \in \{C_I\} \tag{7}$$

Determination of the CI Expansion Coefficients C_I

The CI expansion coefficients C_I determined by variational principle:

- write down the expectation value for the energy
- introduce the determinantal basis set
- vary the energy in order to minimize it

Expectation value for the CI electronic energy:

$$E_{el}^{\mathrm{CI}} = \frac{\left\langle \Psi_{el}^{\mathrm{CI}} \middle| H_{el} \middle| \Psi_{el}^{\mathrm{CI}} \right\rangle}{\left\langle \Psi_{el}^{\mathrm{CI}} \middle| \Psi_{el}^{\mathrm{CI}} \right\rangle} \tag{8}$$

Insert expansion of Slater determinants:

$$E_{el}^{\mathrm{CI}} = \frac{\sum_{K,L} C_K^* C_L \left\langle \Phi_K \middle| H_{el} \middle| \Phi_L \right\rangle}{\sum_{K,L} C_K^* C_L \left\langle \Phi_K \middle| \Phi_L \right\rangle} \tag{9}$$

The CI Eigenvalue Problem

Calculate all derivatives $\partial E_{el}^{\mathrm{CI}} \,/\, \partial C_K^*$ and set them equal to zero, which yields the **CI eigenvalue problem:**

$$\boldsymbol{H} \cdot \boldsymbol{C} = \boldsymbol{E}_{el} \cdot \boldsymbol{C} \tag{10}$$

Essential: $\boldsymbol{H}$ is constructed from matrix elements $\langle \Phi_K | \, H_{el} \, | \Phi_L \rangle$ in the pre-defined determinantal basis $\{\Phi_K\}$

By solving the CI eigenvalue problem, ground and excited electronic states of the system are obtained.

$\boldsymbol{E}_{el}$ is diagonal matrix with total energies of all electronic states that can be expressed in basis given (M determinants yield M electronic states).

Standard 'Technical' Trick: Second Quantization

Operators and wave functions are expressed in terms of creation and annihilation operators to implement the Slater–Condon rules for the evaluation of matrix elements $\langle \Phi_K | H_{el} | \Phi_L \rangle$ directly into the formalism.

H_{el} in second quantization (i, j, k, l are spin orbital indices):

$$\Rightarrow \qquad H_{el} = \sum_{ij} \langle \phi_i | h(i) | \phi_j \rangle a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} \langle \phi_i(1) \langle \phi_k(2) | g(1,2) | \phi_l(2) \rangle \phi_j(1) \rangle a_i^\dagger a_j^\dagger a_k a_l \quad (11)$$

CI wave function in second quantization:

$$\Psi_{el}^{\mathrm{FCI}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} a_a^\dagger a_i \Phi_0 + \sum_{(ai)(bj)} C_{(ai,bj)} a_b^\dagger a_j a_a^\dagger a_i \Phi_0 \cdots \quad (12)$$

CI Energy in Second Quantization

$$
\begin{aligned}
E_{el}^{\mathrm{CI}} &= \left\langle \Psi_{el}^{\mathrm{CI}} \middle| H_{el} \middle| \Psi_{el}^{\mathrm{CI}} \right\rangle && (13)\\
&= \sum_{ij}^{N} \underbrace{\sum_{KL}^{N} C_K^* C_L t_{ij}^{KL}}_{\gamma_{ij}} \underbrace{\langle \phi_i(1) | h(1) | \phi_j(1) \rangle}_{\equiv h_{ij}} \\
&\quad + \sum_{ijkl}^{N} \underbrace{\sum_{KL}^{N} C_K^* C_L T_{ijkl}^{KL}}_{\Gamma_{ijkl}} \underbrace{\langle \phi_i(1) \langle \phi_k(2) | g(1,2) | \phi_l(2) \rangle \phi_j(1) \rangle}_{g_{ijkl}} && (14)\\
&= \sum_{ij}^{N} \gamma_{ij} h_{ij} + \sum_{ijkl}^{N} \Gamma_{ijkl} g_{ijkl} && (15)
\end{aligned}
$$

t_{ij}^{KL} or T_{ijkl}^{KL} are matrix elements of determinantal basis functions over pairs or quadruples of elementary operators $a^\dagger$ and a.

γ_{ij} are Γ_{ijkl} are density matrix elements.

Is there a better way to construct the finite-dimensional determinantal basis set in order to avoid the factorial scaling?

Coupled-Cluster — An Advanced CI-type Wave Function

Ansatz:

$$\Psi_{\mathrm{el}}^{\mathrm{CC}} = \exp\left(T\right)\, \Phi_{\mathrm{el}}^{\mathrm{HF}} \tag{16}$$

Excitation operator:

$$T = T_1 + T_2 + T_3 + \cdots \tag{17}$$

where

$$T_\alpha = \sum_{\underbrace{ab\cdots}_{\alpha \text{ times}}\underbrace{ij\cdots}_{\alpha \text{ times}}} \overbrace{t_{ij\ldots}^{ab\cdots}}^{\text{cluster-amplitudes}} \underbrace{\cdots a_b^\dagger a_j a_a^\dagger a_i}_{\alpha \text{ pairs } a^\dagger a} \quad \Rightarrow \quad T_1 = \sum_{ai} t_i^a a_a^\dagger a_i \tag{18}$$

Notation:

CCS ($T = T_1$), CCSD ($T = T_1 + T_2$), CCSDT ($T = T_1 + T_2 + T_3$) ,$\cdots$

Coupled-cluster improves on truncated CI, because certain (disconnected) higher excited configurations (e.g., $t_i^a a_a^\dagger a_i t_{jk}^{bc} a_c^\dagger a_k a_b^\dagger a_j$) are included.

Is there a better way to construct the finite-dimensional determinantal basis set in order to avoid the factorial scaling?

Let's investigate FCI from a different perspective:

Many-Electron Hamiltonian in Second Quantization

- many-electron Hamiltonian in second quantization

$$H_{el} = \sum_{\substack{i,j \\ \sigma}} h_{ij} a^\dagger_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{\substack{i,j,k,l \\ \sigma,\sigma'}} V_{ijkl} a^\dagger_{i\sigma} a^\dagger_{j\sigma'} a_{k\sigma'} a_{l\sigma} \tag{19}$$

with $\sigma \in \{\alpha, \beta\}$ and the creators and annihilators $a_{i\sigma}$ and $a^\dagger_{i\sigma}$, resp.

- with one-electron integrals h_{ij}

$$h_{ij} = \int \phi^*_i(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{r_I} \right) \phi_j(\boldsymbol{r})\, d^3r \tag{20}$$

- and two-electron integrals V_{ijkl}

$$V_{ijkl} = \int\int \frac{\phi^*_i(\boldsymbol{r}_1)\phi^*_j(\boldsymbol{r}_2)\phi_k(\boldsymbol{r}_2)\phi_l(\boldsymbol{r}_1)}{r_{12}}\, d^3r_1 d^3r_2 \tag{21}$$

with spatial molecular orbitals ϕ_i.

Full CI in (Explicit) Second Quantization

- Elementary operators: $a^\dagger_{i\sigma}$ and $a_{i\sigma}$
- Hamiltonian matrix is now constructed from the matrix representation for the elementary operators by direct products
- **By contrast to standard procedure, instead of evaluating the action of the elementary operators on the determinantal basis functions, we set-up a matrix representation of the elementary operators and construct a matrix representation of the Hamiltonian DIRECTLY.**

  This Hamiltonian matrix can then be diagonalized.

Elementary operators in (Explicit) Second Quantization

- $a^\dagger_{i\sigma}$ and $a_{i\sigma}$ operate on spin orbital with two states: occ. and unocc.

$$|0\rangle_{i\sigma} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |1\rangle_{i\sigma} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{22}$$

- Corresponding matrix representation of elementary operators:

$$a^\dagger_{i\sigma}|0\rangle_{i\sigma} = |1\rangle_{i\sigma} \quad \Longleftrightarrow \quad \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{23}$$

$$a^\dagger_{i\sigma}|1\rangle_{i\sigma} = 0 \quad \Longleftrightarrow \quad \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{24}$$

$$a_{i\sigma}|0\rangle_{i\sigma} = 0 \quad \Longleftrightarrow \quad \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{25}$$

$$a_{i\sigma}|1\rangle_{i\sigma} = |0\rangle_{i\sigma} \quad \Longleftrightarrow \quad \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{26}$$

Matrices for Hamiltonian in (Explicit) Second Quantization

- Dimension of elementary operators defined for orbital space of n spin orbitals with 2 states each: $2^n \Rightarrow$ dimension of the Hamiltonian is 2^n

  (NB: for spatial orbitals we have 4^n where 4 is the number of states per orbital [empty, up, down, doubly occupied])

- 2^n-dimensional elementary operator: (the spin index has been omitted for the sake of clarity)

$$a_i^\dagger = \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \otimes \cdots \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{i-1}}_{\substack{\text{matrix structure needed for anticommutation} \\ \text{cf. Jordan–Wigner transformation}}} \otimes \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}_i \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_{i+1} \otimes \cdots \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_n$$

- Then, $2^n \times 2^n$-matrix of term of the one-electron part of Hamiltonian reads:

$$h_{ij} a_i^\dagger a_j =$$

$$h_{ij} \left[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \otimes \cdots \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{i-1} \otimes \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}_i \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_{i+1} \otimes \cdots \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_n \right]$$

$$\times \left[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_1 \otimes \cdots \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{j-1} \otimes \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}_j \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_{j+1} \otimes \cdots \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_n \right]$$

- Similar expression for the two-electron part, but product of four 2^n-dimensional elementary matrices

Nothing has been gained yet!

Even worse: Huge matrices have been generated which contain mostly zeros and need to be multiplied and added.

Nothing has been gained yet!

Even worse: Huge matrices have been generated which contain mostly zeros and need to be multiplied and added.

Need to find a way to reduce the dimension !

What is the best reduced many-particle basis?

First attempt: Wilson's renormalization group

Wilson's Renormalization Group: Dimension Reduction

1. Choose a number of orbitals l whose many-electron Hamiltonian $H_{el}^{(l)}$ can still be constructed and exactly diagonalized.
2. Diagonalize $H_{el}^{(l)}$ of dimension 2^l (or 4^l for spatial orbitals) and select m lowest-energy eigenvectors out of the 2^l eigenvectors.
3. Reduce the dimension of $H_{el}^{(l)}$ from 2^l to m by transformation with the rectangular $m \times 2^l$ matrix of eigenvectors.
4. Construct $H_{el}^{(l+1)}$ from $H_{el}^{(l)}$ and $H_{el}^{(1)}$ defined for an orbital taken from the $L - l$ remaining orbitals.
5. Continue with 2) until $l + 1 = L$.

Issues with Wilson's Renormalization Group

- $H_{el}^{(l)}$ requires exact diagonalization (or a subspace iteration technique like Lanczos, which produces a large portion of the low-energy eigenvectors) and thus its dimension 2^l is limited and l must therefore be rather small

- No guarantee that reduced basis is optimum choice in some sense.

- No information from those $L - l$ remaining orbitals, which have not yet been considered, are taken into account in the construction of $H_{el}^{(l)}$ (particularly bad, when l is small)

What is the best reduced many-particle basis in terms of a least-squares fit?

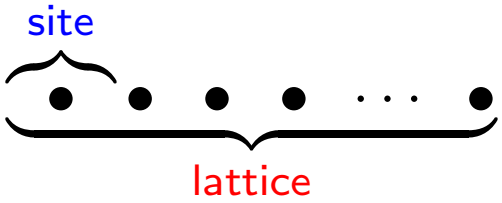
Second attempt: White's DMRG

— transform with eigenvectors of a reduced density matrix

S. R. White, *Phys. Rev. Lett.* **1992** *69* 2863; *Phys. Rev. B* **1993** *48* 10345

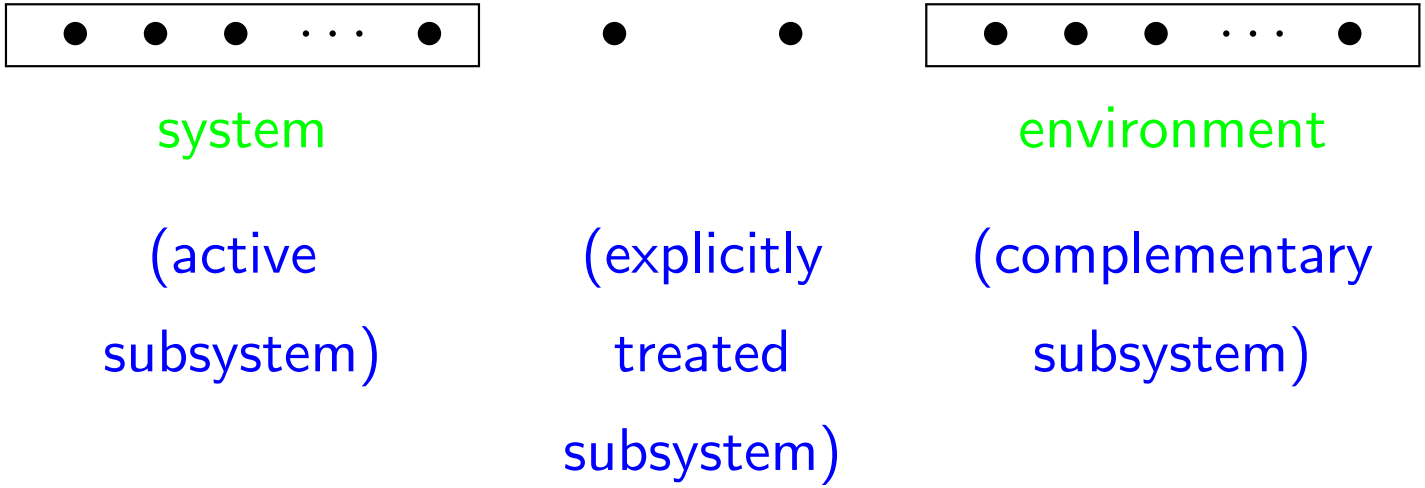
The (two-site) DMRG Algorithm: Terminology

- arrange all **spatial** orbitals as a one-dimensional lattice
- lattice consists of sites



(27)

- the sites of solid state physics are the orbitals in quantum chemistry
- divide lattice into system block, two single sites, environment block



- the joined systems (=CAS) are called the 'superblock'

The DMRG Algorithm: Initialization

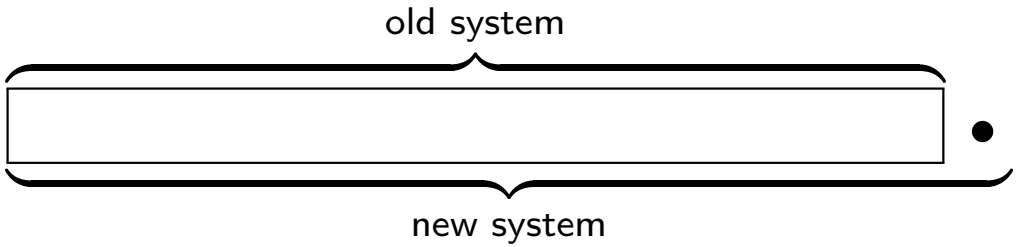
- Construct many-particle states explicitly on active subsystem

$\rightarrow$ actually: find matrix representation of elementary operators defined on this subsystem

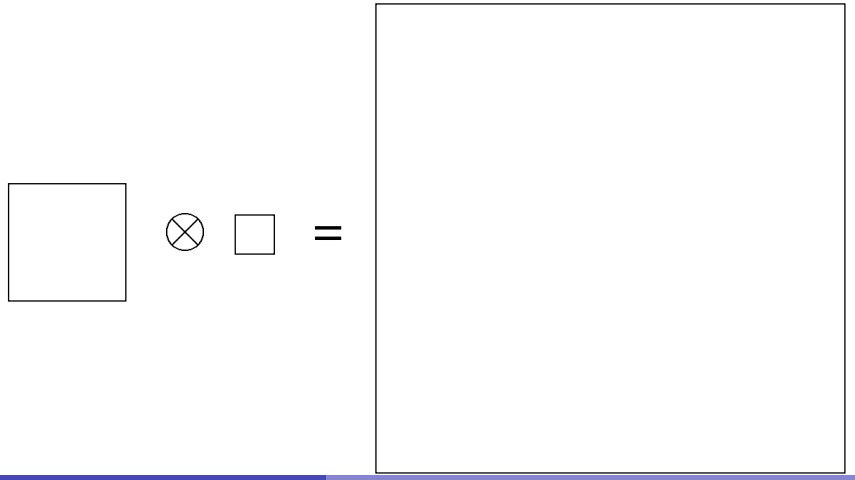
- NB: For a total(!) system of N electrons, many-particle states with 0 to a maximum of N electrons need to be considered
- Hence, active subsystem can comprise only few orbitals (too many sites prohibitive because of factorial scaling of states)
- Find a way to increase the number of orbitals (blocking), while keeping the number of basis states on the active subsystem constant (decimation)

The DMRG Algorithm: Blocking

- enlarge the system (and environment) by one site ('Blocking')



- new states are tensor products of those on old system + those on new site
- calculate operators of new system as direct product of operators defined for old system and new site
- Dimension of operators on old system: m; Dim. of ops. on single site: 4
  $\Rightarrow$ Dimension of operators defined on new system: $4m$



Construction & Diagonalization of Total Hamiltonian

- consider system and environment each enlarged by one of the explicitly treated sites (dimension for both: $4m$)
- any electronic state defined on the total orbital space (superblock) can be written as a tensor product over system $|i\rangle$ and environment $|j\rangle$ basis states

$$\Psi_{el}^{\mathrm{DMRG}} = \sum_{ij} \psi_{ij} \, |i\rangle \otimes |j\rangle \tag{28}$$

- corresponding superblock Hamiltonian $H_{\text{superblock}}$ is calculated as a sum of all elementary operator products defined on enlarged system and enlarged environment (dimension: $4m \times 4m = 16m^2$)
- NB: realize that in the first set of iterations (sweep), in which the active subsystem grows orbital by orbital, guessing of a reduced number of states on the environment is required (warm-up)
- diagonalize $H_{\text{superblock}}$ to obtain CI-type coefficients ψ_{ij} (scaling: $(16m^2)^3 \approx m^6$ for large $m \rightarrow$ subspace methods: Davidson's diagonalizer)

Construction & Diagonalization of Reduced Density Matrix

- The DMRG CI-type coefficients ψ_{ij} carry two indices as they are explicitly obtained for the i-th system and the j-th environment basis state.
- The reduced density matrix $\rho^{s/e}$ (RDM) for the system can be obtained by tracing out all (sub)states j from the environment:

$$\rho^{s/e}_{ii'} = \sum_{j \in \{e\}} \psi_{ij} \psi_{i'j} \tag{29}$$

- This matrix $\rho^{s/e}_{ii'}$ is of dimension $4m$
- m eigenvectors of $\rho^{s/e}$ can be used for the dimension reduction of all elementary operators from $4m$ back to the original dimension m

Understanding Relation of RDM to Least-Squares Fitting

- We have the following bases at our disposal:
  system: $\{|i\rangle; i = 1, \ldots, m_s\}$
  environment: $\{|j\rangle; j = 1, \ldots, m_e\}$

- In the product basis (bipartition) we express a pure state of the superblock (total system; real coefficients assumed):

$$\Psi_{el} = \sum_{ij} \psi_{ij} |i\rangle \otimes |j\rangle \tag{30}$$

- Now search for $m < m_s$ orthogonal, linear-independent system states $\{|u\rangle; u = 1, \ldots, m\}$
  into which we expand the approximate state

$$\widetilde{\Psi}'_{el} = \sum_{uj} c_{uj} |u\rangle \otimes |j\rangle \tag{31}$$

RDM, SVD, and Least-Squares Fitting

- We wish $\Psi_{el} \approx \widetilde{\Psi}'_{el}$ by requiring that

$$S' = \left|\Psi_{el} - \widetilde{\Psi}'_{el}\right|^2 = \text{ min} \tag{32}$$

- Introduce a similar reduced-dimensional basis on the environment: $\{|v\rangle; v = 1, \ldots, m\}$ with $\langle j|v\rangle = c_{vj}$ and $\sum_j |c_{vj}|^2 = 1$ such that the approximate state takes the simple form

$$\widetilde{\Psi}_{el} = \sum_k c_k |u_k\rangle \otimes |v_k\rangle \tag{33}$$

(Schmidt decomposition)

- With $U_{ik} = \langle i|u_k\rangle$ and $V_{jk} = \langle j|v_k\rangle$ we have for the squared norm

$$S = \sum_{ij} \left[\psi_{ij} - \sum_k c_k U_{ik} V_{jk}\right]^2 \tag{34}$$

RDM, SVD, and Least-Squares Fitting

- **Here, we recognize the similarity to the least-squares fitting problem in linear algebra!**
- Hence, we may use singular value decomposition (SVD) of a rectangular matrix to minimize $S \rightarrow$ factorize $\psi = (\psi_{ij})$:

$$\psi = U \cdot D \cdot V^T \tag{35}$$

- The matrix $U = (U_{ik})$ is orthogonal and of dimension $m_s \times m_s$.
- The matrix $V = (V_{jk})$ is column-orthogonal and of dimension $m_e \times m_s$.
- D is an m_s-dimensional diagonal matrix and contains the singular values of ψ (assume $m_s \leq m_e$, otherwise consider ψ^T).

RDM, SVD, and Least-Squares Fitting

- The m largest diagonal elements of D are the desired coefficients c_k and the corresponding column vectors of U and V are the desired $|u_k\rangle$ and $|v_k\rangle$.
- **But how can one make the connection to the RDM?**
- Consider the von Neumann density operator for the superblock

$$\hat{\rho} = |\Psi_{el}\rangle\langle\Psi_{el}| \overset{(30)}{=} \sum_{ii'jj'} \psi_{ij}\psi_{i'j'}|i\rangle\langle i'| \otimes |j\rangle\langle j'| \tag{36}$$

- reduced density operator from tracing out the enviroment states

$$\hat{\rho}_s = Tr_e\hat{\rho} = \sum_{j''}\sum_{ii'jj'} \psi_{ij}\psi_{i'j'}|i\rangle\langle i'|\langle j''|j\rangle\langle j'|j''\rangle \tag{37}$$

$$= \sum_{ii'j} \psi_{ij}\psi_{i'j}|i\rangle\langle i'| \tag{38}$$

RDM, SVD, and Least-Squares Fitting

- The RDM is then obtained as

$$\rho_s = \psi \cdot \psi^T \quad \text{with} \quad (\rho_s)_{ii'} = \sum_j \psi_{ij}\psi_{i'j} \tag{39}$$

- for which we can insert the SVD

$$\rho_s = \psi \cdot \psi^T \overset{(35)}{=} (UDV^T) \cdot (VDU^T) = U \cdot D^2 \cdot U^T \tag{40}$$

- Hence, U diagonalizes ρ_s and thus its eigenvalues D_{ii}^2 are related to the coefficients c_k of the Schmidt decomposition !
- Thus, instead of calculating the SVD, one can diagonalize ρ_s to obtain the $c_k = \sqrt{D_{kk}^2}$ from the m highest eigenvalues of D^2 and the corresponding eigenvectors $|u_k\rangle$.
- I.e., the larger the eigenvalue D_{ii}^2, the better represents $|u_i\rangle$ the system part of the superblock state

RDM, SVD, and Least-Squares Fitting

- Accuracy of approximation can be measured by the truncation error ϵ

$$\epsilon = 1 - \sum_{k=1}^{m} D_{kk}^2 \tag{41}$$

Ö. Legeza, J. Röder, B. A. Hess, Phys. Rev. B 67 (2003) 125114

- This transfers to the accuracy of an observable O as follows

$$\begin{aligned} |\langle O \rangle_{\Psi_{el}} - \langle O \rangle_{\widetilde{\Psi}_{el}}| &= |Tr(O\rho_s) - Tr(O\widetilde{\rho}_s)| = \left| \sum_{i=m+1}^{m_s} O_{ii} D_{ii}^2 \right| \\ &\leq \sum_{i=m+1}^{m_s} |O_{ii}| D_{ii}^2 \leq \max_{i>m} |O_{ii}| \sum_{i=m+1}^{m_s} D_{ii}^2 \\ &= \max_{i>m} |O_{ii}| \epsilon \end{aligned} \tag{42}$$

J. Röder, PhD Thesis, University of Erlangen, 2003

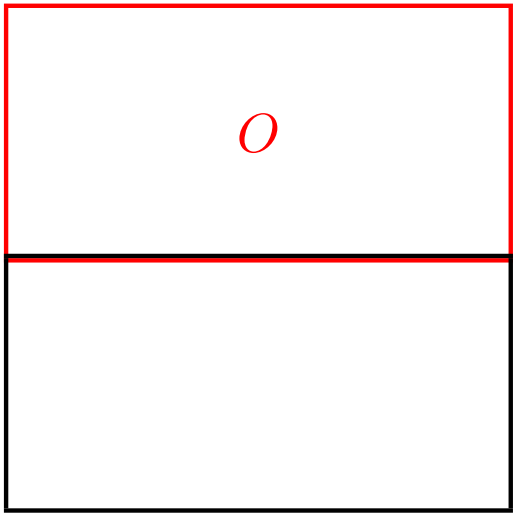
Pictorially: Diagonalization of the RDM

- reduced density matrix is diagonalized $\rightarrow$ $4m$ eigenpairs

$$U = \boxed{4m \times 4m}$$

Pictorially: Diagonalization of the RDM

- reduced density matrix is diagonalized $\rightarrow$ $4m$ eigenpairs

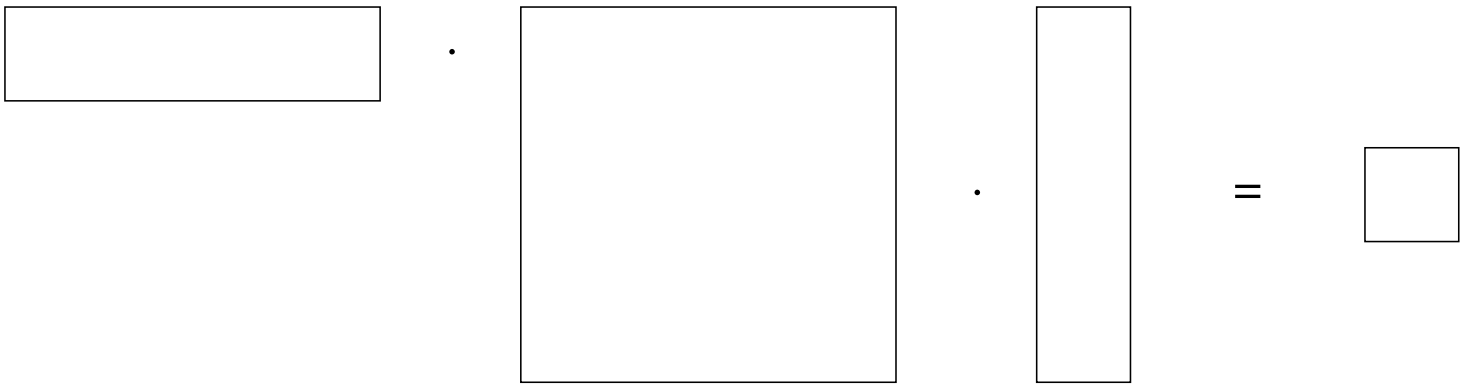
$U =$ 

- choose the m eigenvectors with the highest eigenvalues
- keep m variable to always adjust to the optimum number of relevant eigenvectors (Ö. Legeza: dynamic block-state selection DBSS)
- selected eigenvectors transform the many-particle basis of the (enlarged) system to a reduced basis

Pictorially: Renormalization of Operators

- transformation by selected eigenvectors yields new many-particle basis of the system (optimum reduced m-dimensional basis in a least-squares sense)

- operators are now transformed to the new basis, i.e. renormalized:



$$O^T \, \tilde{a}_{\text{new}} \, O \;=\; a_{\text{new}} \tag{43}$$

- columns of the transformation matrix O consist of the selected eigenvectors

- dimension of the operators is reduced from $4m$ to m

Features of the DMRG Algorithm

- DMRG is a CAS approach!
- DMRG iterations increase AS orbital by orbital until the environment is completely absorbed into the system.
- Then, the iteration direction is reversed to optimize the environment representation.
- This defines a 'linear' algorithm, and explains why the orbital ordering can be important (convergence to local minima possible!).

  G. Moritz, B. A. Hess, M. Reiher, *J. Chem. Phys.* **2005** *122* 024107
- It was thought that DMRG is therefore only beneficial for pseudo-one-dimensional molecules.
- DMRG state is a superposition of FCI-type basis states.
- An FCI/CAS solution can be converged; but the basis cannot be completely known in terms of CSFs if DMRG shall be efficient

DMRG Convergence for Complicated Electronic Structures

- If DMRG calculations shall be competitive, these issues must be addressed:
  - **dynamic correlation effects need to be included**
    see work of G. K.-L. Chan *et al.*, T. Yanai & Y. Kurashige *et al.* on multi-reference perturbation theory;
    problem: requires up to 4-body reduced density matrices !
  - **efficient warm-up sweep (environment guess)**
    see work of Ö. Legeza *et al.* (CI-DEAS and entanglement measures for orbital ordering)
  - **number of renormalized states m should be as small as possible**

- orbital ordering:
  crucial to avoid convergence to local energy minima in case of small m
  (if no noise or perturbative correction are considered)

  G. Moritz, B. A. Hess, M. Reiher, *J. Chem. Phys.* **2005** *122* 024107

- environment states: in principle, the better the approximation of environment states the faster convergence should be

  G. Moritz, M. Reiher, *J. Chem. Phys.* **2006** *124* 034103

Determining Factors of DMRG Convergence

1. (Choice of the one-electron basis set for the representation of the molecular orbitals)
2. Size of the active space (CAS)
3. Choice of the type of molecular orbitals
   (HF, NO's, localized orbitals, ..., DMRG-SCF)
4. Environment-state guess in the first sweep
   (CI-DEAS by Ö. Legeza or noise/perturbation added to RDM)
5. Ordering of orbitals (exploit entanglement measures, see below)
6. Number of renormalized subsystem states m

$\Rightarrow$ **All of these parameters must be documented in a report on DMRG results !**

S. Keller, M. Reiher, Chimia 68 **2014** 200-203 [arXiv: 1401.5497]

Lecture 2

Second-Generation DMRG: Matrix Product and Tensor Network States

1. New Parametrization of the Electronic Wave Function: Tensor Network States (TNS)
2. Matrix Product States (MPSs) and Matrix Product Operators (MPOs)
3. Parameters that Determine DMRG Accuracy

How to Efficiently Represent (Electronic) Quantum States?

- Tensor-product construction of the N-particle Hilbert space from 1-particle Hilbert spaces

$$\Psi_{el} = \sum_{i_1 i_2 \cdots i_L} C_{i_1 i_2 \cdots i_L} \; |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_L\rangle \tag{44}$$

- Dimension inreases exponentially with system size (4^L for spatial orbitals). $C_{i_1 i_2 \cdots i_L}$ ($=C_I$) is element of the coefficient tensor
- In principle, it should be sufficient to parameterize a manifold of states such that there exists a large overlap with the exact state.

  F. Verstraete, *Adv. Phys.* **2008** *57* 143

- How to reduce the complexity of Ψ_{el} and come up with a class of variational wave functions that captures the physics of the electronic Hamiltonian?

Parameterization of the Wave Function

$$\Psi_{el} = \sum_{i_1 i_2 \cdots i_L} C_{i_1 i_2 \cdots i_L} \, |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_L\rangle \tag{45}$$

- Configuration Interaction ansatz

$$|\mathrm{CI}\rangle = \Big(1 + \sum_{\mu} C_\mu \hat{\tau}_\mu\Big)|\mathrm{HF}\rangle \tag{46}$$

- Coupled Cluster ansatz

$$|\mathrm{CC}\rangle = \Big(\prod_{\mu} [1 + t_\mu \hat{\tau}_\mu]\Big)|\mathrm{HF}\rangle \tag{47}$$

- Restricted sum over basis states with a certain substitution pattern generated by 'excitation' operator $\hat{\tau}_\mu$
  $\rightarrow$ yields a pre-defined (!) many-particle basis set
- numerous specialized selection/restriction protocols

Instead of standard CI-type calculations by diagonalization/projection

$$\Psi_{el} = \sum_{i_1 i_2 \cdots i_L} C_{i_1 i_2 \cdots i_L} \, |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_L\rangle \tag{48}$$

construct CI coefficients from correlations among orbitals

$$\Psi_{el} = \sum_{i_1 i_2 \cdots i_L} C_{i_1 i_2 \cdots i_L} \, |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_L\rangle \tag{49}$$

$\Longrightarrow$ tensor construction of expansion coefficients

Some Early Tensor Network (TN) Approaches

... for spin Hamiltonians developed:

- 1-dimensional TN: **Matrix Product States** (MPS) / DMRG

  S. R. White, *Phys. Rev. Lett.* **1992** *69* 2863

  S. Römmer, S. Ostlund, *Phys. Rev. Lett.* **1995** *75* 3537

- 2-dimensional TN: **Projected Entangled Pair States** (PEPS)

  F. Verstraete, M. M. Wolf, D. Perez-Garcia, J. I. Cirac *PRL* **2006** *96* 220601

- higher-dimensional TN:
  Multiscale Entanglement Renormalization Ansatz (MERA)

  M. Aguado, G. Vidal, *Phys. Chem. Rev.* **2008** *100* 070404

MPS & DMRG

- Structure of White's DMRG wave function: Matrix Product States (MPS)

  S. Römmer, S. Ostlund, *Phys. Rev. Lett.* **1995** *75* 3537

$$\Psi_{el}^{\mathrm{MPS}} = \sum_{i_1 i_2 \cdots i_L} \left[A_{i_1}^{[1]} \cdots A_{i_L}^{[L]} \right] |i_1 \otimes i_2 \otimes \cdots \otimes i_L\rangle \tag{50}$$

- **DMRG algorithm defines a protocol for the iterative improvement of the matrices $A^{[i]}$ by using the reduced density matrix (RDM) for the AS of the total system.**
- Transformation matrices $A^{[i]}$ represent the change of the many-electron basis when adding to the *active subsystem* (AS) states on a single orbital taken from the *environment*.
- In the finite-CAS DMRG, the first and last matrices $A_{i_1}^{[1]}$ and $A_{i_L}^{[L]}$, resp., are actually vectors.

Reconstruction of CI coefficients

- Reconstruct a CI-type wave function from the DMRG state, because
  - allows us to interpret/understand the states in the standard way,
  - makes DMRG calculations for different m values comparable,
  - allows us to study DMRG convergence in terms of determinants being picked up.

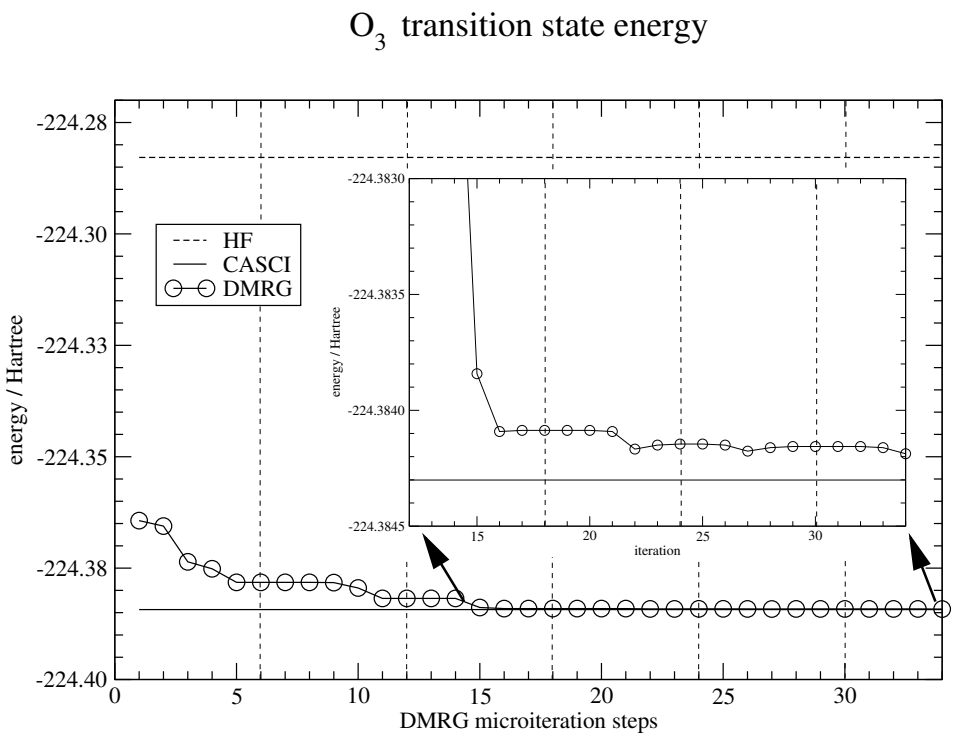
- MPS structure yields the CI coefficients:

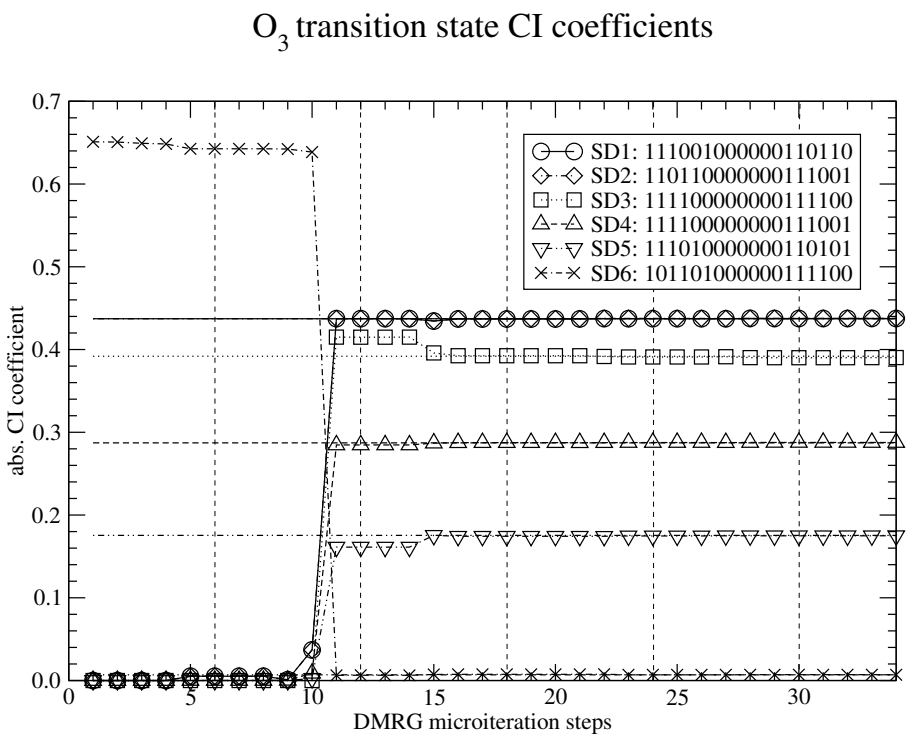
$$C_{\{\mathbf{n}\}} = \sum_{m_s}^{m} \sum_{m_e}^{m} \psi_{m_s n_{l+1} n_{l+2} m_e} \left(A_l^{[n_l]} \dots A_2^{[n_2]} \right)_{m_s;n_1} \times \left(A_{l+3}^{[n_{l+3}]} \dots A_{L-1}^{[n_{L-1}]} \right)_{m_e;n_L} \tag{51}$$

CI coefficient calculated from renormalization matrices and DMRG-state expansion coefficients $\psi_{m_s n_{l+1} n_{l+2} m_e}$ (for active system of size l)

G. Moritz, M. Reiher, *J. Chem. Phys. 126* **2007** 244109

Example: Transition Structure of Ozone

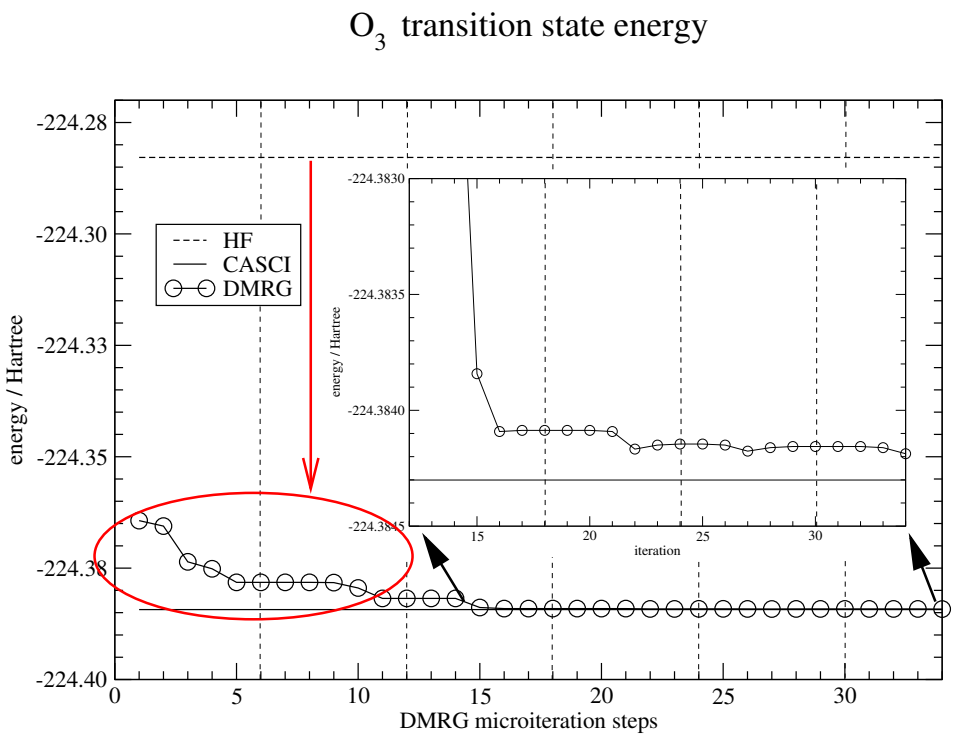


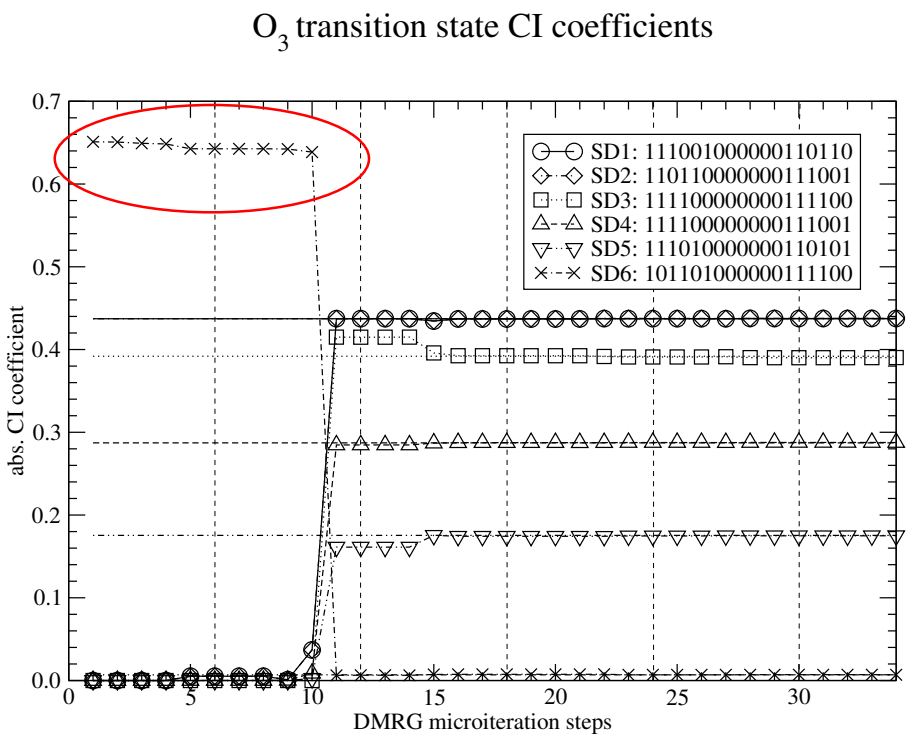


G. Moritz, M. Reiher, *J. Chem. Phys. 126* (2007) 244109

(see this reference also for a DMRG flow chart)

Example: Transition Structure of Ozone

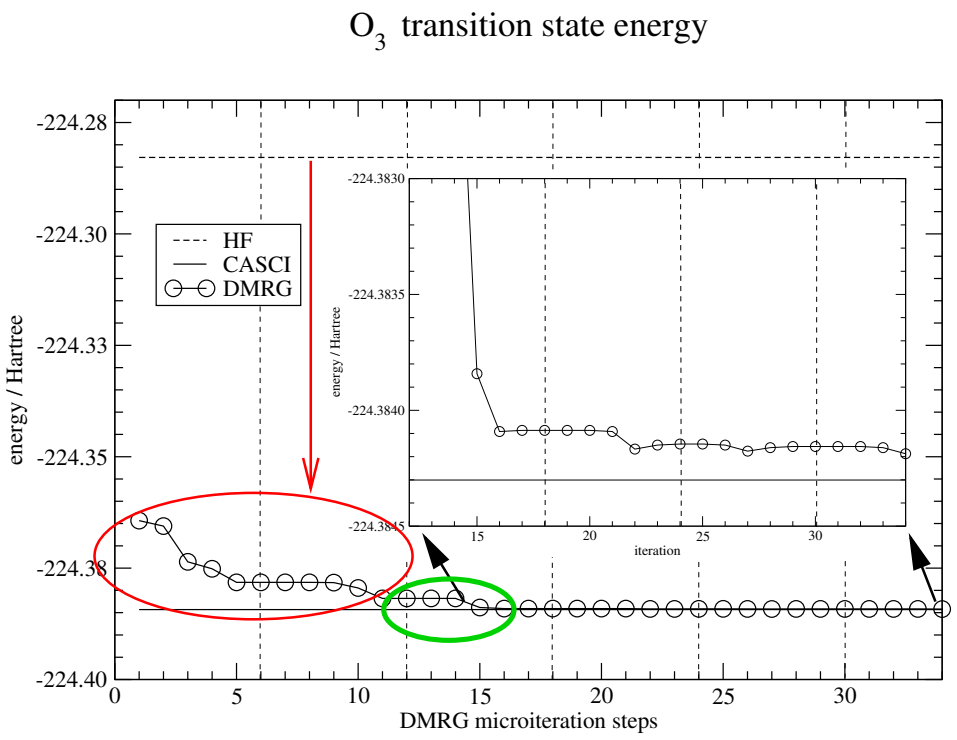


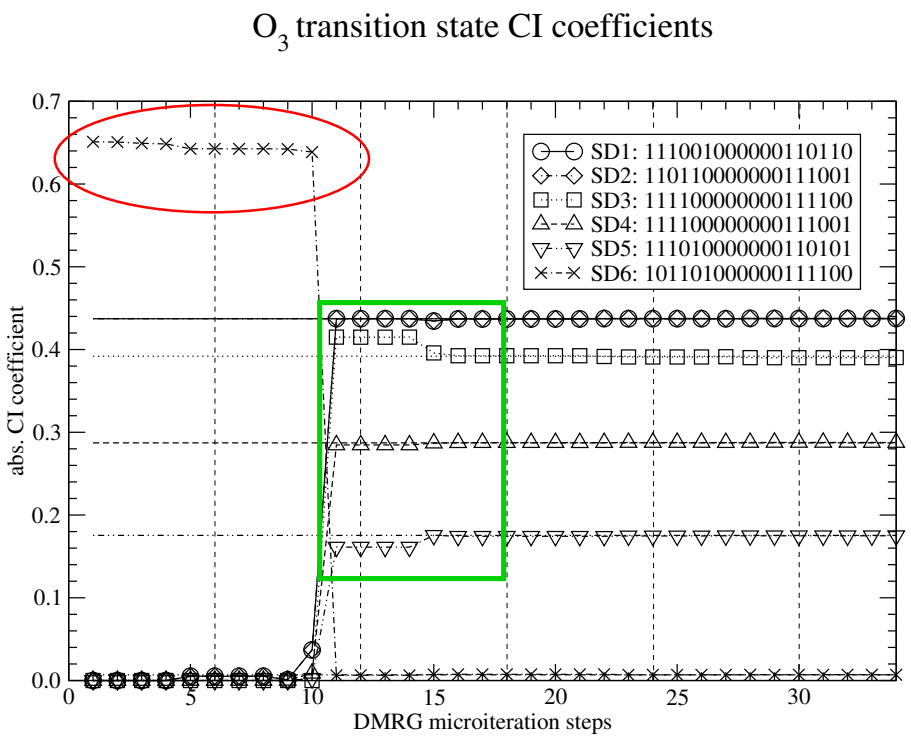


G. Moritz, M. Reiher, *J. Chem. Phys. 126* (2007) 244109

(see this reference also for a DMRG flow chart)

Example: Transition Structure of Ozone





G. Moritz, M. Reiher, *J. Chem. Phys. 126* (2007) 244109

(see this reference also for a DMRG flow chart)

SR-CAS Approach

- Our 2007 scheme could only reconstruct FCI from DMRG wave functions for which a FCI calculation was also possible.

- Cure: Sampling-Reconstruction Complete-Active-Space algorithm:

  Monte Carlo scheme for sampling configurations

- Only the most important configurations are kept.
- The accuracy is easily controlled by a completeness measure COM:

$$\mathrm{COM} = 1 - \sum_{I \in \{\mathrm{sample}\}} C_I^2 \tag{52}$$

K. Boguslawski, K. H. Marti, M. Reiher, *J. Chem. Phys. 134* (2011) 224101

Derivation of MPS Structure of DMRG Wave Function

The CI coefficient tensor $C_{i_1 i_2 \cdots i_L}$

$$\begin{aligned} \Psi_{el} &= \sum_{i_1 i_2 \cdots i_L} C_{i_1 i_2 \cdots i_L} \, |i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_L\rangle \\ &\equiv \sum_{i_1 i_2 \cdots i_L} C_{i_1 i_2 \cdots i_L} \, |i_1, i_2, \ldots i_L\rangle \;\equiv\; \sum_I C_I \Phi_I \end{aligned} \tag{53}$$

can be decomposed by sequential SVDs, which clarifies the MPS structure of the DMRG wave function.

Consider a DMRG state function with the first orbital (from the left) in the AS and $(L-1)$ orbitals in the environment,

$$\Psi_{el}^{\mathrm{DMRG}} = \sum_{i_1, \mathbf{j}} \psi_{i_1 \mathbf{j}} \, |i_1\rangle \otimes |\mathbf{j}\rangle \;\; \text{with} \;\; \mathbf{j} = (i_2 \ldots i_L) \tag{54}$$

Hence, the coefficient tensor $C_{i_1 i_2 \cdots i_L}$ is approximated by a matrix $\psi_{i_1 \mathbf{j}}$.

Derivation of MPS Structure of DMRG Wave Function

$\psi_{i_1\mathbf{j}}$ is of dimension $(m \times m^{L-1})$ and can be subjected to an SVD

$$\begin{aligned} C_{i_1 i_2 \cdots i_L} \;\rightarrow\; \psi_{i_1\mathbf{j}} = \psi_{i_1(i_2 \ldots i_L)} &= \sum_{a_1}^{r_1} U_{i_1 a_1}\; D_{a_1 a_1}\; V^T_{a_1(i_2 \ldots i_L)} \\ &\equiv \sum_{a_1}^{r_1} U_{i_1 a_1}\; C_{a_1 i_2 \ldots i_L} \end{aligned} \tag{55}$$

with the rank $r_1 \leq m$. Now, change notation:

a) matrix U is written as a collection of row vectors A^{i_1} with entries $A^{i_1}_{a_1} = U_{i_1 a_1}$.

b) coefficient tensor $C_{a_1 i_2 \ldots i_L}$ is ordered as a matrix $\psi_{(a_1 i_2)(i_3 \ldots i_L)}$ of dimension $(r_1 \cdot m \times m^{L-2})$

Derivation of MPS Structure of DMRG Wave Function

... so that we obtain for the original coefficient tensor

$$C_{i_1 i_2 \cdots i_L} = \sum_{a_1}^{r_1} A_{a_1}^{i_1} \; \psi_{(a_1 i_2)(i_3 \ldots i_L)} \tag{56}$$

Next, the matrix $\psi_{(a_1 i_2)(i_3 \ldots i_L)}$ is subjected to another SVD

$$\psi_{(a_1 i_2)(i_3 \ldots i_L)} = \sum_{a_2}^{r_2} U_{(a1 i_2) a_2} \; D_{a_2 a_2} \; V^T_{a_2 (i_3 \ldots i_L)} \tag{57}$$

$$\equiv \sum_{a_2}^{r_2} U_{(a_1 i_2) a_2} \; C_{a_2 i_3 \ldots i_L} \tag{58}$$

$$\equiv \sum_{a_2}^{r_2} A_{a_1 a_2}^{i_2} \; \psi_{(a_2 i_3)(i_4 \ldots i_L)} \tag{59}$$

where the last step is again just a change of notation ...

Derivation of MPS Structure of DMRG Wave Function

... which, however, allows us to write the original tensor in compact form

$$C_{i_1 i_2 \cdots i_L} = \sum_{a_1}^{r_1} \sum_{a_2}^{r_2} A^{i_1}_{a_1} A^{i_2}_{a_1 a_2} \; \psi_{(a_2 i_3)(i_4 \ldots i_L)} \tag{60}$$

Now, the new matrix $\psi_{(a_2 i_3)(i_4 \ldots i_L)}$ of dimension $(r_2 \cdot m \times m^{L-3})$ is subjected to the next SVD.

This 'game' continues until we finally obtain

$$C_{i_1 i_2 \cdots i_L} = \sum_{a_1 \ldots a_L} A^{i_1}_{a_1} A^{i_2}_{a_1 a_2} \ldots A^{i_{L-1}}_{a_{L-2} a_{L-1}} A^{i_L}_{a_{L-1}} \tag{61}$$

$$= A^{i_1} A^{i_2} \cdots A^{i_{L-1}} A^{i_L} \tag{62}$$

where the sums are interpreted as matrix multiplications in the last step.

MPS Structure of Operators: MPOs

Consider occupation-number-vector basis states $|\boldsymbol{\sigma}\rangle$ and $|\boldsymbol{\sigma'}\rangle$.

The coefficients $w_{\boldsymbol{\sigma}\boldsymbol{\sigma'}}$ of a general operator

$$\widehat{\mathcal{W}} = \sum_{\boldsymbol{\sigma},\boldsymbol{\sigma'}} w_{\boldsymbol{\sigma}\boldsymbol{\sigma'}} |\boldsymbol{\sigma}\rangle\langle\boldsymbol{\sigma'}|, \tag{63}$$

may be encoded in matrix-product form

$$w_{\boldsymbol{\sigma},\boldsymbol{\sigma'}} = \sum_{i_1,\ldots,i_{L-1}} W^{\sigma_1\sigma_1'}_{1i_1} \cdots W^{\sigma_l\sigma_l'}_{i_{l-1}i_l} \cdots W^{\sigma_L\sigma_L'}_{i_{L-1}1}. \tag{64}$$

Combining Eqs. (63) and (64), operator $\widehat{\mathcal{W}}$ reads

$$\widehat{\mathcal{W}} = \sum_{\boldsymbol{\sigma}\boldsymbol{\sigma'}} \sum_{i_1,\ldots,i_{L-1}} W^{\sigma_1\sigma_1'}_{1i_1} \cdots W^{\sigma_l\sigma_l'}_{i_{l-1}i_l} \cdots W^{\sigma_L\sigma_L'}_{i_{L-1}1} \, |\boldsymbol{\sigma}\rangle\langle\boldsymbol{\sigma'}|. \tag{65}$$

Simplify Eq. (65) by contraction over the local site indices σ_l, σ_l' in $\boldsymbol{\sigma}, \boldsymbol{\sigma'}$:

$$\widehat{W}^l_{i_{l-1}i_l} = \sum_{\sigma_l,\sigma_l'} W^{\sigma_l\sigma_l'}_{i_{l-1}i_l} |\sigma_l\rangle\langle\sigma_l'|, \tag{66}$$

so that Eq. (65) reads

$$\widehat{\mathcal{W}} = \sum_{i_1,\ldots,i_{L-1}} \widehat{W}^1_{1i_1} \cdots \widehat{W}^l_{i_{l-1}i_l} \cdots \widehat{W}^L_{i_{L-1}1}. \tag{67}$$

Motivation for this: Entries of the resulting $\widehat{W}^l_{i_{l-1}i_l}$ matrices are the elementary operators $\hat{a}^\dagger_{l\sigma}$ and $\hat{a}_{l\sigma}$ acting on a single site (=orbital)!

MPS concept has thus been transfered to operators (MPOs).

A program that implements these equations, we call a second-generation DMRG program.

Why write a new code? – Two variants of DMRG:

Traditional DMRG

- $|\psi\rangle = \sum_{LR} C_{LR} |\boldsymbol{\sigma}_L\rangle \otimes |\boldsymbol{\sigma}_R\rangle$
- coefficients valid for one bipartition into L and R (need basis transformations)
- considered to be faster for ground state

MPO-DMRG

- $|\psi\rangle = \sum_{\boldsymbol{\sigma}} M^{\sigma_1} M^{\sigma_2} \cdots M^{\sigma_L} |\boldsymbol{\sigma}\rangle$
- coefficients valid for whole system
- Easy and efficient implementation of observables
- QC-MAQUIS developed in my group by S. Keller, S. Knecht, Y. Ma, C. Stein, S. Battaglia, E. Hedegard is based on the MPO-based DMRG program MAQUIS by Troyer and co-workers for spin Hamiltonians

Other Options: Tensor Network States (TNS)

$$\Psi_{el}^{\mathrm{TNS}} = \sum_{i_1 i_2 \ldots i_L} \prod_{i}^{L} \prod_{j \leq i} f_{ij}^{I[i]I[j]} \underbrace{|i_1\rangle \otimes |i_2\rangle \otimes \cdots \otimes |i_L\rangle}_{|I\rangle} \tag{68}$$

- Idea: Rewrite CI coefficient tensor by reducing number of variational parameters (still obtain qualitatively correct wave function).

- **TNS originally proposed for simple** *Spin Hamiltonians*:
  - String-Bond States

N. Schuch, M. Wolf, F. Verstraete, J. I. Cirac, *Phys. Rev. Lett.* **2008** *100* 040501

  - Entangled-Plaquette States

F. Mezzacapo, N. Schuch, M. Boninsegni, J. I. Cirac **2009** arXiv:0905.3898v3

  - Correlator-Product States

H. J. Changlani, J. M. Kinder, C. J. Umrigar, G. K.-L. Chan, **2009** arXiv:0907.4646v1

Complete-Graph Tensor Network States (CG-TNS)

- First implementation of TNS for full quantum-chemical Hamiltonian
- Considering *all* pairs of parameters f_{ij}: CG-TNS
- Parameters optimized with Monte Carlo techniques
- First studied for methylene and ozone; S/T splitting in ozone:

	$\mathrm{E}_{\mathrm{S}=0}/E_h$	$\mathrm{E}_{\mathrm{S}=1}/E_h$	$\Delta\mathrm{E}/\mathrm{kcalmol}^{-1}$
HF	$-224.282\ 841$	$-224.357\ 167$	46.6
CASCI	$-224.384\ 301$	$-224.416\ 172$	20.0
CG-TNS	$-224.381\ 648$	$-224.412\ 775$	19.5

K. H. Marti, B. Bauer, M. Reiher, M. Troyer, F. Verstraete, New J. Phys. *12* **2010** 103008

Variational Quantum Monte Carlo

$$\Psi_{el}^{\mathrm{TNS}} = \sum_{i_1 i_2 \ldots i_N} \prod_{i}^{N} \prod_{j \leq i} f_{ij}^{I[i]I[j]} \underbrace{|I\rangle}_{|i_1 i_2 \ldots i_N\rangle} = \sum_{I} W(I)|I\rangle$$

$$E = \langle E(I) \rangle = \frac{1}{Z} \sum_{I} W^2(I) E(I) \quad \text{where} \quad Z = \sum_{I} W^2(I)$$

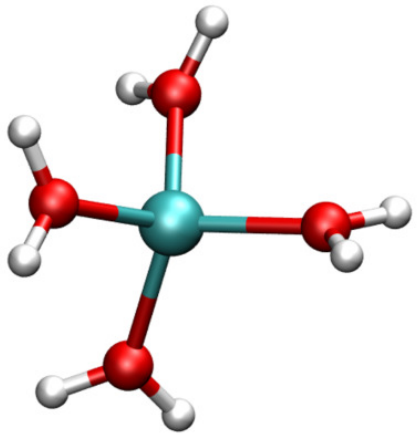
$$E(I) = \sum_{I'} \frac{W(I')}{W(I)} \langle I'|H|I\rangle$$

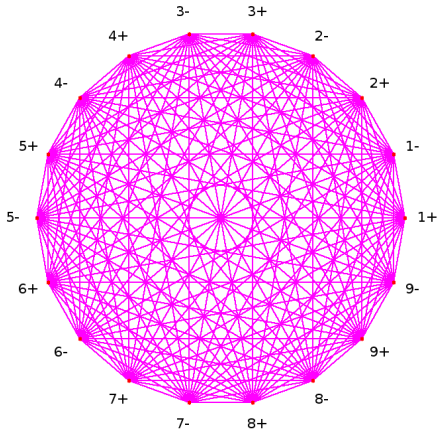
- The energy can be evaluated using importance sampling of the configurations $|I\rangle$ according to the weight $W^2(I)$.

A. W. Sandvik, G. Vidal, *Phys. Rev. Lett.* **2007** *99* 220602

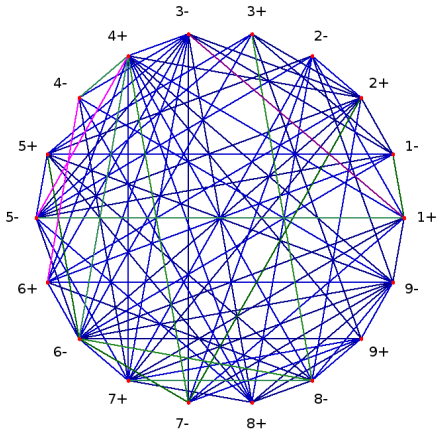
CG-TNS for Transition Metal Compounds

- CG-TNS will be efficient if the molecular structure supports the ansatz (clusters!)
- Problem: One must avoid the explicit construction of all CSFs
- First feasibility test: tetraqua-cobalt
  K. H. Marti, M. Reiher, *PCCP 13* (2011) 6750

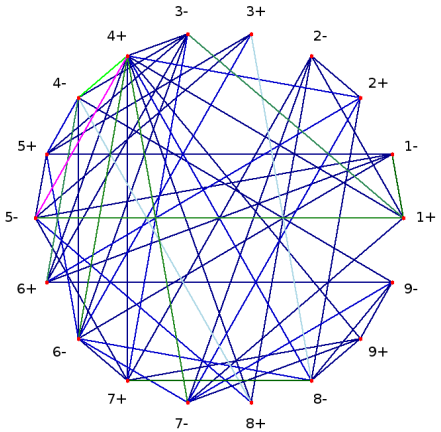




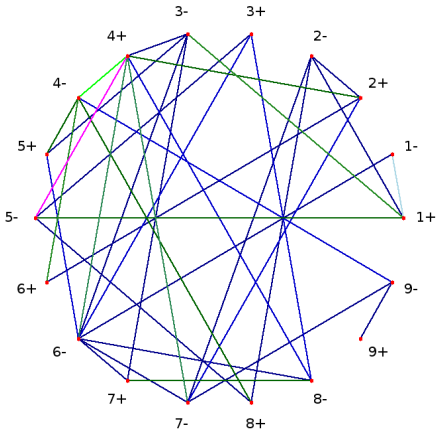
–1676.566 252 E_h



–1685.278 226 E_h



–1685.278 549 E_h



–1685.278 641 E_h

	Hartree–Fock	CAS(9,9)-SCF	CG-TNS
E_{el} / Hartree	−1685.235 055	−1685.293 744	−1685.279 408
Var. Parameters		7056	684

Applications

Results of Actual Quantum-Chemical Calculations

(taken from our group)

1. DMRG for Compact Strongly Correlated Molecules: Transition Metal Complexes
2. DMRG Spin Density
3. Concepts of Quantum Information Theory for Electronic Structures and Chemical Bonding

Does DMRG Work for Compact Molecules?

- Original 'opinion' in the DMRG community:

  Works only for pseudo-one-dimensional, non-compact systems!

- Test for a mononuclear transition metal system CAS(10,10): CoH

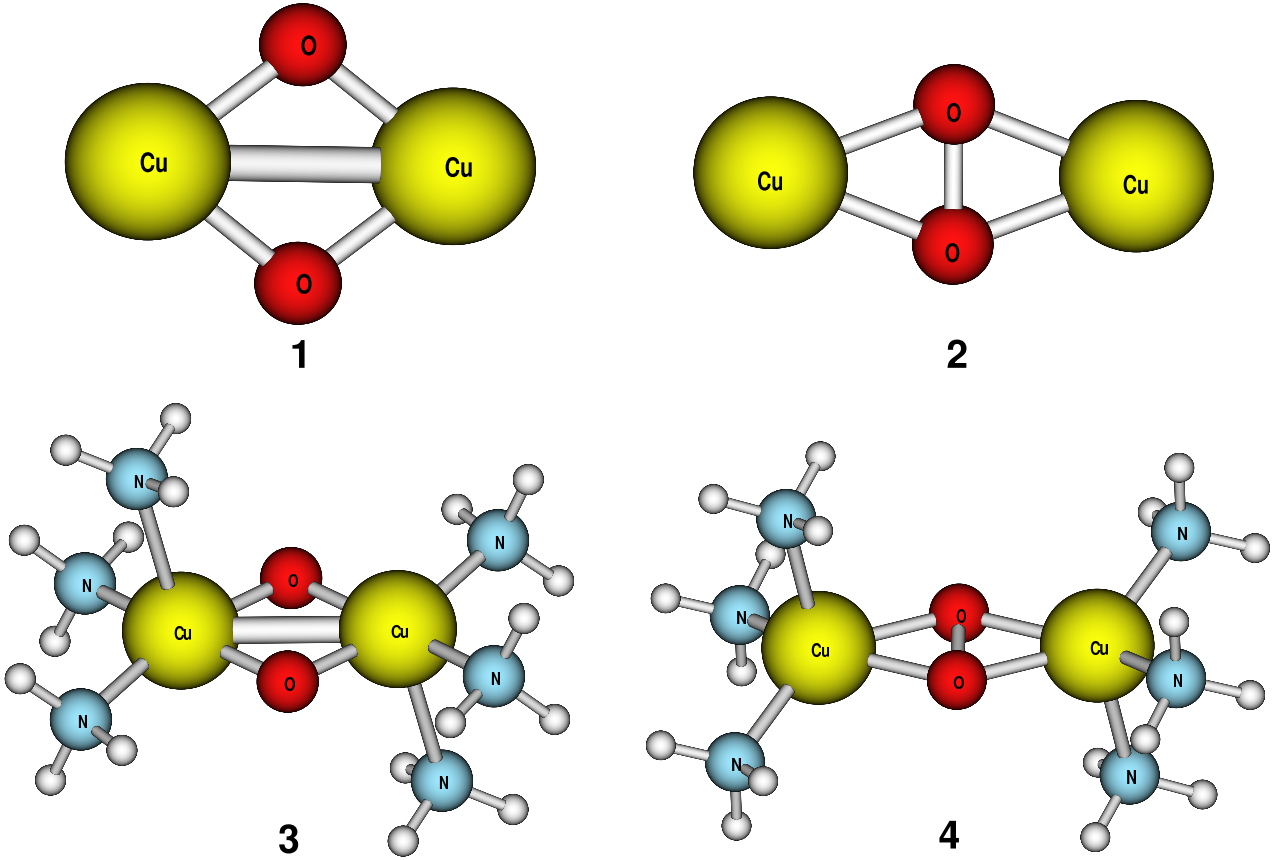
m	$E_{singlet}/\mathrm{E}_h$	$E_{triplet}/\mathrm{E}_h$	$\Delta E/\mathrm{kJmol}^{-1}$
64	−1381.952 054	−1381.995 106	**113.03**
76	−1381.952 063	−1381.995 109	113.02
91	−1381.952 070	−1381.995 110	113.00
109	−1381.952 073	−1381.995 110	112.99
CAS(10,10)	−1381.952 074	−1381.995 110	**112.99**
CASPT2(10,10)	−1382.189 527	−1382.241 333	130.57
DFT/BP86	−1383.504 019	−1383.585 212	213.1
DFT/B3LYP	−1383.202 267	−1383.279 574	203.0

original work to propose DMRG for compact, strongly correlated molecules:

K. Marti, I. Malkin Ondik, G. Moritz, M. Reiher, *J. Chem. Phys 128* (2008) 014104

The Cu_2O_2-Torture Track

- Standard CASSCF fails for large CASs relevant in polynuclear clusters
- Example: two different isomers of dinuclear copper clusters



C. J. Cramer, M. Włoch, P. Piecuch, C. Puzzarini, L. Gagliardi *J. Phys. Chem. A 110* (2006) 1991

Energies of Isomeric Dinuclear Copper Clusters

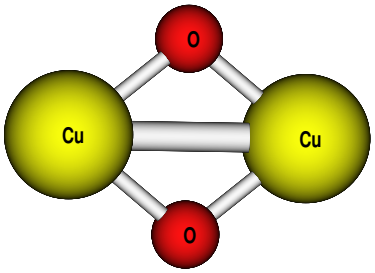
- CASSCF fails since large CASs needed for clusters

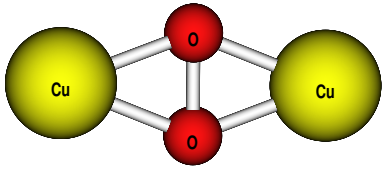
  K. Marti, I. Malkin Ondik, G. Moritz, M. Reiher, *JCP 128* (2008) 014104

- results with new code and including noise:

  44 active orbitals, 26 electrons, basis set: Cu ECP10MDF, O ANO-Sm, charge: +2

  K. Marti, M. Reiher, *Z. Phys. Chem. 224* (2010) 583





m	E_{bisoxo}/E_h	E_{peroxo}/E_h	$\Delta E/\mathrm{kJmol}^{-1}$
DMRG(m=32)	−541.440 272	−541.478 196	99.6
DMRG(m=44)	−541.446 006	−541.483 405	98.2
DMRG(m=64)	−541.458 021	−541.497 468	103.6
DMRG(m=128)	−541.473 082	−541.514 702	109.3
RASPT2(24,28)[a]			119.66

[a] P. Å. Malmqvist, et al. *J. Chem. Phys 128* (2008) 204109

- What is the fully converged DMRG result for this system?

  → Large-scale DMRG: **149 kJ/mol** Y. Kurashige, T. Yanai, *J. Chem. Phys. 130* (2009) 234114 ... Final answer ?

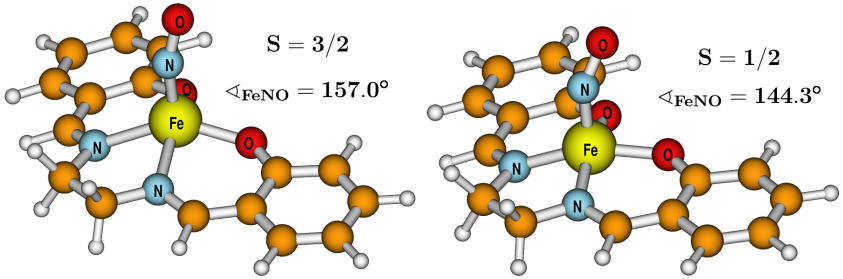
Torture Track: $[Cu_2O_2]^{2+}$

Ref.,method	E_{bisoxo}	E_{peroxo}	ΔE
'Standard' methods			
A),CASSCF(16,14)	−541.50307	−541.50345	1
A),CASPT2(16,14)	−542.06208	−542.06435	6
A),bs-B3LYP	−544.19419	−544.27844	221
B),RASPT2(24,28)			120
Previously published DMRG energies			
C),DMRG(26,44)[800]	−541.46779	−541.49731	78
D),DMRG(26,44)[128]	−541.47308	−541.51470	109
E),DMRG(32,62)[2400]	−541.96839	−542.02514	149
F),DMRG(28,32)[2048]-SCF	−541.76659	−541.80719	107
F),DMRG(28,32)[2048]-SCF/CT			113
our latest DMRG results with QIT, without noise			
G), DMRG(26,44)[256/1024/10^{-5}]	−541.53853	−541.58114	112

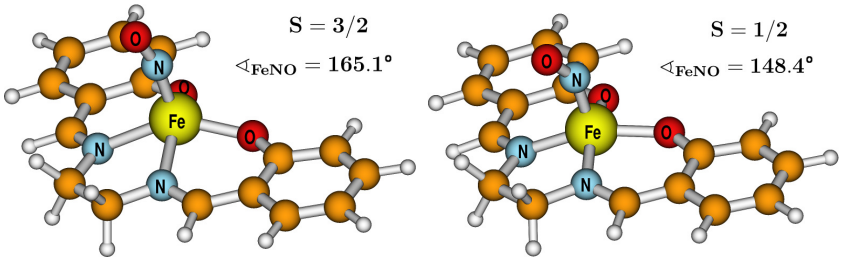
A) C. J. Cramer *et al.*, *J. Phys. Chem. A 110* (2006) 1991; B) P. A. Malmqvist *et al.*, *J. Chem. Phys 128* (2008) 204109; C) K. Marti, *et al.*, *J. Chem. Phys 128* (2008) 014104; D) K. Marti, M. Reiher, *Z. Phys. Chem. 224* (20109 583; E) Y. Kurashige, T. Yanai, *J. Chem. Phys. 130* (2009) 234114; F) T. Yanai *et al.*, *J. Chem. Phys. 132* (2010) 024105; **G) G. Barcza** *et al.*, *Phys. Rev. A 83* **(2011) 012508**

Analysis of Spin Density Distributions with DMRG

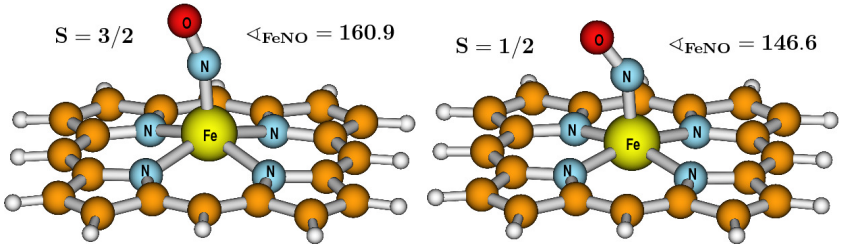
Example 4: Noninnocent Iron Nitrosyl Complexes



(a) Fe(salen)(NO) conformation a



(b) Fe(salen)(NO) conformation b

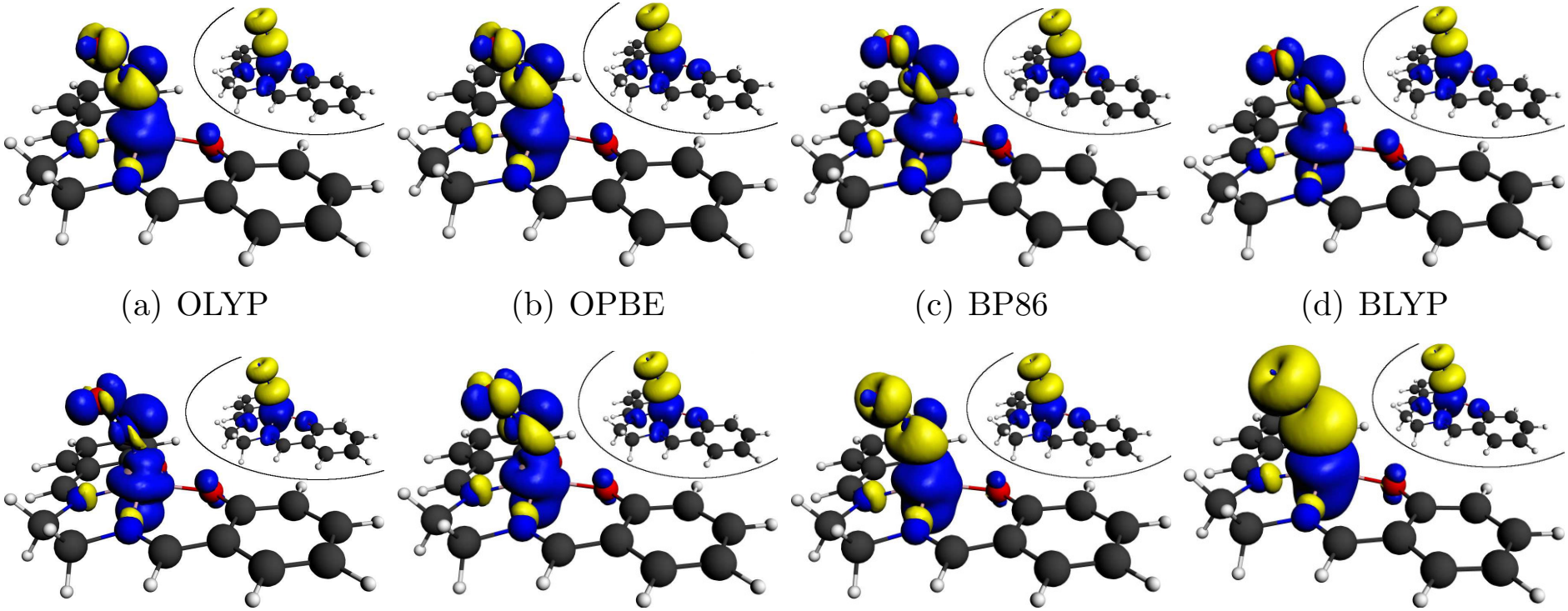


(c) Fe(porphyrin)(NO)

- transition metal nitrosyl complexes have a complicated electronic structure
- qualitatively different spin densities reported by Conradie & Ghosh
  J. Conradie, A. Ghosh, *J. Phys. Chem. B* **2007,** *111,* 12621.
- systematic comparison of DFT spin densities with CASSCF:
  K. Boguslawski, C. R. Jacob, M. Reiher, *J. Chem. Theory Comput.* **2011,** *7,* 2740;

  see also work by K. Pierloot *et al.*

DFT Spin Densities: A Case Study



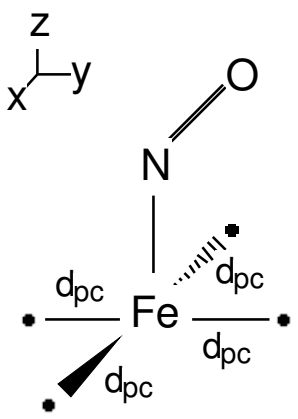
(a) OLYP (b) OPBE (c) BP86 (d) BLYP

(e) TPSS (f) TPSSh (g) M06-L (h) B3LYP

- Only for high-spin complexes similar spin densities are obtained

$\Rightarrow$ $[Fe(NO)]^{2+}$ moiety determines the spin density

The Model System for Accurate Reference Calculations



Structure:

- Four point charges of -0.5 e model a square-planar ligand field ($d_{\mathrm{dp}} = 1.131$ Å)

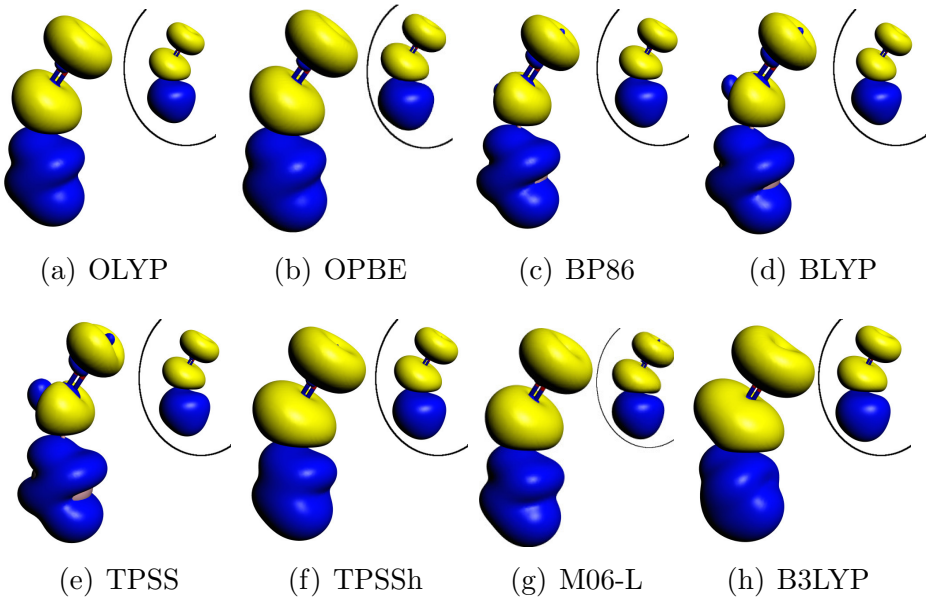
$\Rightarrow$ Similar differences in DFT spin densities as present for larger iron nitrosyl complexes

Advantage of the small system size:

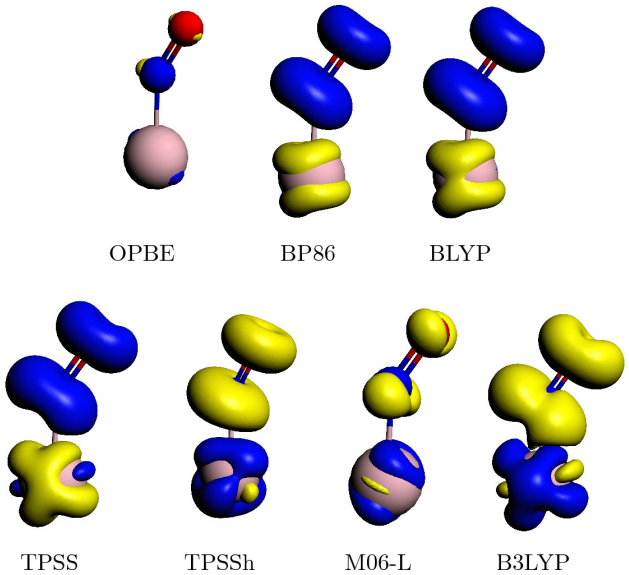
- Standard correlation methods (CASSCF, ...) can be efficiently employed
- Study convergence of the spin density w.r.t. the size of the active orbital space

K. Boguslawski, C. R. Jacob, M. Reiher, *J. Chem. Theory Comput.* **2011,** *7,* 2740.

DFT Spin Densities



Spin density isosurface plots



Spin density difference plots w.r.t. OLYP

⇒ Similar differences as found for the large iron nitrosyl complexes

Reference Spin Densities from Standard Electron Correlation Methods

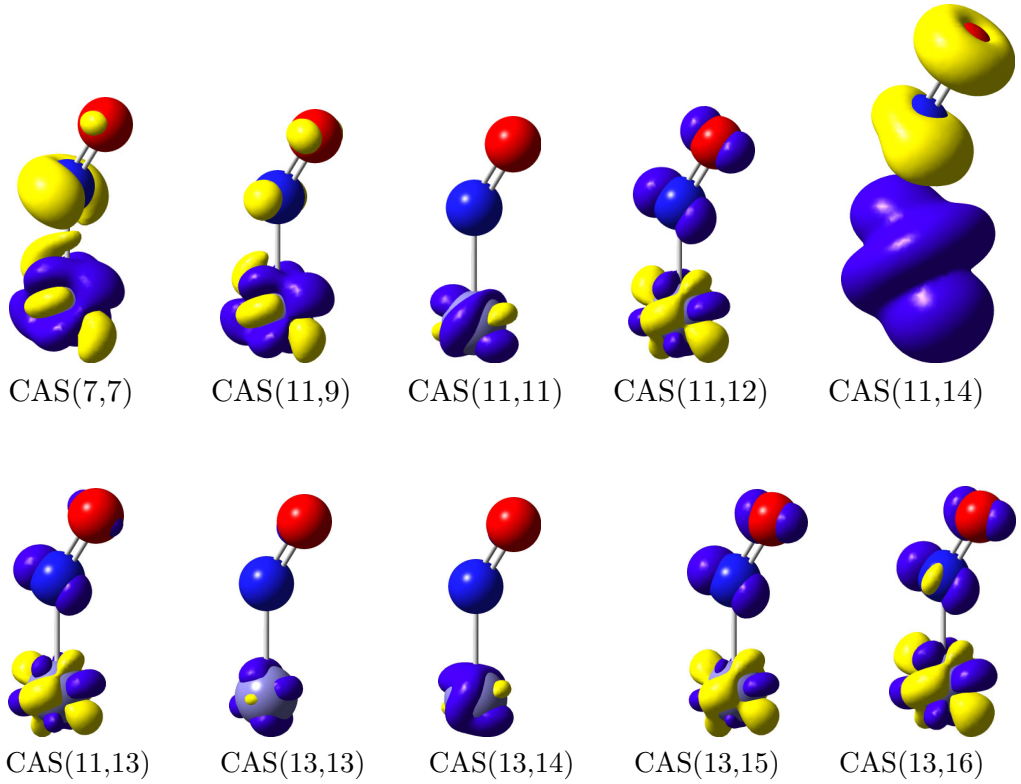
Reference Spin Densities from CASSCF Calculations

Defining the active orbital space:

- Minimal active space: Fe $3d$- and both NO π^*-orbitals $\Rightarrow$ **CAS(7,7)**
- Consider also both NO π-orbitals $\Rightarrow$ **CAS(11,9)**
- Additional shell of Fe d-orbitals (double-shell orbitals) is gradually included $\Rightarrow$ **CAS(11,11)** to **CAS(11,14)**
- Include one ligand σ-orbital and the antibonding σ^*-orbital upon the CAS(11,11) $\Rightarrow$ **CAS(13,13)**

$\Rightarrow$ Analyze convergence of spin density w.r.t. the dimension of the active orbital space

CASSCF Results: Oscillating Spin Densities



- CAS(11,14): spin density; all others: spin density differences
- stable CAS with all important orbitals is difficult to obtain

$\Rightarrow$ Reference spin densities for very large CAS required

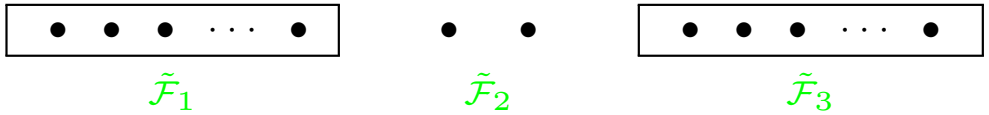
The Non-Relativistic DMRG Spin Density

Calculation of DMRG spin density requires expression in 2nd quantization

$$Q(\boldsymbol{r}) = \frac{1}{2}\sum_{pq}\phi_p^*(\mathbf{r})\phi_q(\mathbf{r})\langle\Psi|a_{p\alpha}^\dagger a_{q\alpha} - a_{p\beta}^\dagger a_{q\beta}|\Psi\rangle \tag{69}$$

Recall:

- The DMRG lattice with natural orbitals $\{\phi_i(\mathbf{r})\}$ as lattice sites



- Operator expression for a_1 and a_2 defined on $\tilde{\mathcal{F}} = \tilde{\mathcal{F}}_1 \otimes \tilde{\mathcal{F}}_2 \otimes \tilde{\mathcal{F}}_3$:

$$a_1^{\tilde{\mathcal{F}}} : \quad a_1 \otimes \mathbf{1}_{\tilde{\mathcal{F}}_2} \otimes \mathbf{1}_{\tilde{\mathcal{F}}_3} \tag{70}$$

$$a_2^{\tilde{\mathcal{F}}} : \quad \mathbf{A}_{\tilde{\mathcal{F}}_1} \otimes a_2 \otimes \mathbf{1}_{\tilde{\mathcal{F}}_3} \tag{71}$$

DMRG Spin Densities — Measures of Convergence

- **Qualitative** convergence measure: spin density difference plots
- **Quantitative** convergence measure:

$$\Delta_{\mathrm{abs}} = \int |\rho_1^{\mathrm{s}}(\mathbf{r}) - \rho_2^{\mathrm{s}}(\mathbf{r})| \mathrm{d}\mathbf{r} \quad < 0.005 \tag{72}$$

$$\Delta_{\mathrm{sq}} = \sqrt{\int |\rho_1^{\mathrm{s}}(\mathbf{r}) - \rho_2^{\mathrm{s}}(\mathbf{r})|^2 \mathrm{d}\mathbf{r}} \quad < 0.001 \tag{73}$$

- **Quantitative** convergence measure: quantum fidelity F_{m_1,m_2}

$$F_{m_1,m_2} = |\langle \Psi^{(m_1)} | \Psi^{(m_2)} \rangle|^2 \tag{74}$$

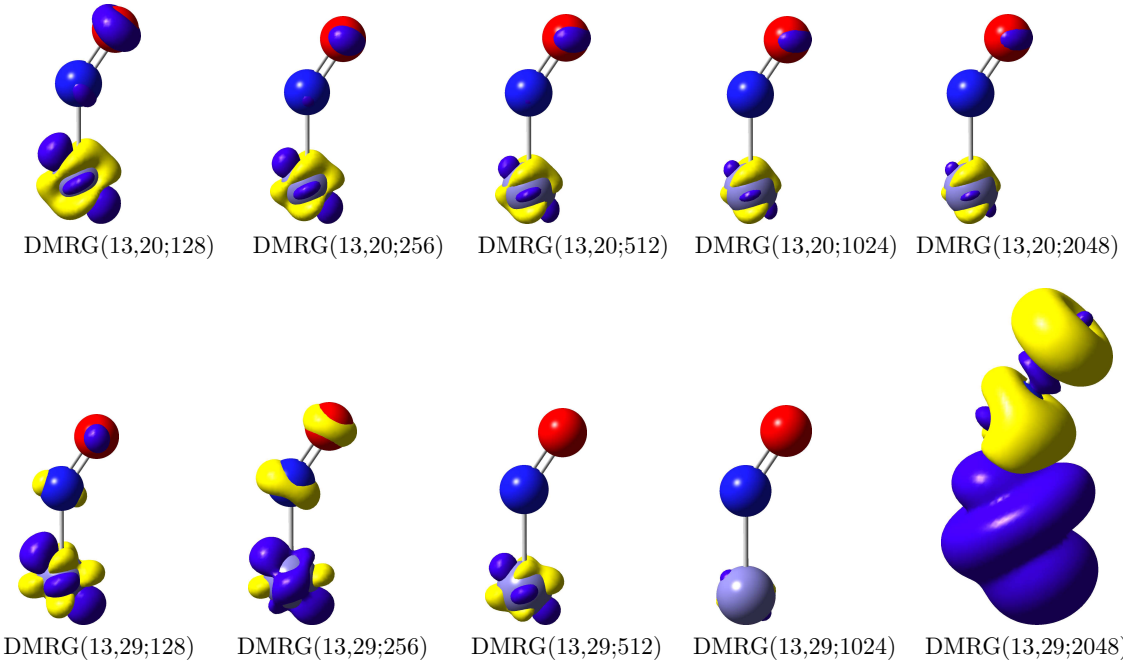
$\Rightarrow$ Reconstructed CI expansion of DMRG wave function can be used!

K. Boguslawski, K. H. Marti, M. Reiher, *J. Chem. Phys.* **2011**, *134*, 224101.

DMRG Spin Densities for Large Active Spaces

Δ_{abs} and Δ_{sq} for DMRG(13,y)[m] calculations w.r.t. DMRG(13,29)[2048] reference

Method	Δ_{abs}	Δ_{sq}	Method	Δ_{abs}	Δ_{sq}
DMRG(13,20)[128]	0.030642	0.008660	DMRG(13,29)[128]	0.032171	0.010677
DMRG(13,20)[256]	0.020088	0.004930	DMRG(13,29)[256]	0.026005	0.006790
DMRG(13,20)[512]	0.016415	0.003564	DMRG(13,29)[512]	0.010826	0.003406
DMRG(13,20)[1024]	0.015028	0.003162	DMRG(13,29)[1024]	0.003381	0.000975
DMRG(13,20)[2048]	0.014528	0.003028			

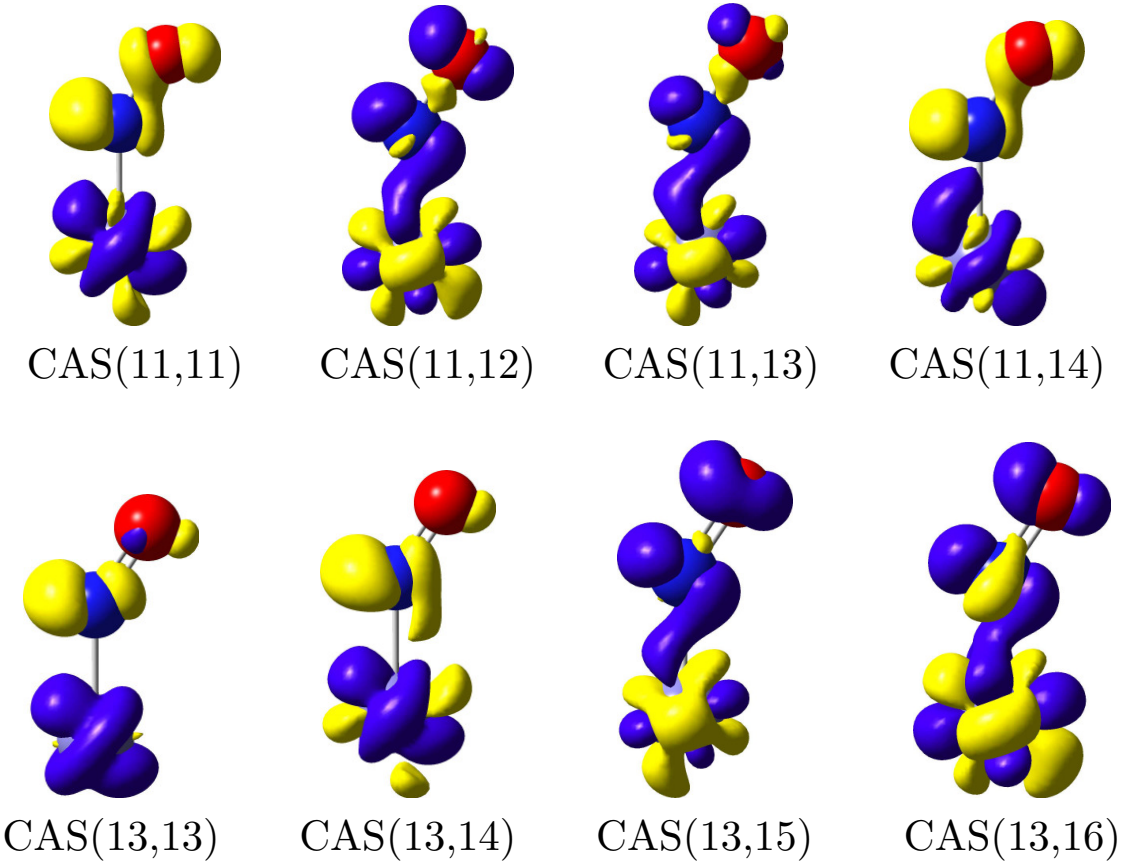


Importance of Empty Ligand Orbitals

Table : Some important Slater determinants with large CI weights from DMRG(13,29)[m] Upper part: Slater determinants containing an occupied $d_{x^2-y^2}$-double-shell orbital (marked in bold face). Bottom part: Configurations with occupied ligand orbitals (marked in bold face). 2: doubly occupied; a: α-electron; b: β-electron; 0: empty.

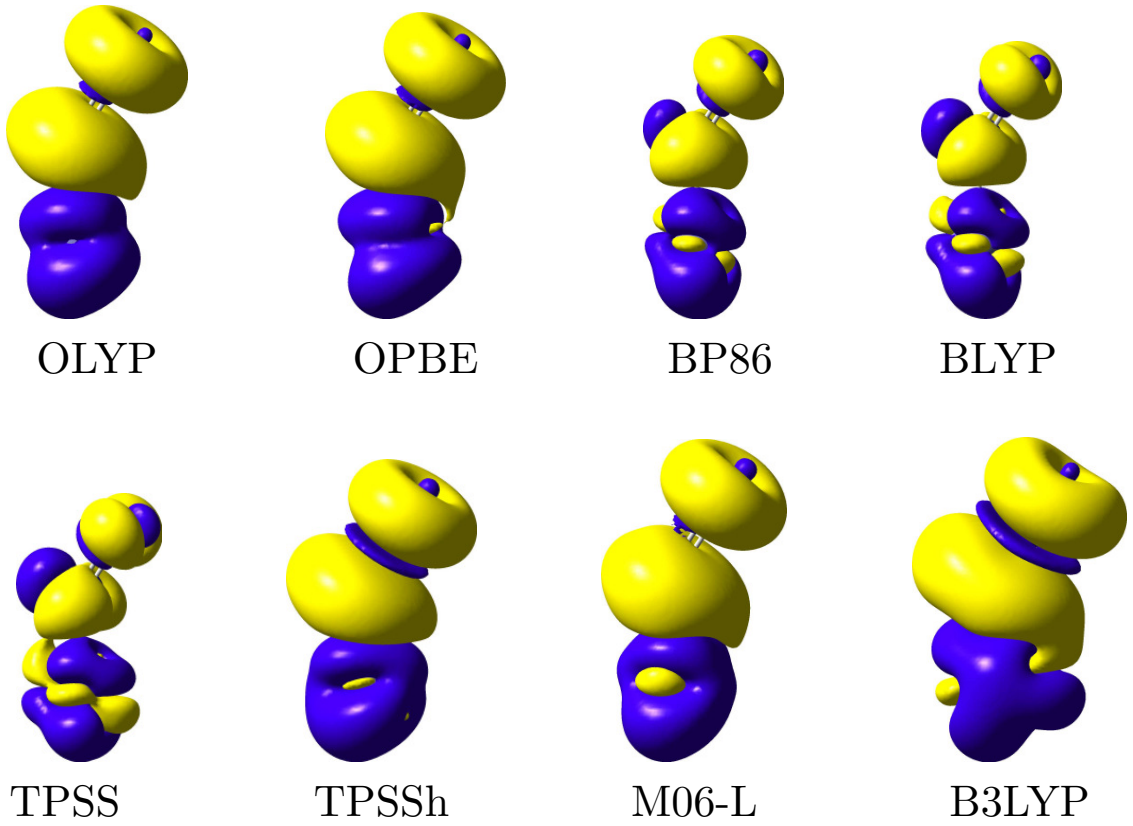
Slater determinant	CI weight	
	$m = 128$	$m = 1024$
b2b222a0a0000000 0000000 **a** 00000	0.003 252	0.003 991
bb2222aa00000000 0000000 **a** 00000	−0.003 226	−0.003 611
222220ab00000000 0000000 **a** 00000	−0.002 762	−0.003 328
ba2222ab00000000 0000000 **a** 00000	0.002 573	0.003 022
b2a222a0b0000000 0000000 **a** 00000	−0.002 487	−0.003 017
202222ab00000000 0000000 **a** 00000	0.002 405	0.002 716
b222a2a0b0000000 **0000000 0 0000a**	0.010 360	0.011 558
22b2a2a0a0000000 **0000000 0 b0000**	0.009 849	0.011 366
22b2a2a0b0000000 **0000000 0 a0000**	−0.009 532	−0.011 457
b2222aab00000000 **0000000 0 0000a**	−0.009 490	−0.010 991
a2222baa00000000 **0000000 0 0000b**	−0.009 014	−0.010 017
b2b222a0a0000000 **0000000 0 0a000**	0.008 820	0.010 327

Assessment of CASSCF Spin Densities (Differences)



$\Rightarrow$ CASSCF spin densities oscillate around DMRG reference distribution

DFT–DMRG Spin Densities Differences



K. Boguslawski, K. H. Marti, Ö. Legeza, M. Reiher, *J. Chem. Theory Comput.* *8* **2012** 1970

Analyzing DMRG and correlated wave functions with concepts from quantum information theory

Entanglement Measures for Embedded Subsystems

- see pioneering work by Ö. Legeza !
- Consider one or two orbitals embedded in a CAS
- Measure for the entanglement of orbital i with the environment:

  Ö. Legeza, J. Sólyom, *Phys. Rev. B* **2003**, *68*, 195116.

von-Neumann-type single-orbital entropy

$$s(1)_i = -\sum_{\alpha=1}^{4} \omega_{\alpha,i} \ln \omega_{\alpha,i} \tag{75}$$

($\omega_{\alpha,i}$ is an eigenvalue of the RDM of spatial orbital i — states defined on all other orbitals of the CAS have been traced out)

Entanglement Measures for Embedded Subsystems

- Measure for the entanglement of orbital i **and** orbital j with the environment:

von-Neumann-type two-orbital entropy

$$s(2)_{ij} = -\sum_{\alpha=1}^{16} \omega_{\alpha,ij} \ln \omega_{\alpha,ij} \tag{76}$$

($\omega_{\alpha,ij}$ is an eigenvalue of the RDM of two spatial orbitals i and j — states defined on all other orbitals of the CAS have been traced out)

Entanglement Measures for Embedded Subsystems

- $s(2)_{ij}$ contains also the 'on-site' entropies for the two orbitals

$\Rightarrow$ Subtract these contributions to obtain the 'inter-orbital entropy':

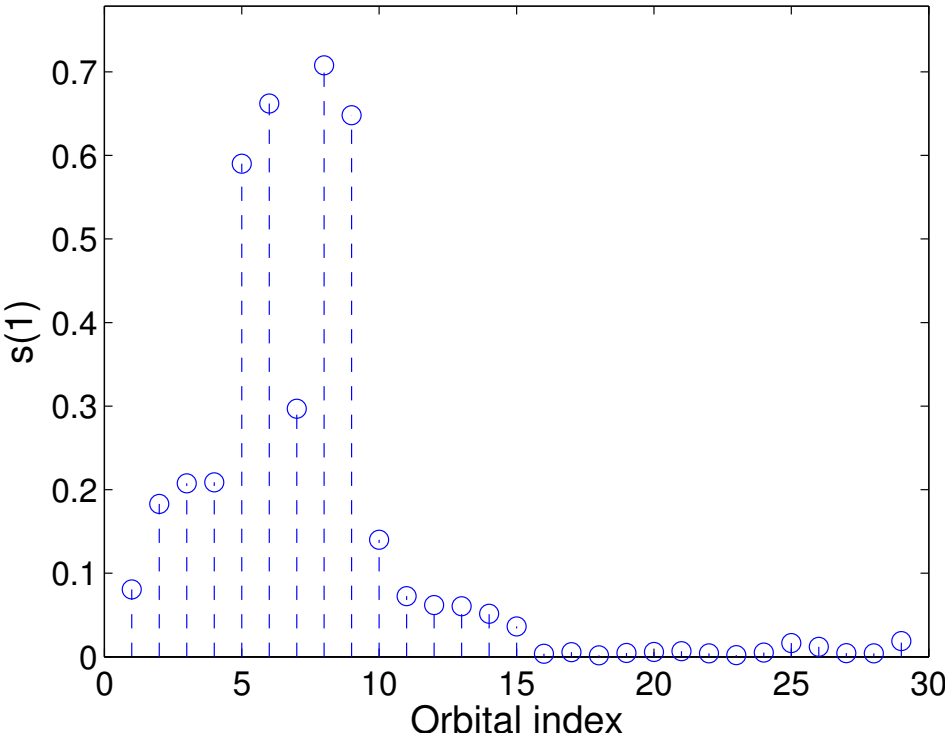
J. Rissler, R.M. Noack, S.R. White, *Chem. Phys.* **2006**, *323*, 519.

Mutual information

$$I_{ij} \propto s(2)_{ij} - s(1)_i - s(1)_j \tag{77}$$

- Successfully applied to optimize orbital ordering and to enhance DMRG convergence by Ö. Legeza

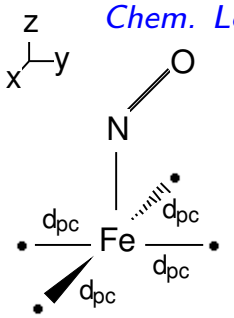
Entanglement and Orbitals — Single Orbital Entropy



K. Boguslawski, P. Tecmer, Ö. Legeza, M. Reiher, *J. Phys. Chem. Lett.* **2012**, *3*, 3129.

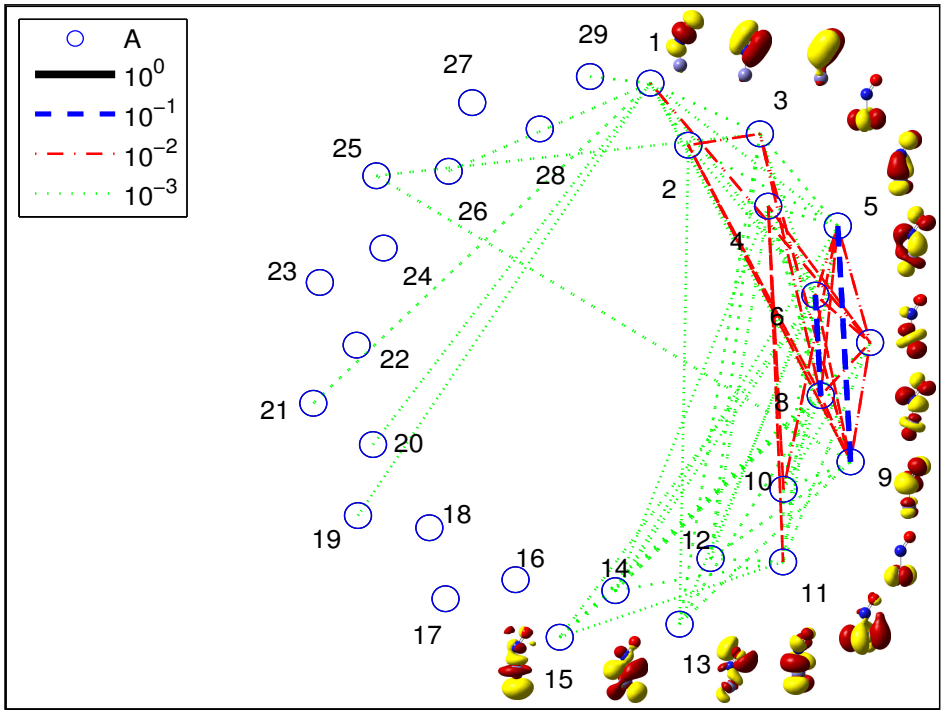
- Three groups of orbitals
  - ⇒ large single orbital entropy
  - ⇒ medium single orbital entropy
  - ⇒ (very) small single orbital entropy
- Configurations with occupied orbitals belonging to the third block have small C_I coefficients

⇒ Important for dynamic correlation



- 4 point charges in xy-plane at $\mathrm{d_{pc}} = 1.133$ Å
- Natural orbital basis: CAS(11,14)SCF/cc-pVTZ
- DMRG(13,29) with DBSS ($m_{\min} = 128, m_{\max} = 1024$)

Entanglement and Orbitals — Mutual Information



- Three groups of orbitals
  - ⇒ high entanglement
  - ⇒ medium entanglement
  - ⇒ weak entanglement
- Strong entanglement for pairs:

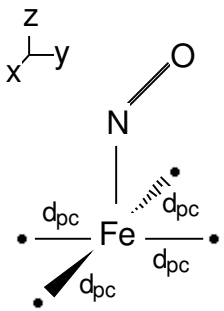
$$(d, \pi^*) \Longleftrightarrow (d, \pi^*)^*$$

$$\pi \Longleftrightarrow \pi^*$$

$$\sigma_{\mathrm{Metal}} \Longleftrightarrow \sigma_{\mathrm{Ligand}}$$

K. Boguslawski, P. Tecmer, Ö. Legeza, M. Reiher, *J. Phys. Chem. Lett.* **2012**, *3*, 3129.

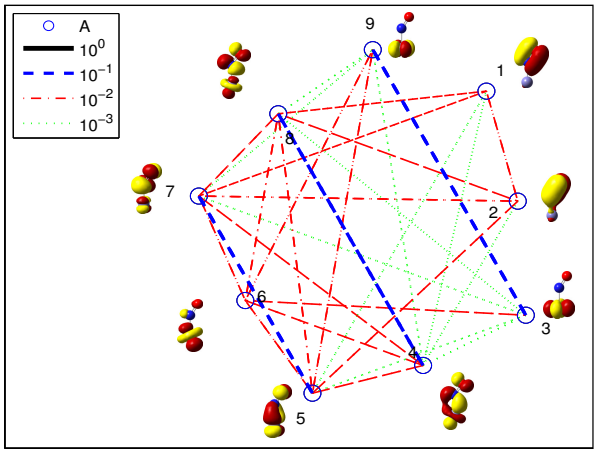
⇒ Important for static and nondynamic correlation (⟺ chemical intuition of constructing a CAS)

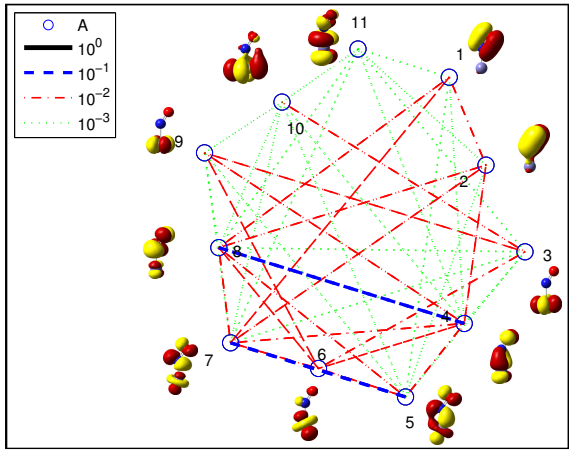


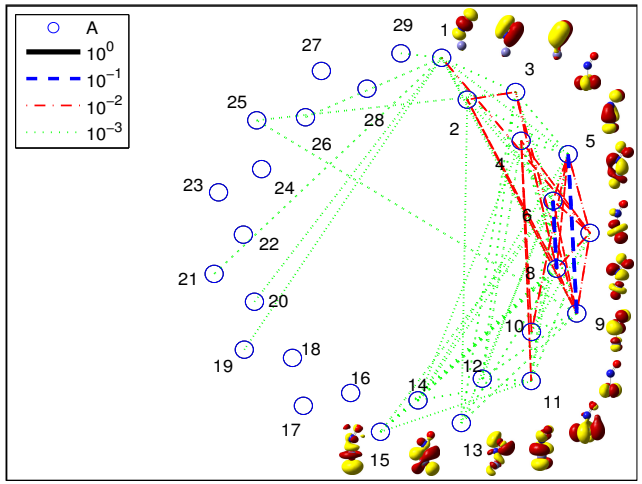
- 4 point charges in xy-plane at $d_{pc} = 1.133$ Å
- Natural orbital basis: CAS(11,14)SCF/cc-pVTZ
- DMRG(13,29) with DBSS ($m_{\min} = 128, m_{\max} = 1024$)

Artifacts of Small Active Space Calculations

Comparison of DMRG(11,9)[220] and DMRG(11,11)[790] to DMRG(13,29)[128,1024,10^{-5}] for $[Fe(NO)]^{2+}$







- I_{ij} (and $s(1)_i$) overestimated for small active spaces

$\Rightarrow$ Entanglement of orbitals too large

$\Rightarrow$ Missing dynamic correlation is captured in an artificial way

Entanglement and Correlation Effects in Chemical Bonding

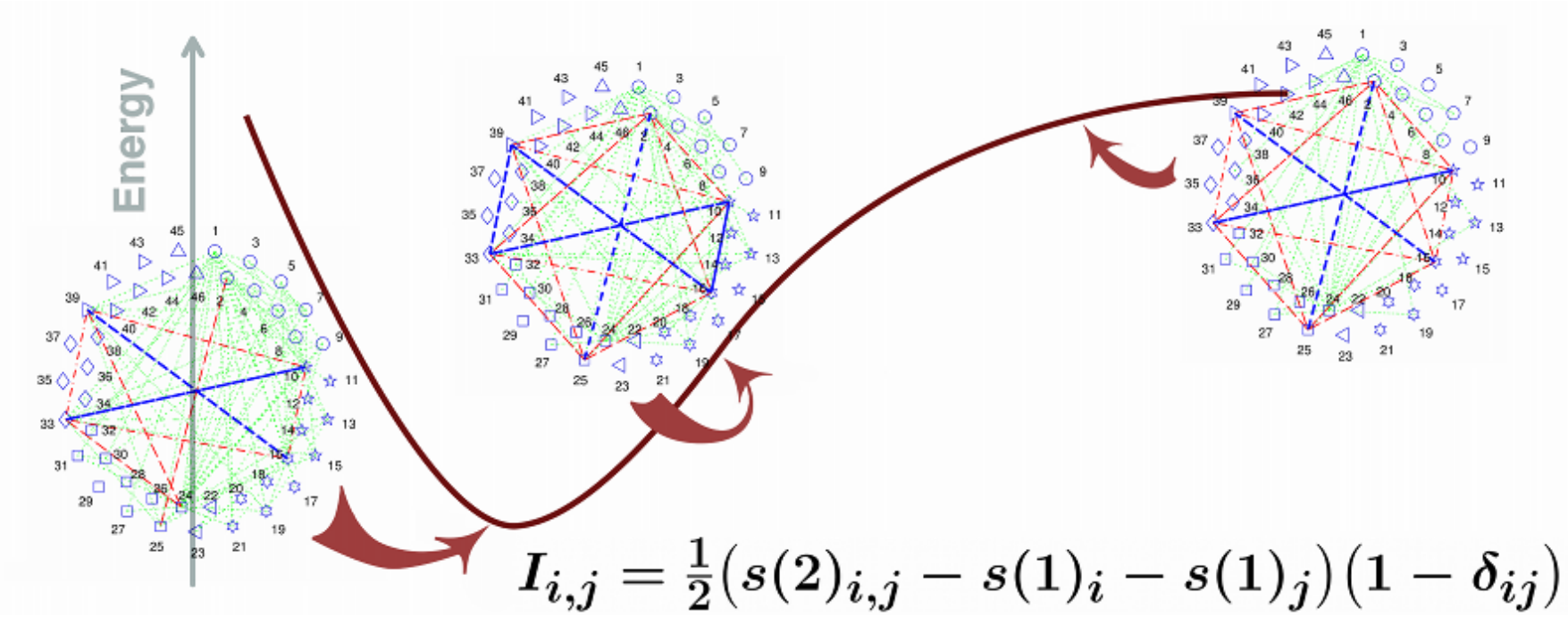
- Mutual information I_{ij} and single orbital entropy $s(1)_i$ can serve as measures of correlation effects:
  - Dynamic correlation: large number of configurations with small (absolute) weights
    $\Rightarrow$ can be captured by including orbitals with small $s(1)_i$ and I_{ij}
  - Static correlation: emerges from nearly degenerate orbitals
    $\Rightarrow$ can be captured by including orbitals with large $s(1)_i$ and I_{ij}

$\Rightarrow$ Gradual transition between both correlation effects is encoded in medium-valued I_{ij} and $s(1)_i$

$\Rightarrow$ A balanced active space can be defined by entanglement measures to uncover (the most important) static and dynamic correlation

K. Boguslawski, P. Tecmer, Ö. Legeza, M. Reiher, *J. Phys. Chem. Lett.* **2012**, *3*, 3129.

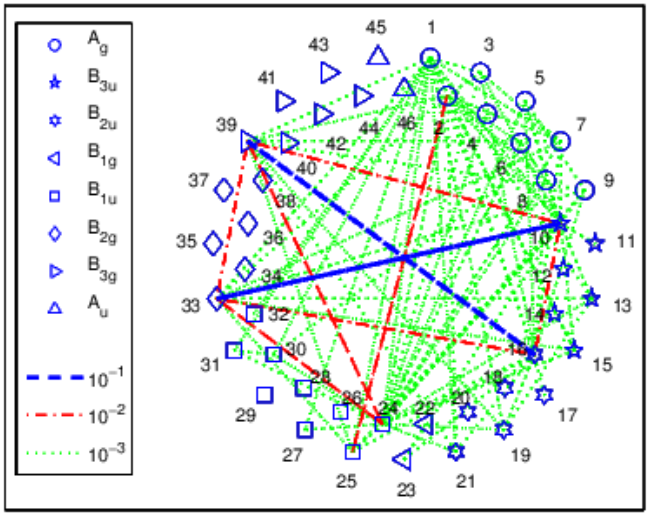
Entanglement Measures can Monitor Bond Breaking/Formation Processes: Dinitrogen



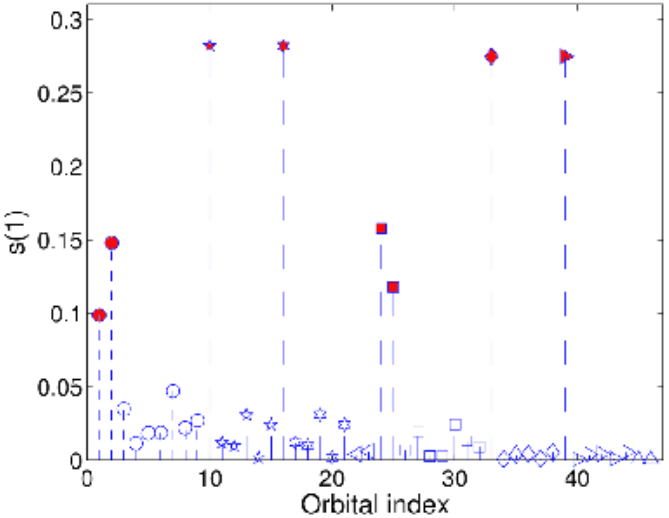
$$I_{i,j} = \frac{1}{2}\big(s(2)_{i,j} - s(1)_i - s(1)_j\big)\big(1 - \delta_{ij}\big)$$

K. Boguslawski, P. Tecmer, G. Barcza, O. Legeza, M. Reiher, *J. Chem. Theory Comput. 9* **2013** 2959–2973 [arxiv: 1303.7207]

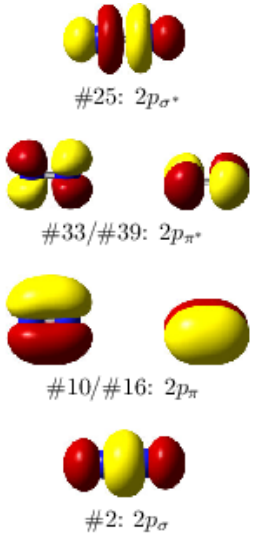
Bond Breaking in Dinitrogen at 1.12 Ångström



Mutual information



Single orbital entropy

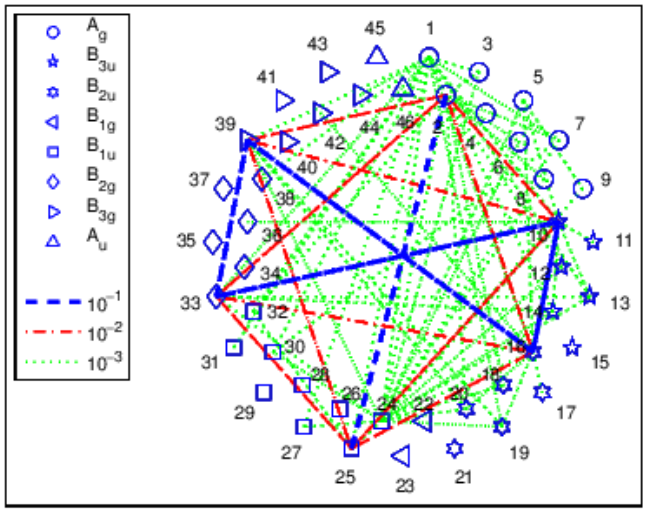


(a) $d_{\mathrm{NN}} = 1.12$Å

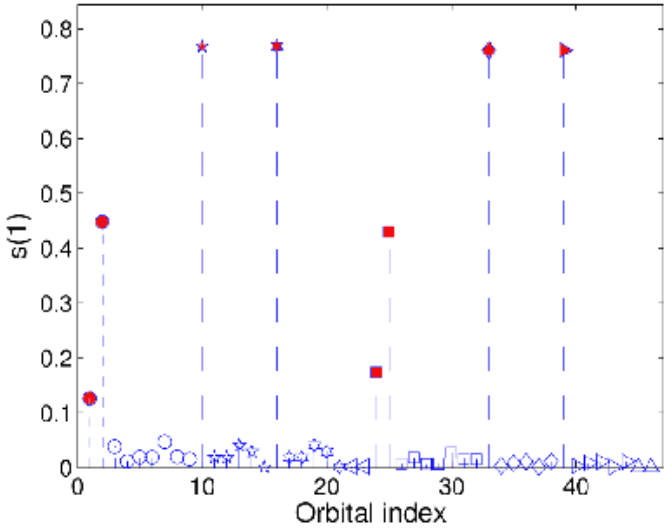
Part of entanglement is already encoded in molecular orbitals changing with the structure !

Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.

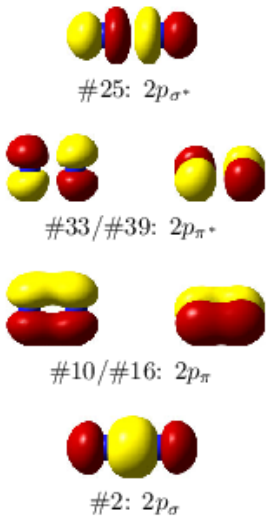
Bond Breaking in Dinitrogen at 1.69 Ångström



Mutual information



Single orbital entropy

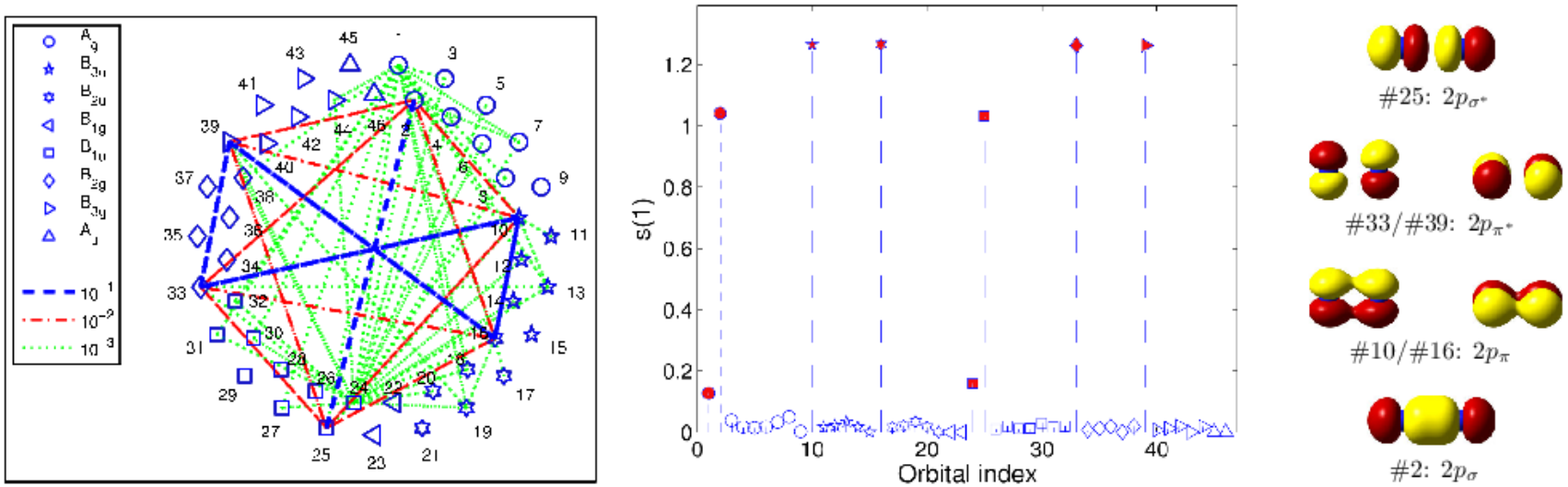


(b) $d_{\mathrm{NN}} = 1.69$Å

Part of entanglement is already encoded in molecular orbitals changing with the structure !

Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.

Bond Breaking in Dinitrogen at 2.22 Ångström



Mutual information

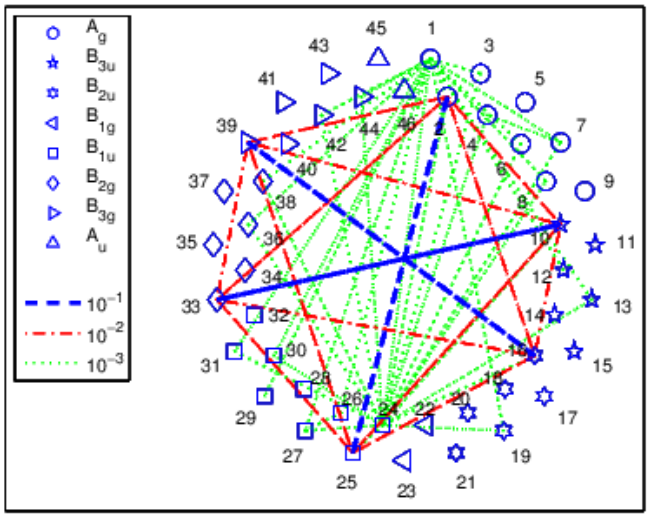
Single orbital entropy

(d) $d_{\mathrm{NN}} = 2.22\text{Å}$

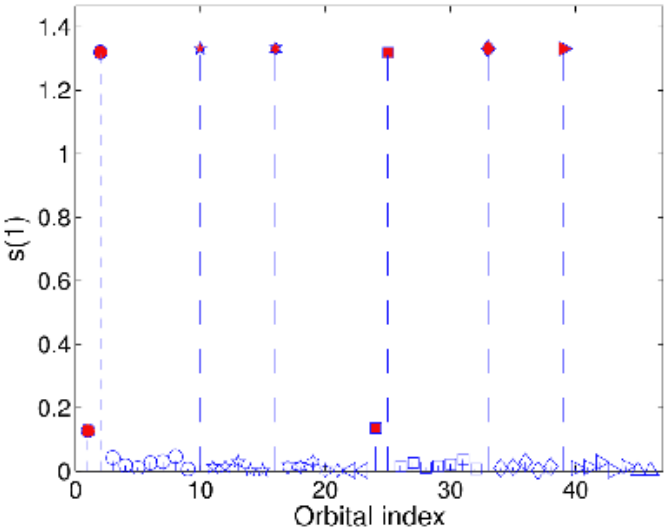
Part of entanglement is already encoded in molecular orbitals changing with the structure !

Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.

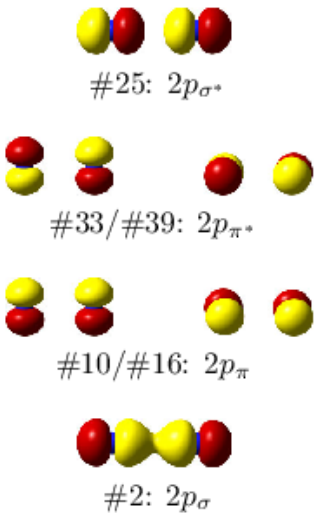
Bond Breaking in Dinitrogen at 3.18 Ångström



Mutual information



Single orbital entropy

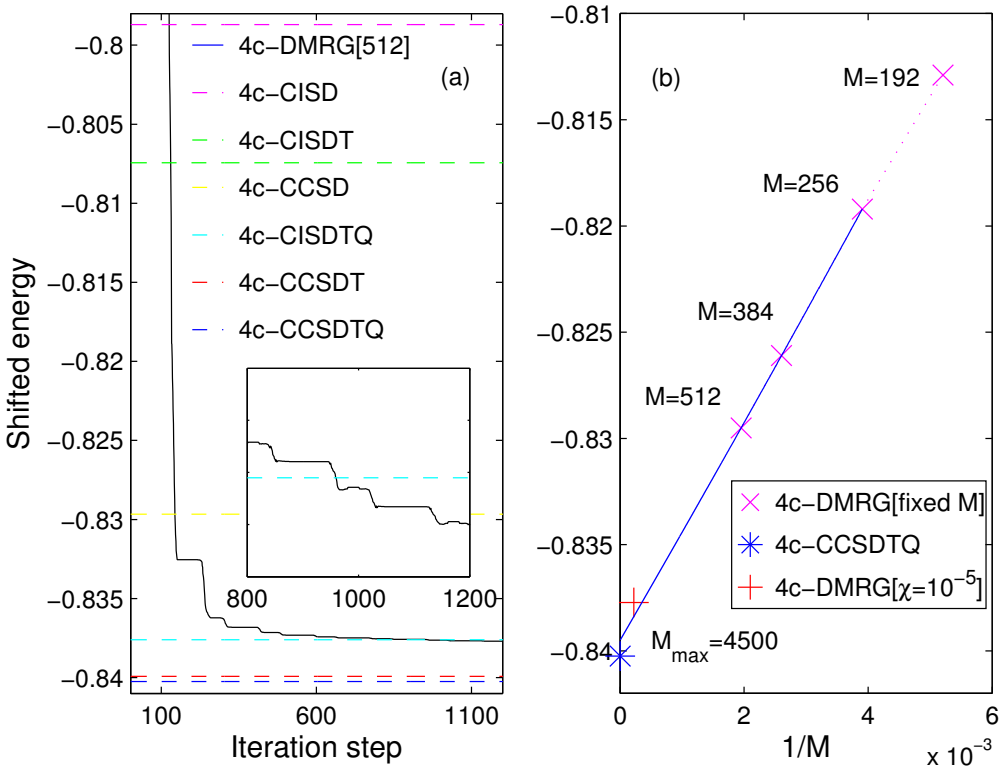


(f) $d_{\mathrm{NN}} = 3.175$Å

Part of entanglement is already encoded in molecular orbitals changing with the structure !

Atomic-like non-orthogonal basis fcts. exhibit large entanglement measures among each other.

'Fully-Relativistic' Four-Component DMRG: TlH



method	r_e Å	ω_e $\frac{1}{cm}$	$\omega_e x_e$ $\frac{1}{cm}$
4c-DMRG(14,94)[512]	1.873	1411	26.64
4c-CISD(14,94)	1.856	1462	23.11
4c-CISDTQ(14,94)	1.871	1405	20.11
4c-MP2(14,94)	1.828	1546	47.27
4c-CCSD(14,94)	1.871	1405	19.36
4c-CCSD(T)(14,94)	1.873	1400	23.52
4c-CCSDT(14,94)	1.873	1398	22.28
4c-CCSDT(Q)(14,94)	1.873	1397	21.01
4c-CCSDTQ(14,94)	1.873	1397	22.24
CCSD(T)[a]	1.876	1385	n/a
CCSD(T)[b]	1.877	1376	n/a
MRD-CI[c]	1.870	1420	n/a
SO-MCQDPT[d]	1.876	1391	29.42
experiment[e]	1.872	1390.7	22.7

[a] 4c-DC CCSD(T) [14 electrons], Visscher et al. 2001.
[b] 4c-DC-Gaunt CCSD(T) [36 electrons], Visscher et al. 2001.
[c] GRECP spin-orbit MRD-CI, Titov et al. 2000.
[d] model-core potential spin-orbit MCQDPT, Zeng et al. 2010.

S. Knecht, Ö. Legeza, M. Reiher, *J. Chem. Phys 140* (2014) 041101

Recent Developments in QC-MAQUIS 1: DFT-embedding for MPO-DMRG

DMRG embedded into a quantum environment

Energy decomposition into system and (spectator) enviroment

$$E_{\mathsf{tot}} = E_{\mathsf{act}}^{\mathsf{DMRG}} + E_{\mathsf{env}}^{\mathsf{KS\text{-}DFT}} + E_{\mathsf{int}}^{\mathrm{OF-DFT}}$$

with

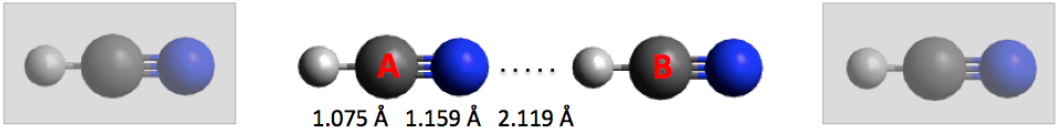
$$E_{\mathsf{act}}^{\mathrm{DMRG}} = \langle \Psi^{\mathrm{act}} | \hat{H}_{\mathrm{act}} | \Psi^{\mathrm{act}} \rangle$$

and

$$E_{\mathsf{int}}^{\mathrm{OF-DFT}}[\rho_{\mathsf{act}}, \rho_{\mathsf{env}}] = T_{\mathsf{s}}^{\mathsf{nad}}[\rho_{\mathsf{act}}, \rho_{\mathsf{env}}] + E_{\mathsf{xc}}^{\mathsf{nad}}[\rho_{\mathsf{act}}, \rho_{\mathsf{env}}] + E_{\mathsf{elstat}}^{\mathsf{int}}[\rho_{\mathsf{act}}, \rho_{\mathsf{env}}]$$

T. Dresselhaus, J. Neugebauer, S. Knecht, S. Keller, Y. Ma, M. Reiher, *J. Chem. Phys.* 142 **2015** 044111

DMRG embedding: Dipole moment of a HCN chain



Dipole moment μ in Debye per HCN molecule.

Method	Active fragment(s)	Env.	μ (per HCN)
	monomer		
DMRG(10,9)[4096]-SCF	A	—	3.09
DFT	A	—	2.96
DMRG(10,9)[4096]-SCF	A	DFT	3.54
DFT	A	DFT	3.42
DMRG(10,9)[4096]-SCF	B	DFT	3.43
DFT	B	DFT	3.32
	dimer		
DMRG(20,18)[4096]-SCF	A+B	—	3.44
DMRG(20,18)[4096]-SCF	A+B	DFT	3.91
DFT	A+B	DFT	3.93
	tetramer		
DMRG(40,36)[2048]-SCF	all	—	3.81

T. Dresselhaus, J. Neugebauer, S. Knecht, S. Keller, Y. Ma, M. Reiher,

J. Chem. Phys. 142 **2015** 044111 (Erratum: ibid. 189901)

Recent Developments in QC-MAQUIS 2: Dynamic Correlation through DFT

Dynamic correlation through short-range DFT

Decomposition into active and inactive system

$$E_{\text{CAS-CI}} = E_{\mathsf{I}} + E_{\mathsf{A}}$$

where

$$E_{\mathrm{I}} = \frac{1}{2}\sum_{ij}\left(h_{ij} + f^{\mathsf{I}}_{ij}\right)D^{\mathsf{I}}_{ij} + V_{\mathsf{nn}} = \sum_{i}\left(h_{ii} + f^{\mathsf{I}}_{ii}\right) + V_{\mathsf{nn}}$$

$$E_{\mathrm{A}} = \sum_{uv} f^{\mathsf{I}}_{uv} D^{\mathsf{A}}_{uv} + \frac{1}{2}\sum_{uvxy} g_{uvxy} P^{\mathrm{A}}_{uvxy}$$

with

$$f^{\mathsf{I}}_{pq} = h_{pq} + \sum_{k}\left(2g_{pqkk} - g_{pkqk}\right)$$

and

$$g_{pqrs} = \langle \phi_p(\boldsymbol{r}_1)\phi_r(\boldsymbol{r}_2)|\hat{g}(1,2)|\phi_q(\boldsymbol{r}_1)\phi_s(\boldsymbol{r}_2)\rangle$$

Dynamic correlation through short-range DFT

Introduce the range separation into the electron–electron interaction

$$\hat{g}(1,2) = \hat{g}^{\mu,\mathsf{lr}}(1,2) + \hat{g}^{\mu,\mathsf{sr}}(1,2)$$

with

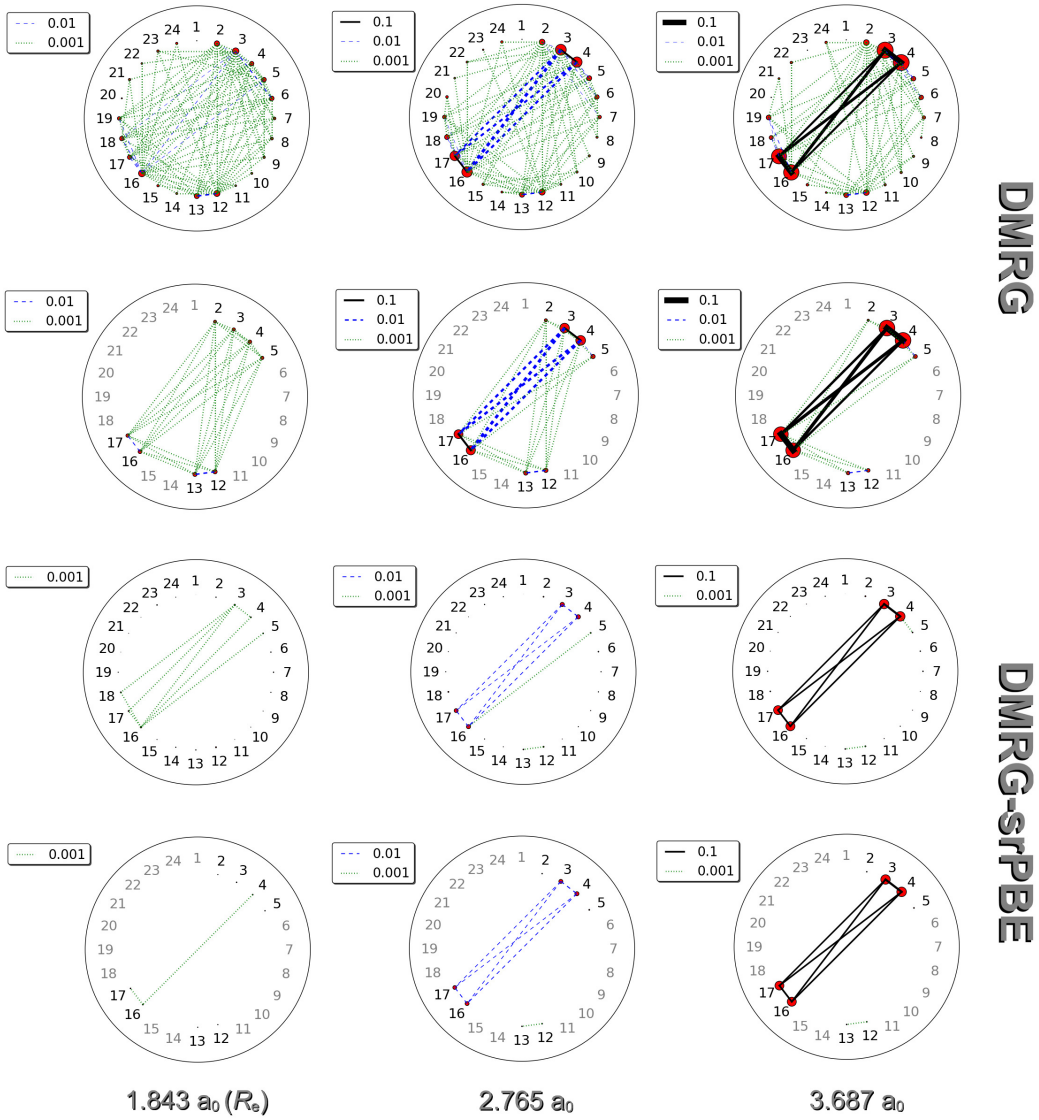
$$\hat{g}^{\mu,\mathsf{lr}}(1,2) = \frac{\mathsf{erf}(\mu|\boldsymbol{r}_1 - \boldsymbol{r}_2|)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

$$\hat{g}^{\mu,\mathsf{sr}}(1,2) = \frac{1 - \mathsf{erf}(\mu|\boldsymbol{r}_1 - \boldsymbol{r}_2|)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

Then, the energy can be set up as

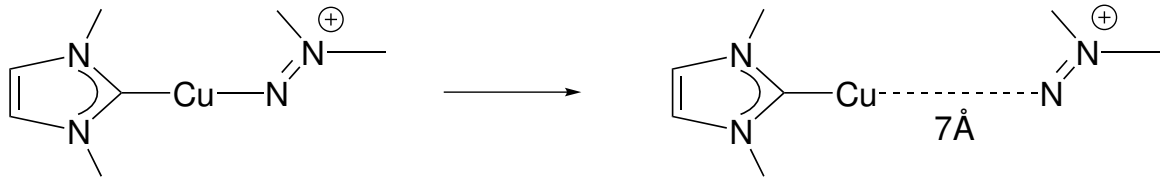
$$E^{\mathsf{srDFT}}_{\mathsf{CAS\text{-}CI}} = E^{\mathsf{lr}}_{\mathsf{I}} + E^{\mathsf{lr}}_{\mathsf{A}} + E^{\mathsf{sr}}_{\mathsf{H}}[\rho] + E^{\mathsf{sr}}_{\mathsf{xc}}[\rho]$$

Regularizing effect of srDFT on small CAS: Water



E. D. Hedegård, S. Knecht, J. S. Kielberg, H. J. A. Jensen, and M. Reiher, *J. Chem. Phys.* 142 **2015** 224108

DMRG–srDFT for the WCCR10 test set



Calculated dissociation energies in kJ/mol

Method	D_e (kJ/mol)	D_0 (kJ/mol)
DMRG[2000](30,22)	173.5	165.1
DMRG[2000](20,18)	169.9	161.5
DMRG[2000](10,10)	132.8	124.3
DMRG[2000](30,22)-srPBE	225.1	216.6
DMRG[2000](20,18)-srPBE	227.9	219.4
DMRG[2000](10,10)-srPBE	216.5	208.0
PBE	240.2	231.8
PBE (full complex/def2-TZVP)	257.5	249.0
PBE (full complex/def2-QZVPP from WCCR10)	247.5	239.0
Exp. (from WCCR10)	226.7	218.2

E. D. Hedegård, S. Knecht, J. S. Kielberg, H. J. A. Jensen, and M. Reiher, *J. Chem. Phys.* 142 **2015** 224108;
WCCR10: T. Weymuth, E. P. A. Couzijn, P. Chen, M. Reiher, *J. Chem. Theory Comput.* 10 **2014** 3092