Multiconfigurational Quantum Chemistry with a Simple Tensor Network: The Matrix-Product-State Ansatz

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## What's to come...

- Multiconfigurational wave function ansätze
- From CI to MPS: optimizing an MPS with the DMRG algorithm
- Recent developments based on an MPS ansatz

Picking up where we ("Titou") left off on Monday...

How could we improve on a truncated CI approach?

$$\Psi^{\text{CISD...}} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} \Phi_i^a + \sum_{(ai)(bj)} C_{(ai,bj)} \Phi_{ij}^{ab} + \dots$$

 $C_0, C_{(ai)}, C_{(ai,bj)} \in \{C_{\mathsf{I}}\}$  and  $\Phi_0 \equiv \Phi^{\mathrm{HF}}$ 

**(1)** Use a CI-type  $\Phi_0$  as reference wave function  $\rightarrow$  multireference CI

**2** Optimize  $E_{el}$  wrt CI coefficients  $\{C_l\}$  and MO basis  $\{\phi_i\}$ 

#### $\rightarrow$ Multi-configuration self-consistent field (MCSCF) approach

## First-order MCSCF

Alternately optimize CI-coefficients and MO basis



BUT: First-order MCSCF typically converges poorly!

## Second-generation MCSCF

- To accelerate convergence use gradient and Hessian information
- Rewrite the wave function ansatz as follows

$$\Psi^{\text{MCSCF}} = \sum_{I} \tilde{\phi}_{I} C_{I}$$

with  $\{\tilde{\phi}_I\}$  and  $\{\phi_I\}$  connected by a unitary transformation  $U = e^{\kappa}$ ( $\kappa$  being anti-hermitian, ( $\kappa^T$ )\* = - $\kappa$ )

$$egin{pmatrix} ilde{\phi_1} \ ilde{\phi_2} \ dots \ ilde{\phi_m} \end{pmatrix} = oldsymbol{U} \cdot egin{pmatrix} \phi_1 \ \phi_2 \ dots \ \phi_m \end{pmatrix}$$

NB:  $\kappa_{pq} \; (\kappa = \{\kappa_{pq}\})$  are usually called orbital rotation parameter.

## Newton–Raphson approach I

• Write electronic energy as a function of parameters p and Taylor-expand for  $p_0 = 0$ :

$$E_{\rm el}(\boldsymbol{p}) = E_{\rm el}(0) + \boldsymbol{g}^{\dagger}\boldsymbol{p} + \frac{1}{2}\boldsymbol{p}^{\dagger}\boldsymbol{H}\boldsymbol{p} + \cdots$$

with g and H given by

$$g_i = \left(\frac{\partial E_{\text{el}}}{\partial p_i}\right)_0$$
 (gradient)  $H_{ij} = \left(\frac{\partial^2 E_{\text{el}}}{\partial p_i \partial p_j}\right)_0$  (Hessian)

• Optimize p with (Newton-step)

$$p = -H^{-1} \cdot g$$

$$E_{I}^{(1)} \equiv \frac{\partial E_{\rm el}^{\rm MCSCF}}{\partial C_{I}^{*}} \quad , \qquad E_{pq}^{(1)} \equiv \frac{\partial E_{\rm el}^{\rm MCSCF}}{\partial \kappa_{pq}^{*}}$$
$$E_{IJ}^{(2)} \equiv \frac{\partial^{2} E_{\rm el}^{\rm MCSCF}}{\partial C_{I}^{*} \partial C_{J}^{*}} \quad , \qquad E_{I,pq}^{(2)} \equiv \frac{\partial^{2} E_{\rm el}^{\rm MCSCF}}{\partial C_{I}^{*} \partial \kappa_{pq}^{*}}, \quad E_{pq,rs}^{(2)} \equiv \frac{\partial^{2} E_{\rm el}^{\rm MCSCF}}{\partial \kappa_{pq}^{*} \partial \kappa_{rs}^{*}}$$

Use the above derivatives to perform the Newton step:

$$\begin{pmatrix} \boldsymbol{C}_A \\ \boldsymbol{\kappa} \end{pmatrix} = - \begin{pmatrix} \{E_{IJ}^{(2)}\} & \{E_{I,pq}^{(2)}\} \\ \{E_{pq,I}^{(2)}\} & \{E_{pq,rs}^{(2)}\} \end{pmatrix}^{-1} \cdot \begin{pmatrix} \{E_I^{(1)}\} \\ \{E_{pq}^{(1)}\} \end{pmatrix}$$

Problem: How to choose the truncated CI wave function for an MCSCF ansatz?

## Complete Active Space SCF — CASSCF

Pick an active orbital space (CAS) within which one solves a FCI problem and optimises the MO basis.



## The active orbital space problem

• Traditional CASCI hits "exponential" scaling wall at  $\approx$  CAS(18,18)



- Requires efficient wave function parametrizations
  - Selected CI (SHCI, CIPSI, ...)
  - QMC (FCIQMC, DMC, ...)
  - incremental FCI approaches
  - DMRG

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## Multiconfigurational methods for large CAS

#### **Standard Cl approach**

• CI-type diagonalization for a **preselected** set of many-particle basis states in a given CAS(N,L) (N electrons in L orbitals)

$$|\Psi
angle = \sum_{k_1,k_2,...,k_L} c_{k_1,k_2,...,k_L} |k_1
angle \otimes |k_2
angle \otimes \ldots \otimes |k_L
angle$$
 (1)

#### Density matrix renormalization group

• Determine CI coefficients from correlations among orbitals

$$|\Psi\rangle = \sum_{k_1, k_2, \dots, k_L} c_{k_1, k_2, \dots, k_L} |k_1\rangle \otimes |k_2\rangle \otimes \dots \otimes |k_L\rangle$$
(2)

• Local space  $k_l$  of *l*-th spatial orbital is of dimension d = 4

 $k_{l}=\left\{ \left|\uparrow\downarrow
ight
angle ,\left|\uparrow
ight
angle ,\left|\downarrow
ight
angle ,\left|0
ight
angle 
ight\}$ 

(3)

## From CI to MPS: optimizing an MPS with the DMRG algorithm

# Optimizing an MPS wave function with the DMRG algorithm

- Optimisation algorithm
- Optimal bipartition
- Parameters that determine DMRG accuracy

Very useful introductory reference:

U. Schollwöck, *The density-matrix renormalization group in the age of matrix product states*, Annals of Physics, 326 (2011) 96–192.

# Some reviews on about 20 years of DMRG in quantum chemistry

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## Intermission: singular value decomposition

• Singular value decomposition (SVD) of a matrix **M**  $(n_a \times n_b)$ **M** = **U S V**<sup>†</sup>

yields:

- Left-singular matrix **U**  $(n_a \times \min(n_a, n_b))$  with  $\mathbf{U}^{\dagger}\mathbf{U} = 1$
- Right-singular matrix V (min $(n_a, n_b) \times n_b$ ) with V<sup>†</sup>V = 1
- Diagonal singular value matrix **S**  $(\min(n_a, n_b) \times \min(n_a, n_b))$  with r nonzero singular values  $\rightarrow r$  is the (Schmidt) rank of **M**



(4)

## From a CI to an MPS parametrization I

 $\bullet\,$  Successive application of SVD to CI tensor  $\rightarrow\,$  MPS wave function



## From a CI to an MPS parametrization II

- Reshape coefficient tensor  $c_{k_1,k_2,...,k_L}$  into a  $d \times d^{L-1}$  matrix  $\Gamma$  $\Gamma_{k_1,(k_2,...,k_L)} = c_{k_1,k_2,...,k_L}$ (5)
- SVD of  $\Gamma_{k_1,(k_2,\ldots,k_L)}$  yields

$$\Gamma_{k_1,(k_2,\dots,k_L)} = \sum_{a_1}^{r_1} U_{k_1,a_1} S_{a_1,a_1} (V^{\dagger})_{a_1,(k_2,\dots,k_L)}$$

$$\equiv \sum_{a_1}^{r_1} A_{a_1}^{k_1} c_{a_1,(k_2,\dots,k_L)}$$
(6)
with
(7)

\*\*\*

- **S** and **V**<sup>†</sup> multiplied and reshaped into coefficient tensor  $c_{a_1,(k_2,...,k_L)}$
- $r_1 < d$
- collection of d row vectors  $A^{k_1}$  with entries  $A^{k_1}_{a_1} = U_{k_1,a_1}$

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## From a CI to an MPS parametrization III

• Reshape coefficient tensor  $c_{a_1,(k_2,...,k_L)}$  into a  $r_1d imes d^{L-2}$  matrix  $\Gamma$ 

$$c_{k_{1},k_{2},...,k_{L}} = \sum_{a_{1}}^{r_{1}} A_{a_{1}}^{k_{1}} \Gamma_{(a_{1}k_{2}),(k_{3},...,k_{L})}$$
(8)  

$$\stackrel{\text{SVD}}{=} \sum_{a_{1}}^{r_{1}} \sum_{a_{2}}^{r_{2}} A_{a_{1}}^{k_{1}} U_{(a_{1}k_{2}),a_{2}} S_{a_{2},a_{2}} (V^{\dagger})_{a_{2},(k_{3},...,k_{L})}$$
(9)  

$$\stackrel{\text{reshape}}{=} \sum_{a_{1}}^{r_{1}} \sum_{a_{2}}^{r_{2}} A_{a_{1}}^{k_{1}} A_{a_{1},a_{2}}^{k_{2}} \Gamma_{(a_{2}k_{3}),(k_{4},...,k_{L})}$$
(10)  
with

• 
$$r_2 < r_1 d < d^2$$

• collection of d matrices  $A^{k_2}$  with entries  $A^{k_2}_{a_1,a_2} = U_{(a_1k_2),a_2}$ 

## From a CI to an MPS parametrization IV

Continue with SVDs until last site which then gives

$$c_{k_{1},k_{2},\dots,k_{L}} = \sum_{a_{1},a_{2},\dots,a_{L}-1} A_{1,a_{1}}^{k_{1}} A_{a_{1},a_{2}}^{k_{2}} \cdots A_{a_{L-2,L-1}}^{k_{L-1}} A_{a_{L-1},1}^{k_{L}}$$
(11)  
$$\equiv A^{k_{1}} A^{k_{2}} \cdots A^{k_{L-1}} A^{k_{L}}$$
(12)

with

- interpretation of sums as matrix-matrix multiplications
- first and last "matrices" are row- and column vectors!
- CI wave function rewritten as MPS wave function:

$$|\Psi\rangle = \sum_{\boldsymbol{k}} c_{\boldsymbol{k}} |\boldsymbol{k}\rangle = \sum_{k_1, k_2, \dots, k_L} A^{k_1} A^{k_2} \cdots A^{k_{L-1}} A^{k_L} |\boldsymbol{k}\rangle$$
(13)

## From a CI to an MPS parametrization V

... schematically



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Matrix Product States

## Properties of the MPS I

- Matrix dimensions grow exponentially up to dim(d<sup>L/2−1</sup> × d<sup>L/2</sup>)
   <u>if no truncation</u> occurs, i.e., all singular values are kept
   → Optimal truncation scheme (in a least-square sense) required!
- From  $U^{\dagger}U = I$  follows that all matrices  $\{A^{k_l}\}$  are left-normalized

- MPS built from left-normalized matrices is called left-canonical
- For any lattice bipartition at site *l*, the states on sites 1,...,*l*

$$|a_l\rangle_{\mathcal{L}} = \sum_{k_1, k_2, \dots, k_l} \left( A^{k_1} \cdots A^{k_l} \right)_{1, a_l} |k_1, \dots, k_l\rangle$$
(15)

spanning a left subsystem  $\ensuremath{\mathcal{L}}$  form an orthonormal basis

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Matrix Product States

## Properties of the MPS II

• Starting SVD on coefficient tensor in Eq. (5) from right-hand side  $\Gamma_{(k_1,k_2,...,k_{L-1}),k_L} = c_{k_1,k_2,...,k_L}$ (16)

yields right-normalized matrices  $\{B^{k_l}\}$  (as  $V^{\dagger}V = I$ ), e.g.,

- MPS built from right-normalized matrices is called right-canonical
- For any lattice bipartition at site l + 1, the states on sites  $l + 1, \ldots, L$  $|a_l\rangle_{\mathcal{R}} = \sum_{k_{l+1}, k_{l+2}, \ldots, k_L} \left( B^{k_{l+1}} \cdots B^{k_L} \right)_{a_l, 1} |k_{l+1}, \ldots, k_L\rangle$  (18)

spanning a right subsystem  $\ensuremath{\mathcal{R}}$  form an orthonormal basis

## Gauge freedom and mixed-canonical form

- MPS representations are not unique ↔ existence of a gauge degree of freedom
- Consider two adjacent matrices  $M^{k_l}$  and  $M^{k_{l+1}}$  of shared column/row dimension D and a square invertible matrix X ( $D \times D$ )
- Invariance of MPS immediately follows from

$$M^{k_l} \to M^{k_l} X; \quad M^{k_{l+1}} \to X^{-1} M^{k_{l+1}}$$
 (19)

#### since

$$M^{k_l} \underbrace{XX^{-1}}_{=I} M^{k_{l+1}} = M^{k_l} \cdot M^{k_{l+1}}$$
(20)

## Mixed-canonical MPS representation

• Gauge freedom allows to write an MPS in **mixed canonical** form at sites {*l*, *l* + 1}

$$|\Psi\rangle = \sum_{\boldsymbol{k}} A^{k_1} \cdots A^{k_{l-1}} M^{k_l k_{l+1}} B^{k_{l+2}} \cdots B^{k_L} |\boldsymbol{k}\rangle$$
(21)

by starting from a general MPS wave function

$$|\Psi\rangle = \sum_{\boldsymbol{k}} M^{k_1} M^{k_2} \cdots M^{k_L} |\boldsymbol{k}\rangle$$
(22)

and the two-site MPS tensor in Eq. (21) reading as

$$M^{k_l k_{l+1}} \equiv M^{k_l k_{l+1}}_{a_{l-1}, a_{l+1}} = \sum_{a_l} M^{k_l}_{a_{l-1}, a_l} M^{k_{l+1}}_{a_l, a_{l+1}}$$
(23)

## Matrix product operators I

• MPS concept applied to operators  $\rightarrow$  matrix product operators (MPOs)



• N-electron operator  $\widehat{W}$  in MPO form

$$\widehat{\mathcal{W}} = \sum_{\boldsymbol{k}\boldsymbol{k'}} \sum_{b_1,\dots,b_{L-1}} W_{1,b_1}^{k_1k'_1} W_{b_1,b_2}^{k_2k'_2} \cdots W_{b_{L-1},1}^{k_Lk'_L} |\boldsymbol{k}\rangle \langle \boldsymbol{k'}| \qquad (24)$$

$$= \sum_{\boldsymbol{k}\boldsymbol{k'}} W^{k_1k'_1} W^{k_2k'_2} \cdots W^{k_Lk'_L} |\boldsymbol{k}\rangle \langle \boldsymbol{k'}| \qquad (25)$$

$$\equiv \sum_{\boldsymbol{k}\boldsymbol{k'}} w_{\boldsymbol{k}\boldsymbol{k'}} |\boldsymbol{k}\rangle \langle \boldsymbol{k'}| \qquad (26)$$

## Matrix product operators II

 For efficiency, rearrange summations in Eq. (24) such that the contraction proceeds first over the local site indices k<sub>l</sub>k'<sub>l</sub>

$$W_{b_{l-1},b_{l}}^{l} = \sum_{k_{l}k_{l}'} W_{b_{l-1},b_{l}}^{k_{l}k_{l}'} \left| k_{l} \right\rangle \left\langle k_{l}' \right| .$$
<sup>(27)</sup>

- By means of Eq. (27) we can write Eq. (24) as  $\widehat{W} = \sum_{b_1, \dots, b_{L-1}} W_{1, b_1}^1 \cdots W_{b_{l-1}, b_l}^l \cdots W_{b_{L-1}, 1}^L .$ (28)
- Note: the entries of  $\{W_{b_{l-1},b_l}^l\}$  matrices comprise the elementary, *local* operators acting on the *l*-th orbital, e.g.,

$$\tilde{a}_{\uparrow l}^{\dagger} = \left|\uparrow\downarrow\right\rangle\left\langle\downarrow\right| + \left|\uparrow\right\rangle\left\langle0\right| \tag{29}$$

## Variational MPS optimization I



- Goal: find optimal approximation  $|\tilde{\Psi}\>\rangle$  to  $|\Psi\>\rangle$  (in a least-square sense)
- Prerequisite: initialize suitable (valid) trial MPS wave function  $| ilde{\Psi}\,
  angle$ 
  - choices for warm-up guess: random guess, encode HF determinant, CI-DEAS by Ö. Legeza, ...
  - assume normalization, i.e.,  $\langle \Psi | \Psi \rangle = 1$

## Variational MPS optimization II



• Ansatz for variational MPS optimization: extremize the Lagrangian  $\mathcal{L} = \langle \Psi | \hat{H} | \Psi \rangle - \lambda \langle \Psi | \Psi \rangle$ (30)

with the two-site  $\{M^{k_l k_{l+1}}\}$  matrices as optimization parameters

- Optimize at each step of a "sweep" entries of site matrices of two orbitals ("two-site DMRG") while keeping all the others fixed
- Sweep through all sites multiple times until energy converges

## Variational MPS optimization III

- At sites  $\{l, l+1\}$ , take derivative in Eq. (30) with respect to complex conjugate of  $M^{k_l,k_{l+1}}$  $\frac{\partial}{\partial M^{k_{l},k_{l+1}*}} (\langle \Psi | \hat{H} | \Psi \rangle - \lambda \langle \Psi | \Psi \rangle) = 0$ (31)which then yields  $\sum_{a_{l-1}'a_{l}'} \sum_{k_{l}'k_{l+1}'} L_{a_{l-1},a_{l-1}'}^{b_{l-1}} W_{b_{l-1},b_{l+1}}^{k_{l}k_{l+1},k_{l}'k_{l+1}'} R_{a_{l+1}',a_{l+1}}^{b_{l+1}} M_{a_{l-1}',a_{l+1}'}^{k_{l}'k_{l+1}'} = \lambda \sum_{a_{l-1}',a_{l-1}'} \Psi_{a_{l-1}',a_{l-1}}^{A} \times (1 - 1)^{a_{l-1}'} M_{a_{l-1}',a_{l+1}'}^{b_{l-1}} M_{a_{l-1}',a_{l+1}'}^{b_{l-1}'} = \lambda \sum_{a_{l-1}',a_{l-1}'} \Psi_{a_{l-1}',a_{l-1}'}^{A} \times (1 - 1)^{a_{l-1}'} M_{a_{l-1}',a_{l+1}'}^{b_{l-1}'} M_{a_{l-1}',a_{l+1}'}^{b_{l-1}'} = \lambda \sum_{a_{l-1}',a_{l+1}'} \Psi_{a_{l-1}',a_{l-1}'}^{A} \times (1 - 1)^{a_{l-1}'} M_{a_{l-1}',a_{l+1}'}^{b_{l-1}'} = \lambda \sum_{a_{l-1}',a_{l+1}'} \Psi_{a_{l-1}',a_{l+1}'}^{A} \times (1 - 1)^{a_{l-1}'} M_{a_{l-1}',a_{l+1}'}^{b_{l-1}'} = \lambda \sum_{a_{l-1}',a_{l+1}'} \Psi_{a_{l-1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l-1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l-1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l-1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l-1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l+1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l+1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l+1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l+1}',a_{l+1}',a_{l+1}'} \Psi_{a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l+1}',a_{l+1}',a_{l+1}',a_{l+1}'}^{A} = \lambda \sum_{a_{l+1}',a_{l+1$  $\times M^{k'_lk'_{l+1}}_{a'_{l-1},a'_{l+1}}\times$  $\times \Psi^B_{a'_{l+1},a_{l+1}}$ (32)
  - L and R are the so-called *left* and *right boundaries* obtained by contracting the MPO with the bra and ket MPS starting from left (right) up to sites l 1 (l + 1)

## Variational MPS optimization IV

Schematically



## Variational MPS optimization V

- NB: Eq. (32) defines a generalized eigenvalue problem which can be simplified to a standard eigenvalue problem (Eq. (33)) if the MPS is a canonical MPS!
- The latter requires the initial MPS to be right-normalized!
- Hence, assuming correct normalization Eq. (32) simplifies to



R

## Variational MPS optimization VI

- Recast Eq. (33) into a matrix eigenvalue equation  $\mathcal{H}v - \lambda v = 0$ ,
  - by defining a local Hamiltonian matrix  $\mathcal{H}$  at sites  $\{l, l+1\}$

$$H_{(k_{l}k_{l+1}a_{l-1}a_{l+1}),(k_{l}'k_{l+1}'a_{l-1}'a_{l+1}')} = \sum_{b_{l-1},b_{l+1}} L_{a_{l-1},a_{l-1}'}^{b_{l-1}} W_{b_{l-1},b_{l+1}}^{k_{l}k_{l+1}'} R_{a_{l+1}',a_{l+1}}^{b_{l+1}}$$
(35)  
• and a vector  $v$   
 $v_{k_{l}'k_{l+1}'a_{l-1}'a_{l+1}'} = M_{a_{l-1}',a_{l+1}'}^{k_{l}'k_{l+1}'}.$  (36)

• Solve Eq. (34) by an iterative eigensolver

 $\rightarrow$  eigenvalue  $\lambda^0$  and corresponding eigenvector  $v^0_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}}$ 

(34)

## Variational MPS optimization VII

- Reshape  $v_{k'_lk'_{l+1}a'_{l-1}a'_{l+1}}^0$  back to  $M_{a'_{l-1},a'_{l+1}}^{k'_lk'_{l+1}}$ •  $M_{a'_{l-1},a'_{l+1}}^{k'_lk'_{l+1}}$  is subsequently subject to a left- or right-normalization  $M_{a'_{l-1},a'_{l+1}}^{k'_lk'_{l+1}} = M_{(k'_l,a'_{l-1})(k'_{l+1},a'_{l+1})} = U_{(k'_l,a'_{l-1})s_l}S_{s_ls_l}V_{s_l(a'_{l+1},k'_{l+1})}$  (37)
- By discarding the 3m smallest singular values in  $S_{s_l s_l}$  to obtain  $S_{a'_l a'_l}$  we achieve the desired reduction in bond dimensionality!
- The maximum (fixed) number *m* of retained singular values is usually called **number of renormalized block states**

## Variational MPS optimization VIII

• Discarding the 3m smallest singular values corresponds to discarding the last 3m columns (rows) of U(V) such that for the two site matrices  $M_{a'_{l-1},a'_{l}}^{k'_{l}}$  and  $M_{a'_{l},a'_{l+1}}^{k'_{l+1}}$  we obtain

$$M_{a'_{l-1},a'_{l}}^{k'_{l}} = U_{(k'_{l},a'_{l-1})a'_{l}}$$
(38)

$$M_{a'_{l},a'_{l+1}}^{k'_{l+1}} = \frac{1}{1 - \sum_{s_{l}=m+1}^{4m} S_{s_{l}s_{l}}} S_{a'_{l}a'_{l}} V_{a'_{l}(a'_{l+1},k'_{l+1})}$$
(39)

• Energy calculated as a function of the truncation error  $\epsilon$ 

$$\epsilon = \sum_{s_l=m+1}^{4m} S_{s_l s_l} = ||\Psi_{16m^2} - \Psi_{4m^2}||$$
(40)

can be employed to obtain an error estimate through extrapolation

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Matrix Product States

## Variational MPS optimization IX

- Moving from sites {l, l + 1} to sites {l + 1, l + 2} completes the local optimization step
- **BUT**: Is the chosen approximation optimal in a least-square sense as we set out to do so?

## Optimal bipartition in a least square sense I



• Given: many-body state  $|\Psi
angle$  of composite system AB

$$|\Psi\rangle = \sum_{ij} C_{ij} |i\rangle_A \otimes |j\rangle_B \tag{41}$$

• { $|i\rangle_A$ } ({ $|j\rangle_B$ }) are orthonormal bases of **A** (**B**) with dimension  $N_A$  ( $N_B$ )

## Optimal bipartition in a least square sense II

• SVD of 
$$|\Psi\rangle$$
 yields  

$$|\Psi\rangle = \sum_{ij} \sum_{a=1}^{\min(N_A, N_B)} U_{ia} S_{aa} V_{ja}^* |i\rangle_A |j\rangle_B \qquad (42)$$

$$= \sum_{a=1}^{\min(N_A, N_B)} \left(\sum_i U_{ia} |i\rangle_A\right) s_a \left(\sum_j V_{ja}^* |j\rangle_B\right) \qquad (43)$$

$$= \sum_{a=1}^{\min(N_A, N_B)} s_a |a\rangle_A |a\rangle_B \qquad (44)$$

## Optimal bipartition in a least square sense III

Restricting the sum in Eq.(44) to some value *r* ≤ min(*N<sub>A</sub>*, *N<sub>B</sub>*) yields the *Schmidt decomposition*

$$|\Psi\rangle = \sum_{a=1}^{\prime} s_a |a\rangle_A |a\rangle_B \tag{45}$$

where r = 1 corresponds to (classical) product states and r > 1 to entangled (quantum) states

• For orthonormal states in **A** and **B**, the two-norm  $||\Psi||_2^2$  is identical to the Frobenius norm of the matrix  $\{C_{ij}\}, ||\mathbf{C}||_F^2$ 

$$||\Psi||_2^2 = ||\mathbf{C}||_F^2 = \sum_{a=1}^{\min(N_A, N_B)} s_a^2$$
(46)

## Optimal bipartition in a least square sense IV

Hence, an optimal approximation |Ψ ⟩ to |Ψ ⟩ with respect to the 2-norm immediately follows from optimal approximation of C by C in the Frobenius norm, with C being a matrix of rank r' ≤ r

$$\left|\tilde{\Psi}\right\rangle = \sum_{a=1}^{r'} s_a |a\rangle_A |a\rangle_B \tag{47}$$

• **BUT** how does this relate to the truncation (dimensionality reduction) in the variational MPS optimization?

## Optimal bipartition in a least square sense V

 Last line in Eq. (44) can be realized for site *l* by an MPS in mixed-canonical form (cf. Eq. (21))

$$\Psi \rangle = \sum_{\substack{a_{1},...,a_{L-1} \\ a_{1,...,a_{L-1}} \\ = \sum_{\substack{a_{l} \\ a_{1},...,a_{L-1} \\ a_{l},...,a_{L-1} \\ \\ \left( \sum_{\substack{k_{1},...,k_{l} \\ a_{1},...,a_{l-1} \\ a_{l},...,a_{l-1} \\ A_{1,a_{1}}^{k_{1}} \cdots A_{a_{l-1},a_{l}}^{k_{l}} |k_{1},...,k_{l}\rangle \right) \cdot S_{a_{l},a_{l}} \cdot \left( 48 \right)$$

$$= \sum_{\substack{a_{l} \\ a_{l+1},...,k_{L} \\ a_{l+1},...,a_{L-1} \\ B_{a_{l},a_{l+1}}^{k_{l+1}} \cdots B_{a_{L-1},1}^{k_{L}} |k_{l+1},...,k_{L}\rangle \right)$$

$$= \sum_{a_{l}} S_{a_{l},a_{l}} |a_{l}\rangle_{\mathcal{L}} |a_{l}\rangle_{\mathcal{R}}$$
(49)

## Optimal bipartition in a least square sense VI

Comparison of Eqs. (50) and (45) immediately reveals that an optimal bipartition in a least square sense can be obtained for |Ψ̃ > from an SVD retaining the lowest r (≡ m as usually referred to in DMRG terminology) values with r < dim(|Ψ >)

$$|\tilde{\Psi}\rangle = \sum_{a_l=1}^r S_{a_l a_l} |a_l\rangle_{\mathcal{L}} |a_l\rangle_{\mathcal{R}}$$
(51)

## Scaling of variational MPS optimization

- Scaling is dominated by the cost of contracting the operator with the MPS on one site and is proportional to the number of non-zero elements in the MPO matrices  $\{\widehat{W}\}$ 
  - in a naïve MPO ansatz this step scales as  $\mathcal{O}(L^5)$
  - in an optimized code scaling reduces to  $\mathcal{O}(L^4)$

Keller, Dolfi, Troyer, Reiher, J. Chem. Phys., 143, 244118 (2015)

• Further reduction through symmetry: U(1) and SU(2)

Keller and Reiher, J. Chem. Phys., 144, 134101 (2016)

- SVD scales as  $\mathcal{O}(m^3)$  (but there are *L* of them in a sweep)
- Taking into account all operations a sweep scales  $\approx \mathcal{O}(L^4 m^3)$

Wouters and van Neck, Eur. Phys. J. D, 68, 272 (2014)

## Extrapolation

• Extrapolate E based on truncation error  $\epsilon$  for different values of m

$$\ln\left(\frac{E_{\mathsf{DMRG}} - E_{\mathsf{FCI}}}{E_{\mathsf{FCI}}}\right) = a\ln\epsilon + b \tag{52}$$

Ö. Legeza, et al., Phys. Rev. B, 67, 124114 (2003)

• Example: ground-state calculation for F<sub>2</sub> molecule



S. Keller, M. Reiher, Chimia, 68, 200 (2014)

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## **Properties of DMRG**

#### DMRG

- Variational
- Size consistent
- (approximate) FCI for a CAS
- Polynomial scaling ( $\approx L^4 m^3$ )
- MPS wave function
- For large *m* invariant wrt orbital rotations

#### CASCI

- Variational
- Size consistent
- FCI for a CAS
- Factorial scaling
- Linearly parametrized wave function
- Invariant wrt orbital rotations

#### MPS/MPO code: https://github.com/qcscine/qcmaquis

Keller, Dolfi, Troyer, Reiher, J. Chem. Phys., 143, 244118 (2015)

Keller, Reiher, J. Chem. Phys., 144, 134101 (2016)

Matrix Product States

## Determining factors of DMRG convergence

- Size *L* of the CAS
- Type of molecular orbitals (HF, NO's, localized orbitals, ...)
- Guess of states in the right subsystem in the first sweep (for example CI-DEAS by Ö. Legeza or random guess)
- Ordering of orbitals (exploit entanglement measures)

Stein, Reiher, J. Chem. Theory Comput., 12, 1760 (2016)

- Number of renormalized block states *m*
- NB: One should never calculate results for just a single m, but increase it in various runs until results converge!

## Recent developments based on an MPS ansatz

# Many beautiful and original works of DMRG in QC by pioneers in the field

- Ö. Legeza
- Garnet Chan
- Takeshi Yanai
- Marcel Nooijen
- Yuki Kurashige
- Dominika Szgid
- Sandeep Sharma
- Dimitry van Neck
- Sebastian Wouters
- ... many other whom I might have forgotten to mention here

## A biased view on our work...



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#### Matrix Product States

## Assessing electron correlation effects

- Exploit the "regularization" effect in a hybrid range-separated short-range DFT ansatz to distinguish strong from dynamical electron correlation effects
- Based on the decomposition of two-electron repulsion into longand short-range contributions,

$$1/r_{12} = w_{ee}^{lr,\mu}(r_{12}) + w_{ee}^{sr,\mu}(r_{12}) ,$$
 (53)

$$w_{\rm ee}^{\rm lr,\mu}(r_{12}) = {\rm erf}(\mu r_{12})/r_{12},$$
 (54)

where  $\operatorname{erf}$  is the error function and  $\mu$  is a parameter in  $[0, +\infty[$  that controls the range separation

• CAS-CI-like energy expression becomes

$$E_{\mathsf{CAS-CI}}^{\mathsf{srDFT}} = E_{\mathsf{I}}^{\mathsf{lr}} + E_{\mathsf{A}}^{\mathsf{lr}} + E_{\mathsf{H}}^{\mathsf{sr}}[n] + E_{\mathsf{xc}}^{\mathsf{sr}}[n]$$
(55)

## Assessing electron correlation effects II

- Use measures obtained from quantum information theory to quantify orbital correlations
- Single-orbital von Neumann entropy  $s_i(1)$

$$s_i(1) = -\sum_{\alpha=1}^4 n_{\alpha,i} \ln(n_{\alpha,i}),$$
 (56)

where  $n_{\alpha,i}$  are the eigenvalues of the **one-orbital** RDM

• Mutual information  $I_{ij}$  between orbitals i and j is defined in terms of  $s_i(1)$  and  $s_{ij}(2)$ 

$$I_{ij} = \frac{1}{2} \left( s_i(1) + s_j(1) - s_{ij}(2) \right) \left( 1 - \delta_{ij} \right)$$
(57)

Ö. Legeza and J. Solyom, Phys. Rev. B 68, 195116 (2003)

Ö. Legeza and J. Solyom, Phys. Rev. B 70, 205118 (2004)

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Matrix Product States

### Assessing electron correlation effects III

One-orbital RDM contains elements of the 1- and 2-RDM!

$$\rho_i(1) = \begin{pmatrix} 1 - \gamma_i^i - \gamma_{\overline{i}}^{\overline{i}} + \Gamma_{i\overline{i}}^{i\overline{i}} & 0 & 0 & 0\\ 0 & \gamma_i^i - \Gamma_{i\overline{i}}^{i\overline{i}} & 0 & 0\\ 0 & 0 & \gamma_{\overline{i}}^{\overline{i}} - \Gamma_{i\overline{i}}^{i\overline{i}} & 0\\ 0 & 0 & 0 & \Gamma_{i\overline{i}}^{i\overline{i}} \end{pmatrix}$$

Two-orbital RDM contains elements of the 1-, 2-, 3- and 4-RDM!

Boguslawski and Tecmer, I. J. Quant. Chem., 115, 1289 (2015)

(58)

### Assessing electron correlation effects IV

## Stretching N2...



Hedegaard, Knecht, Kielberg, Jensen, Reiher, J. Chem. Phys., 142, 224108 (2015)

Stef	an	Kn	ec	ht

### Assessing electron correlation effects V

## Stretching N2...



Hedegaard, Knecht, Kielberg, Jensen, Reiher, J. Chem. Phys., 142, 224108 (2015)

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## Intermission: Relativistic quantum chemistry

#### **One-step approaches**

"j-j coupling"

- Include scalar-relativistic effects and SO coupling variationally *ab initio*
- Use Dirac Hamiltonian ("four-component")

or

block-diagonalization /

elimination techniques for

"two-component" form

## Two-step approaches

"L-S coupling"

• "State-interaction" for *a posteriori* inclusion of SO coupling:

 $\mathbf{Hc} = E\mathbf{Sc}$ 

- Express **H** in basis of scalar-relativistic wave functions
- Use Hamiltonian of form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}^{\mathsf{e}l,sf} + \hat{\mathcal{H}}^{\mathsf{S}O}$$

## The state-interaction (SI) approach

- Property calculations for CAS-type wave functions often require an evaluation of matrix elements between individually optimized (nonorthogonal) electronic states calculated
  - in a state-specific approach and/or
  - which differ in their total spin: singlet, triplet, quintet, ...
- **Key**: transformation of MOs/wave functions to biorthonormal orbital basis (representation)

P. A. Malmqvist, Int. J. Quant. Chem. 30, 479 (1986)



S. Knecht, S. Keller, J. Autschbach, M. Reiher, JCTC, 12, 5881 (2016)

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Matrix Product States

## MPS-SI: property calculations for NpO $_2^{2+}$

S. Knecht, S. Keller, J. Autschbach, M. Reiher, JCTC, 12, 5881 (2016)

- Magnetic properties of a prototypical 5f<sup>1</sup> molecule
- Relative energies of spin-orbit coupled electronic states arising from the spinfree  ${}^{2}\Phi_{u}$  and  ${}^{2}\Delta_{u}$  manifold

Qualitative molecular orbital diagram



<sup>a</sup> F. Gendron et al., IC, 53, 8577 (2014)

## MPS-SI: low-lying excited state spectrum of NpO $_2^{2+}$

S. Knecht, S. Keller, J. Autschbach, M. Reiher, JCTC, 12, 5881 (2016)

Computational details: ANO-RCC-VTZ, no symmetry, Cholesky decomposition, m = 256 for all DMRG-SCF calculations, pc-NEVPT2 with CAS(7,10) reference

state	DMRG-SCF			NEVPT2	CASPT2 <sup>a</sup>	
	$\Delta E$	composition	$\Delta E$	composition	$\Delta E$	composition
	$[cm^{-1}]$	%	$[cm^{-1}]$	%	$[cm^{-1}]$	%
${}^{2}\Phi_{5/2u}$	0	89 $\phi$ , 11 $\delta$	0	88 $\phi$ , 12 $\delta$	0	88 $\phi$ , 12 $\delta$
$^{2}\Delta_{3/2u}$	3294	99 $\delta$ , 1 $\pi$	3086	98 $\delta$ , 2 $\pi$	3107	98 $\delta$ , 2 $\pi$
$^{2}\Phi_{7/2u}$	8067	100 $\phi$	8086	100 $\phi$	8080	100 $\phi$
$^{2}\Delta_{5/2u}$	9402	89 $\delta$ , 11 $\phi$	9280	88 $\delta$ , 12 $\phi$	9313	88 $\delta$ , 12 $\phi$

<sup>a</sup> F. Gendron, B. Pritchard, H. Bolvin, J. Autschbach, Inorg. Chem., 53, 8577 (2014)

## MPS-SI: electronic g-factors of NpO $_2^{2+}$

S. Knecht, S. Keller, J. Autschbach, M. Reiher, JCTC, 12, 5881 (2016)

- Computational details: ANO-RCC-VTZ, no symmetry, Cholesky decomposition, m = 256 for all DMRG-SCF calculations
- All data for the  ${}^2\Phi_{5/2u}$  state
- Reference value for g<sub>∥</sub> from a four-component SD(9)MRCI(1,4)SDT calculation: 4.283

active space	DMRG-SCF		NEVPT2		CASPT2 <sup>a</sup>		
	g∥	g⊥	g∥	g⊥	g∥	g⊥	
$NpO_2^{2+}$							
CAS(1,4)	4.211	0.001	4.214	0.002	4.225	0.001	
CAS(7,10)	4.228	0.002	4.235	0.002	4.233	0.002	
CAS(13,16)	4.223	0.002					

<sup>a</sup> F. Gendron, B. Pritchard, H. Bolvin, J. Autschbach, Inorg. Chem., 53, 8577 (2014)

## Relativistic DMRG with QCMaquis

Battaglia, Keller, Knecht, J. Chem. Theory Comput., 14, 2353 (2018)

• General formulation that works with 4- and 2-component Hamiltonian, e.g.

$$\begin{split} \hat{H}_{\mathsf{Dirac}} &= \sum_{i} \left[ c^{2} (\beta - I_{4}) + c (\boldsymbol{\alpha} \cdot \hat{\boldsymbol{p}}_{i}) + \hat{V}_{i} \right] + \sum_{i < j} \hat{V}_{ij} \\ \hat{V}_{ij} &= \frac{1}{r_{ij}} - \frac{\boldsymbol{\alpha}_{i} \cdot \boldsymbol{\alpha}_{j}}{r_{ij}} - \frac{\left[ (\boldsymbol{\alpha}_{i} \cdot \boldsymbol{\nabla}_{i}) (\boldsymbol{\alpha}_{j} \cdot \boldsymbol{\nabla}_{j}) r_{ij} \right]}{2} \end{split}$$

- Exploits time-reversal symmetry for one- and two-electron integrals
- Based on a Kramers-unrestricted spinor model with k<sub>l</sub> = { ||⟩, |0⟩ }
   → spinor lattice (!)

## Relativistic DMRG with QCMaquis

Battaglia, Keller, Knecht, J. Chem. Theory Comput., 14, 2353 (2018)

## Block-matrix structure of (fermionic) operators in second quantization defines the Hamiltonian model in QCMaquis

#### non-relativistic Hamiltonian

op\_t create\_up\_op, create\_down\_op, destroy\_up\_op, destroy\_down\_op, count\_up\_op, count\_down\_op, count\_up\_down\_op, docc\_op, e2d\_op, d2e\_op, d2u\_op,u2d\_op, ident\_op, fill\_op;

typename SymmGroup::charge A(0), B(0), C(0), D(1); B[0]=1; C[1]=1;

ident\_op.insert\_block(Matrix(1, 1, 1), A, A); ident\_op.insert\_block(Matrix(1, 1, 1), B, B); ident\_op.insert\_block(Matrix(1, 1, 1), C, C); ident\_op.insert\_block(Matrix(1, 1, 1), D, D);

create\_up\_op.insert\_block(Matrix(1, 1, 1), A, B); create\_up\_op.insert\_block(Matrix(1, 1, 1), C, D); create\_down\_op.insert\_block(Matrix(1, 1, 1), A, C); create\_down\_op.insert\_block(Matrix(1, 1, 1), B, D);

destroy\_up\_op.insert\_block(Matrix(1, 1, 1), B, A); destroy\_up\_op.insert\_block(Matrix(1, 1, 1), D, C); destroy\_down\_op.insert\_block(Matrix(1, 1, 1), C, A); destroy\_down\_op.insert\_block(Matrix(1, 1, 1), D, B);

#### relativistic Hamiltonian

op\_t create\_op, destroy\_op, count\_op, ident\_op, fill\_op; typename SymmGroup::charge A(0), B(0); B[0]=1; ident\_op.insert\_block(Matrix(1, 1, 1), A, A); ident\_op.insert\_block(Matrix(1, 1, 1), B, B); create\_op.insert\_block(Matrix(1, 1, 1), A, B); destroy\_op.insert\_block(Matrix(1, 1, 1), B, A); count\_op.insert\_block(Matrix(1, 1, 1), B, B); fill op.insert\_block(Matrix(1, 1, 1), A, A);

fill\_op.insert\_block(Matrix(1, 1, 1), A, A);
fill\_op.insert\_block(Matrix(1, 1, -1), B, B);

Knecht, in preparation (2021)

- Relativistic DMRG-SCF calculations (*m* = 1024)
- State-averaged optimization
  - (UCl<sub>6</sub>)<sup>1-</sup>: 14 roots
  - (UCl<sub>6</sub>)<sup>2-</sup>: 17 roots
- Basis sets
  - U: uncontracted ANO-RCC
  - CI: ANO-RCC-TZVP
- Customized fitting basis sets
- Excitation energies in eV

• octahedral  $f^1$  and  $f^2$  complexes



Knecht, in preparation (2021)

#### • Ground- and excited-state properties of (UCI<sub>6</sub>)<sup>1-</sup>

state	$aU_{3/2u}$	$aE_{5/2u}$	$\mathrm{bU}_{3/2\mathrm{u}}$	$aE_{1/2u}$	g-factor
CAS(7,20)	0.41	0.91	1.31	1.48	-1.15
CAS(19,32) <sup>†</sup>	0.46	0.85	1.32	1.48	-
CAS(19,32) <sup>‡</sup>	0.46	0.82	1.30	1.46	-
experiment <sup>a</sup>	0.47	0.84	1.26	1.43	-1.1
CAS-SOC <sup>b</sup>	-	0.89	1.34	1.53	-1.05
SO-CASPT2°	0.47	0.91	1.39	1.54	-1.06
CAS/CCSD(T)/SO <sup>d</sup>	0.39	0.73	1.13	1.30	-

<sup>†</sup> Dirac-Coulomb; <sup>‡</sup> Dirac-Coulomb-Breit

<sup>a</sup> Selb *et al.*, Inorg. Chem., 7, 976 (1968); <sup>b</sup> Ganyushin and Neese, J. Chem. Phys., 138, 104113 (2013)

<sup>c</sup> Notter and Bolvin, J. Chem. Phys., 130, 184310 (2009); <sup>d</sup> Su et al., J. Chem. Phys., 142, 134308 (2015)

Stefan Knecht

Knecht, in preparation (2021)

#### • Ground- and excited-state properties of (UCI<sub>6</sub>)<sup>2-</sup>

state	${\sf aT}_{1{\sf g}}$	aEg	$aT_{2g}$	bEg	$bT_{2g}$	$bT_{1g}$
CAS(2,14) <sup>†</sup>	0.10	0.15	0.27	0.77	0.77	0.78
CAS(2,14) <sup>‡</sup>	0.10	0.15	0.27	0.76	0.76	0.76
CAS(20,32)	0.10	0.15	0.26	0.68	0.72	0.80
experiment <sup>a</sup>	0.11	0.16	0.28	0.63	0.61	0.79
SO-CASPT2 <sup>b</sup>	0.09	0.14	0.24	0.66	0.67	0.66

<sup>†</sup> Dirac-Coulomb; <sup>‡</sup> Dirac-Coulomb-Breit

<sup>a</sup> Flint et al., Mol. Phys., 61, 389 (1987); <sup>b</sup> Su et al., J. Chem. Phys., 142, 134308 (2015)

• g-factor in the A<sub>1g</sub> ground state:  $g_{\parallel}$ =0.57 (0.58),  $g_{\perp}$ =1.92 (1.91)

Knecht, in preparation (2021)

• Valence spinors (only one Kramers-partner shown) of (UCl<sub>6</sub>)<sup>2-</sup>



Matrix Product States



#### Electron localization function (ELF)



### ELF from non-relativistic and relativistic HF calculations

Jerabek et al., Phys. Rev. Lett., 120, 053001 (2018)



•  $\Delta_{\mathsf{ELF}}^{\mathsf{relativistic}}(\mathsf{HF}\text{-}\mathsf{DMRG}(40,130))$ 

Knecht, Nachr. Chem., 67, 57 (2019)

#### ELF as a function of the distance from the nucleus



Jerabek et al., Phys. Rev. Lett., 120, 053001 (2018)



Knecht, Nachr. Chem., 67, 57 (2019)

## Copernicium and Flerovium

ELF as a function of the distance from the nucleus

Copernicium

Flerovium



Knecht, unpublished (2020)

## Coupling to (strong) external fields

Exploit template-based code structure of QCMAQUIS to implement a coupling to

• (uniform) external magnetic fields





DMRG(3,4)-SCF for  $N_2^+$  with uniform magnetic field of 20,000 T

- quantized photon fields, i.e. optimize an MPS for a mixed fermonic and bosonic Hamiltonian
  - $\rightarrow$  follow work on polaritonic CC by Manby and co-workers

Phys. Rev. Res., 2, 023262 (2020)

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