Strong correlation in quantum chemistry and density matrix renormalization group method

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Problem of electron correlation

1. Born-Oppenheimer approximation:

$$H_{\mathrm{el}} = -\sum_i \frac{\nabla_i^2}{2} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I}\frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \qquad \Rightarrow \qquad \Psi_{\mathrm{el}}(\mathbf{r}_1 \ldots \mathbf{r}_n)$$

2. Hartree-Fock approximation:
    - Single Slater determinant ⇒ one-electron problems

3. Post-Hartree-Fock methods:

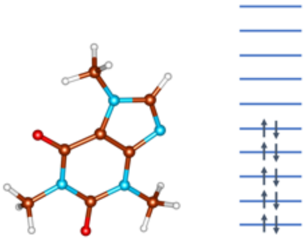
$$\Psi_{\mathrm{el}} = \Psi_{\mathrm{HF}} + \Psi_{\mathrm{corr}} \qquad E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{\mathrm{HF}} \quad \ldots$$ correlation energy

Dynamical versus static electron correlation

Weakly correlated regime

Dynamical correlation

DFT, CCSD(T)

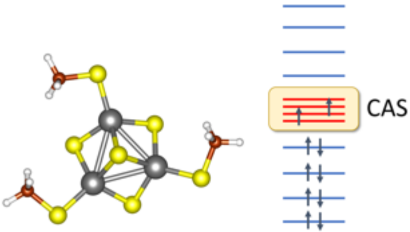


Caffeine

Strongly correlated regime

Static correlation

Complete active space (CAS) methods

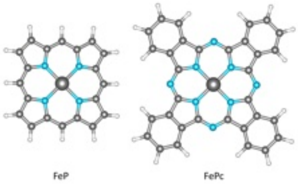


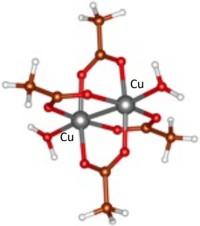
[3Fe-4S] model cluster

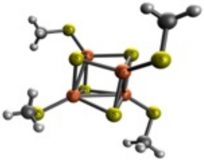
- Our targets: molecules requiring very large active spaces
- We employ DMRG for proper description of static correlation and other methods (CC, AC) for the missing dynamical correlation

What systems can we study?

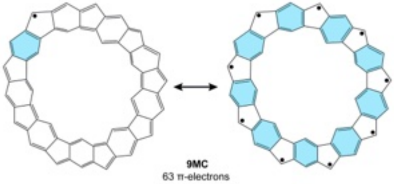
Transition metal complexes

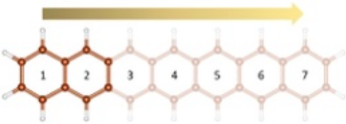






Polyradical polycyclic aromatic hydrocarbons (PAHs)





What are the strong and weak points of DMRG?

Strong points

- Variational
- Genuinely multireference
- Size consistent

Weak(er) points

Not suitable for dynamical correlation

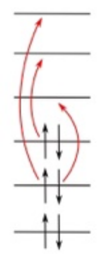
Not truly black-box

Complexity of the exact (FCI) solution

- Full configuration interaction (FCI) active space expansion:

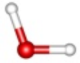
$$\Psi_{\mathrm{el}} = \sum_{n_1 n_2 \dots n_k} \psi^{n_1 n_2 \dots n_k} \left| n_1 n_2 \cdots n_k \right\rangle$$

- $|n_i\rangle \in \{|\text{empty}\rangle, |\downarrow\rangle, |\uparrow\rangle, |\downarrow\uparrow\rangle\}, \qquad \sum_i n_i = N$
- Dimension of the vector (Hilbert) space increases exponentially with system size: $\sim 4^k$

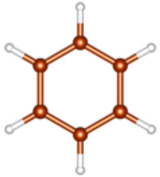


- in PVDZ basis set:

100



$\approx 10^7$



$\approx 10^{46}$

- With FCI one can treat at most 16 (20) active orbitals.

Complexity of the exact (FCI) solution

- Do we really need to exploit the full Hilbert space?
- Most of quantum phase space *is not* explored by physical ground states
- How to reduce the complexity of Ψ_{el} and come up with a class of variational wave functions that captures the physics of electronic Hamiltonian?
- Introduction of locality into the wave function parametrization

- The simplest approach: $\psi^{n_1 n_2 \cdots n_k} \approx \psi^{n_1} \psi^{n_2} \cdots \psi^{n_k}$
- $4^k \Rightarrow 4k$ parameters, however not very accurate!

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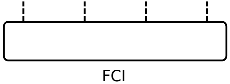
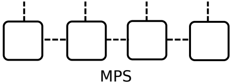
Matrix Product State (MPS) ansatz

$$\Psi_{\mathrm{el}} = \sum_{n_1 n_2 \ldots n_k} \psi^{n_1 n_2 \ldots n_k} \left| n_1 n_2 \cdots n_k \right\rangle , \qquad \left| n_i \right\rangle \in \{ \left|0\right\rangle , \left|\downarrow\right\rangle , \left|\uparrow\right\rangle , \left|\downarrow\uparrow\right\rangle \}$$

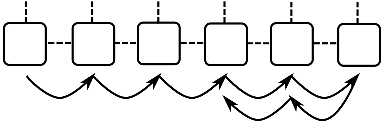


- DMRG: Matrix product state (MPS) ansatz:



$$\psi^{n_1 n_2 \ldots n_k} \approx \sum_{i_1 i_2 \ldots i_{k-1}} \psi^{n_1}_{i_1} \psi^{n_2}_{i_1 i_2} \psi^{n_3}_{i_2 i_3} \cdots \psi^{n_k}_{i_{k-1}} , \qquad 4^k \Rightarrow \mathcal{O}(4M^2 k) \text{ parameters}$$

- Bond dimension M governs accuracy as well as computational cost: $M \to \dim(\mathrm{FCI})$, $E_{\mathrm{DMRG}} \to E_{\mathrm{exact}}$
- One or two individual MPS tensors are variationally optimized at a time (sweeping)



Singular value decomposition (SVD)

- Very versatile tool of linear algebra
- Arbitarary (rectangular) matrix M can be decomposed as

$$M = UDV^\dagger \qquad D \ldots \text{diagonal matrix}$$

$$\text{singular values:} \quad d_1 \geq d_2 \geq \ldots \geq d_r > 0 \qquad r \ldots \text{Schmidt rank}$$

- SVD provides optimal approximation of M by M' with lower Schmidt rank $r' < r$

$$M' = UD'V^\dagger \qquad D' = \text{diag}(d_1, d_2, \ldots, d_{r'}, 0, \ldots)$$

Schmidt decomposition

- In DMRG, as we will see, we group orbitals into the left and right blocks - bipartite splitting

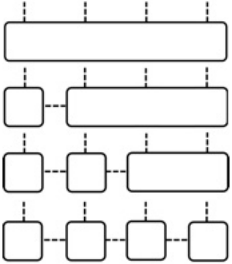
$$\begin{aligned}
|\Psi\rangle &= \sum_{ij} \Psi_{ij} \, |i\rangle_L \, |j\rangle_R \\
&= \sum_{ij} \sum_{a} U_{ia} D_{aa} V^*_{ja} \, |i\rangle_L \, |j\rangle_R \\
&= \sum_{a} d_a \Big(\sum_{i} U_{ia} \, |i\rangle_L \Big) \Big(\sum_{j} V^*_{ja} \, |j\rangle_R \Big) \\
&= \sum_{a=1}^{r} d_a \, |a\rangle_L \, |a\rangle_R
\end{aligned}$$

- Schmidt rank is a measure of entanglement between the left and right parts!
- $r = 0 \ldots$ product state, $r > 0 \ldots$ entangled state

Matrix Product State (MPS) ansatz

- Any wavefunction can be *exactly* factorized into the MPS form:

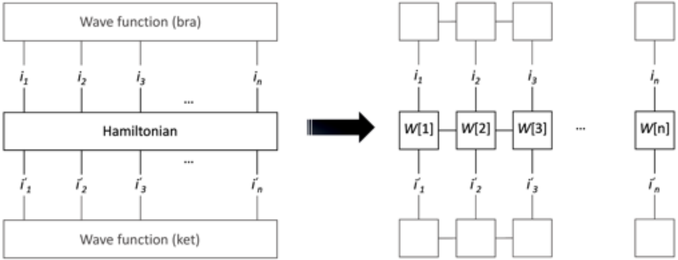
$$
\begin{aligned}
\psi^{n_1 n_2 \dots n_k} &\equiv \psi_{n_1,(n_2 \dots n_k)} = \sum_{a_1} U_{n_1 a_1} D_{a_1 a_1} (V^\dagger)_{a_1,(n_2 \dots n_k)} = \sum_{a_1} A^{n_1}_{a_1} \psi_{a_1 n_2 \dots n_k} \\
&= \sum_{a_1} A^{n_1}_{a_1} \psi_{(a_1 n_2),(n_3 \dots n_k)} = \sum_{a_1} \sum_{a_2} A^{n_1}_{a_1} U_{(a_1 n_2),a_2} D_{a_2 a_2} (V^\dagger)_{a_2,(n_3 \dots n_k)} \\
&= \sum_{a_1} \sum_{a_2} A^{n_1}_{a_1} A^{n_2}_{a_1 a_2} \psi_{a_2 n_3 \dots n_k} \dots
\end{aligned}
$$



- Non-truncated auxiliary dimensions would leed to the original, i.e. exponential scaling!

Tensor networks

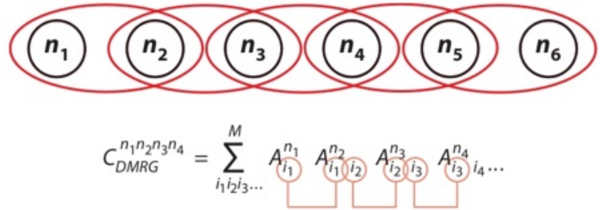
- Hamiltonian can be exactly factorized into the matrix product operator (MPO) form



- Computation of $\langle \Psi_{\mathrm{MPS}} | H_{\mathrm{MPO}} | \Psi_{\mathrm{MPS}} \rangle$ can be done *efficiently* by contraction of the tensor network e.g. from the left to the right
- DMRG/MPS - simplest (1D) tensor network method

Locality in DMRG

- DMRG encodes locality through the structure of contractions of auxiliary indices



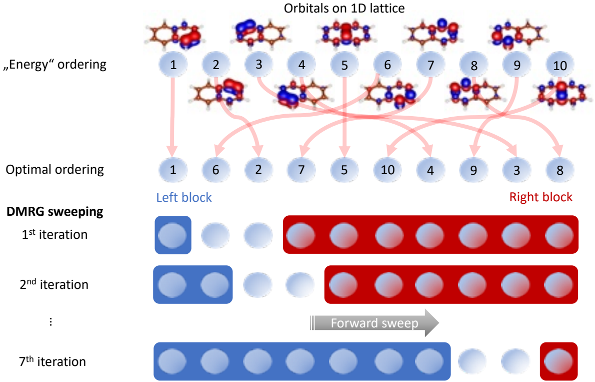
$$C_{DMRG}^{n_1 n_2 n_3 n_4} = \sum_{i_1 i_2 i_3 \dots}^{M} A_{i_1}^{n_1} A_{i_1 i_2}^{n_2} A_{i_2 i_3}^{n_3} A_{i_3 i_4 \dots}^{n_4}$$

- E.g. i_1 and its contraction give rise to correlations between occupancies n_1 and n_2
- It can be shown that when the underlying orbital (entanglement) topology is linear, DMRG ansatz is optimal
- DMRG is a powerful method even for non-linear topologies

Basics of the DMRG algorithm

$$H = \sum_{\substack{pq=1\\ \sigma\in\{\uparrow,\downarrow\}}}^{k} h_{pq}\, a^{\dagger}_{p\sigma} a_{q\sigma} + \sum_{\substack{pqrs=1\\ \sigma,\sigma'\in\{\uparrow,\downarrow\}}}^{k} v_{pqrs}\, a^{\dagger}_{p\sigma} a^{\dagger}_{q\sigma'} a_{r\sigma'} a_{s\sigma}\,, \qquad v_{pqrs} = \frac{1}{2}\langle pq|sr\rangle$$

- MO integrals h_{pq} and v_{pqrs} are input parameters
- Zero$^{\text{th}}$ step - ordering of orbitals on 1D lattice



Two-site DMRG algorithm

- First iteration:$\{l\} = \{|0\rangle, |\downarrow\rangle, |\uparrow\rangle, |\uparrow\downarrow\rangle\}$ and is *complete*
- Explicit matrix form of second-quantized operators:

$$a_\uparrow^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad a_\downarrow^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ \downarrow \\ \uparrow \\ \uparrow\downarrow \end{pmatrix}$$

- Hamiltonian of a single site (orbital) can be easily formed from them
- Right part $\{r\}$ is guessed (may be even random matrices)
- Increasing the left block by remaining orbitals without truncation $\Rightarrow$ curse of dimensionality!
- Renormalization - finding the *optimal* block basis with bounded dimension M

$$\{l_{p-1}, \dim = M\} \otimes \{s, \dim = 4\} \Rightarrow \{l_p, \dim = M\}$$

$$|l_p\rangle = \sum_{l_{p-1}s} O_{l_{p-1}s,l_p} |l_{p-1}\rangle \otimes |s\rangle \qquad \mathbf{O} \ldots 4M \times M \text{ renorm. matrix}$$

Two-site DMRG algorithm

- Determinant representation of many-body basis is not stored, rather matrix representations of second-quantized operators needed for $H \cdot \psi$
- Notice that due to truncation (in-completeness of many-body basis)

$$(a^{\dagger}_{p\uparrow} a_{q\downarrow})_{\alpha\beta} \neq \sum_{\gamma} (a^{\dagger}_{p\uparrow})_{\alpha\gamma} (a_{q\downarrow})_{\gamma\beta}$$

- Due to efficient treatment of intermediates, no need for four-index entities
- Pre-summation:

$$\mathcal{A}^{\uparrow\uparrow}_{rs} = \sum_{pq \in \text{left}} v_{pqrs} a^{\dagger}_{p\uparrow} a^{\dagger}_{q\uparrow}, \qquad rs \notin \text{left}$$

$$H^{\uparrow\uparrow\uparrow\uparrow}_{\text{int}} \ni \sum_{\substack{pq \in \text{left} \\ rs \notin \text{left}}} v_{pqrs} a^{\dagger}_{p\uparrow} a^{\dagger}_{q\uparrow} a_{r\uparrow} a_{s\uparrow} = \sum_{rs \notin \text{left}} \mathcal{A}^{\uparrow\uparrow}_{rs} a_{r\uparrow} a_{s\uparrow}.$$

⇒ at most two-index operators

Two-site DMRG algorithm

- Projecting Schrödinger equation onto $\{l\} \otimes \{s_l\} \otimes \{s_r\} \otimes \{r\}$

$$|\Psi\rangle = \sum_{l s_l s_r r} \psi_{l s_1 s_2 r} \, |l\rangle \otimes |s_l\rangle \otimes |s_r\rangle \otimes |r\rangle$$

$$n_\uparrow(l) + n_\uparrow(s_l) + n_\uparrow(s_r) + n_\uparrow(r) = n_\uparrow^{\text{tot}}$$
$$n_\downarrow(l) + n_\downarrow(s_l) + n_\downarrow(s_r) + n_\downarrow(r) = n_\downarrow^{\text{tot}}$$

- Hamiltonian has a tensor product structure:

$$H = \sum_\alpha H_l^{(\alpha)} \otimes H_{s_l}^{(\alpha)} \otimes H_{s_r}^{(\alpha)} \otimes H_r^{(\alpha)}$$

- Since single site operators are due to symmetry reasons scalars:

$$\psi_{l s_1 s_2 r} \Rightarrow \psi_{lr} \equiv \mathbf{C}$$
$$H\,|\psi\rangle \Rightarrow \sum_\alpha f_\alpha \mathbf{H}_l^{(\alpha)} \cdot \mathbf{C} \cdot (\mathbf{H}_r^{(\alpha)})^{\mathrm{T}}$$

- Diagonalization of H by means of iterative solvers like Davidson or Lanczos

Renormalization with truncation

$$\{\phi_{\text{left}}\}_p \otimes \{\phi_{\text{site}}\}_{p+1} \Rightarrow \{\phi_{\text{left}}\}_{p+1}$$

- Truncation pushes the (bond) dimension from $M \cdot 4$ back to M
- Formation of a reduced density matrix of the enlarged Left (Right) block

$$\mathbf{D}_{\text{Left}} = \mathbf{c}\mathbf{c}^\dagger \qquad \text{where} \quad \mathbf{c} = \psi_{(ls_1)(s_2r)}$$

  and form the *rectangular* transformation matrix $\mathbf{O}$ from M eigenvectors corresponding to the largest eigenvalues
- All the operators $\{\mathbf{H}_i\}$ are transformed to the new basis $\{\phi_{\text{left}}\}_{p+1}$

$$\tilde{\mathbf{H}}_i = \mathbf{O}^\dagger \mathbf{H}_i \mathbf{O}$$

Equivalence of SVD and RDM approaches

$$
\begin{aligned}
|\Psi\rangle &= \sum_{ij} \Psi_{ij} |i\rangle_L |j\rangle_R \\
&= \sum_{ij} \sum_{a} U_{ia} D_{aa} V^*_{ja} |i\rangle_L |j\rangle_R \\
&= \sum_{a} d_a \Big(\sum_{i} U_{ia} |i\rangle_L \Big) \Big(\sum_{j} V^*_{ja} |j\rangle_R \Big) \\
&= \sum_{a=1}^{r} d_a |a\rangle_L |a\rangle_R
\end{aligned}
$$

$$
\begin{aligned}
\rho_L &= tr_R(\rho) = tr_R |\Psi\rangle \langle\Psi| \\
&= \sum_{a=1}^{r} \omega_a |a\rangle_L \langle a|_L \qquad \omega_a = d_a^2
\end{aligned}
$$

- Diagonal form
- ρ_L anf ρ_R share the spectrum
- **U** formed by eigenvectors of ρ_L

$$\sum_{a=1}^{r} \omega_a = 1$$

$\chi = 1 - \sum_{a=1}^{r'} \omega_a \ldots$ truncation error, e.g. $10^{-5}, 10^{-6}$

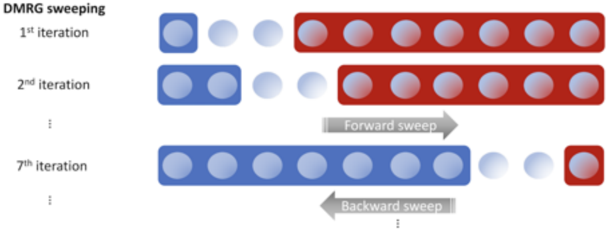
Renormalization produces MPS wave function

$$
\begin{aligned}
|\phi_{p+1}\rangle &= \sum O_{(p\ \ i_{p+1}),p+1} \, |\phi_p\rangle \otimes |i_{p+1}\rangle \qquad \text{where} \quad |i_{p+1}\rangle \in \{|0\rangle\,, |{\downarrow}\rangle\,, |{\uparrow}\rangle\,, |{\downarrow\uparrow}\rangle\} \\
&= \sum A^{i_{p+1}}_{p,p+1} \, |\phi_p\rangle \otimes |i_{p+1}\rangle \\
&= \sum A^{i_p}_{p-1,p} \cdot A^{i_{p+1}}_{p,p+1} \, |\phi_{p-1}\rangle \otimes |i_p\rangle \otimes |i_{p+1}\rangle \\
&= \sum A^{i_1}_1 \cdots A^{i_p}_{p-1,p} \cdot A^{i_{p+1}}_{p,p+1} \, |i_1\rangle \otimes \ldots \otimes |i_p\rangle \otimes |i_{p+1}\rangle
\end{aligned}
$$

- **A** matrices are reshapes of **O** matrices!

Two-site DMRG algorithm scaling

DMRG algorithm recap:



QC-DMRG scaling

$$\mathcal{O}(M^3k^3) + \mathcal{O}(M^2k^4)$$

- k . . . number of molecular orbitals, $\mathcal{O}(10)$
- M . . . bond dimension, $\mathcal{O}(1000)$

Entanglement entropies

$$\rho_L \ldots \text{info about L} \leftrightarrow \text{R interaction} \quad \Rightarrow \quad S = -\text{tr}\rho_L \ln \rho_L \ldots \text{entanglement entropy}$$

- Single-orbital entropy (S_i): entanglement between a given molecular orbital and the rest

$$\rho_i = \text{tr}_{\forall j \neq i}\rho \qquad S_i = -\text{tr}\rho_i \ln \rho_i$$

- Can be employed for selection of the active space
- Two-orbital entropy (S_{ij}): entanglement between a given orbital pair and the rest

$$\rho_{ij} = \text{tr}_{\forall k \neq i,j}\rho \qquad S_{ij} = -\text{tr}\rho_{ij} \ln \rho_{ij}$$

- Mutual information (I_{ij}): correlation between two orbitals i and j when embedded in the whole system

$$I_{ij} = S_i + S_j - S_{ij}$$

- Can be employed for orbital ordering optimization
- S_i and S_{ij} (and I_{ij}) can be calculated *efficiently from MPS*

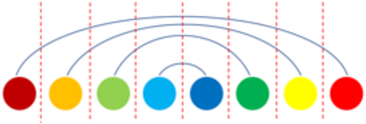
Orbital ordering

- Proper ordering of molecular orbitals on a 1D lattice is in the hearth of *efficient* DMRG - huge impact on accuracy/convergence!
- In order to minimize an error of truncation, the highly entangled orbitals should be as close as possible and located in the center of a lattice.

Good ordering

- We cut at most one entanglement bond
- ⇒ low truncation error

Bad ordering



- We cut the same bond many times
- ⇒ huge truncation error

- Pairwise entanglement (more precissely correlation) is described by mutual information I_{ij}.
- d_{ij} . . . distance of two sites: $d_{ij} = |i - j|$.
- Our aim is to minimize cost functions of the following form:

$$\text{cost}_\eta = \sum_{ij} I_{ij} d_{ij}^\eta$$

Orbital ordering

- Brute for approach for optimization is certainly not feasable - factorial cost!
- For $\eta = 2$, concepts from spectral graph theory can be employed:
- Graph: orbitals (sites) = vertices, I_{ij} = edge weights.
- It turns out that solving the eigenvalue problem of a discrete graph Laplacian corresponds to cost_2 minimization

$$L_{ij} = \delta_{ij} D_{ii} - I_{ij} \qquad D_{ii} = \sum_j I_{ij}$$

- The second eigenvector (so called Fiedler vector) provides the optimal ordering.
- General cost_η can be minimized using *genetic algorithms*.
- It turns out that I_{ij} from cheap approximate calculations with small D works excellent!

Mutual information for bonding analysis

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On-Surface Strain-Driven Synthesis of Nonalternant Non-Benzenoid Aromatic Compounds Containing Four- to Eight-Membered Rings

Benjamin Mallada,[†] Bruno de la Torre,[*,†] Jesús I. Mendieta-Moreno, Dana Nachtigallová,[*] Adam Matěj, Mikulas Matoušek, Pingo Mutombo, Jiri Brabec, Libor Veis,[*] Timothée Cadart, Martin Kotora,[*] and Pavel Jelínek[*]

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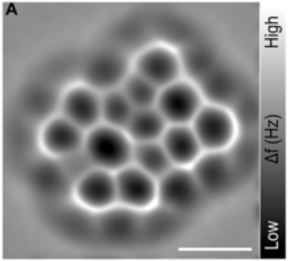
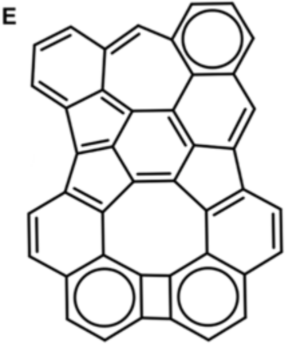
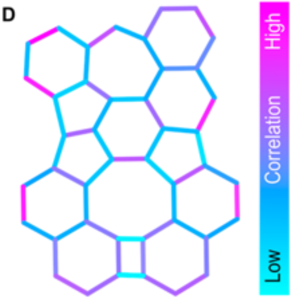
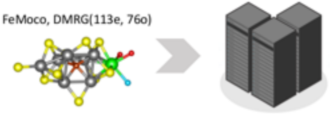






MoLMPS scalable QC-DMRG code

- Motivated by large-scale DMRG applications and accessibility of supercomputers, we have developed the scalable quantum chemical DMRG implementation



MOLMPS features

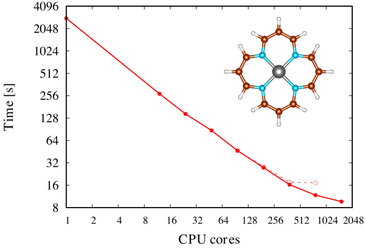
- Highly templated C++ code, flexible in Hamiltonian definition: Hubbrad-like, RHF, UHF, relativistic (4c)
- Low level lightweight tensor library allowing global memory storage
- Post-DMRG features: CASCCF, tailored CC, AC
- Interfaced to NWChem, Orca

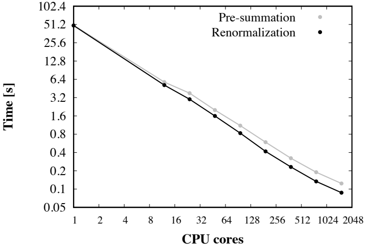
J. Brabec, J. Brandejs, K. Kowalski, S. Xantheas, Ö. Legeza, and L. V., *J. Comp. Chem.* **2021**, 42, 534–544.

MolMPS scaling tests

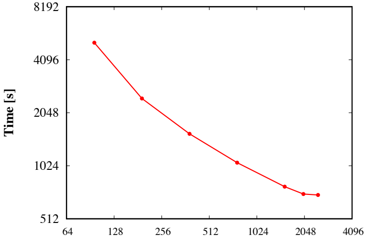
- Fe(II)-porphyrin model, CAS(32,34), left - Davidson, right Renormalization

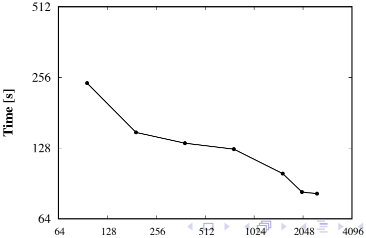
$M = 2048$, local data model





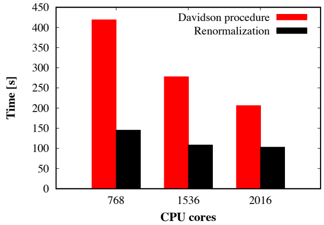
$M = 8192$, global data model

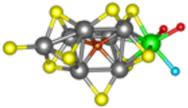




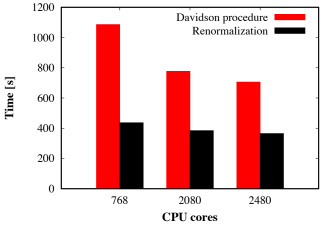
scaling tests

π-conjugated system, CAS(63, 63), $M = 4096$





FeMoco cluster, CAS(113, 76)*, $M = 6000$



*https://github.com/zhendongli2008/Active-space-model-for-FeMoco

J. Brabec, J. Brandejs, K. Kowalski, S. Xantheas, Ö. Legeza, and L. V., *J. Comp. Chem.* **2021**, 42, 534–544.

Post-DMRG

- DMRG-SCF:
- Replacing FCI by DMRG in CASSCF orbital optimization
- The simplest case - *decoupled* optimization of MPS and MO coefficients

$$\text{initial orbitals} \Rightarrow h_{pq}, v_{pqrs} \Rightarrow \text{DMRG: } \gamma_{pq}, \Gamma_{pqrs} \Rightarrow \text{orbital rotation} \Rightarrow \text{new set of } h_{pq}, v_{pqrs} \ldots$$

- Dynamical electron correlation:
- DMRG can treat dozens of active orbitals, but usually not the full orbital space
- Missing out-of-CAS dynamical electron correlation - important for chemical accuracy (1 kcal/mol)
- DMRG-NEVPT2, DMRG-TCCSD, DMRG-AC

Dynamical correlation extensions

- DMRG active space in spite of being large usually cannot be the full space
- DMRG active space: tens of orbitals, full space: hundreds of orbitals
- To achieve chemical accuracy (1 kcal/mol) methods for computation of the missing dynamical correlation are necessary!
- Most of the existing methods (e.g. DMRG-NEVPT2) require higher-body RDMs $\Gamma^{(n)}$
- Recently, we have presented/tested two methods, which avoid this problem

1. Tailored coupled clusters: DMRG-TCCSD(T) (plus DLPNO)
2. Adiabatic connection: DMRG-SCF-AC0

L. V., A. Antalík, J. Brabec, F. Nesse, Ö. Legeza, J. Pittner, *J. Phys. Chem. Lett.* **2016**, 7, 4072.

P. Beran, M. Matoušek, M. Hapka, K. Pernal, L. V., *J. Chem. Theor. Comput.*, **2021**, 17, 7575.

Tailored coupled clusters

- Essentially single reference theory
- Split-amplitude ansatz

$$|\Psi_{\mathrm{TCC}}\rangle = e^{\mathcal{T}}\,|\Psi_{\mathrm{ref}}\rangle = e^{\mathcal{T}^{\mathrm{ext}}+\mathcal{T}^{\mathrm{CAS}}}\,|\Psi_{\mathrm{ref}}\rangle$$

- $\mathcal{T}^{\mathrm{CAS}}$
  - amplitudes extracted from DMRG (CASCI) calculation
  - frozen during CC calculation
  - account for static correlation
- $\mathcal{T}^{\mathrm{ext}}$
  - determined through the usual CC
  - account for dynamic correlation

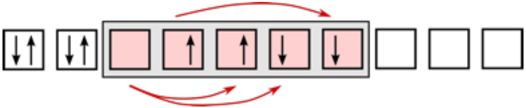
$$\begin{aligned} |\Psi_{\mathrm{TCCSD}}\rangle &= e^{\left(\mathcal{T}_1^{\mathrm{ext}}+\mathcal{T}_2^{\mathrm{ext}}\right)}\,e^{\left(\mathcal{T}_1^{\mathrm{CAS}}+\mathcal{T}_2^{\mathrm{CAS}}\right)}\,|\Psi_{\mathrm{ref}}\rangle \\ &\approx e^{\left(\mathcal{T}_1^{\mathrm{ext}}+\mathcal{T}_2^{\mathrm{ext}}\right)}\,|\Psi_{\mathrm{CASCI}}\rangle \end{aligned}$$

- Requires minimal modifications of the CC code

T. Kinoshita, O. Hino, and R. J. Bartlett, *J. Chem. Phys.* **2005**, 123, 074106.

CCSD tailored by MPS wave functions

- Small active space DMRG calculation



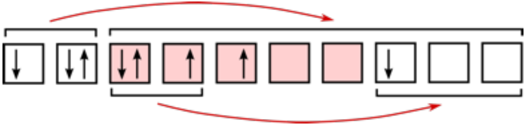
- Acquisition of CI coefficients by efficient contraction of MPS matrices

$$|\Psi_{\mathrm{MPS}}\rangle = \sum_{\{n\}} \mathbf{A}^{n_1}\mathbf{A}^{n_2}\cdots\mathbf{A}^{n_k}|n_1 n_2 \cdots n_k\rangle$$

- Calculation of CAS amplitudes

$$T_1^{\mathrm{CAS}} = C_1 \qquad T_2^{\mathrm{CAS}} = C_2 - \frac{1}{2}(C_1)^2$$

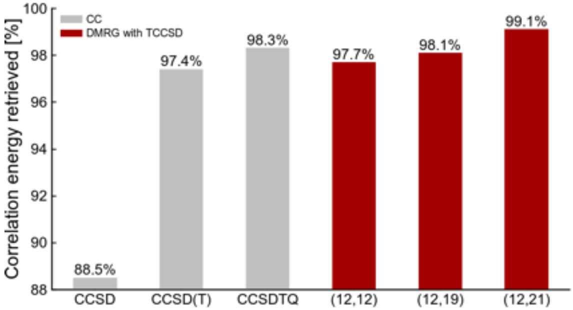
- CCSD calculation for T_1^{ext} and T_2^{ext}



  - Implemented in ORCA

DMRG-TCCSD performance: Cr_2

- One of the most notorious and demanding systems
- Excellent level of theory for dymamical and static correlation required
- Single-point calculation at 1.5 Å, Ahlrichs' SV basis set → FCI energy available



L. V., A. Antalík, J. Brabec, F. Nesse, Ö. Legeza, J. Pittner, *J. Phys. Chem. Lett.* **2016**, 7, 4072.

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