DMRG-SCF study of the singlet, triplet, and quintet states of oxo-Mn(Salen)

Sebastian Wouters,[1] Thomas Bogaerts,[1,2] Pascal Van Der Voort,[2] Veronique Van Speybroeck,[1] and Dimitri Van Neck[1]

[1]Center for Molecular Modelling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium
[2]Center for Ordered Materials, Organometallics and Catalysis, Ghent University, Krijgslaan 281 (S3), 9000 Gent, Belgium

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1. Density matrix renormalization group [DMRG]

- Exact wavefunction for L orbitals grows exponentially fast [4^L]:

$$|\Psi\rangle = \sum_{\{n_{j\sigma}\}} C^{n_{1\uparrow}n_{1\downarrow}n_{2\uparrow}\ldots n_{L\downarrow}} \left(\hat{a}^\dagger_{1\uparrow}\right)^{n_{1\uparrow}} \left(\hat{a}^\dagger_{1\downarrow}\right)^{n_{1\downarrow}} \left(\hat{a}^\dagger_{2\uparrow}\right)^{n_{2\uparrow}} \ldots \left(\hat{a}^\dagger_{L\downarrow}\right)^{n_{L\downarrow}} |-\rangle$$

- DMRG uses a matrix product state [MPS] with $\dim(\alpha_k) = \min(4^k, 4^{L-k}, D)$:

$$C^{n_{1\uparrow}n_{1\downarrow}n_{2\uparrow}n_{2\downarrow}n_{3\uparrow}n_{3\downarrow}\ldots n_{L\uparrow}n_{L\downarrow}} \approx \sum_{\{\alpha_k\}} A[1]^{n_{1\uparrow}n_{1\downarrow}}_{\alpha_1}\ A[2]^{n_{2\uparrow}n_{2\downarrow}}_{\alpha_1;\alpha_2}\ A[3]^{n_{3\uparrow}n_{3\downarrow}}_{\alpha_2;\alpha_3}\ \ldots\ A[L]^{n_{L\uparrow}n_{L\downarrow}}_{\alpha_{L-1}}$$

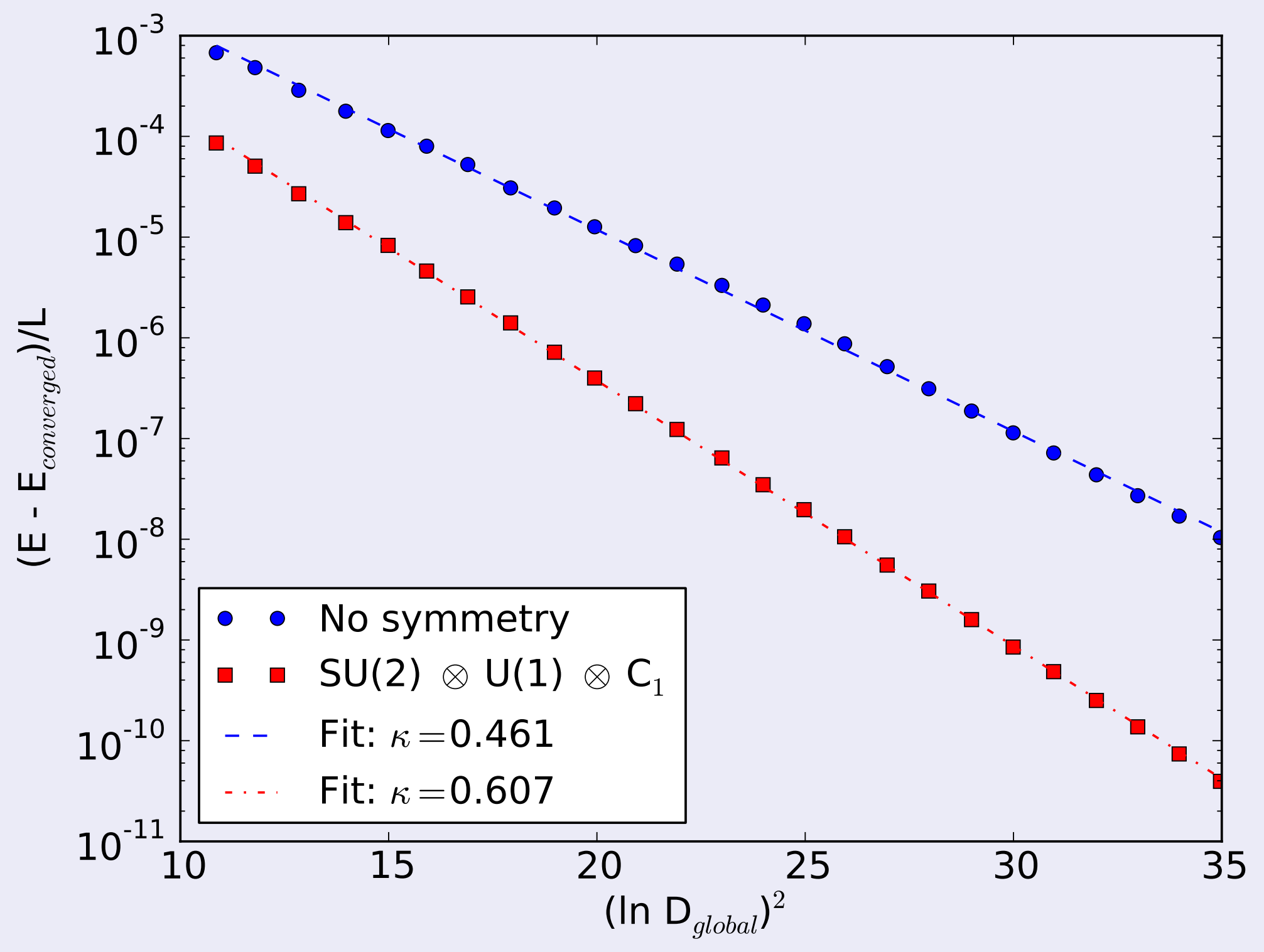
- Virtual dimension D controls the accuracy
- Simultaneous optimization of two neighbouring MPS site tensors can be formulated as a numerically stable standard Hermitian eigenvalue problem
- DMRG sweeps through the chain back and forth while locally optimizing
- Numerically exact results in active spaces up to (40e, 40o)

2. CheMPS2

- Quantum chemistry Hamiltonians (often) have
  - SU(2) spin symmetry
  - U(1) particle-number symmetry
  - Molecular point-group symmetry P [in CheMPS2 P $\in \{C_1, C_i, C_2, C_s, D_2, C_{2v}, C_{2h}, D_{2h}\}$]
- Block-sparse and *reduced* MPS site tensors

$$A^{(ss^zNI)}_{(j_Lj^z_LN_LI_L\alpha_L);(j_Rj^z_RN_RI_R\alpha_R)} = \langle j_Lj^z_Lss^z \mid j_Rj^z_R\rangle\, \delta_{N_L+N,N_R}\delta_{I_L\otimes I,I_R}\, T^{(sNI)}_{(j_LN_LI_L\alpha_L);(j_RN_RI_R\alpha_R)}$$

reduce the computational cost significantly



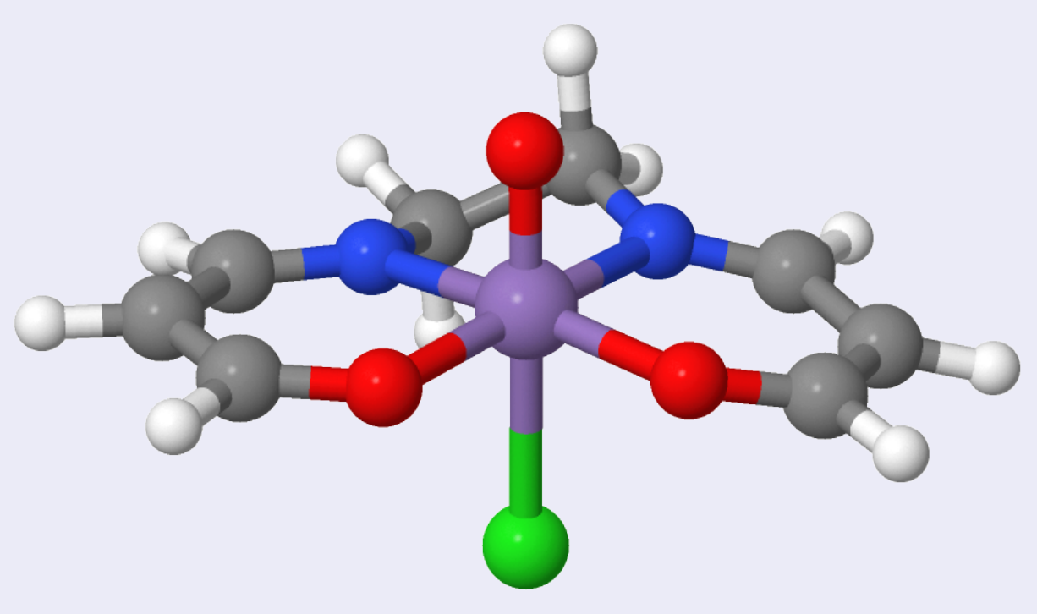
Hubbard model OBC, 36 sites, 22 electrons, spin 0, $U = 6$

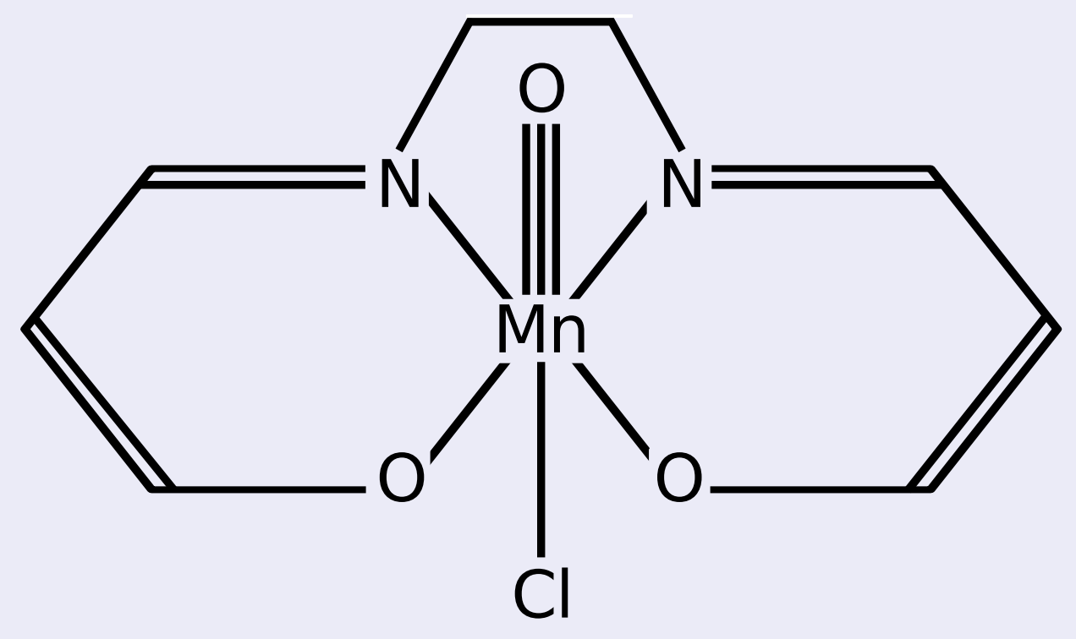
D_{global} is the *reduced* virtual dimension for SU(2) $\otimes$ U(1) $\otimes$ C$_1$

$\mathbb{C}he[\mathcal{M}][\mathcal{P}][\mathcal{S}]$ 2

- CheMPS2 is free open-source software [1]
  - GNU General Public License v2.0
  - https://github.com/SebWouters/CheMPS2
  - With augmented Hessian Newton-Raphson DMRG-SCF loop

3. Oxo-Mn(Salen): Introduction





- Oxo-Mn(Salen) is a reaction intermediate in the enantioselective epoxidation of unfunctionalized olefins with the Mn(Salen) catalyst
- Relevant active space & relative stability singlet, triplet, and quintet?

ΔE [kcal/mol]	CASSCF(12e,10o) 6-31G* [2]	CASSCF(12e,10o) 6-31G* [3]	GASSCF(18e,17o) ANO-RCC-VDZP+DKH2 [4]
E(^3A) - E(^1A)	-2.9	0.26	-3.6
E(^5A) - E(^1A)	39.7	42.88	

- Relative shifts due to
  - Relativistic corrections: ~ 0.2 kcal/mol [2][3]
  - Dynamic correlation: ~ 5 kcal/mol [2][4]
  - Basis set choice: ~ 1.3 kcal/mol [3]
- Singlet → triplet corresponds to $3d_{x^2-y^2} \rightarrow \pi^*_1(O_{ax})$ [2][3] [see Section 5]
- Triplet → quintet corresponds to $\pi_2(O_{ax}) \rightarrow \pi^*_2(O_{ax})$ [2][3]

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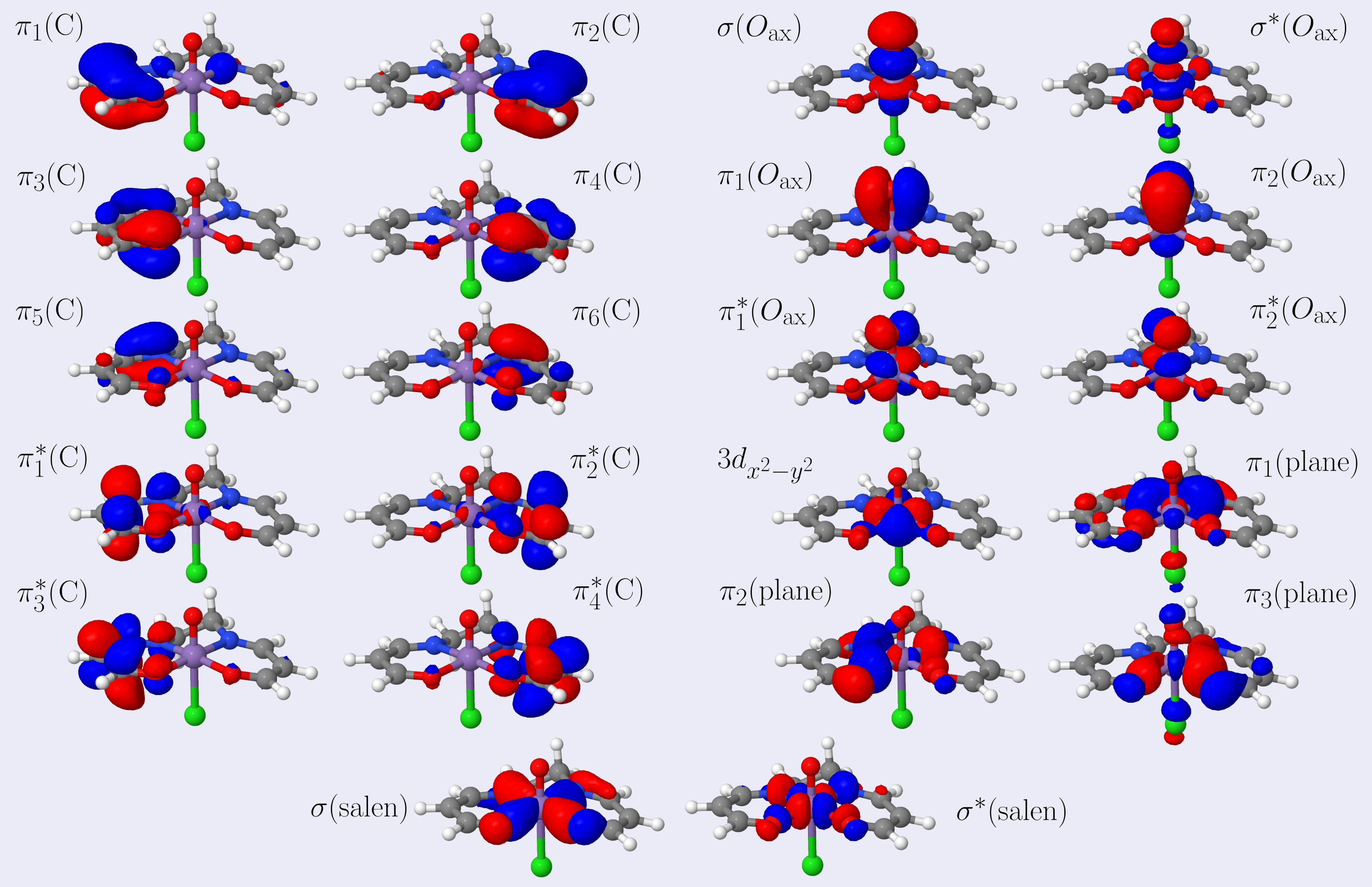
4. Our approach

- RHF molecular orbitals in 3 double ζ basis sets with polarization functions: 6-31G* ; cc-pVDZ ; ANO-RCC-VDZP+DKH2
- Normal approach: localization + manual selection of the active space [2][3][4]
- Orbitals with occupations close to 0 or 2 lie close to Fermi surface → approximate DMRG calculation in large window around the Fermi level
- For the singlet, the same (28e, 22o) active space is obtained for the 3 basis sets by truncating the approximate active spaces to 0.015 ≤ NOON ≤ 1.985
- When the DMRG-SCF gradient is sufficiently small for the singlet calculations, separate DMRG-SCF calculations are started for the triplet and quintet with this active space

5. Results

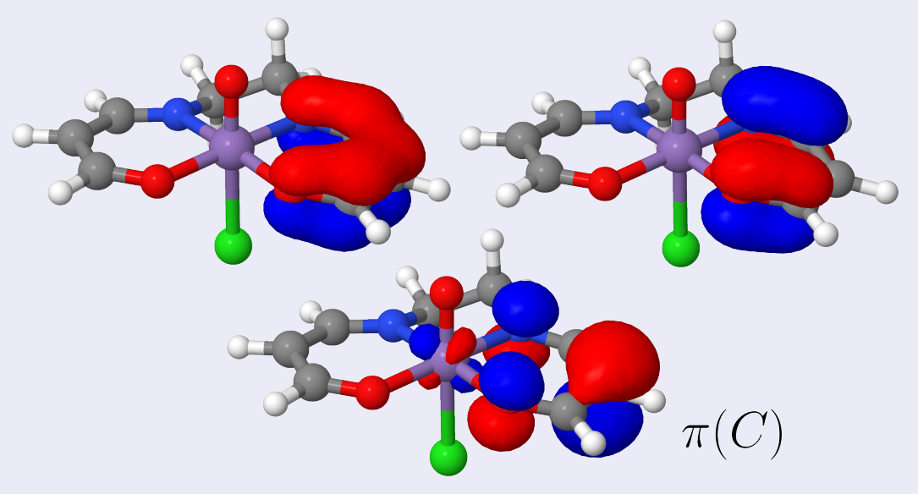
Converged DMRG-SCF(28e, 22o)/ANO-RCC-VDZP+DKH2 singlet active space



Corresponding occupation numbers for the singlet, triplet, and quintet

	^1A	^3A	^5A		^1A	^3A	^5A
$\pi_1(C)$	1.99	1.99	1.99	$\sigma(O_{ax})$	1.91	1.90	1.89
$\pi_2(C)$	1.99	1.99	-	$\sigma^*(O_{ax})$	0.11	0.11	0.12
$\pi_3(C)$	1.96	1.96	1.96	$\pi_1(O_{ax})$	1.86	1.77	1.94
$\pi_4(C)$	1.96	1.96	-	$\pi_2(O_{ax})$	1.85	1.95	1.94
$\pi_5(C)$	1.94	1.94	1.94	$\pi^*_1(O_{ax})$	**0.17**	**1.04**	**1.05**
$\pi_6(C)$	1.94	1.94	-	$\pi^*_2(O_{ax})$	**0.17**	**0.24**	**1.04**
$\pi^*_1(C)$	0.07	0.07	0.07	$3d_{x^2-y^2}$	**1.97**	**1.00**	**1.00**
$\pi^*_2(C)$	0.07	0.07	0.11	π_1(plane)	1.99	1.99	1.99
$\pi^*_3(C)$	0.03	0.03	0.03	π_2(plane)	1.98	1.98	1.99
$\pi^*_4(C)$	0.03	0.03	0.06	π_3(plane)	1.98	1.98	1.99
σ(salen)	1.95	1.93	1.98	σ^*(salen)	0.08	0.10	0.07

For the quintet, the natural orbitals $\pi_2(C)$, $\pi_4(C)$, and $\pi_6(C)$ are rotated



with occupation numbers (top left, top right, $\pi(C)$) = (1.93, 1.89, **1.01**).

The triplet → quintet transition hence corresponds to $\pi(C) \rightarrow \pi^*_2(O_{ax})$.
The bond order of the axial oxygen atom in the quintet is hence 2, and not 1.5.

DMRG-SCF(28e, 22o) energies [extrapolated with discarded weight]

	6-31G*	cc-pVDZ	ANO-RCC-VDZP+DKH2
E(^1A) [Hartree]	-2251.5498	-2251.7509	-2261.0226
E(^3A) [Hartree]	-2251.5578	-2251.7593	-2261.0290
E(^5A) [Hartree]	-2251.5268	-2251.7316	-2260.9994
E(^3A) - E(^1A) [kcal/mol]	-5.0	-5.3	-4.0
E(^5A) - E(^1A) [kcal/mol]	14.5	12.1	14.5

References

[1] Wouters, Poelmans, Ayers, and Van Neck, *Comput. Phys. Commun.* **185**, 1501-1514 (2014)
[2] Ivanic, Collins, and Burt, *J. Phys. Chem. A* **108**, 2314-2323 (2004)
[3] Sears and Sherrill, *J. Chem. Phys.* **124**, 144314 (2006)
[4] Ma, Li Manni, and Gagliardi, *J. Chem. Phys.* **135**, 044128 (2011)