

# Modern Multi-Determinantal Total-State Wave Functions and their Relation to One-Electron Pictures like Valence Bond Theory

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- General Theory
  - Solution of the Schrödinger equation
  - Single-particle and many-particle states
  - Density matrices
- Ansätze to approximate the FCI wave function
  - Conventional approaches
  - Unconventional approaches: tensor network states
- Extraction of local quantities
- Case study: spin densities

## The molecular Schrödinger equation

$$\hat{\mathcal{H}}\Psi = (\hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{NN} + \hat{V}_{eN})\Psi = E\Psi$$

- A molecular structure is *a priori* not defined
- For a general solution: do not make assumptions on particle properties
- ⇒ General wave function and distribution functions
- ⇒ Molecular structures can be derived from the mass distribution functions

E. Mátyus, J. Hutter, U. Müller-Herold, M. Reiher, *J. Chem. Phys.* **2011**, *135*, 204302.

E. Mátyus, J. Hutter, U. Müller-Herold, M. Reiher, *Phys. Rev. A* **2011**, *83*, 052512.

- Practical Solution: Born–Oppenheimer approximation and solve only electronic Schrödinger equation for fixed nuclear coordinates

## The electronic Schrödinger equation

$$\hat{\mathcal{H}}_{\text{el}}\Psi_{\text{el}} = E_{\text{el}}\Psi_{\text{el}}$$

with target quantity  $E_{\text{el}}$

- Solution: expand  $\Psi_{\text{el}}$  in a complete many electron basis set ( $\equiv$  electronic configurations  $\Phi_I$ )

$$\Psi_{\text{el}} = \sum_{I=0}^m C_I \hat{\mathcal{A}}(\phi_{I_1}(\mathbf{r}_1)\phi_{I_2}(\mathbf{r}_2)\dots\phi_{I_N}(\mathbf{r}_N)) = \sum_{I=0}^m C_I \Phi_I$$

with expansion coefficients  $C_I$ , antisymmetrizer  $\hat{\mathcal{A}}$  and a set of one-particle functions  $\{\phi_{I_i}\}_{i=1}^k$  from which the Slater determinant  $\Phi_I$  can be constructed

$\Rightarrow$  Full configuration interaction solution ( $m \rightarrow \infty$ )

- 1 For practical purposes,  $m$  should be **as small as possible**:

multi-determinantal result ( $m$  finite)

vs.

single-determinant independent particle model picture  
( $m = 1$ , easy interpretable, Koopmans' theorem)

- 2 Choice of **one-particle functions**:

orthogonal orbitals (MO)

vs.

nonorthogonal orbitals (VB)

Many-electron basis functions (determinants) constructed from:

- 1 non-orthogonal local orbital basis (VB)  
⇒ small number of configurations, technically demanding
- 2 orthogonal, local orbitals  
⇒ small number of configurations, technically simple
- 3 orthogonal, non-local orbitals (MO)  
⇒ large number of configurations, technically simple

# Relation total state $\iff$ single-particle state

One-electron density matrix with elements  $D_{pq}$

$$D_{pq} = \langle \Psi | a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta} | \Psi \rangle$$

- The diagonal elements  $D_{pp}$  are the **orbital occupation numbers**
- Restricted to the interval  $0 \leq D_{pp} \leq 2$
- Particularly useful set of occupation numbers: *natural-orbitals occupation numbers*  $n_p$  obtained by diagonalizing  $\mathbf{D}$

$$\mathbf{D} = \mathbf{U}\mathbf{n}\mathbf{U}^\dagger \quad 0 \leq n_p \leq 2, \quad \sum_p n_p = N$$

- The eigenvectors  $\mathbf{u}_p$  of  $\mathbf{D}$  form the *natural orbitals*
- Example: bonding analysis in terms of effective bond order  
B. O. Roos, A. C. Borin, L. Gagliardi, *Angew. Chem. Int. Ed. Engl.* **2007**, 46, 1469.

$\Rightarrow$  All orbitals contribute

# Density matrices

- The expectation value of  $\hat{\mathcal{H}}_{el}$  in second quantized form

$$\hat{\mathcal{H}}_{el} = \sum_{pq} \sum_{\sigma} t_{pq} a_{p\sigma}^{\dagger} a_{q\sigma} + \frac{1}{2} \sum_{pqrs} \sum_{\sigma\tau} g_{pqrs} a_{p\sigma}^{\dagger} a_{r\tau}^{\dagger} a_{s\tau} a_{q\sigma}$$

for some normalized reference state  $\Psi$  reads

$$\langle \Psi | \hat{\mathcal{H}}_{el} | \Psi \rangle = \sum_{pq} t_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} d_{pqrs}$$

with the one-electron orbital density matrix elements  $D_{pq}$  and the *two-electron orbital density matrix* elements  $d_{pqrs}$

$$d_{pqrs} = \langle \Psi | \sum_{\sigma\tau} a_{p\sigma}^{\dagger} a_{r\tau}^{\dagger} a_{s\tau} a_{q\sigma} | \Psi \rangle$$

⇒ All information is contained in the density matrices  $D_{pq}$  and  $d_{pqrs}$



# Density matrices: orbital $\iff$ spin-orbital basis

## One-electron density matrix in spin-orbital basis

$$D_{pq} = \bar{D}_{p\alpha,q\alpha} + \bar{D}_{p\beta,q\beta}$$

where the overbars are used for the density matrix elements in the spin-orbital basis

- The natural-orbital occupation numbers are obtained by diagonalizing  $\bar{\mathbf{D}}$

$$\bar{\mathbf{D}} = \mathbf{U}\bar{\mathbf{n}}\mathbf{U}^\dagger \quad 0 \leq \bar{n}_p \leq 1, \quad \sum_p \bar{n}_p = N$$

- Similarly, the two-electron density matrix can be resolved for each electron spin:

## Two-electron density matrix in spin-orbital basis

$$d_{pqrs} = \bar{d}_{p\alpha,q\alpha,r\alpha,s\alpha} + \bar{d}_{p\beta,q\beta,r\beta,s\beta} + \bar{d}_{p\alpha,q\alpha,r\beta,s\beta} + \bar{d}_{p\beta,q\beta,r\alpha,s\alpha}$$

# Ansätze to approximate the FCI wave function

# Conventional approaches with non-optimized orbitals

Restrict the many-electron basis  $\{\Phi_I\}$  to a set of *preselected* configurations

- Truncated CI wave function (single reference):
  - Restrict FCI wave function to contain only single, double, triple, ... excitations with respect to a reference configuration  $|\Phi_0\rangle$

## CISD wave function

$$|\Psi_{\text{el}}^{\text{CISD}}\rangle = |\Psi_0\rangle + \sum_i^{\text{occ}} \sum_a^{\text{unocc}} C_i^a a_a^\dagger a_i |\Psi_0\rangle + \sum_{j<i}^{\text{occ}} \sum_{b<a}^{\text{unocc}} C_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |\Psi_0\rangle$$

- Truncated coupled cluster (CC) (single reference):
  - Exponential Ansatz for the wave function with truncated cluster operator  $\hat{T}$

## CC wave function

$$|\Psi_{\text{el}}^{\text{CC}}\rangle = \exp(\hat{T})|\Psi_0\rangle, \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$$

where  $\exp(\hat{T}) = 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots$

# Conventional Approaches with non-optimized orbitals

- Customized approaches, e.g., difference dedicated CI (DDCI):
  - Variational method specifically designed to calculate energy differences (optical transitions, ionization potentials, electron affinities, . . .)
  - FCI space is rationally truncated by means of second order perturbation theory (PT) considerations
    - ⇒ Include only configurations of interest
  - ① Choose a minimal model space ( $\equiv$  minimal active space including orbitals relevant for the transition)
  - ② Include external correlations (quasi-degenerate PT) up to 2nd order
  - ③ Construct CI subspace of active space and single and double excitations involving at least one active orbital
  - ④ Perform diagonalization
- Results depend on the MO basis
  - ⇒ Active orbitals can be improved iteratively (IDDCI)

J. Miralles, O. Castell, R. Caballol, J.-P. Malrieu, *Chem. Phys.* **1993**, *172*, 33.

- Multi-configuration self-consistent field (MCSCF):
  - Choose a truncated CI expansion  $\{\Phi_I\}$
  - Optimize both **expansion coefficients**  $C_I$  and **one-particle functions**  $\{\phi_i\}$  which are used to construct  $\{\Phi_I\}$
- Special case: complete-active-space self-consistent-field (CASSCF):
  - Choose a subspace of one-particle functions  $\{\phi_i\}$  ( $\equiv$  active orbitals) which are occupied by  $N_{\text{active}}$  electrons (active electrons) in the reference wave function  $\Phi_0$
  - Construct the **full CI space** ( $\equiv$  active space) for the orbital subspace
  - Optimize both  **$\{C_I\}$**  and **all  $\{\phi_i\}$**
- Collect effect of neglected virtual orbitals ( $\equiv$  dynamic correlation) through perturbation theory
  - $\Rightarrow$  CASPT2

# Unconventional approaches

- Reduce variational degrees of freedom in FCI wave function expansion, i.e., number of  $C_I$  coefficients  
⇒ Find a more **local notation** of a quantum state
- ① The density matrix renormalization group (DMRG) ansatz by White (1992):

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

G. K.-L Chan, S. Sharma, *Annu. Rev. Phys. Chem.* **2011**, 62, 465.

$$\Psi^{\text{DMRG}} = \sum_{ij} \psi_{ij} |i\rangle \otimes |j\rangle,$$

with expansion coefficients  $\psi_{ij}^{(m)}$  and orthonormal product bases  $\{|i\rangle\}$  and  $\{|j\rangle\}$

- Iterative optimization of reduced-dimensional many-electron basis in a least-square sense
- The DMRG algorithm optimizes a **matrix product state** (MPS)

## 2 MPS:

- Define **projection operators**  $\hat{A}_i[n_i]$  which depend on the local site  $n_i$  and map from one  $m$ -dimensional subspace spanned by  $\{|m_{l-1}\rangle\}$  to another  $m$ -dimensional subspace spanned by  $\{|m_l\rangle\}$
- ⇒ Represent  $\hat{A}_i[n_i]$  by  **$(m \times m)$  matrices**  $A_{m_{l-1}, m_l}^{n_i}$

S. Rommer, S. Östlund, *Phys. Rev. B* **1997**, 55, 2164.

## Mixed-canonical MPS

$$\Psi^{\text{MPS}} = \sum_{\{\mathbf{n}\}} A^{n_1} \dots A^{n_{l-1}} \Psi^{n_l n_{l+1}} A^{n_{l+2}} \dots A^{n_L} |n_1 \dots n_L\rangle,$$

where  $\{\mathbf{n}\}$  is the set of all Slater determinants constructed from  $L$  one-particle states

- ⇒ Number of variational parameters is reduced to  **$4L$  local matrices**

# Relation MPS $\iff$ CI expansion

- $C_I$  coefficients can be reconstructed from the position-dependent transformation matrices and the expansion coefficients:

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

## $C_I$ coefficient corresponding to a Slater determinant $\mathbf{n}$

$$C_{\mathbf{n}} = \sum_{m^S}^m \sum_{m^E}^m \psi_{m^S n_{I+1} n_{I+2} m^E} (A_2[n_2] \dots A_I[n_I])_{n_1; m^S} (A_{I+3}[n_{I+3}] \dots A_{L-1}[n_{L-1}])_{m^E; n_L}$$

- Unfeasible to create the entire basis of the  $N$ -particle Hilbert space
- $C_I$  vector is sparse: only a subspace of the  $N$ -particle Hilbert space is decisive for a reliable representation of the wave function

$\Rightarrow$  Collect only the most important configurations  $\{\tilde{\mathbf{n}}\}$



# Sampling the $N$ -particle Hilbert space: the SRCAS algorithm

## Sampling-reconstruction CAS (SRCAS) routine

- Perform excitation of the type:

$$a_{p_1}^\dagger a_{q_1} a_{p_2}^\dagger a_{q_2} \dots a_{p_i}^\dagger a_{q_i}$$

from a predefined reference (Hartree–Fock) with random numbers

$$i \in \{1, \dots, N\}, \quad p_j, q_j \in \{1, \dots, L\}$$

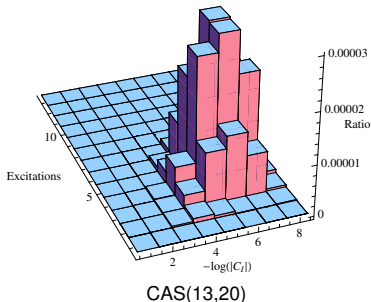
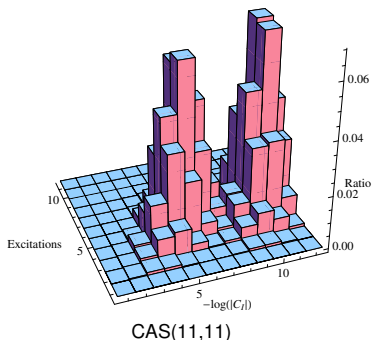
- Number of particles, projected spin, and point-group symmetry are preserved

## Completeness measure (COM) to monitor the accuracy:

$$\text{COM} = 1 - \sum_{\{\tilde{\mathbf{n}}\}} |c_{\{\tilde{\mathbf{n}}\}}|^2$$

# Excitation patterns

- Substitution pattern for predefinition of many-electron basis states
- Example: excitation pattern for CAS(11,11) and CAS(13,20) for  $[\text{FeNO}]^{2+}$  in a point charge environment from DMRG calculations



- A large number of determinants is of little importance (small absolute  $C_I$  coefficient)

# Unconventional approaches

- For an MPS parameterization, the orbital basis must be mapped on a **1-dimensional lattice**
  - ⇒ Quantum information theory (mutual information, single-orbital entropies)
  - ⇒ Correlation is transmitted over the lattice
  - ⇒ MPS state difficult to optimize for a general molecule (long-range correlation, non-localized orbitals)
  - ⇒ Incorporate **non-local correlation in a non-local tensor network ansatz**
- ① Complete-Graph Tensor-Network-States (CGTNS)
  - Replace  $C_I$  coefficient by a network of tensors which connect all orbitals (**pair correlations**)

## CGTN ansatz

$$|\Psi^{\text{CGTN}}\rangle = \sum_{n_1 \dots n_L} \prod_{\alpha} \prod_{\beta \leq \alpha} f_{\alpha\beta}^{n_{\alpha} n_{\beta}} |n_1 \dots n_L\rangle$$

- Optimize CGTN state by a variational Monte Carlo scheme

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

# Unconventional approaches

⇒ Increase flexibility of tensors by

- 1 **higher-order correlators** (three-orbital, four-orbital, etc.)

H. J. Changlani, J. M. Kinder, C. J. Umrigar, G. K.-L. Chan, *Phys. Rev. B* **2009**, *80*, 245116.

- 2 larger **bond dimension** (scalars → matrices)

## 2 Tree-tensor network state (TTNS)

- **Generalization of MPS:**

Consider arbitrary structure of network with different coordination numbers  $z$  per site

- $C_l$  coefficients emerge from the contraction of a set of tensors for each vertex  $m$  of the form

$$[A_m]_{a_1 \dots a_z}^{n_i}$$

- For  $z = 2$ , the one-dimensional MPS is recovered

V. Murg, Ö. Legeza, R. M. Noack, F. Verstraete, *Phys. Rev. B* **2010**, *82*, 205105.

# Extraction of local quantities from multi-reference wave function: Local spin

- **Decomposition** of the expectation value of the total spin-square operator  $\langle \hat{S}^2 \rangle$  into one- and two-electron terms

- 1 Determine spin state of an atom or group of atoms
- 2 Describe magnetic interactions between the atoms

A. E. Clark, E. R. Davidson, *J. Chem. Phys.* **2001**, *115*, 7382.

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{\substack{A,B \\ A \neq B}} \langle \hat{S}^2 \rangle_{AB}$$

- Partitioning into several components is usually not unique

E. Ramos-Cordoba, E. Matito, I. Mayer, P. Salvador, *J. Chem. Theory Comput.* **2012**, *8*, 1270.

- **Two requirements** are important for the decomposition of  $\langle \hat{S}^2 \rangle$ 
  - 1 No spins for covalent systems described by closed-shell singlets
  - 2 Asymptotic values of atomic spins for large distances should be equivalent to the atomic spins of the free atoms

C. Herrmann, M. Reiher, B. A. Hess, *J. Chem. Phys.* **2005**, *122*, 034102.

# Extraction of local quantities from multi-reference wave function: Local spin

$\langle \hat{S}^2 \rangle$  in terms of density matrices in the orbital basis

$$\langle \hat{S}^2 \rangle = \frac{3}{4} \sum_i D_{ii} - \frac{1}{2} \sum_{ik} d_{iikk} - \sum_{ik} d_{ikki}$$

- Rewrite equation in spin-orbital basis and introduce cumulant matrix  $\Gamma_{j\sigma | \sigma'}^{i\sigma k\sigma'}$  ( $\equiv$  correction term if  $d_{pqrs}$  is written in terms of  $D_{pq}$ )
- Partitioning requires knowledge about the second-order density matrix in the **spin-orbital representation**  $\bar{d}_{pqrs}$
- For non-singlet states:  $\bar{d}_{pqrs}$  matrix elements **depend on**  $S_z$  substates

I. Mayer, *Chem. Phys. Lett.* **2009**, 478, 323.

# Extraction of local quantities from multi-reference wave function: Spin-free treatment

- Introduce a spin-free second order density matrix and cumulant matrix  $\Lambda_{pqrs}$  and the effectively unpaired electron matrix  $u_{ij}$

$\langle \hat{S}^2 \rangle$  partitioning in terms of a spin-free treatment

$$\langle \hat{S}^2 \rangle = \frac{1}{2} \sum_i (uS)_{ii} - \frac{1}{2} \sum_{ik} \sum_{jl} (S)_{ij} \Lambda_{jkli} (S)_{kl},$$

given in the atomic orbital basis with overlap matrix elements  $(S)_{ij}$

One-center local spins (trace over redundant indices)

$$\langle \hat{S}^2 \rangle_A = \frac{1}{2} \sum_{i \in A} (uS)_{ii} - \frac{1}{2} \sum_{i,k \in A} \sum_{jl} (S)_{ij} \Lambda_{jkli} (S)_{kl}$$

⇒ One-center and two-center terms are  **$S_z$ -independent**

⇒ Required: **S**, **D** and **d** (all matrices are available)

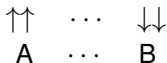
D. R. Alcoba, A. Torre, L. Lain, R.C. Bochicchio, *J. Chem. Theory Comput.* **2011**, *7*, 3560.

# Single-determinant description of multi-determinant cases: broken (spin) symmetry

- To enforce a one-determinant picture may lead in general to breaking symmetries

G. E. Scuseria, C. A. Jimenez-Hoyos, T. M. Henderson, K. Samanta, J. K. Ellis, *J. Chem. Phys.* **2011**, *135*, 124108.

- Typical example: description of antiferromagnetically (or ferromagnetically) coupled states in terms of a Heisenberg coupling model



- Broken symmetry (BS) determinants:  
determinants with certain amount of spin excess on one (metal) atom and the opposite spin excess on other (metal) atoms

L. Noodleman, *J. Chem. Phys.* **1981**, *74*, 5737.



# Single-determinant description of multi-determinant cases: broken (spin) symmetry

- Construction of BS states:

- 1 Chose suitable starting approximation for the orbitals
- 2 Constrained DFT approach

Q. Wu, T. van Voorhis, *Phys. Rev. A* **2005**, *72*, 024502.

I. Rudra, Q. Wu, T. van Voorhis, *J. Chem. Phys.* **2006**, *124*, 024103.

C. Herrmann, M. Podewitz, M. Reiher, *Int. J. Quantum Chem.* **2009**, *109*, 2430.

- ⇒ 'VB-like' description with semi-localized magnetic orbitals (nonorthogonal spatial orbitals)
- ⇒ Extraction of magnetic orbitals for spin-unrestricted calculations not obvious for many-electron systems

# Relation of BS orbitals to magnetic orbitals

- Especially problematic for the calculation of the overlap of BS magnetic orbitals (strong mixing with other orbitals, . . .)
- ⇒ Corresponding orbital transformation (COT) generates new set of orbitals
  - orbitals of  $\alpha$ -set overlap at most with one orbital from the  $\beta$ -set
  - ⇒ BS wave function invariant, but spin-orbitals with largest similarity are paired together:
    - 1 MOs with spatial overlap close to unity (closed-shell orbitals)
    - 2 MOs with spatial overlap very different than zero or unity (VB-like magnetic pairs)
    - 3 If  $M_S > 0$ , additional  $\alpha$  MOs (SOMOs)
- ⇒ COT straightforward to apply to the BS wave function
- ⇒ Interacting non-orthogonal VB-like orbital pairs can be extracted

A. T. Amos, G. G. Hall, *Proc. R. Soc. Lond. A* **1961**, 263, 483.

H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, R. G. Parr *J. Chem. Phys.* **1967**, 47, 1936.

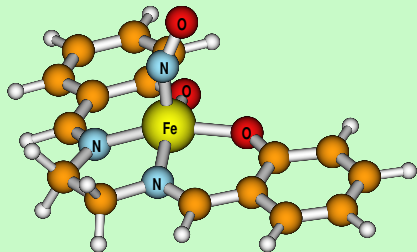
F. Neese, *J. Phys. Chem. Solids* **2004**, 65, 781.

# Case Study:

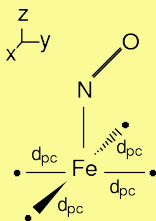
Magnetic open-shell molecules

⇒ spin densities

# Example: $[\text{FeNO}]^{2+}$ model of a salen complex



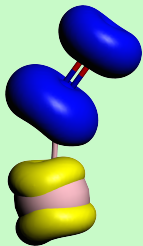
Full complex:  
 $\text{Fe}(\text{salen})(\text{NO})$



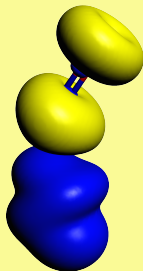
- 4 point charges in  $xy$ -plane at  $d_{\text{pc}} = 1.133 \text{ \AA}$
- Square planar ligand field emulates one-particle states of full complex
- $d_{\text{pc}}$  determines character of wave function

Model complex:  $[\text{FeNO}]^{2+}$

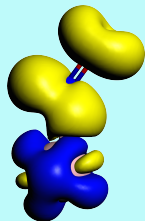
- Spin density difference plots with respect to OLYP



BP86



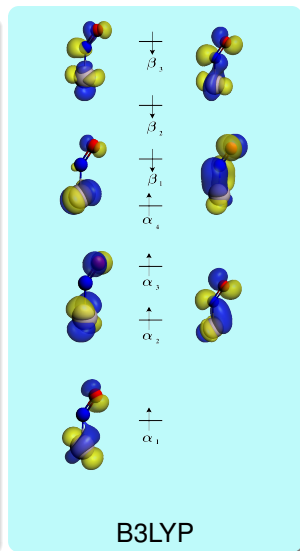
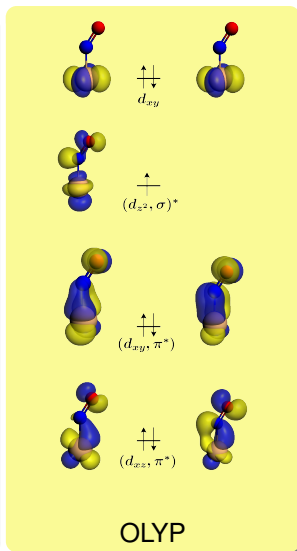
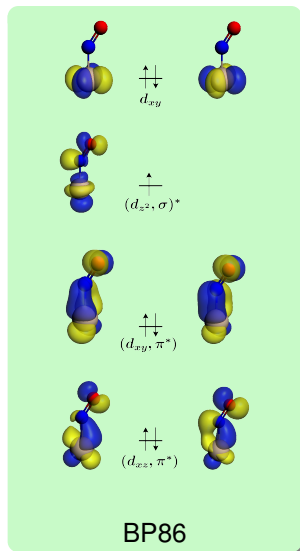
OLYP



B3LYP

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

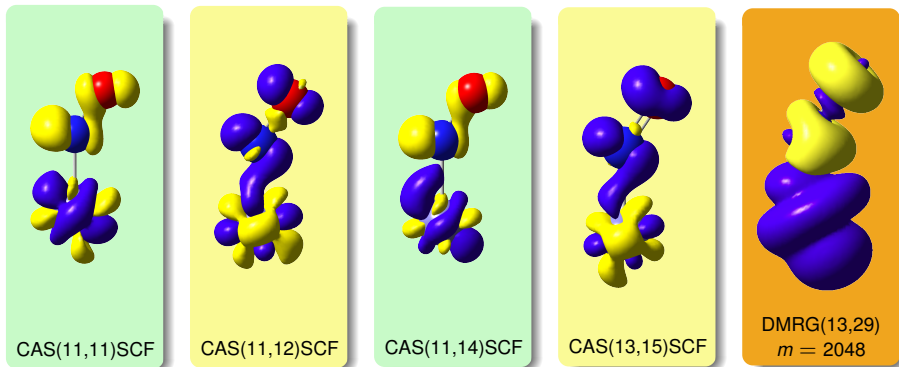
# Understandable in terms of orbitals



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

# The multi-determinantal picture

- CASSCF spin density distribution with respect to a DMRG(13,29)[2048] reference spin density

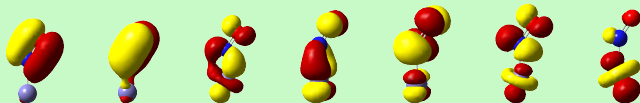


- CASSCF spin densities oscillate around DMRG(13,29)[2048] reference distribution

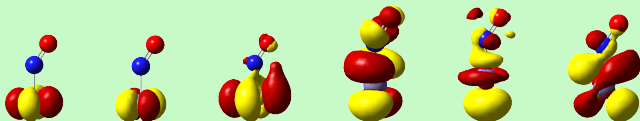
K. Boguslawski, K. H. Marti, Ö. Legeza, M. Reiher, *J. Chem. Theory Comput.* **2012**, *8*, 1970.

# Interpreted in terms of natural orbitals

- Natural orbitals obtained from a CAS(11,14)SCF calculation



|                   |       |       |       |       |       |       |       |
|-------------------|-------|-------|-------|-------|-------|-------|-------|
| CAS(11,11)SCF     | 1.967 | 1.945 | 1.755 | 1.809 | 0.229 | 0.275 | 1.006 |
| CAS(11,12)SCF     | 1.960 | 1.946 | 1.777 | 1.792 | 0.244 | 0.257 | 1.003 |
| CAS(11,14)SCF     | 1.959 | 1.946 | 1.746 | 1.815 | 0.218 | 0.278 | 1.003 |
| CAS(13,15)SCF     | 1.964 | 1.952 | 1.770 | 1.816 | 0.210 | 0.254 | 1.004 |
| DMRG(13,29)[2048] | 1.958 | 1.947 | 1.746 | 1.802 | 0.228 | 0.276 | 1.011 |

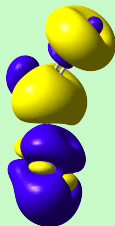


|                   |       |       |       |       |       |       |
|-------------------|-------|-------|-------|-------|-------|-------|
| CAS(11,11)SCF     | 1.943 | 0.067 | 0.012 | 0.010 | 0.000 | 0.000 |
| CAS(11,12)SCF     | 1.943 | 0.045 | 0.012 | 0.010 | 0.009 | 0.000 |
| CAS(11,14)SCF     | 1.945 | 0.043 | 0.013 | 0.010 | 0.008 | 0.005 |
| CAS(13,15)SCF     | 1.944 | 0.045 | 0.012 | 0.011 | 0.008 | 0.000 |
| DMRG(13,29)[2048] | 1.943 | 0.042 | 0.013 | 0.010 | 0.006 | 0.008 |

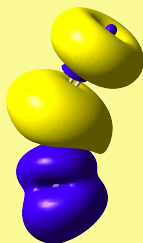


# Deviation of one-particle picture from present-day DFT compared to *ab initio* reference

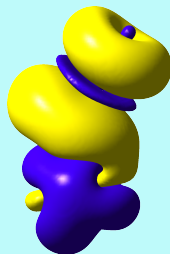
- DFT-DMRG(13,29)[2048] spin density difference distributions



BP86



OLYP



B3LYP

- Best agreement obtained for BP86, BLYP and TPSS

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

# Conclusions & Perspective

- Accurate multi-determinantal wave-function calculations are feasible and accurate, but not easy to interpret
- As a consequence, quantitative quantum chemistry has a hard time with Coulson's appeal "give me insights, not numbers"
- Moreover, novel wave function approximations introduce new ingredients/concepts (tensor networks) which lead to an even larger diversity of notions to describe/understand electronic structures
- This also holds true for concepts from quantum information theory that measure the entanglement of subsystems and the entropy among orbitals

Review: K.H. Marti, M. Reiher, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6750.

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