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

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Outline

- 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

Solution of the complete Schrödinger equation

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

$\Rightarrow$ General wave function and distribution functions

$\Rightarrow$ 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

Exact solution of the electronic Schrödinger equation

The electronic Schrödinger equation

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

with target quantity E_{el}

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

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

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 Φ_I can be constructed

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

Dilemmas

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)

Technical remark

Many-electron basis functions (determinants) constructed from:

1. non-orthogonal local orbital basis (VB)
   $\Rightarrow$ small number of configurations, technically demanding

2. orthogonal, local orbitals
   $\Rightarrow$ small number of configurations, technically simple

3. orthogonal, non-local orbitals (MO)
   $\Rightarrow$ large number of configurations, technically simple

Relation total state $\Longleftrightarrow$ 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 **D**

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

- The eigenvectors $\mathbf{u}_p$ of **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 Ψ 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}

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

$\Rightarrow$ 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

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

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

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

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

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

Two-electron density matrix in spin-orbital basis

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

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

CISD wave function

$$|\Psi_{\mathrm{el}}^{\mathrm{CISD}}\rangle = |\Phi_0\rangle + \sum_i^{\mathrm{occ}} \sum_a^{\mathrm{unocc}} C_i^a a_a^\dagger a_i |\Phi_0\rangle + \sum_{j<i}^{\mathrm{occ}} \sum_{b<a}^{\mathrm{unocc}} C_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle$$

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

CC wave function

$$|\Psi_{\mathrm{el}}^{\mathrm{CC}}\rangle = \exp(\hat{T})|\Phi_0\rangle, \qquad \hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$$

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
    $\Rightarrow$ 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
    $\Rightarrow$ Active orbitals can be improved iteratively (IDDCI)

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

Conventional Approaches with optimized orbitals

- Multi-configuration self-consistent field (MCSCF):
  - $\rightarrow$ Choose a truncated CI expansion $\{\Phi_I\}$
  - $\rightarrow$ 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):
  - $\rightarrow$ Choose a subspace of one-particle functions $\{\phi_i\}$ ($\equiv$ active orbitals) which are occupied by N_{active} electrons (active electrons) in the reference wave function Φ_0
  - $\rightarrow$ Construct the full CI space ($\equiv$ active space) for the orbital subspace
  - $\rightarrow$ 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

  $\Rightarrow$ 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.

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

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)

Unconventional approaches

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 $\{|m_l\rangle\}$

   $\Rightarrow$ Represent $\hat{A}_i[n_i]$ by $(m \times m)$ matrices $A^{n_i}_{m_{l-1},m_l}$

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

Mixed-canonical MPS

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

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

$\Rightarrow$ Number of variational parameters is reduced to $4L$ local matrices

Relation MPS $\Longleftrightarrow$ 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 **n**

$$C_{\mathbf{n}} = \sum_{m^S}^m \sum_{m^E}^m \psi_{m^S n_{l+1} n_{l+2} m^E} \left(A_2[n_2] \ldots A_l[n_l] \right)_{n_1; m^S}$$
$$\left(A_{l+3}[n_{l+3}] \ldots A_{L-1}[n_{L-1}] \right)_{m^E; n_L}$$

- 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:

$$\mathrm{COM} = 1 - \sum_{\{\tilde{\mathbf{n}}\}} |C_{\{\tilde{\mathbf{n}}\}}|^2$$

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

Excitation patterns

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

CAS(11,11)

CAS(13,20)
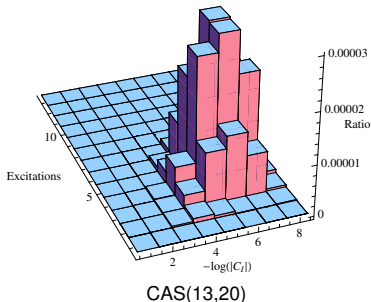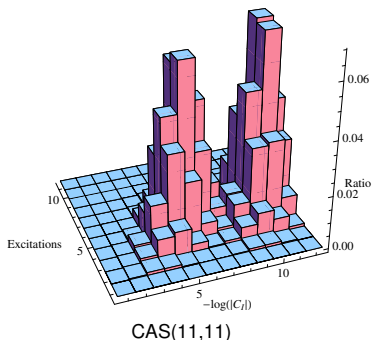
- A large number of determinants is of little importance (small absolute C_l coefficient)

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

$$|\Psi^{\mathrm{CGTN}}\rangle = \sum_{n_1 \ldots n_L}^{q} \prod_{\alpha}^{L} \prod_{\beta \leq \alpha} f_{\alpha\beta}^{n_\alpha n_\beta} |n_1 \ldots n_L\rangle$$

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

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

   - 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.

$\langle \hat{S}^2 \rangle$ 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 $\Gamma_{j^\sigma l^{\sigma'}}^{i^\sigma k^{\sigma'}}$ ($\equiv$ 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 $\overline{d}_{pqrs}$

- ⊖ For non-singlet states: $\overline{d}_{pqrs}$ 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 Λ_{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)

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

$\Rightarrow$ One-center and two-center terms are S_z-independent

$\Rightarrow$ 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

$$\begin{array}{ccc} \uparrow\uparrow & \cdots & \downarrow\downarrow \\ A & \cdots & B \end{array}$$
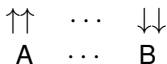
- Broken symmetry (BS) determinants:
  determinants with certain amount of spin excess on one (metal) atom and the opposite spin excess on other (metal) atoms

  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.

$\Rightarrow$ 'VB-like' description with semi-localized magnetic orbitals (nonorthogonal spatial orbitals)

$\Rightarrow$ 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 α-set overlap at most with one orbital form the β-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 α 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

$\Rightarrow$ spin densities
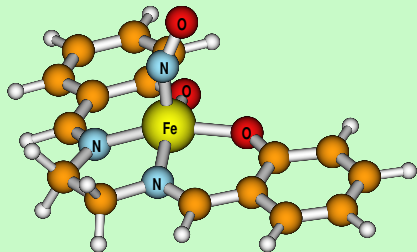
Full complex:
Fe(salen)(NO)
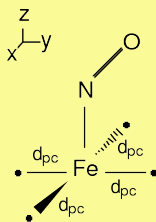
- 4 point charges in *xy*-plane at $d_{pc} = 1.133$ Å
- Square planar ligand field emulates one-particle states of full complex
- d_{pc} determines character of wave function
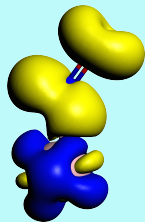
Model complex: $[FeNO]^{2+}$

DFT single-particle picture
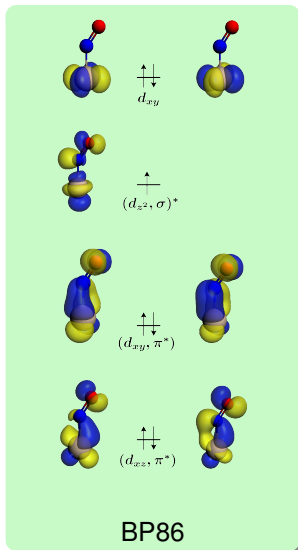
- Spin density difference plots with respect to OLYP
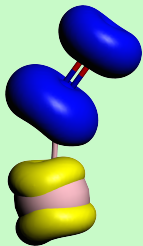
BP86
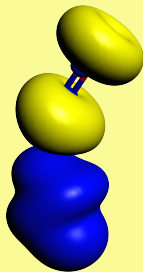
OLYP

B3LYP

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

Understandable in terms of orbitals

BP86

OLYP

B3LYP
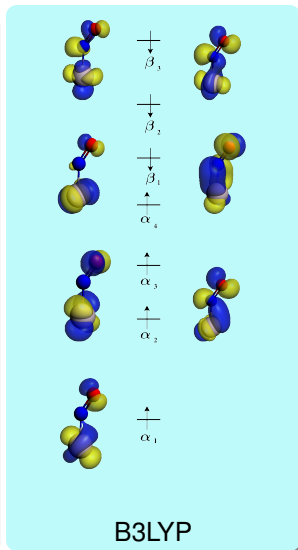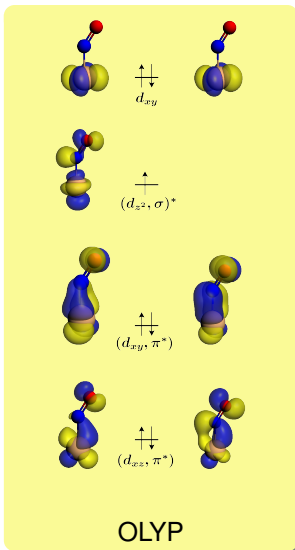
K. Boguslawski, C. R. Jacob, M. Reiher, *J. Chem. Theory Comput.* **2011,** *7,* 2740.

The multi-determinantal picture

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

CAS(11,11)SCF   CAS(11,12)SCF   CAS(11,14)SCF   CAS(13,15)SCF   DMRG(13,29) $m = 2048$
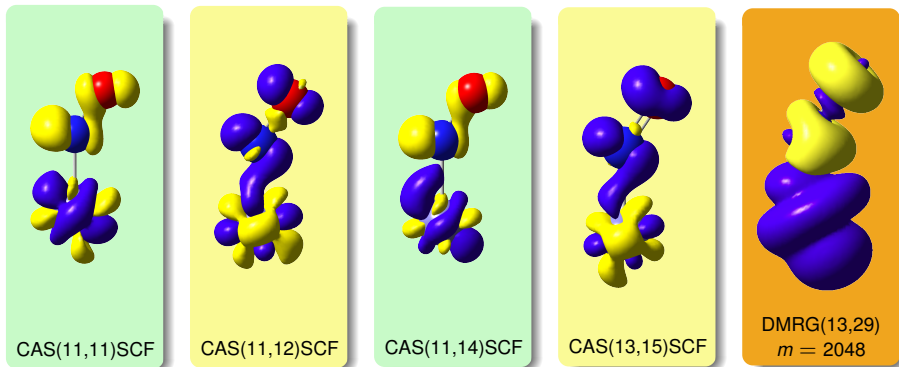
- CASSCF spin densities oscillate around DMRG(13,29)[2048] reference distribution

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
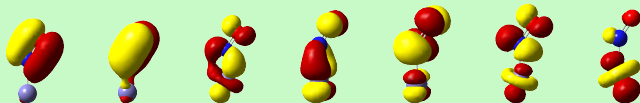
CAS(11,11)SCF	1.967	1.945	1.755	1.809	0.229	0.275	1.006
CAS(11,12)SCF	1.960	1.946	1.777	1.792	0.244	0.257	1.003
CAS(11,14)SCF	1.959	1.946	1.746	1.815	0.218	0.278	1.003
CAS(13,15)SCF	1.964	1.952	1.770	1.816	0.210	0.254	1.004
DMRG(13,29)[2048]	1.958	1.947	1.746	1.802	0.228	0.276	1.011
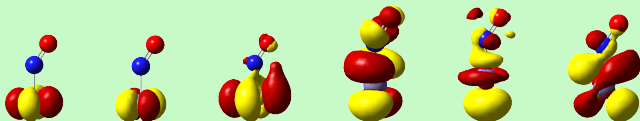
CAS(11,11)SCF	1.943	0.067	0.012	0.010	0.000	0.000
CAS(11,12)SCF	1.943	0.045	0.012	0.010	0.009	0.000
CAS(11,14)SCF	1.945	0.043	0.013	0.010	0.008	0.005
CAS(13,15)SCF	1.944	0.045	0.012	0.011	0.008	0.000
DMRG(13,29)[2048]	1.943	0.042	0.013	0.010	0.006	0.008

Deviation of one-particle picture from present-day DFT compared to *ab initio* reference
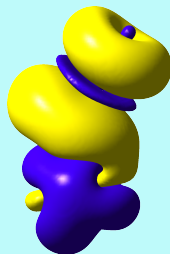
- DFT–DMRG(13,29)[2048] spin density difference distributions
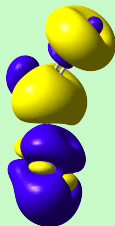
BP86
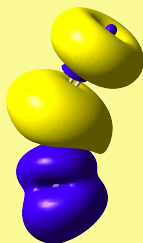
OLYP

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

- 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

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