

REDUCED DENSITY MATRICES IN QUANTUM CHEMISTRY

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1- AND 2- ELECTRON RDMS

- Full Correlation Interaction equation

$$\mathbf{HC} = \mathbf{EC},$$

- provides a numerically exact solution

$$|\Psi\rangle = \sum_{n_1 n_2 \dots n_N} C_{n_1 n_2 \dots n_N} |n_1 n_2 \dots n_N\rangle$$

- CI coefficients $C_{n_1 n_2 \dots n_N}$ are elements of vector \mathbf{C}
- q is dimension of the local Hilbert space
- $|n_1 n_2 \dots n_3\rangle$ occupation number vector (ONV)

- 1-electron reduced density matrix (RDM)**

$$D_{pq} = \langle \Psi | a_p^\dagger a_p | \Psi \rangle$$

- first-order reduced density matrix

$$\gamma_1(\mathbf{x}_1, \mathbf{x}'_1) = \sum_{pq} \phi_q(\mathbf{x}'_1) \phi_p(\mathbf{x}_1) D_{pq}$$

- 2-electron reduced density matrix (RDM)**

$$d_{pqrs} = \langle \Psi | a_p^\dagger a_s^\dagger a_q a_r | \Psi \rangle$$

- expectation value of any 1- and 2-electron Hermitian operator $\hat{\Omega}$ in spin-orbital basis is

$$\langle \Psi | \hat{\Omega} | \Psi \rangle = \sum_{pq} D_{pq} \Omega_{pq} + \sum_{pqrs} d_{pqrs} \Omega_{pqrs}$$

- if $i = +$ and $\bar{i} = +$ are occupations for i -th orbital, the **spinless 1- and 2- electron RDMS** are

$$\bar{d}_{ijkl} = d_{ijkl} + d_{i\bar{j}\bar{k}\bar{l}} + d_{i\bar{j}k\bar{l}} + d_{i\bar{j}\bar{k}l}$$

$$\bar{D}_{ij} = D_{ij} + D_{i\bar{j}}$$

LOCAL PARTITIONING

- \mathbf{S}^{MO} is **overlap matrix**

$$S_{i,j}^{\text{MO}} = \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \langle i | j \rangle$$

- $\mathbf{S}^{\text{A,MO}}$ defines contribution to $\langle S^2 \rangle$ from atom A

- $\mathbf{S}^{\text{A,MO}}$ is **atomic overlap matrix**

$$S_{i,j}^{\text{A,MO}} = \int \phi_i^*(\mathbf{r}) w_A(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} = \langle i | w_A | j \rangle$$

- $w_A(\mathbf{r})$ are the weight functions fulfilling

$$0 \leq w_A(\mathbf{r}) \leq 1$$

$$\sum_A w_A(\mathbf{r}) = 1$$

- the choice of $w_A(\mathbf{r})$ is defined by partition scheme: Bader, Hirshfeld, Mulliken *etc.*

- Mulliken partitioning** employs

$$\phi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \psi_{\mu}(\mathbf{r})$$

$$S_{\mu\nu}^{\text{A}} = \sum_{ij} c_{\mu i} S_{ij}^{\text{A,MO}} c_{\nu j}$$

$w_A(\mathbf{r})$ is specially chosen so that elements of \mathbf{S}^{A} are

$$S_{\mu\nu}^{\text{A}} = \begin{cases} S_{\mu\nu} & \forall \mu \in A \\ 0 & \forall \mu \notin A \end{cases}$$

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LOCAL SPIN CALCULATION

- expectation value of \hat{S}^2 can be decomposed

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

- local spin** – atomic contributions to $\langle \hat{S}^2 \rangle$

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4} (2 \text{Tr}(\bar{\mathbf{D}} \mathbf{S}^{\text{A,MO}}) - \text{Tr}(\bar{\mathbf{D}} \mathbf{S}^{\text{A,MO}} \bar{\mathbf{D}} \mathbf{S}^{\text{MO}}))$$

$$- \frac{1}{4} \text{Tr}(\mathbf{P}^{\text{s}} \mathbf{S}^{\text{A,MO}} \mathbf{P}^{\text{s}} \mathbf{S}^{\text{A,MO}}) + \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S_{ki}^{\text{A,MO}} S_{lj}^{\text{A,MO}}$$

$$- \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S_{kj}^{\text{A,MO}} S_{li}^{\text{A,MO}} + \frac{1}{4} \text{Tr}(\mathbf{P}^{\text{s}} \mathbf{S}^{\text{A,MO}})^2$$

- diatomic contributions to $\langle \hat{S}^2 \rangle$

$$\langle \hat{S}^2 \rangle_{AB} = -\frac{1}{4} \text{Tr}(\mathbf{P}^{\text{s}} \mathbf{S}^{\text{A,MO}} \mathbf{P}^{\text{s}} \mathbf{S}^{\text{B,MO}})$$

$$+ \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S_{ki}^{\text{A,MO}} S_{lj}^{\text{B,MO}} - \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl} S_{kj}^{\text{A,MO}} S_{li}^{\text{B,MO}}$$

$$+ \frac{1}{4} \text{Tr}(\mathbf{P}^{\text{s}} \mathbf{S}^{\text{A,MO}}) \text{Tr}(\mathbf{P}^{\text{s}} \mathbf{S}^{\text{B,MO}})$$

- \mathbf{P}^{s} is **spin-density matrix**

$$P_{ij}^{\text{s}} = D_{ij} - D_{i\bar{j}}$$

- Γ_{ijkl} is a **cumulant** of spinless 2-electron RDM

$$\Gamma_{ijkl} = -\bar{D}_{ik} \bar{D}_{jl} + \frac{1}{2} \bar{D}_{jk} \bar{D}_{il} + \frac{1}{2} P_{jk}^{\text{s}} P_{il}^{\text{s}} + \frac{1}{2} \bar{d}_{ijkl}$$

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1- AND 2-ORBITAL RDMS

- 1-orbital reduced density matrix operator

$$|\Psi^{n_i}\rangle = \sum_{n_i, e} C_{n_i, e_1, e_2} |e_1\rangle |n_i\rangle |e_2\rangle$$

$$\hat{\rho}_i = \text{Tr}_{e_1, e_2} |\Psi^{n_i}\rangle \langle \Psi^{n_i}|$$

- $\hat{\rho}_i$ is represented in the basis of one-orbital states

$$|n_i\rangle = \{ - ; + ; ++ \}$$

- matrix representation of $\hat{\rho}_i$, **1-orbital RDM**, can be defined in terms of 1- and 2-electron RDMS

	-	+	++
-	$1 - D_{ii} - D_{\bar{i}\bar{i}} + d_{i\bar{i}\bar{i}\bar{i}}$	0	0
+	0	$D_{ii} - d_{i\bar{i}\bar{i}\bar{i}}$	0
++	0	0	$D_{\bar{i}\bar{i}} - d_{i\bar{i}\bar{i}\bar{i}}$
	0	0	$d_{i\bar{i}\bar{i}\bar{i}}$

- 2-orbital reduced density matrix operator

$$|\Psi^{n_i, n_j}\rangle = \sum_{n_i, n_j, e} C_{e_1, n_i, e_2, n_j, e_3} |e_1\rangle |n_i\rangle |e_2\rangle |n_j\rangle |e_3\rangle$$

$$\hat{\rho}_{i,j} = \text{Tr}_{e_1, e_2} |\Psi^{n_i, n_j}\rangle \langle \Psi^{n_i, n_j}|$$

- $\hat{\rho}_{i,j}$ is represented in the basis of two-orbital states

$$|n_i\rangle |n_j\rangle = \{ - - ; - + ; \dots ; ++ ++ \}$$

- matrix representation of $\hat{\rho}_{i,j}$, **2-orbital RDM**, can be defined in terms of 1-, 2-, 3-, and 4-electron RDMS

K. Boguslawski *et al.*, *J. Chem. Theory Comput.*, **2013**, *9*, 2959-2973.

SINGLE-ORBITAL ENTROPIES AND MUTUAL INFORMATION FROM 1- AND 2-ORBITAL RDMS

- eigenvalues $\lambda_{\alpha, i}$ of ρ_i give **single-orbital entropy**

$$s_i(1) = - \sum_{\alpha} \lambda_{\alpha, i} \ln \lambda_{\alpha, i}$$

- eigenvalues $\lambda_{\alpha, ij}$ of ρ_{ij} give **two-orbital entropy**

$$s_{ij}(2) = - \sum_{\alpha} \lambda_{\alpha, ij} \ln \lambda_{\alpha, ij}$$

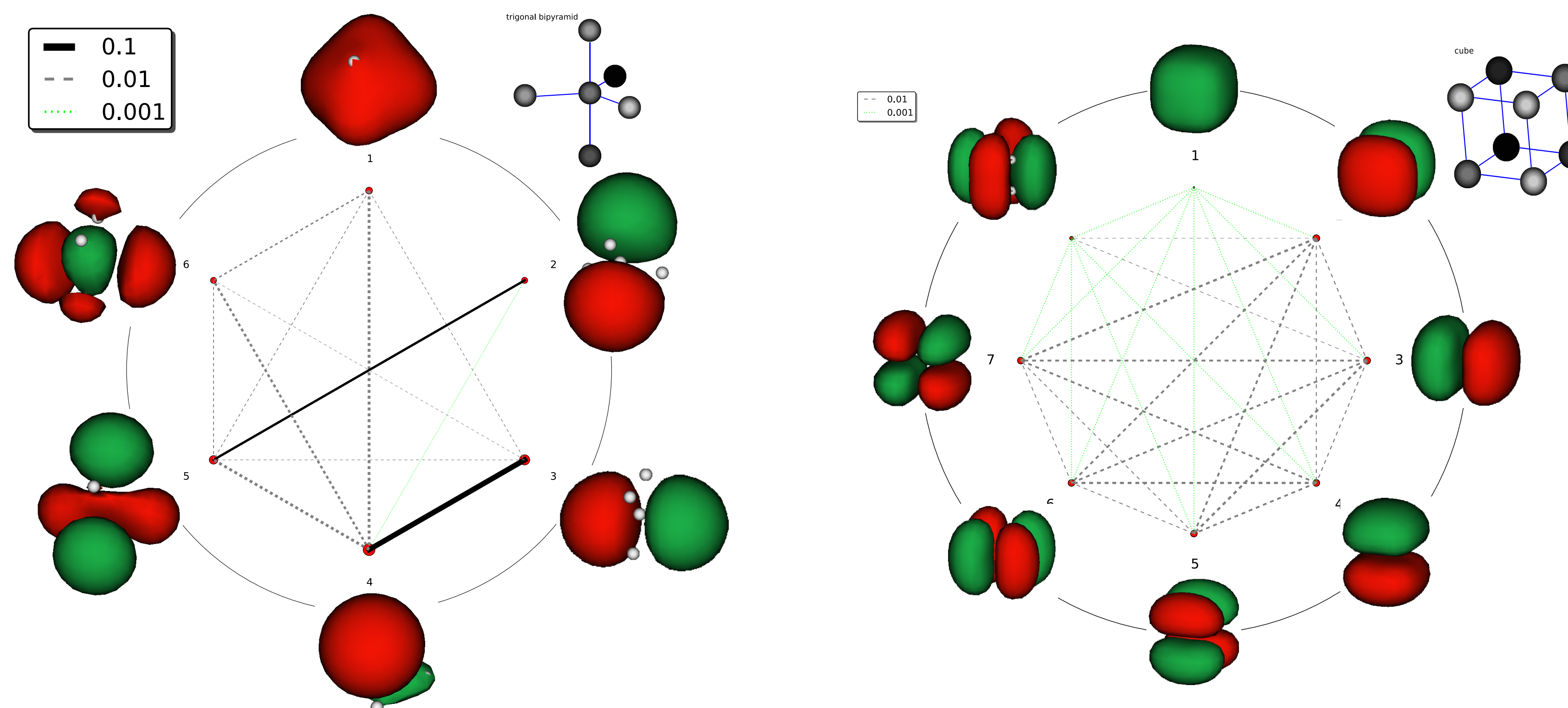
- and finally one can define **mutual information** as

$$I_{i,j} = \frac{1}{2} [s_{ij}(2) - s_i(1) - s_j(1)] (1 - \delta_{ij})$$

O. Legeza and J. Solyom, *Phys. Rev. B*, **2003**, *68*, 195116.

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Mutual information plots for hydrogen clusters



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CONCLUSIONS

- all information required for the evaluation of expectation values is embodied in the one- and two-electron RDMS
- RDMS can give insight into the nature of correlations between molecular orbitals of chemical systems