# Lesson 6, Summer 2017

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## One-particle reduced density matrix

## Natural orbitals

- 1-particle reduced density

$$\rho(\vec{x}_1) = N \int d\vec{x}_2 \dots d\vec{x}_N \, \Phi(\vec{x}_1 \dots \vec{x}_N) \Phi^*(\vec{x}_1 \dots \vec{x}_N)$$

- 1-particle reduced density matrix (generalization)

$$\gamma(\vec{x}_1, \vec{x}_1') = N \int d\vec{x}_2 \dots d\vec{x}_N \, \Phi(\vec{x}_1 \dots \vec{x}_N) \Phi^*(\vec{x}_1', \vec{x}_2 \dots \vec{x}_N)$$

Properties

$$\rho(\vec{x}_1) = \gamma(\vec{x}_1, \vec{x}_1) \quad , \quad \gamma^*(\vec{x}_1, \vec{x}_1') = \gamma(\vec{x}_1', \vec{x}_1)$$

- Each function of 2 variables can be expanded into orthonormal basis $\{\chi_i\}$:

$$\gamma(\vec{x}_1, \vec{x}_1') = \sum_{ij} \chi_i(\vec{x}_1) \gamma_{ij} \chi_j^*(\vec{x}_1')$$

$$\gamma_{ij} = \int d\vec{x}_1 \, d\vec{x}_1' \, \chi_i^*(\vec{x}_1) \gamma(\vec{x}_1, \vec{x}_1') \chi_j(\vec{x}_1')$$

$$\gamma_{ij}^* = \int d\vec{x}_1 \, d\vec{x}_1' \, \chi_i(\vec{x}_1) \gamma(\vec{x}_1', \vec{x}_1) \chi_j^*(\vec{x}_1') = \gamma_{ji} \quad \dots \text{Hermitian}$$

- Special case: HF ~~orbital~~ wave function $\Phi$

$$\gamma^{HF}(\vec{x}_1, \vec{x}_1') = \frac{N}{N!} \int d\vec{x}_2 \dots d\vec{x}_N \, |\varphi_1(1) \varphi_2(2) \dots \varphi_N(N)| \, |\varphi_1(1') \varphi_2(2) \dots \varphi_N(N)|$$

$$= \frac{N(N-1)!}{N!} \sum_{i=1}^{N} \varphi_i(\vec{x}_1) \varphi_i^*(\vec{x}_1')$$

$$\gamma^{RHF}(\vec{x}_1, \vec{x}_1') = \sum_{a=1}^{N/2} 2\,\varphi_a(\vec{x}_1)\,\varphi_a^*(\vec{x}_1') \Rightarrow \gamma_{ij}^{RHF} = 2\delta_{ij} \quad i,j \in \text{occupied}$$

$$= 0 \quad i,j \text{ virtual}$$

$$\gamma^{RHF} = \begin{pmatrix} 2 & & & & & \\ & 2 & & & & \\ & & 2 & & & \\ & & & 0 & & \\ & & & & 0 & \\ & & & & & 0 \end{pmatrix}$$

- For a general $\Phi(1 \ldots N)$ the matrix $\gamma_{ij}$ is non-diagonal but still Hermitian — it can be diagonalized

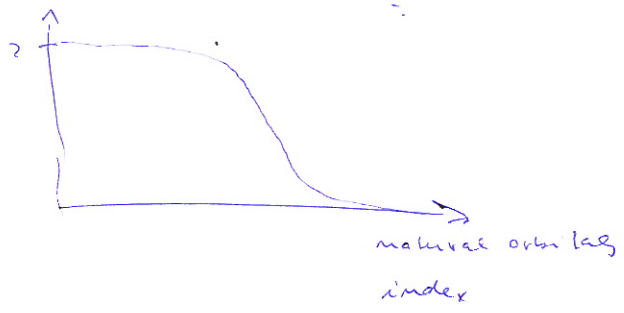
$$U^+ \gamma U = \lambda \Rightarrow \gamma(\vec{x}_1, \vec{x}_1') = \sum_i \lambda_i \eta_i(\vec{x}) \eta_i^*(\vec{x}_1')$$

Natural orbitals $\longrightarrow$ $\eta_i(\vec{x}_1) = \sum_j \chi_j(\vec{x}_1) U_{ji}$

Use of natural orbitals:

for CI, CC

$$\lambda = \begin{pmatrix} 2 & & & & & & \\ & 1.98 & & & & & \\ & & 1.9 & & & & \\ & & & 1.2 & & & \\ & & & & 1.0 & & \\ & & & & & 0.8 & \\ & & & & & & \ddots \end{pmatrix}$$



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# Introduction to Coupled – clusters

Help of the second quantization:

a.) $|\Psi_a^r\rangle = a_r^\dagger a_a |\Psi_0\rangle$

b.) $|\Psi_{ab}^{rs}\rangle = a_r^\dagger a_s^\dagger a_a a_b |\Psi_0\rangle$

c.) .....

$$|\Psi^{CISD}\rangle = \left(1 + \underbrace{\sum_{ar} c_a^r a_r^\dagger a_a}_{T_1 \text{ operator}} + \underbrace{\frac{1}{4}\sum_{\substack{ab\\rs}} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_a a_b}_{T_2 \text{ operator}}\right)|\Psi_0\rangle$$

Motivation, Čížek 1966

FCI Beryllium gives $C_{abcd}^{rstu} \sim C_{ab}^{rs} * C_{cd}^{tu}$

Coupled Clusters Ansatz

$$|\Psi^{CCD}\rangle = e^{T_2}|\Psi_0\rangle = \left(1 + T_2 + \frac{T_2^2}{2} + \dots\right)|\Psi_0\rangle$$

← Terminates at $T^N$

$$|\Psi^{CCSDT}\rangle = e^{T_1+T_2+T_3}|\Psi_0\rangle$$

⋮

In principle CC is similar to FCI – it contains all the excitations, but not all of them are independent variations

## How to solve CC problem?

$$|\Psi^{CCD}\rangle = |\Psi_0\rangle + \frac{1}{4}\sum_{\substack{ab\\rs}} C_{ab}^{rs}\, a_r^\dagger a_s^\dagger a_a a_b |\Psi_0\rangle + \frac{1}{32}\sum_{\substack{abcd\\rstu}} C_{ab}^{rs} C_{cd}^{tu} |\Psi_{abcd}^{rstu}\rangle + \dots$$

($|\Psi_{ab}^{rs}\rangle$)

$$H|\Psi^{CCD}\rangle = E|\Psi^{CCD}\rangle = (E_0 + E_{corr})|\Psi^{CCD}\rangle$$

$$(H - E_0)|\Psi^{CCD}\rangle = E_{corr}|\Psi^{CCD}\rangle$$

1.) $\langle\Psi_0|$ gives:

$$E_{corr} = \frac{1}{4}\sum_{\substack{ab\\rs}} \langle\Psi_0|H|\Psi_{ab}^{rs}\rangle C_{ab}^{rs}$$

only double-excitations contribute to the correlation energy!

But $C_{ab}^{rs}$ depend on the higher orders!

2.) $\langle\Psi_{ef}^{xy}|$ gives:

$$\langle\Psi_{ef}^{xy}|H|\Psi_0\rangle + \frac{1}{4}\sum_{\substack{ab\\rs}} \langle\Psi_{ef}^{xy}|H-E_0|\Psi_{ab}^{rs}\rangle C_{ab}^{rs} + \frac{1}{32}\sum_{\substack{abcd\\rstu}} C_{ab}^{rs} C_{cd}^{tu} \langle\Psi_{ef}^{xy}|H-E_0|\Psi_{abcd}^{rstu}\rangle$$

$$= E_{corr}\frac{1}{4}\sum_{\substack{ab\\rs}} \langle\Psi_{ef}^{xy}|\Psi_{ab}^{rs}\rangle C_{ab}^{rs} = \frac{1}{4} E_{corr}\, C_{ef}^{xy}$$

Quadratic system of equations, iterative solutions

Amplitude equations