Lesson 6, Summer 2017

by Roman Čurík

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)

$$\gamma(\vec{x}_1, \vec{x}_1') = N \int d\vec{x}_2 \dots d\vec{x}_N \quad \phi(\vec{x}_1, \dots \vec{x}_N) \, \phi^*(x_1', \vec{x}_2 \dots \vec{x}_N)$$

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 $\{\chi_i\}$:

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

$$\Downarrow$$

$$\gamma_{ij} = \int d\vec{x}_1 d\vec{x}_1' \, \chi_i^*(\vec{x}_1) \, \gamma(\vec{x}_1, \vec{x}_1') \, \chi_j(x_1')$$

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

- Special case: HF ~~orbit~~ wave funcion ϕ

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

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

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

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

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

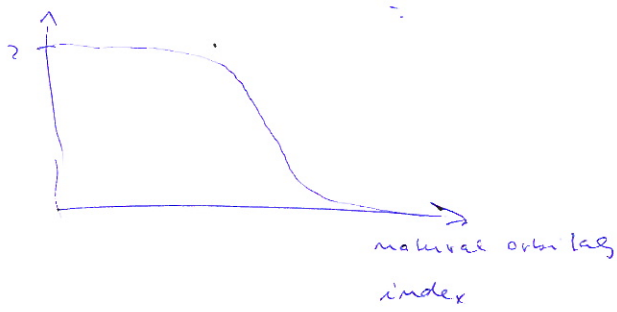
- For a general $\phi(1 \ldots N)$ the matrix γ_{ij} is non-diagonal but still Hermitian – it can be diagonalized

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

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

Use of natural orbitals for CI, CC

$$\lambda = \begin{pmatrix} 2.0 & & & & & & \\ & 1.98 & & & & & \\ & & 1.9 & & & & \\ & & & 1.2 & & & \\ & & & & 1.0 & & \\ & & & & & 0.8 & \\ & & & & & & \ddots \end{pmatrix}$$



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Introduction to Coupled - clusters

Help of the second quantization:

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

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

c.) ....

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

Motivation, Čížek 1966

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

Coupled Clusters Ansatz

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

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?

$$|\Psi^{CCD}\rangle = |\Psi_0\rangle + \frac{1}{4}\sum_{\substack{ab\\rs}} C_{ab}^{rs} \underbrace{a_r^+ a_s^+ a_a a_b |\Psi_0\rangle}_{|\Psi_{ab}^{rs}\rangle} + \frac{1}{32}\sum_{\substack{abcd\\rstu}} \overset{C_{ab}^{rs}\cdot C_{cd}^{tu}}{\cancel{C_{abcd}^{rst}}} \, |\Psi_{abcd}^{rstu}\rangle + \ldots$$

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

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

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 doube-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