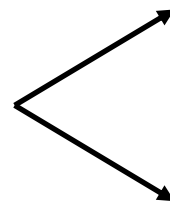


„Size – Extensivity vs. Consistency“

$$A + B \rightarrow C \quad N_A \neq N_B \neq N_C$$

$$SC \equiv E_A + E_B \cong \lim_{\substack{A \rightarrow \infty \\ B \rightarrow -\infty}} N_{A+B}$$

$$E_{(N)} \underset{N \rightarrow \infty}{\cong} N$$



Hartree-Fock (uzavřená slupka)

Full-CI

~~Double-CI~~

$$2\mathbf{H}_2: \quad |\Psi_0\rangle = |1_1 \bar{1}_1 1_2 \bar{1}_2\rangle \quad \begin{matrix} 1_1 & \dots \psi_1 & 1_2 \psi_1(2.H_2) \\ & \dots 1.H_2 & \end{matrix}$$

$$r_{12} = \infty \quad \left(1_1 \bar{1}_1 | 1_2 \bar{1}_2\right) \approx \frac{1}{r_{12}} = 0$$

$$J_{11} = \left(1_1 \bar{1}_1 | 1_1 \bar{1}_1\right) = \left(1_2 \bar{1}_2 | 1_2 \bar{1}_2\right) \quad {}^2E_0 = 2(2\varepsilon_1 - J_{11}) \quad HF$$

$$|\Psi_{1_1}\rangle = (\sqrt{2(1+S_{12})})^{-1} \left(\phi_{1s}^{1.H_2}(1) + \phi_{1s}^{1.H_2}(2)\right) \quad \begin{matrix} \text{proměnné (1), (2)} \\ \text{elektrony z 1. H}_2 \end{matrix}$$

$$|\Psi_{2_1}\rangle = (\sqrt{2(1-S_{12})})^{-1} \left(\phi_{1s}^{1.H_2}(1) - \phi_{1s}^{1.H_2}(2)\right)$$

$$|\Psi_{1_2}\rangle = (\sqrt{2(1+S_{12})})^{-1} \left(\phi_{1s}^{2.H_2}(3) + \phi_{1s}^{2.H_2}(4)\right) \quad \begin{matrix} \text{proměnné (3), (4)} \\ \text{elektrony z 2. H}_2 \end{matrix}$$

$$|\Psi_{2_2}\rangle = (\sqrt{2(1-S_{12})})^{-1} \left(\phi_{1s}^{2.H_2}(3) - \phi_{1s}^{2.H_2}(4)\right)$$

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1 |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle + c_2 |1_1 \bar{1}_1 2_2 \bar{2}_2\rangle + c_3 |1_1 \bar{1}_1 2_1 \bar{2}_1\rangle + \\ + c_4 |2_2 \bar{2}_2 1_2 \bar{1}_2\rangle + c_5 |1_1 \bar{2}_1 2_2 \bar{1}_2\rangle$$

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1 | \rangle + c_2 | \rangle + 0 = |\Psi_0\rangle + \sum_{i=1}^2 c_1 |^1\Psi_{1i, \bar{1}i}^{2i, \bar{2}i}\rangle$$

Příklad 1: $|1_1 \bar{1}_1 2_1 \bar{2}_1\rangle \quad \langle \Phi_0 | H | 1_1 \bar{1}_1 2_1 \bar{2}_1 \rangle = 0$



1. H₂

2. H₂

$$\langle \Psi_0 | H | 1_2 \bar{1}_2 2_1 \bar{2}_1 \rangle = \langle 1_1 \bar{1}_1 | | 2_1 \bar{2}_1 \rangle = \langle 1_1 \bar{1}_1 | 2_1 \bar{2}_1 \rangle - \langle 1_1 \bar{1}_1 | \bar{2}_1 2_1 \rangle = K_{12}$$

$$| {}^1 \Psi_{1, \bar{1}}^{2_1, \bar{2}_1} \rangle$$

$$DCI = \begin{pmatrix} 0 & K_{12} & K_{12} \\ K_{12} & 2\Delta & 0 \\ K_{12} & 0 & 2\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \end{pmatrix} = {}^2 E_c \begin{pmatrix} 1 \\ c_1 \\ c_2 \end{pmatrix} \quad \begin{aligned} K_{12}(c_1 + c_2) &= E \\ K_{12} + 2\Delta c_1 &= E c_1 \\ K_{12} + 2\Delta c_2 &= E c_2 \end{aligned}$$

$$c_1 = c_2 = \frac{K_{12}}{E - 2\Delta} \rightarrow E = \frac{2(K_{12})^2}{E - 2\Delta}$$

$$E_c = \Delta - \left(\Delta^2 + 2(K_{12})^2 \right)^{1/2} \neq 2 \left[\Delta - \left(\Delta^2 + (K_{12})^2 \right)^{1/2} \right]$$

=> Double-CI není konzistentní

N-krát H₂

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{i=1}^N c_i |{}^1\Psi_{1i, \bar{1}i}^{2i, \bar{2}i}\rangle$$

$$\left(\begin{array}{cccccc} 0 & K & K & K & \dots & K \\ K & 2\Delta & & & & \\ K & & 2\Delta & & & \emptyset \\ K & & & 2\Delta & & \\ \dots & & & & \dots & \\ K & \emptyset & & & & 2\Delta \end{array} \right) \quad \begin{aligned} c_1 = c_2 = \dots = c_N &= \frac{K_{12}}{E - 2\Delta} \\ E = K_{12} \sum c_i = NK_{12}c_1 &= \frac{N(K_{12})^2}{E - 2\Delta} \\ E_c &= \Delta - \left(\Delta^2 + N(K_{12})^2 \right)^{1/2} \end{aligned}$$

$$\text{SC} \approx \Rightarrow {}^N E_c \simeq N^1 E_c = N \left[\Delta - \left(\Delta^2 + (K_{12})^2 \right)^{1/2} \right]$$

Příklad 2: *FCI je SC? 2H₂ v minimální bázi*

$$|\Phi_0\rangle = |\Psi_0\rangle + c_1 |2_1 \bar{2}_1 1_2 \bar{1}_2\rangle + c_2 |1_1 \bar{1}_1 2_2 \bar{2}_2\rangle + \underline{c_3 |2_1 \bar{2}_1 2_2 \bar{2}_2\rangle}$$

a) *FCI* :

$$\begin{pmatrix} 0 & K & K & 0 \\ K & 2\Delta & 0 & K \\ K & 0 & 2\Delta & K \\ 0 & K & K & 4\Delta \end{pmatrix}$$

b) $c_1 = c_2$ ${}^2E_c = 2K_{12}c_1$

c) $c_3 = \frac{E}{E - 4\Delta}$ $c_1 = \frac{2K_{12}}{E - 4\Delta} \rightarrow {}^2 E_c = 2\left[\Delta - \left(\Delta^2 + (K_{12})^2\right)^{1/2}\right]$

d) $c_Q \doteq (c_D)^2$ $c_3 = \frac{E}{E - 4\Delta} = \frac{2K_{12}c_1}{E - 4\Delta} = (c_1)^2$

Příklad 3:

je-li $K^2/\Delta^2 \ll 1$:

$$E_{PT} \doteq \frac{(K_{12})^2}{2\Delta} \quad \sqrt{1+x} \doteq 1 + \frac{x}{2} \quad x \ll 1$$

$${}^N E_{PT} \doteq \frac{N(K_{12})^2}{2\Delta} \quad \leftarrow \quad \frac{N(K_{12})^2}{\Delta^2} \ll 1$$

$${}^N E_{PT} = N^1 E_{PT} ! \quad \text{PT je SC!}$$

Příklad 4:

$$\text{je DCI přibližně SC?} \quad E_c = E_c(\text{DCI}) + \Delta E_{\text{Dav.}}$$

$$\Delta E_D = (1 - c_0^2) E_c(\text{DCI}) \quad c_0 : \langle \Phi'_0 | \Phi'_0 \rangle = 1$$
$$|\Phi'_0\rangle = c_0 |\Psi_0\rangle + \dots$$

N-krát H₂

$$\Delta \gg K_{12}$$

a) $\frac{N(K_{12})^2}{\Delta^2} < 1 \quad \sqrt{1+x} = 1 + x/2 - x^2/8$

$${}^N E_c(\text{DCI}) = -\frac{NK^2}{2\Delta} + \frac{N^2 K^4}{8\Delta^3} + \dots$$

...SC ...? ...?

b) $1 - c_0'^2 = \frac{Nc_1^2}{1 + Nc_1^2}$ plyne z úplné normalizace:

$$c_0'^2 = \frac{1}{1 + Nc_1^2}; \quad c_1'^2 = \frac{c_1^2}{1 + Nc_1^2}; \quad c_0'^2 + Nc_1'^2 = 1$$

c) $c_1 = \frac{-K}{2\Delta} + \dots$ členy s N pak pokud lze Nc^2 zanedbat oproti 1 (pro c_0 blízke 1)

d) $\Delta E_D = -\frac{N^2 K^4}{8\Delta^3} + \dots$

Příklad 5: \mathbf{H}_2 (min.báze) $|\Phi'_0\rangle = \frac{1}{\sqrt{1+c^2}}|1\bar{1}\rangle + \frac{c}{\sqrt{1+c^2}}|2\bar{2}\rangle$

N-krát \mathbf{H}_2

$$c = {}^1E_c / K_{12} \quad \langle \Psi_0 | \Phi'_0 \rangle = (1 + c^2)^{-N/2}$$

$$|\Phi'_0\rangle \doteq \prod_{i=1..N} \left\{ \frac{1}{\sqrt{1+c^2}} |1_i \bar{1}_i\rangle + \frac{c}{\sqrt{1+c^2}} |2_i \bar{2}_i\rangle \right\}$$

$$|\Psi_0\rangle = \prod_{i=1..N} |1_i \bar{1}_i\rangle$$

Size-Extensivity and Size-Consistency

Two important concepts in electronic structure theory are *size-consistency* and *size-extensivity*. Though these terms are sometimes used interchangeably in the literature, there are very important distinctions to be made between them.

There are two primary definitions of *size-consistency* in use. The first was employed by **Pople** as one criterion for a well-constructed quantum chemical method. If we imagine two molecules, separated by a large distance (large enough that we may consider them to be non-interacting) then the energy calculated for both molecules simultaneously should be exactly twice that calculated for only one, isolated molecule of , just like the exact energy. This "non-interacting limit" description is the original concept of size-consistency. From this perspective, size-consistency describes what has been referred to as the "additive separability" of the wavefunction.

However, a more recently imposed (**Barlett**) definition requires that the method not only correctly describe the fragmentation limit, but the entire process (in a qualitative sense). That is, the entire potential energy curve mapped out when we bring our two non-interacting molecules close together must be correctly described as well.

For example, both spin-unrestricted Hartree-Fock (UHF) and spin-restricted Hartree-Fock (RHF) wavefunctions are size-consistent for the separated dimer system described above. However, for a closed-shell molecule dissociating into open-shell fragments, a RHF wavefunction does not conform to the second definition of size-consistency, as we will discuss further below.

Size-extensivity, on the other hand, is a more mathematically formal characteristic which refers to the correct (linear) scaling of a method with the number of electrons.

All **Hartree-Fock methods qualify as size-extensive, as well as many-body perturbation theory and coupled-cluster theories**.

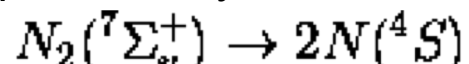
Truncated configuration interaction methods, however, are not size-extensive.

An important advantage of a size-extensive method is that it allows straightforward comparisons between calculations involving variable numbers of electrons, e.g. ionization processes or calculations using different numbers of active electrons.

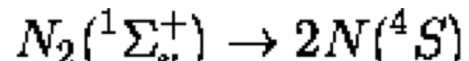
Lack of size-extensivity implies that errors from the exact energy increase as more electrons enter the calculation.

Size-extensivity and size-consistency are not mutually exclusive properties, by any means. At the non-interacting limit, size-extensivity of a method is a **necessary and sufficient condition** to ensure size-consistency, implying that the former is more general than the latter. However, size-extensivity does not ensure correct fragmentation.

For example, we may consider two different fragmentation processes for :



and



The first process is correctly described by both RHF and UHF wavefunctions, and hence, both methods are size-consistent. However, the second process is not correctly described by a RHF wavefunction (and, therefore, perturbation theory and coupled-cluster theory methods which use this as a reference will not be size-consistent.)

Both RHF and UHF are *always* size-extensive, though.

This implies, then, that size-consistency is more general than size-extensivity, but this is also incorrect.

At non-interacting limits, **size-extensivity is a more general property**, and its existence implies that of size-consistency.

However, size-consistency has the additional requirement of correct fragmentation that is not necessarily dependent on the mathematical scaling of the energy.

■ Size-extensive

- The energy of a non-interacting system computed with this model scales correctly with the size of the system, which satisfy

$$E(N\text{He}) = NE(\text{He})$$

■ Size-consistency

- The energies of two systems A and B and of the combined system AB with A and B very far apart, computed in equivalent ways, satisfy

$$E(\text{AB}) = E(\text{A}) + E(\text{B})$$