Separation of dynamic and nondynamic correlation

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CECAM, Lausanne (2017).

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Electron Correlation Definition

The term electron correlation was coined by Wigner and Seitz in 1934, and defined as we know it today by Löwdin in 1959:

$$E_{\text{CORR}} = E_{\text{EXACT}} - E_{\text{HF}}$$

Although it is more convenient to take Pines' definition from 1955,

$$E^{X}_{\text{CORR}} = E_{X} - E_{\text{HF}}$$

which is taken as an intrinsic property of the method of calculation X. There are different correlation types that now belong to the chemistry jargon: dynamic, nondynamic, long-range, short-range, angular, radial, in-out, left-right, etc.

Pines, *Solid State Physics*, **1**, 367 (**1955**)
Löwdin, *Adv. Chem. Phys.*, **2**, 207 (**1959**)

What do we need it for?

Naively, there have been many attemps to find a *holy grail*:
a simple functional of E_{CORR} in terms of Hartree-Fock property X,

$$E_{\text{EXACT}} = E_{\text{HF}} + E_{\text{CORR}}[X]$$

For instance, for atoms $E_{corr}[Z]$ was found within an accuracy of 0.01 a.u. Some others, in the context of DFT, have tried to find $E_c[\rho]$ or other momentums of the density.

However, its most important role has been in method development, as a guide to identify most complicated systems and the inherent difficulties of existing methods. Nowadays it is often used in **hybrid methods** to separate for instance, dynamic and nondynamic correlation or short- and long-range correlation.

Dynamic and nondynamic correlation

Dynamic correlation accounts for correlation between pairs of electrons that do not give rise to one configuration that mixes strongly with HF in a CI wavefunction. It involves *local* changes in the electron distribution.

e.g.: He dimer, He isoelectronic series.

Nondynamic correlation arises from degeneracies and near-degeneracies. It involves *global* changes in the electron distribution.

e.g.: Stretched H_2, Be atom, radicals.

Valderrama, Ludeña, Hinze *JCP* **110** 2343 (**1999**)

Handy's definition of DC & NDC

Nondynamic correlation:

$$E_{ND} = E_{\text{CASSCF}} - E_{\text{HF}}$$

Dynamic correlation:

$$E_D = E_{\text{CORR}} - E_{ND} = E_{\text{FCI}} - E_{\text{CASSCF}}$$

- The CASSCF calculation should use the full-valence space.
- It associates FV-CASSCF to NDC.
- It assumes FV-CASSCF introduces zero DC.

Mok, Neumann, Handy *JPC* **100**, 6625 (**1996**)
Davidson et. al *PRA* **44**, 7071 (**1991**)

Cioslowski's definition of D & ND correlation

Dynamic correlation:

$$E_D = E_{\mathsf{FCI}}[\rho_{\mathsf{HF}}] - E_{\mathsf{HF}}[\rho_{\mathsf{HF}}]$$

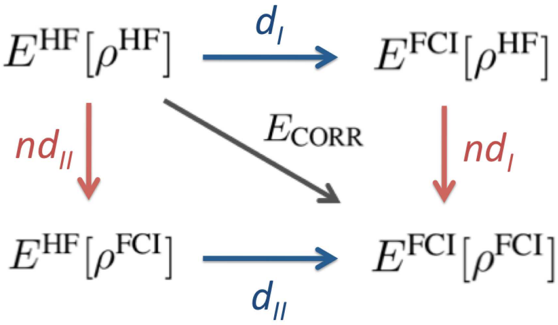
Nondynamic correlation:

$$E_{ND} = E_{\mathsf{CORR}} - E_D = E_{\mathsf{FCI}}[\rho_{\mathsf{FCI}}] - E_{\mathsf{FCI}}[\rho_{\mathsf{HF}}]$$

$E_{\mathsf{FCI}}[\rho_{\mathsf{HF}}]$ requires the calculation of a density-constrained FCI procedure.

Cioslowski, *PRA* **43**, 1223 (**1991**)

Cioslowski-Ludeña D & ND corrrelation



Cioslowski, *PRA* **43**, 1223 (**1991**)
Valderrama, Ludena, Hinze, *JCP* **106**, 9227 (**1997**)

"*Matters such as electron correlation should show in the two-particle density matrix.*"

Coulson
Rev. Mod. Phys. 32, 170 **1960**

First and Second-Order Densities. The Cumulant.

The density and the 1-RDM

$$\rho(\mathbf{1}) = N \int |\Psi(\mathbf{1},\mathbf{2},\ldots,\mathbf{N})|^2 d\mathbf{2}\cdots d\mathbf{N} = \rho_1(\mathbf{1};\mathbf{1})$$

$$\rho_1(\mathbf{1};\mathbf{1}') = N \int \Psi^*(\mathbf{1},\ldots,\mathbf{N})\Psi(\mathbf{1}',\ldots,\mathbf{N}) d\mathbf{2}\cdots d\mathbf{N}$$

The pair density

$$\rho_2(\mathbf{1},\mathbf{2}) = N(N-1) \int |\Psi(\mathbf{1},\mathbf{2},\ldots,\mathbf{N})|^2 d\mathbf{3}\cdots d\mathbf{N}$$

$$\rho_2^{\mathsf{SD}}(\mathbf{1},\mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) - \rho_1(\mathbf{1};\mathbf{2})\rho_1(\mathbf{2};\mathbf{1})$$

The two-particle cumulant matrix:

$$\gamma(\mathbf{1},\mathbf{2}) = \rho_2(\mathbf{1},\mathbf{2}) - \rho_2^{\mathsf{SD}}(\mathbf{1},\mathbf{2})$$

First and Second-Order Densities.

The 1-RDM can be expanded in terms of 1-DM:

$$\rho_1(\mathbf{1};\mathbf{1}') = \sum_{ij} {}^1D^i_j \chi_i^*(\mathbf{1})\chi_j(\mathbf{1}') = \sum_i n_i \phi_i^*(\mathbf{1})\phi_j(\mathbf{1}')$$

where $\{\chi_i\}$ are molecular orbitals and $\{\phi_i\}$ and $\{n_i\}$ natural orbitals and their occupancies. The 2-PD

$$\rho_2(\mathbf{1}',\mathbf{2}';\mathbf{1},\mathbf{2}) = \sum_{ijkl} {}^2D^{ij}_{kl}\chi_i^*(\mathbf{1}')\chi_j^*(\mathbf{2}')\chi_k(\mathbf{1})\chi_l(\mathbf{2})$$

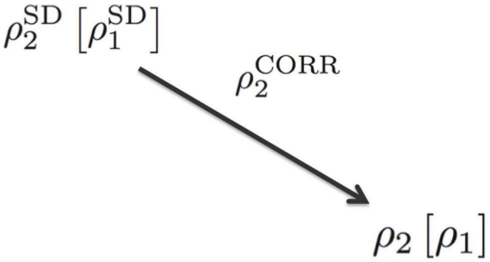
The two-particle cumulant representation:

$$\Gamma^{ij}_{kl} = {}^2D^{ij}_{kl} - \left({}^2D^{\mathsf{SD}}\right)^{ij}_{kl} = {}^2D^{ij}_{kl} - {}^1D^i_j\,{}^1D^k_l + {}^1D^k_j\,{}^1D^i_l \qquad \Gamma^{\mathsf{HF}} = \mathbf{0}$$

Pair density decomposition

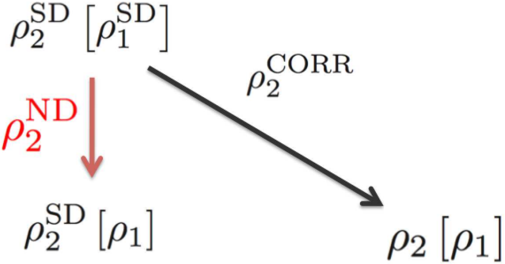
Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).
Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).
Rodriguez-Mayorga, Via-Nadal, Ramos-Cordoba, Matito, *in preparation*.

Decomposition of the correlated 2-PD



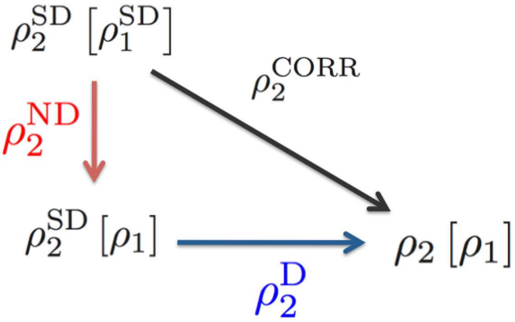
Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).

Decomposition of the correlated 2-PD



Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).

Decomposition of the correlated 2-PD

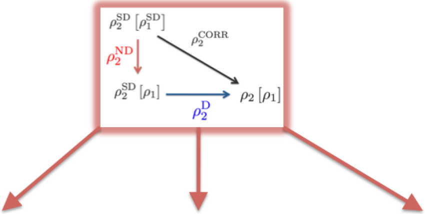


$$\rho_2(\mathbf{1},\mathbf{2}) = \rho_2^{\mathsf{SD}}(\mathbf{1},\mathbf{2}) + \rho_2^{\mathsf{D}}(\mathbf{1},\mathbf{2}) + \rho_2^{\mathsf{ND}}(\mathbf{1},\mathbf{2})$$

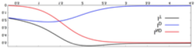
Hypothesis: 1RDM does not change with dynamic elect. corr.

Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).

Decomposition of the correlated 2-PD

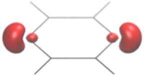


GLOBAL CORRELATION



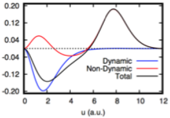
PCCP (**2016**)

LOCAL CORRELATION



JCTC (**2017**)

RANGE-SEPARATION OF CORRELATION



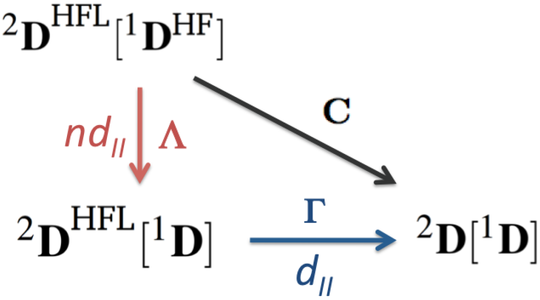
(*in preparation*)

Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).
Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).
Rodriguez-Mayorga, Via-Nadal, Ramos-Cordoba, Matito, *in preparation*.

Global Correlation

Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).

Decomposition of the correlated 2RDM



$$C^{ij}_{kl} = {}^2D^{ij}_{kl} - ({}^2D^{\mathsf{HF}})^{ij}_{kl}$$
$$C^{ij}_{kl} = \Lambda^{ij}_{kl} + \Gamma^{ij}_{kl}$$

Ramos-Cordoba, Salvador, Matito, PCCP 18, 24015 (**2016**).

A simple two-electron model to extract information.

We take the average interaction of electrons occupying two non-overlapping regions:

$$I_{\mathsf{D}} = \sum_{ijkl} \Gamma^{ij}_{kl} S^{A}_{ik} S^{B}_{jl} \qquad\qquad I_{\mathsf{ND}} = \sum_{ijkl} \Lambda^{ij}_{kl} S^{A}_{ik} S^{B}_{jl}$$

and assume the two-electron model in two identical regions of the space and sufficiently delocalized orbitals so that

$$S^{A}_{ii} = S^{B}_{ii} = 1/2$$

A two-electron system

A two-electron singlet wavefunction can be retrieved exactly

$$\Psi(\mathbf{1},\mathbf{2}) = \sqrt{\frac{1}{2}}\,(\alpha_1\beta_2 - \alpha_2\beta_1)\sum_k c_k \phi_k(\mathbf{r}_1)\phi_k(\mathbf{r}_2)$$

where $2c_k^2 = n_k$, n_k and ϕ_k being the natural occupancies and orbitals, respectively. The cumulant can be expressed as:

$$\Gamma^{ij}_{kl} = 2\left[\phi_{ik}\, n_i^{1/2} n_k^{1/2} \delta_{ij}\delta_{kl} - 2n_i n_j \delta_{ik}\delta_{jl} + n_i n_j (\delta_{il}\delta_{jk})\right]$$

where $\phi_{ik} = \{-1, 1\}$ is an undetermined phase factor.

In a minimal basis set $\phi_{12} = 1$ (ϕ_{ii} is always 0).

Löwdin, Shull, *PR*, **101**, 1730 (1956)

The indices in a two-electron system

If we assume minimal basis:

$$\begin{aligned}\Gamma^{22}_{11} &= \Gamma^{11}_{22} = -2n^{1/2}(1-n)^{1/2} \\ \Gamma^{11}_{11} &= \Gamma^{22}_{22} = \Gamma^{12}_{21} = \Gamma^{21}_{12} = 2n(1-n) \\ \Gamma^{12}_{12} &= \Gamma^{21}_{21} = -4n(1-n)\end{aligned}$$

where n is the strongly-occupied natural orbital. Then

$$\begin{aligned}I_D &= -4n(1-n) + 2n^{1/2}(1-n)^{1/2} \\ I_{ND} &= 4n(1-n) \\ I_T &= 2n^{1/2}(1-n)^{1/2}\end{aligned}$$

Ramos-Cordoba, Salvador, Matito, PCCP 18, 24015 (**2016**).

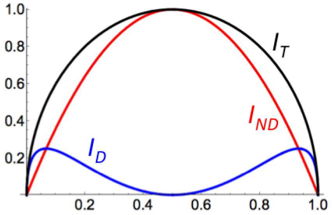
Global Correlation Indices

Assuming additive individual orbital contributions to correlation:

$$I_D[\{n_i\}] = \frac{1}{2N}\sum_i \left(n_i^{1/2}(1-n_i)^{1/2} - 2n_i(1-n_i)\right)$$

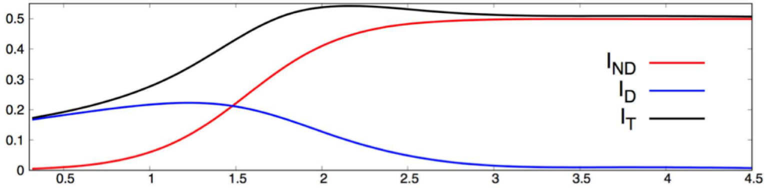
$$I_{ND}[\{n_i\}] = \frac{1}{N}\sum_i n_i(1-n_i)$$

$$I_T[\{n_i\}] = \frac{1}{2N}\sum_i n_i^{1/2}(1-n_i)^{1/2}$$



Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).

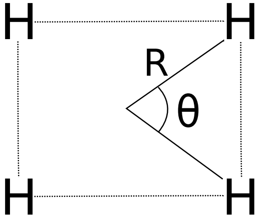
Correlation Upon Dissociation: H_2



Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).

The H_4 molecule.

The transition of D_{2h} to D_{4h} symmetry in H_4 molecule is among the most simple archetypal examples to illustrate the consequences of missing dynamic/nondynamic correlation effects.

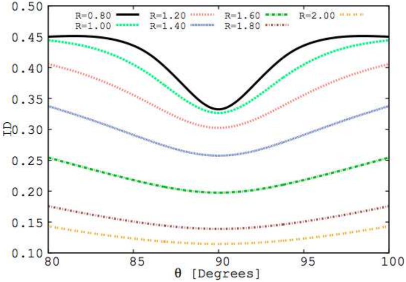


Playing out with θ and R one can introduce variable correlation effects.

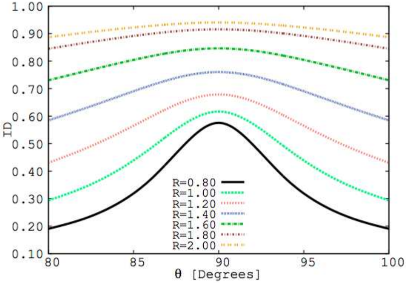
Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).

Correlation in the H_4 molecule.

I_D



I_{ND}



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Local Correlation

Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).

A local account of electron correlation.

One can easily devise a local version of these quantities.

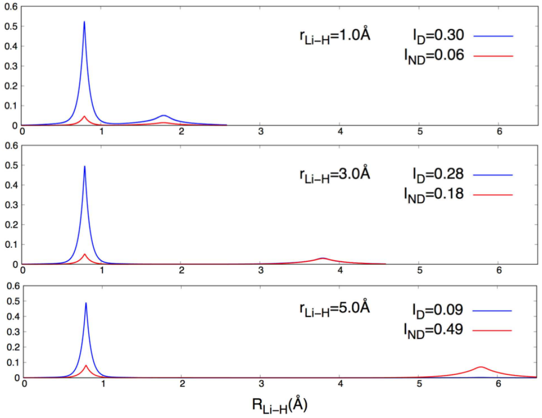
$$I_D[\{n_i\},\{\phi_i\}](r) = \frac{1}{2N}\sum_i \left(n_i^{1/2}(1-n_i)^{1/2} - 2n_i(1-n_i)\right)|\phi_i(r)|^2$$

$$I_{\mathsf{ND}}[\{n_i\},\{\phi_i\}](r) = \frac{1}{N}\sum_i (n_i(1-n_i))\,|\phi_i(r)|^2$$

$$I_T[\{n_i\},\{\phi_i\}](r) = \frac{1}{2N}\sum_i n_i^{1/2}(1-n_i)^{1/2}\,|\phi_i(r)|^2$$

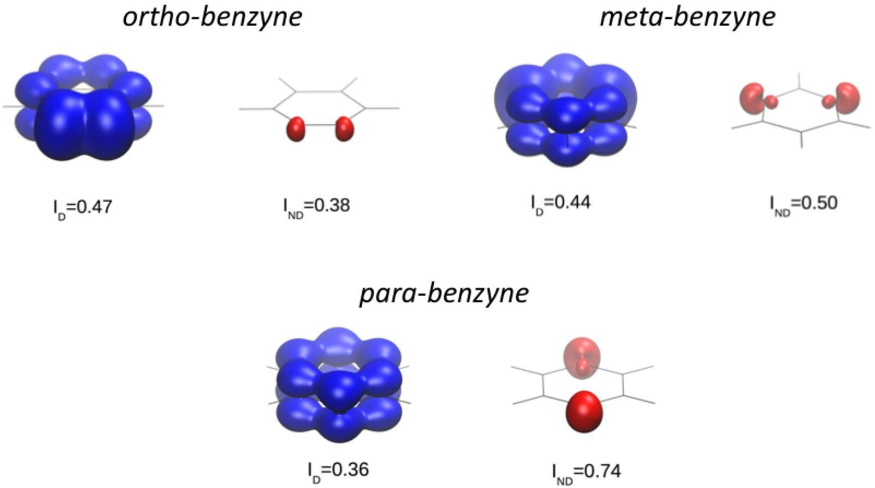
Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).

Local Correlation in Dissociation: LiH



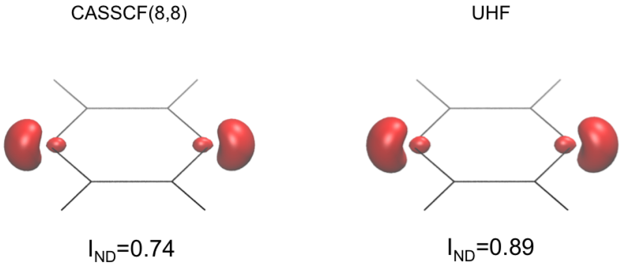
Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).

Electron correlation in benzynes



Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).

Unrestricted natural orbitals (UNOs) provide a similar NDC description:



Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).

Conclusions and future perspectives

- Correlation matrices: $\mathbf{C} = \mathbf{\Gamma} + \mathbf{\Lambda}$
- Global correlation indicators: $I_T = I_D + I_{ND}$
  - Global hybridization in DFT
- Local correlation indicators: $I_T(\mathbf{r}) = I_D(\mathbf{r}) + I_{ND}(\mathbf{r})$
  - Local-scaling and local hybrid functionals
- Range-separation correlation indicators: $\mathbf{C}(\mathbf{r_{12}}) = \mathbf{\Gamma}(\mathbf{r_{12}}) + \mathbf{\Lambda}(\mathbf{r_{12}})$
  - Range-separated methods (*e.g.* RSF-functionals)

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Rodriguez-Mayorga, Via-Nadal, Ramos-Cordoba, Matito, *in preparation*.
Via-Nadal, Rodríguez-Mayorga, Matito, *in preparation*.

Acknowledgements

Dr. Pedro Salvador

Dr. Eloy Ramos-Cordoba
Mr. Mauricio Rodríguez
Ms. Mireia Via

Funding: MINECO/FEDER
CTQ2014-52525-P

Ramos-Cordoba, Salvador, Matito, *PCCP* 18, 24015 (**2016**).
Ramos-Cordoba, Matito, *JCTC*, 13, 2705 (**2017**).
Rodríguez-Mayorga, Via-Nadal, Ramos-Cordoba, Matito, *in preparation*.
Via-Nadal, Rodríguez-Mayorga, Matito, *in preparation*.

Decomposition of the correlated 2RDM

The following matrix contains most electron correlation effects:

$$
\begin{aligned}
C^{ij}_{kl} &= {}^2D^{ij}_{kl} - ({}^2D^{\mathsf{HF}})^{ij}_{kl} \\
C^{ij}_{kl} &\approx {}^2D^{ij}_{kl} - ({}^2D^{\mathsf{PHF}})^{ij}_{kl}
\end{aligned}
$$

Let us decompose $\mathbf{C}$ as

$$C^{ij}_{kl} = \Lambda^{ij}_{kl} + \Gamma^{ij}_{kl}$$

where

$$\Lambda^{ij}_{kl} = (n_i n_j - \epsilon_{ijkl}) \left(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \right)$$

$$\Gamma^{ij}_{kl} = {}^2D^{ij}_{kl} - (n_i n_j) \left(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \right)$$

$\boldsymbol{\Lambda}$ is an antisymmetric diagonal matrix that measures the pairwise deviation of NOO from a single-determinant picture and $\boldsymbol{\Gamma}$ is the cumulant matrix.