Localizing electron pairs with the Electron Pair Localization Function

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What is EPLF?

- EPLF: Electron Pair Localization Function
- 3D local function which measures the degree of pairing of electrons
- Introduced in the QMC framework in 2004[1]
- Modified for analytical calculations in 2010[2]

[1] A. Scemama, P. Chaquin, M. Caffarel *J. Chem. Phys.* **121** 1725 (2004)

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Outline

QMC Background

- Calculation of an expectation value as a stochastic average:

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\begin{aligned}
O &= \frac{\langle \Psi | \mathcal{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\
&= \frac{\int \Psi^2(\vec{r_1}, \dots, \vec{r_N}) \left[\frac{\mathcal{O}\Psi(\vec{r_1}, \dots, \vec{r_N})}{\Psi(\vec{r_1}, \dots, \vec{r_N})} \right] d\vec{r_1} \dots d\vec{r_N}}{\int \Psi^2(\vec{r_1}, \dots, \vec{r_N}) d\vec{r_1} \dots d\vec{r_N}} \\
&= \langle \frac{\mathcal{O}\Psi(\vec{r_1}, \dots, \vec{r_N})}{\Psi(\vec{r_1}, \dots, \vec{r_N})} \rangle_{\Psi^2}
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- Definition of a local property $\frac{\mathcal{O}\Psi}{\Psi}$
- Statistical sampling of the $3N$-electron density Ψ^2

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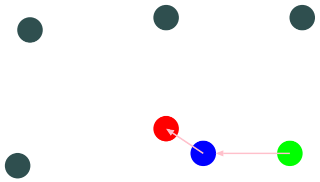
Electron pairing as a local property

An electron i at $\vec{r}_i$ is paired to an electron j at $\vec{r}_j$ if j is the closest electron to i.

The local pairing at $\vec{r}_i$ is proportional $d(\vec{r}_i)^{-1}$ where

$$d(\vec{r}_i) = \min_{j \neq i} |\vec{r}_j - \vec{r}_i|$$



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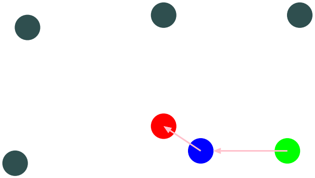

Electron pairing as a local property

We distinguish two different cases:

- pairs of same-spin electrons (σ, σ)
- pairs of opposite-spin electrons $(\sigma, \bar{\sigma})$

and introduce the two following quantities

$$d_{\sigma\sigma}(\vec{r}) = \int \Psi^2(\vec{r}_1, \dots, \vec{r}_N) \left[\sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \min_{j \neq i; \sigma_j = \sigma_i} |\vec{r}_i - \vec{r}_j| \right] d\vec{r}_1 \dots d\vec{r}_N$$

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$$\mathrm{EPLF}(\vec{r}) = \frac{d_{\sigma\sigma}(\vec{r}) - d_{\sigma\bar{\sigma}}(\vec{r})}{d_{\sigma\sigma}(\vec{r}) + d_{\sigma\bar{\sigma}}(\vec{r})} \qquad -1 \leq \mathrm{EPLF}(\vec{r}) \leq 1$$

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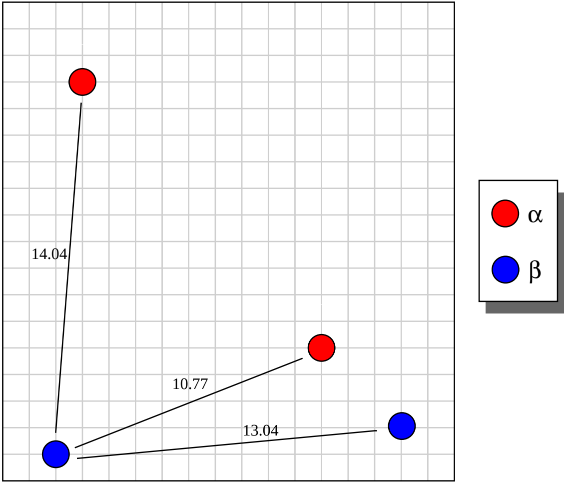
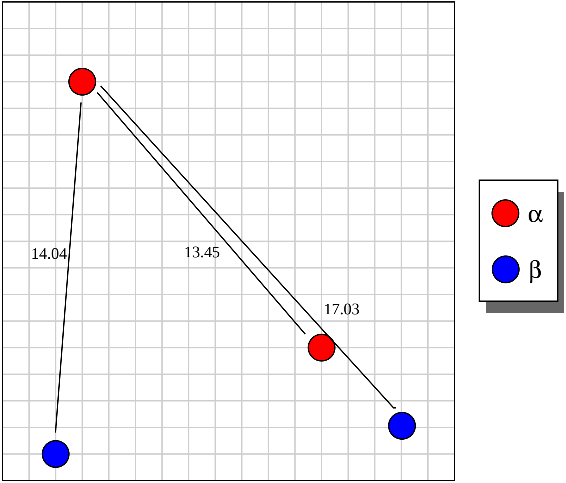
Electron pairing as a local property



$d_{\sigma\sigma}$ = 13.04
$d_{\sigma\bar{\sigma}}$ = 10.77
EPLF = 0.09

EPLF > 0
Slight anti-parallel pairing

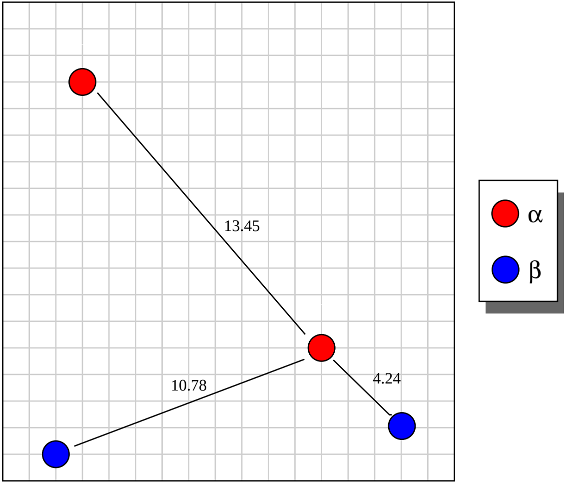
Electron pairing as a local property



$d_{\sigma\sigma}$ = 14.04
$d_{\sigma\bar{\sigma}}$ = 13.45
EPLF = -0.12

EPLF < 0
Slight parallel pairing

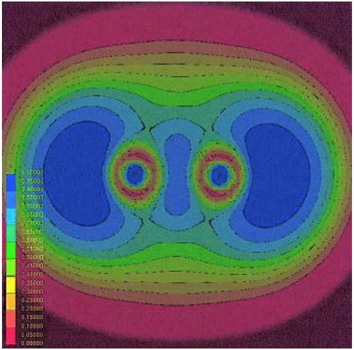
Electron pairing as a local property



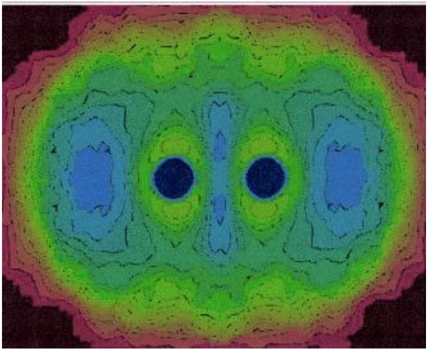
$d_{\sigma\sigma}$ = 4.24
$d_{\sigma\bar{\sigma}}$ = 13.45
EPLF = 0.52

EPLF $\gg 0$
Strong anti-parallel pairing

Examples : N_2 (Hartree-Fock)

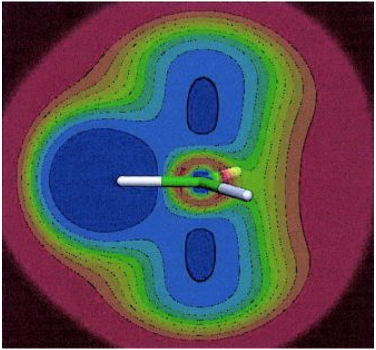


ELF



EPLF

Examples : CH_3 (Hartree-Fock)



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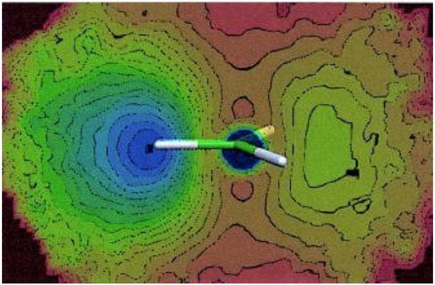

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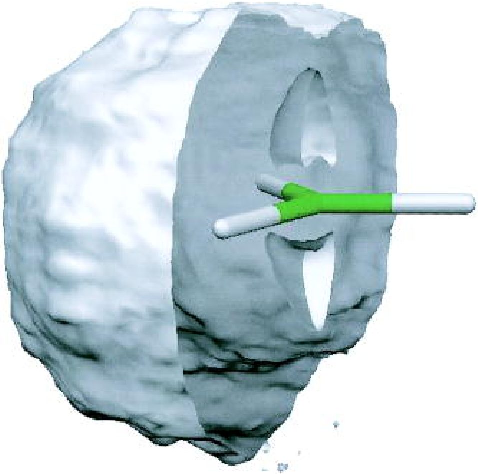

Outline

1. EPLF in quantum Monte Carlo
2. Reformulation for analytical calculations

Need for an analytical expression

- With the QMC estimators, images are very noisy
- An analytical expression of EPLF is more suitable for more conventional methods (Hartree-Fock, CI, CAS,. . .)
- An analytical expression helps to reduce the noise of the QMC estimators (work in progress) via zero-variance improved estimators.
- The $\min$ function in the expressions of $d_{\sigma\sigma}$ and $d_{\sigma\bar{\sigma}}$ yields difficulties for analytical integration

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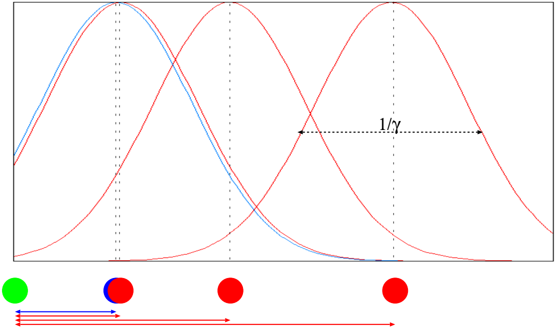
Suppression of the min function

Approximation of the min in terms of gaussian functions

$$\min_{j \neq i} |\vec{r}_i - \vec{r}_j| = \lim_{\gamma \to \infty} \sqrt{-\frac{1}{\gamma} \ln \left(\sum_{j \neq i} e^{-\gamma |\vec{r}_i - \vec{r}_j|^2} \right)}$$



Introduction of bi-electronic operators

As $\sum_{j\neq i} e^{-\gamma|\vec{r}_i-\vec{r}_j|^2}$ has small fluctuations in the regions of interest, we can do the approximation

$$\langle \ln X \rangle \sim \ln \langle X \rangle$$

The expectation values of the minimum distances are now

$$d_{\sigma\sigma}(\vec{r}) \sim \lim_{\gamma\to\infty} \sqrt{-\frac{1}{\gamma}\ln\left\langle \Psi \left| \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) \sum_{j\neq i;\sigma_i=\sigma_j}^{N} e^{-\gamma|\vec{r}_i-\vec{r}_j|^2} \right| \Psi \right\rangle}$$

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Expression of γ

Remember:

$$\min_{j\neq i} |\vec{r}_i - \vec{r}_j| = \lim_{\gamma\to\infty} \sqrt{-\frac{1}{\gamma} \ln \left(\sum_{j\neq i} e^{-\gamma|\vec{r}_i-\vec{r}_j|^2} \right)}$$

- γ needs to be very large when electrons are close and not too large when electrons are far apart.
- γ is chosen to depend on the density, such that the largest possible value of d is the radius of a sphere that contains around 0.1 electron:

$$\gamma(\vec{r}) = \left(\frac{4\pi}{3n} \rho(\vec{r}) \right)^{2/3} (-\ln(\epsilon))$$

where $n = 0.1$ and ϵ is the smallest floating point number representable on 64 bits ($\sim 2.10^{-308}$).

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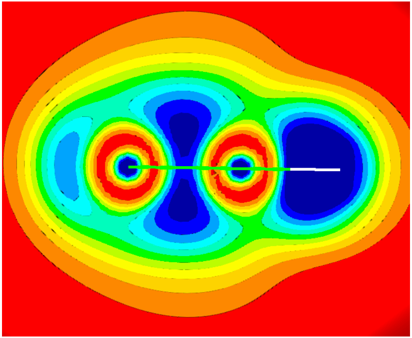
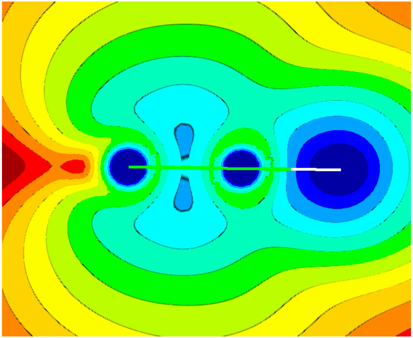
Examples : C_2H (ROHF)



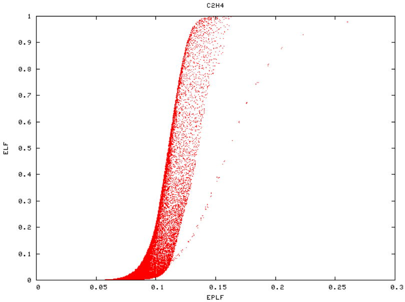
ELF

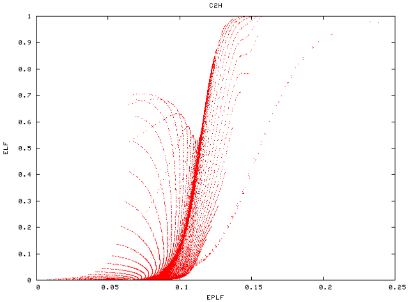


EPLF

Correlation between ELF and EPLF

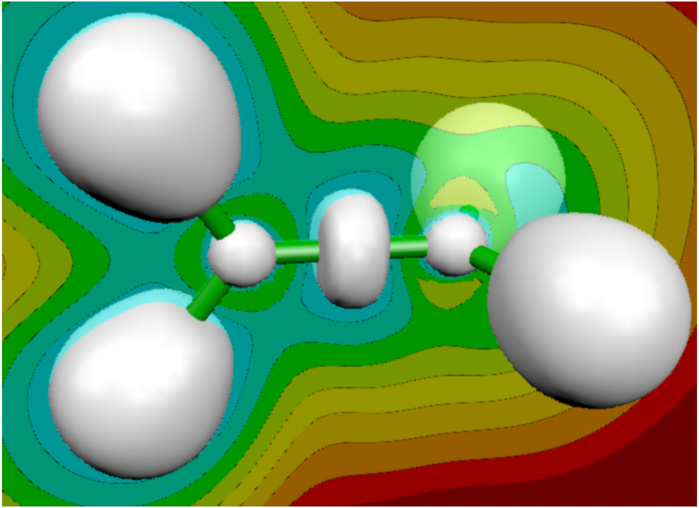
For each value $\vec{r}$, $\mathrm{ELF}(\vec{r})$ and $\mathrm{EPLF}(\vec{r})$ was computed.
We plot $\mathrm{EPLF}(\vec{r}) = f(\mathrm{ELF}(\vec{r}))$



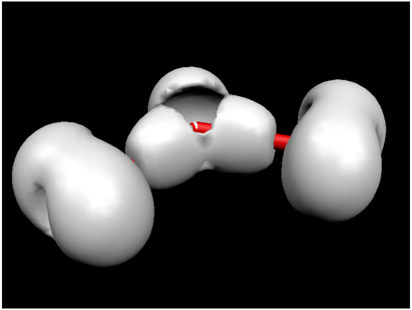


C_2H_4 (Planar) C_2H

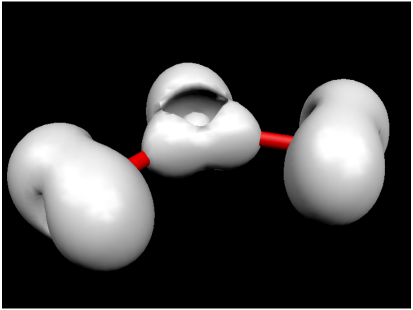
Examples : Twisted C_2H_4 (Singlet CAS (2,2))



Examples : Ozone (Hartree-Fock)

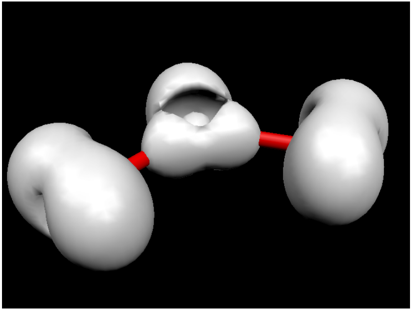


ELF

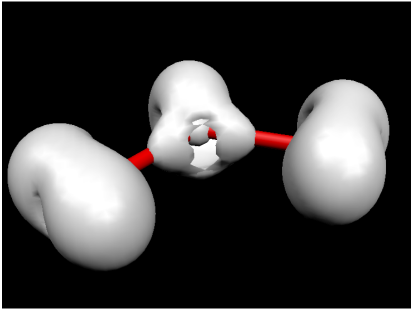


EPLF

Examples : Ozone (Hartree-Fock, CAS(8,8))

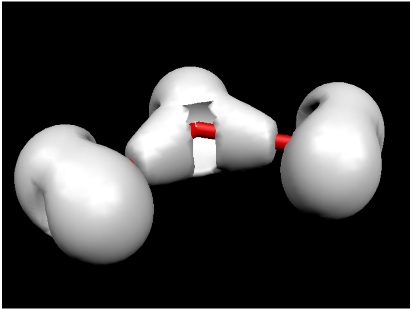


EPLF HF

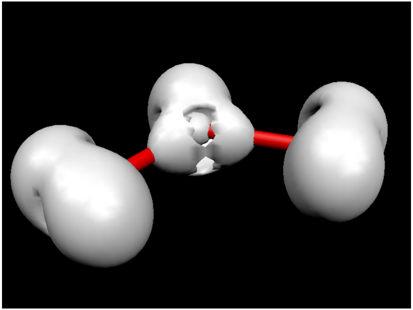


EPLF CAS(8,8)

Examples : Ozone (B3LYP)

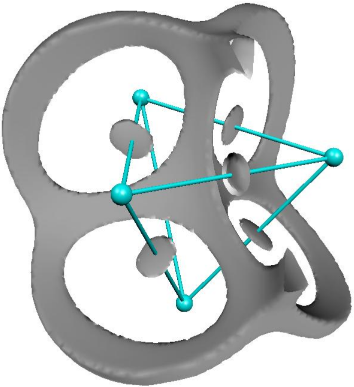


ELF



EPLF

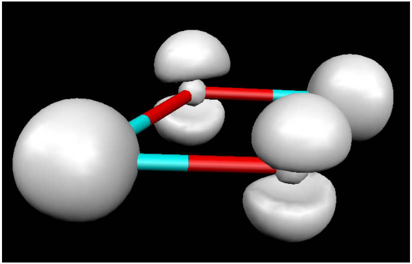
Examples : Li_4 (Quintet, ROHF)



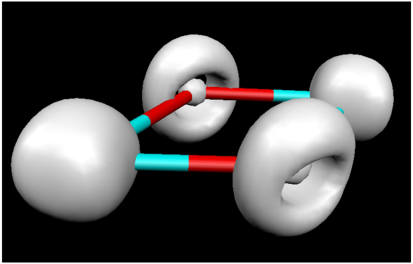
EPLF < 0 !

A. Scemama, A. Monari, M. Caffarel, S. Evangelisti
work in progress

Examples : $Cu_2O_2^{2+}$ (Hartree-Fock, B3LYP, CAS(4,4))



HF (B3LYP almost identical)



CAS(4,4)

A. Scemama, M. Caffarel, J. Pilmé, R. Chaudret, J.-P. Piquemal
to be analyzed... work in progress

Conclusions

The Electron Pair Localization Function:

- Is a combination of two bi-electronic operators
- Is similar to ELF for single determinant closed-shells (HF or DFT)
- Is different from ELF when unpaired electrons are localized (ROHF)
- Is naturally defined for multi-configurational wave functions (CI,MCSCF,MR-CI,VB,. . .)
- Can be used with any type of wave function using the QMC formulation (Hylleraas, Slater-Jastrow, Fixed-Node DMC, . . .)

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Acknowledgments

- The “disorganizers”
- Collaborators:
  - Paris: J.-P. Piquemal, J. Pilmé, R. Chaudret, P. Chaquin, . . .
  - Mexico: A. Ramirez-Solis (O_4, Li-thiophene)
  - Toulouse: A. Monari (Li_4), J.-L. Heully, F. Alary (Nickel bisdithiolene complex)

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