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\(^2\)

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Outline

1. EPLF in quantum Monte Carlo

2. Reformulation for analytical calculations
QMC Background

Calculation of an expectation value as a stochastic average:

\[ O = \frac{\langle \Psi | O | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \Psi^2(r_1, \ldots, r_N) \left[ \frac{O\Psi(r_1, \ldots, r_N)}{\Psi(r_1, \ldots, r_N)} \right] dr_1 \ldots dr_N}{\int \Psi^2(r_1, \ldots, r_N) dr_1 \ldots dr_N} = \langle \frac{O\Psi(r_1, \ldots, r_N)}{\Psi(r_1, \ldots, r_N)} \rangle \Psi^2 \]

- Definition of a local property \( \frac{O\Psi}{\Psi} \)
- Statistical sampling of the \( 3N \)-electron density \( \Psi^2 \)
QMC Background

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- Definition of a local property \( \frac{O\Psi}{\Psi} \)
- Statistical sampling of the \( 3N \)-electron density \( \Psi^2 \)
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 to \( d(\vec{r}_i)^{-1} \) where

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

$$d(\vec{r}_i) = \min_{j \neq i} |\vec{r}_j - \vec{r}_i|$$
Electron pairing as a local property

We distinguish two different cases:

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

and introduce the two following quantities

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

**Definition**

\[
EPLF(\vec{r}) = \frac{d_{\sigma\sigma}(\vec{r}) - d_{\sigma\bar{\sigma}}(\vec{r})}{d_{\sigma\sigma}(\vec{r}) + d_{\sigma\bar{\sigma}}(\vec{r})}
\]

\(-1 \leq EPLF(\vec{r}) \leq 1\)
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\mathcal{d}_{\sigma\bar{\sigma}}(\vec{r}) & = \int \Psi^2(\vec{r}_1, \ldots, \vec{r}_N) \left[ \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \min_{j; \sigma_j \neq \sigma_i} |\vec{r}_j - \vec{r}_i| \right] d\vec{r}_1 \ldots d\vec{r}_N
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Definition

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\text{EPLF}(\vec{r}) = \frac{\mathcal{d}_{\sigma\sigma}(\vec{r}) - \mathcal{d}_{\sigma\bar{\sigma}}(\vec{r})}{\mathcal{d}_{\sigma\sigma}(\vec{r}) + \mathcal{d}_{\sigma\bar{\sigma}}(\vec{r})} \quad -1 \leq \text{EPLF}(\vec{r}) \leq 1
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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})}
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Electron pairing as a local property

\[ d_{\sigma\sigma} = 13.04 \]
\[ d_{\sigma\bar{\sigma}} = 10.77 \]
\[ \text{EPLF} = 0.09 \]

Slight anti-parallel pairing

EPLF > 0
Electron pairing as a local property

\[ d_{\sigma\sigma} = 14.04 \]
\[ d_{\sigma\bar{\sigma}} = 13.45 \]
\[ \text{EPLF} = -0.12 \]

\[ \text{EPLF} < 0 \]
Slight parallel pairing

[Diagram with labeled points and distances]
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

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Examples: $\text{CH}_3$ (Hartree-Fock)
Examples: CH$_3$ (Hartree-Fock)
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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The min function in the expressions of $d_{\sigma\sigma}$ and $d_{\sigma\bar{\sigma}}$ yields difficulties for analytical integration.
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

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

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Expression of $\gamma$

Remember:

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

- $\gamma$ needs to be very large when electrons are close and not too large when electrons are far apart.
- $\gamma$ 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:

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

where $n = 0.1$ and $\epsilon$ is the smallest floating point number representable on 64 bits ($\sim 2.10^{-308}$).
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Examples: $C_2H$ (ROHF)

ELF

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

C$_2$H$_4$ (Planar)  

C$_2$H
Examples: Twisted $\text{C}_2\text{H}_4$ (Singlet CAS (2,2))
Examples: Ozone (Hartree-Fock)

ELF

EPLF

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

EPLF HF

EPLF CAS(8,8)
Examples: Ozone (B3LYP)

ELF

EPLF

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Examples: \( \text{Li}_4 \) (Quintet, ROHF)

\[ \text{EPLF} < 0 \]

A. Scemama, A. Monari, M. Caffarel, S. Evangelisti
work in progress
Examples: $\text{Cu}_2\text{O}_2^{2+}$ (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
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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EPLF in quantum Monte Carlo
Reformulation for analytical calculations

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