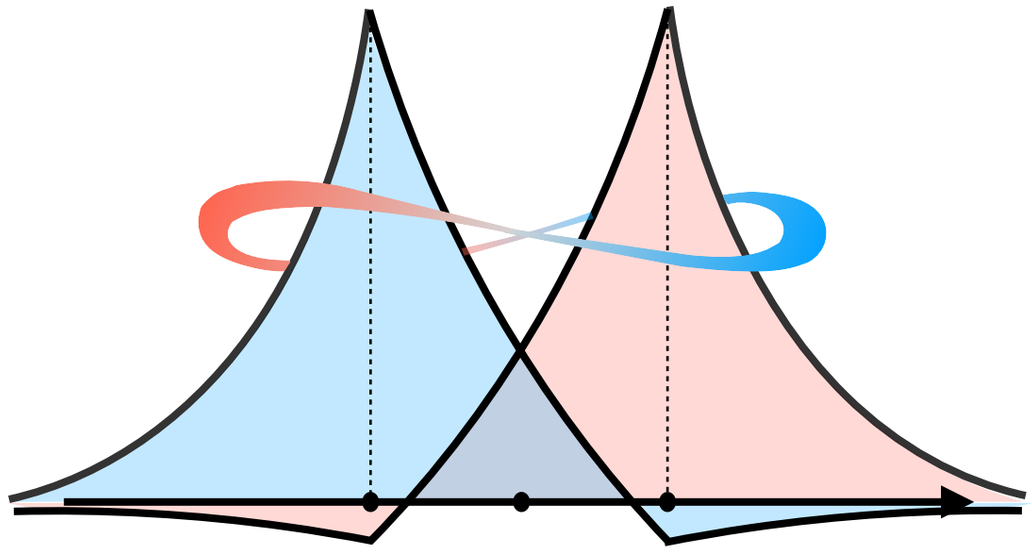
Electron Entanglement: State Complexity and Chemical Bonding

Lexin Ding

Trento 2022

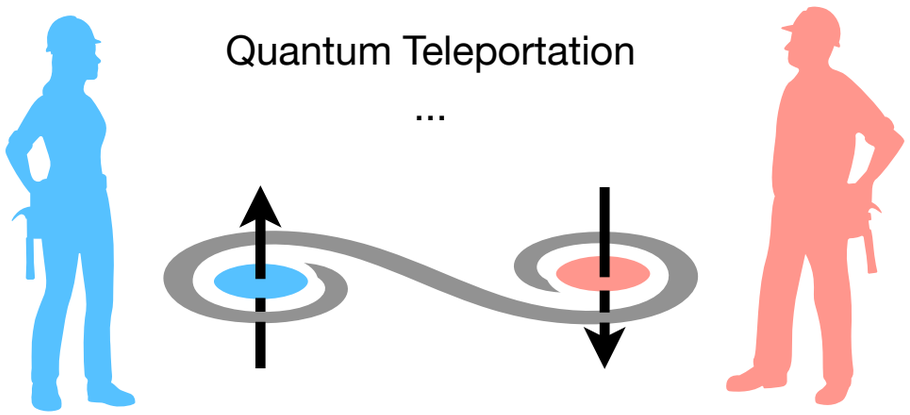


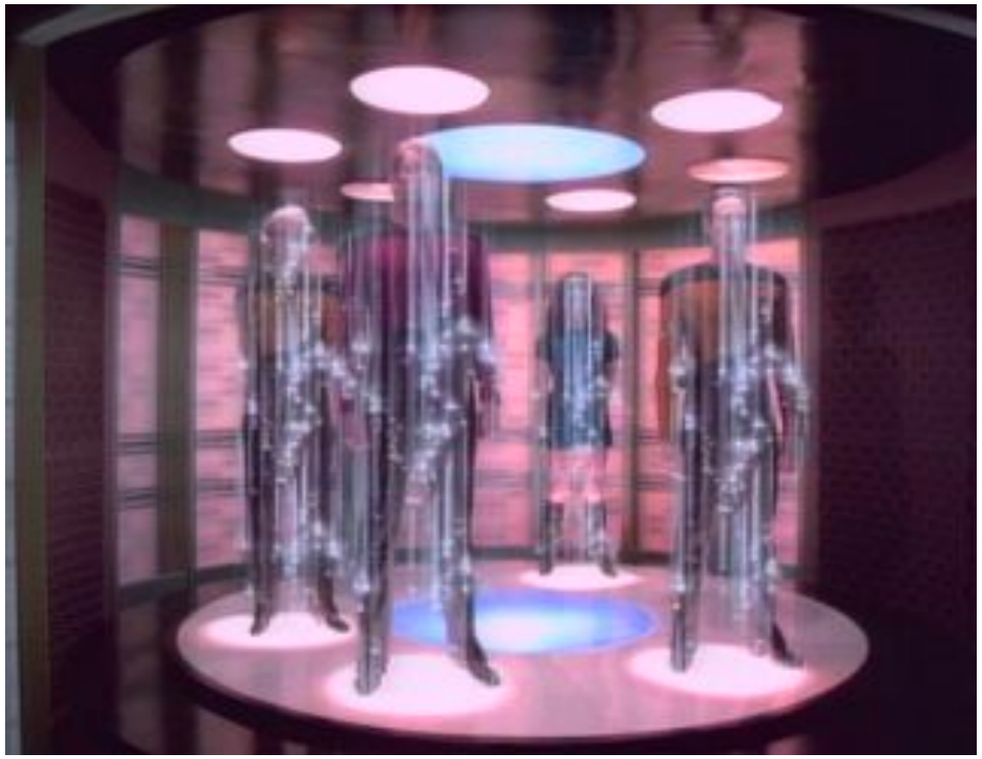
LD, S. Knecht, Z. Zimborás, C. Schilling, Quantum correlation in molecules: A quantum information toolbox for chemists. arXiv: 2205.15881 (2022)

LD, Z. Zimborás, C. Schilling, Quantifying Electron Entanglement Faithfully. arXiv: 2207.03377 (2022)

The Ubiquitous Entanglement

Quantum Information Processing

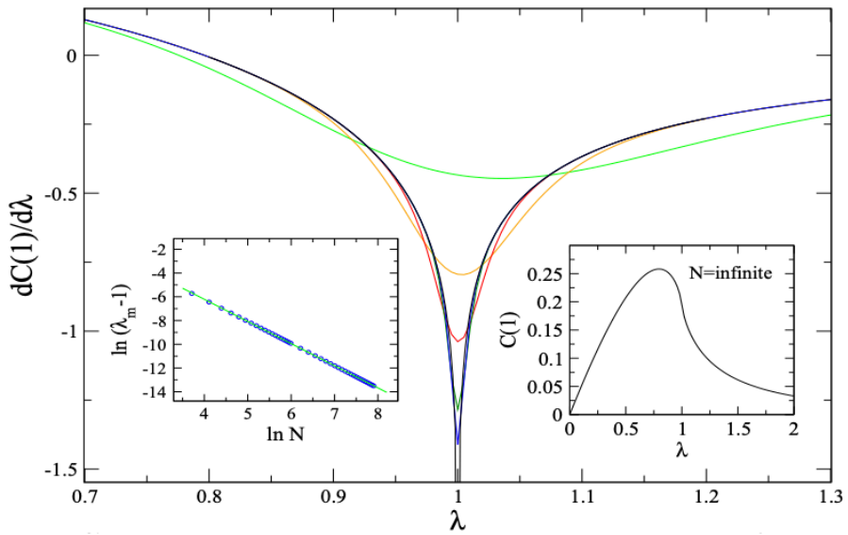




"Star Trek: The Next Generation." (Image credit: Paramount Television)

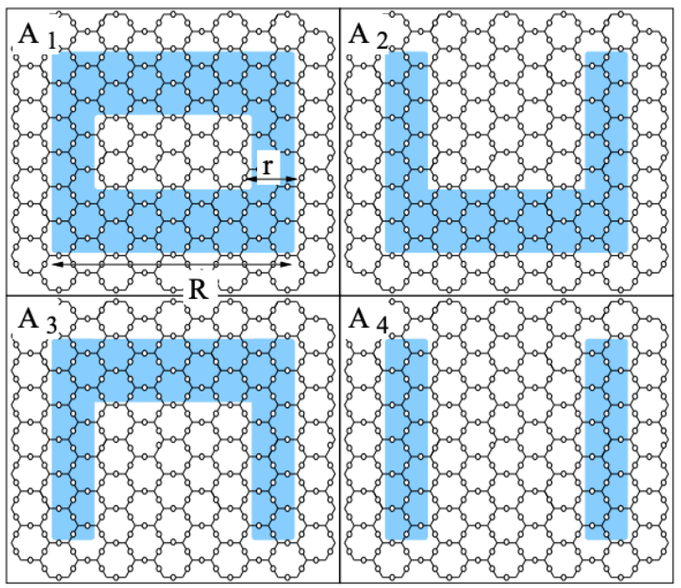
Condensed Matter Physics

Quantum Phase Transition



A. Osterloh, L. Amico, G. Falci, R. Fazio, *Nature* **416**, 608–610 (2002)

Topological Order



M. Levin and X.-G. Wen, *Phys. Rev. Lett*. **96**, 110405 (2006)

Orbital Correlation in Quantum Chemistry

JCTC Journal of Chemical Theory and Computation

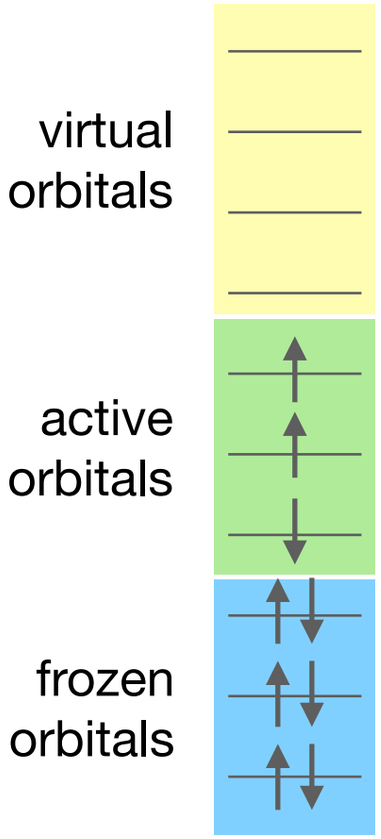
Article

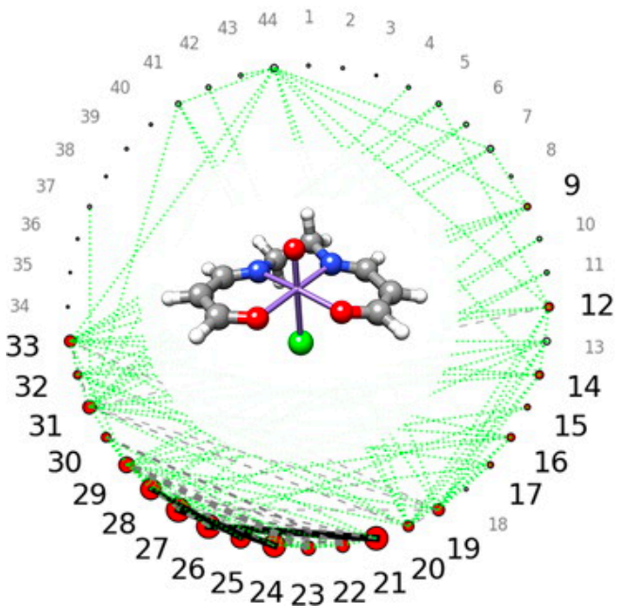
pubs.acs.org/JCTC

Automated Selection of Active Orbital Spaces (2016)

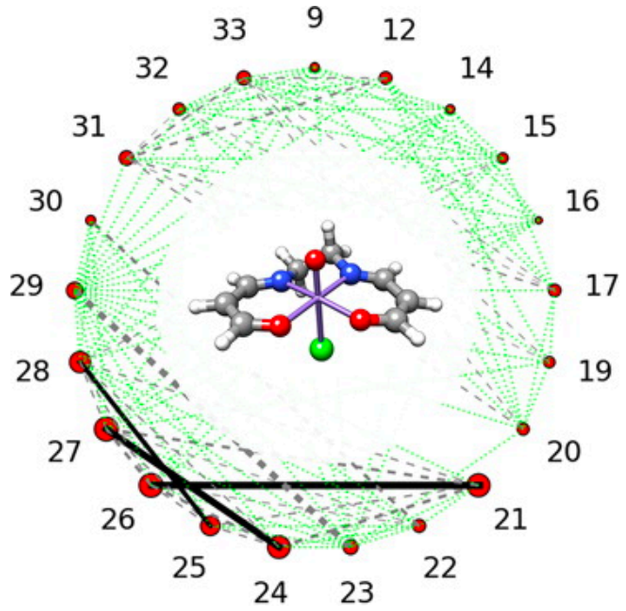
Christopher J. Stein and Markus Reiher*

Laboratorium für Physikalische Chemie, ETH Zürich, Vladimir-Prelog-Weg 2, CH-8093 Zürich, Switzerland





essential CAS selection



General Goals of Our Studies

1. Quantify various aspects of correlation in molecules

2. Minimize computational resource for molecular ground state calculation

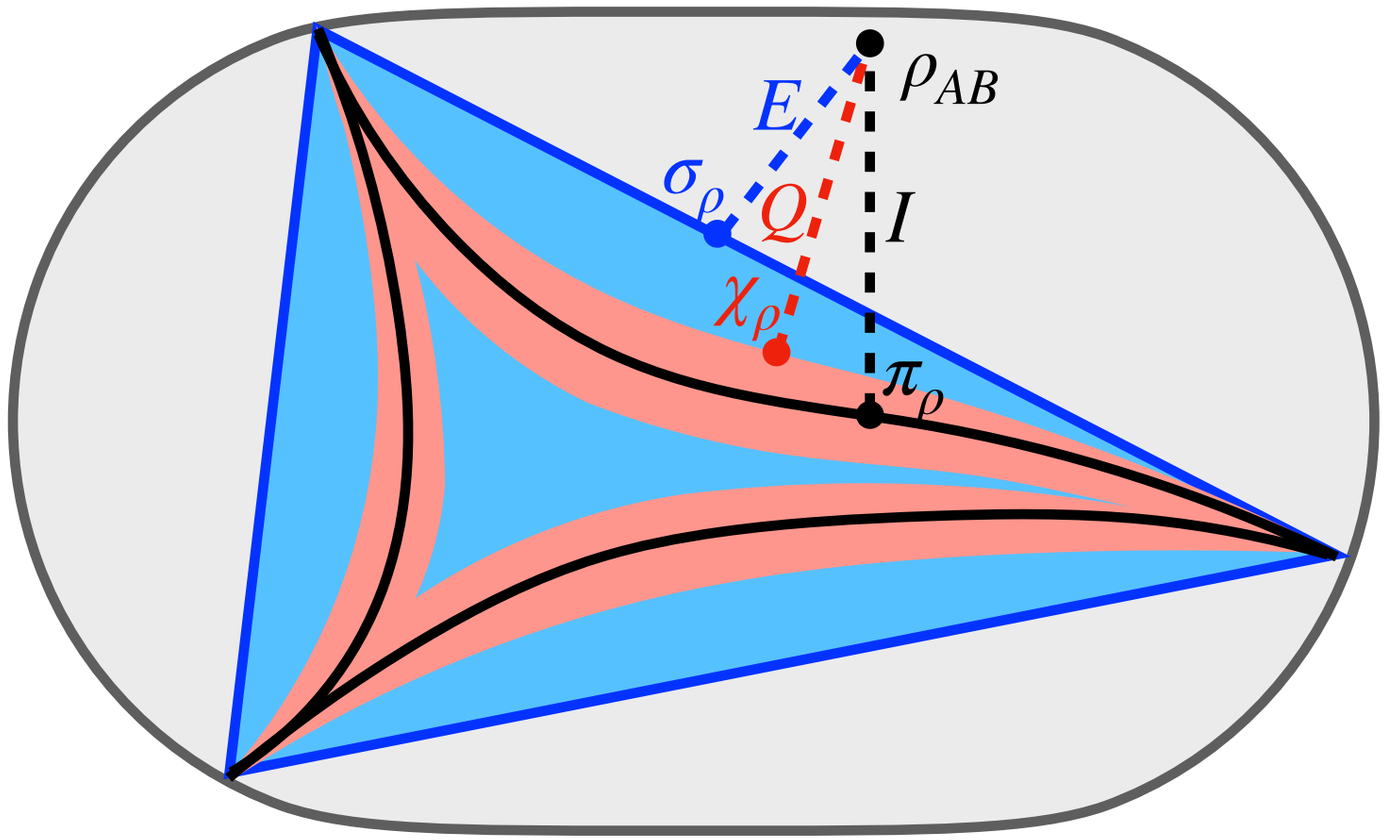
3. Maximize the entanglement resource in molecules for 2nd quantum revolution

4. Use orbital entanglement to study electronic structures/solve fundamental problems in quantum chemistry

Defining Correlation Types - Geometric Picture

Relative Entropy "Distance"

$$S(\rho\|\sigma)=\mathrm{Tr}[\rho(\log\rho-\log\sigma)]$$



K. Modi, et al., *Phys. Rev. Lett.* 104, 080501 (2010)

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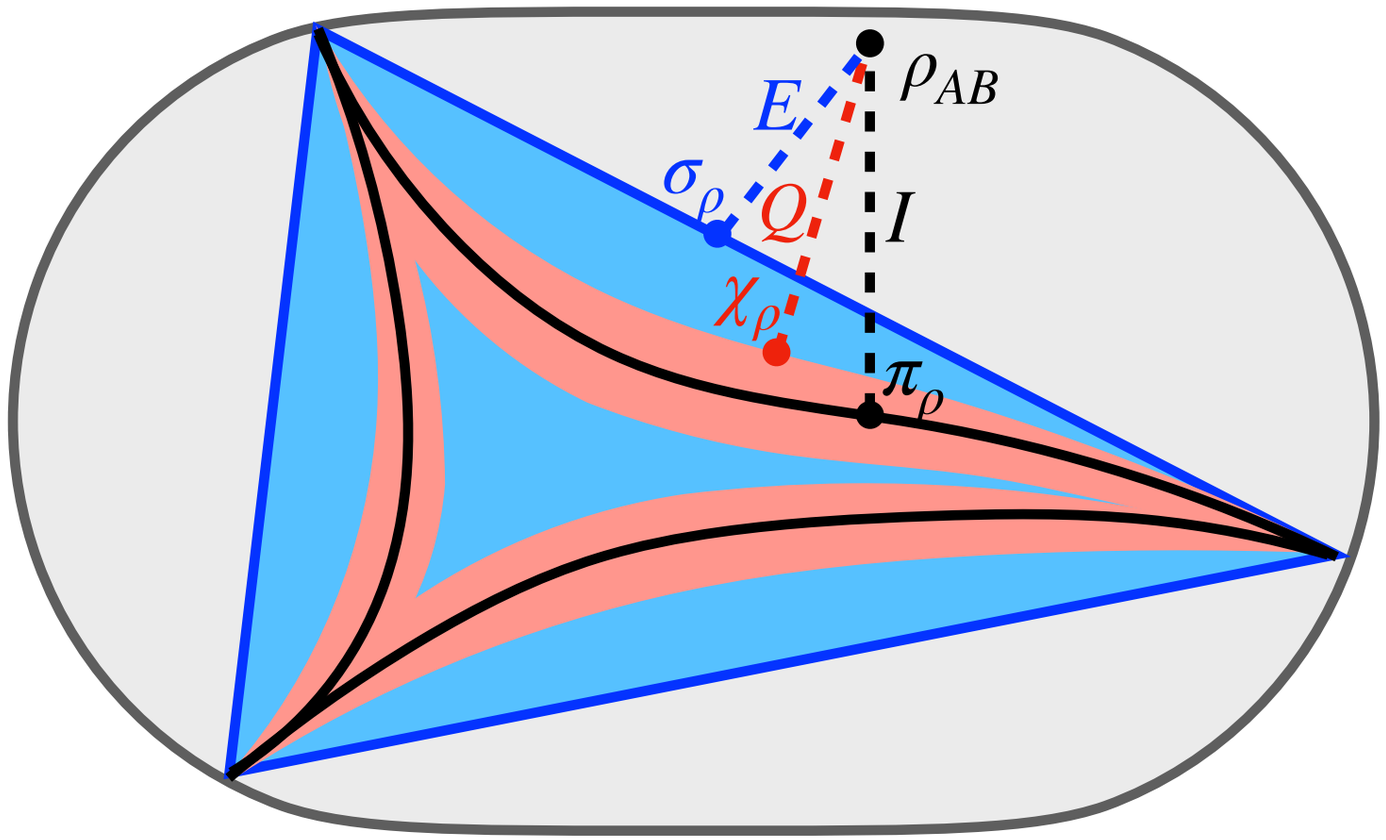

Uncorrelated States: D_0

$$\sigma_A \otimes \sigma_B$$

Total Correlation:

$$I=\min_{\pi\in D_0} S(\rho\|\pi)=S(\rho\|\pi_\rho)$$

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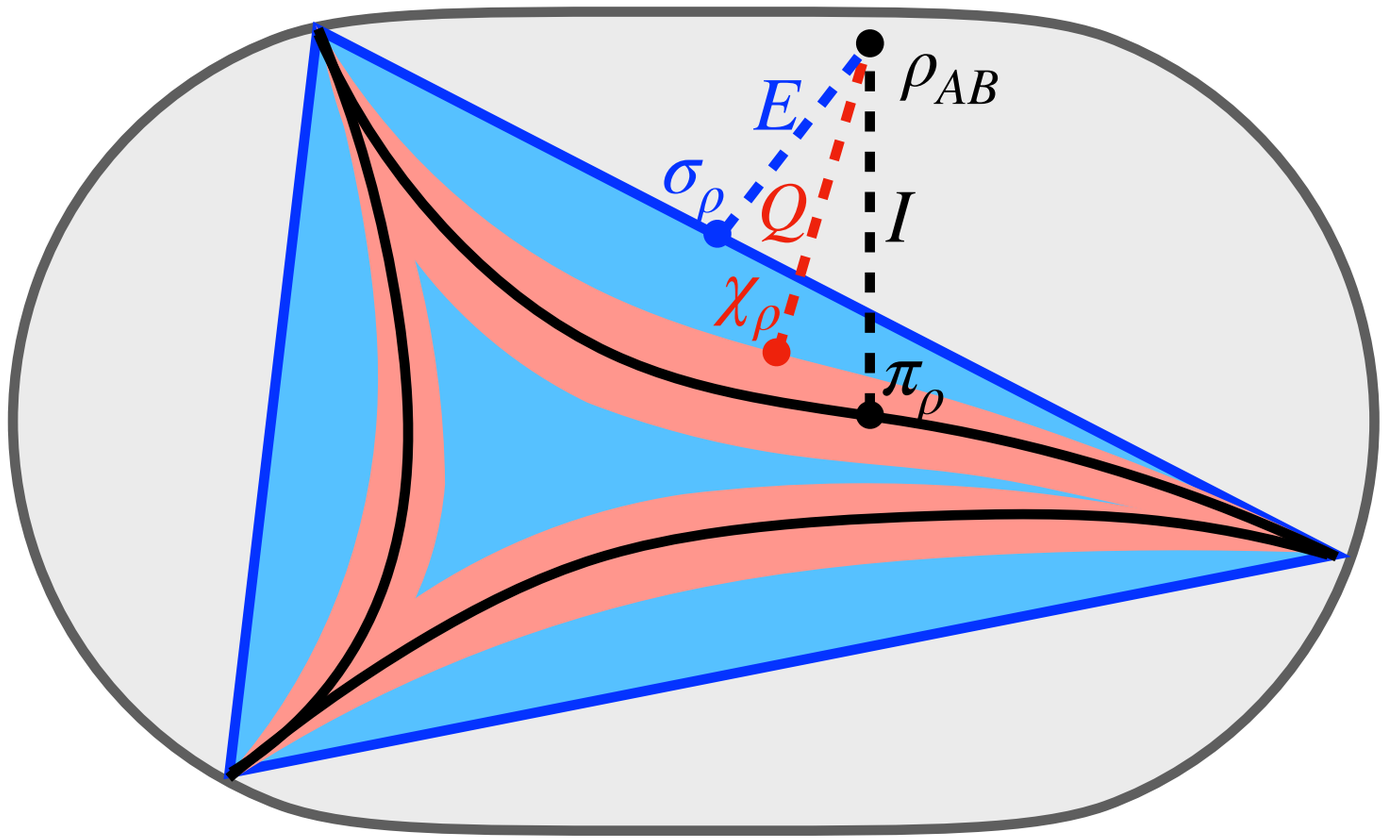

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Classical States: D_{cl}

$$\sum_{i,j} p_{ij}\,|i\rangle\langle i|\otimes|j\rangle\langle j|$$

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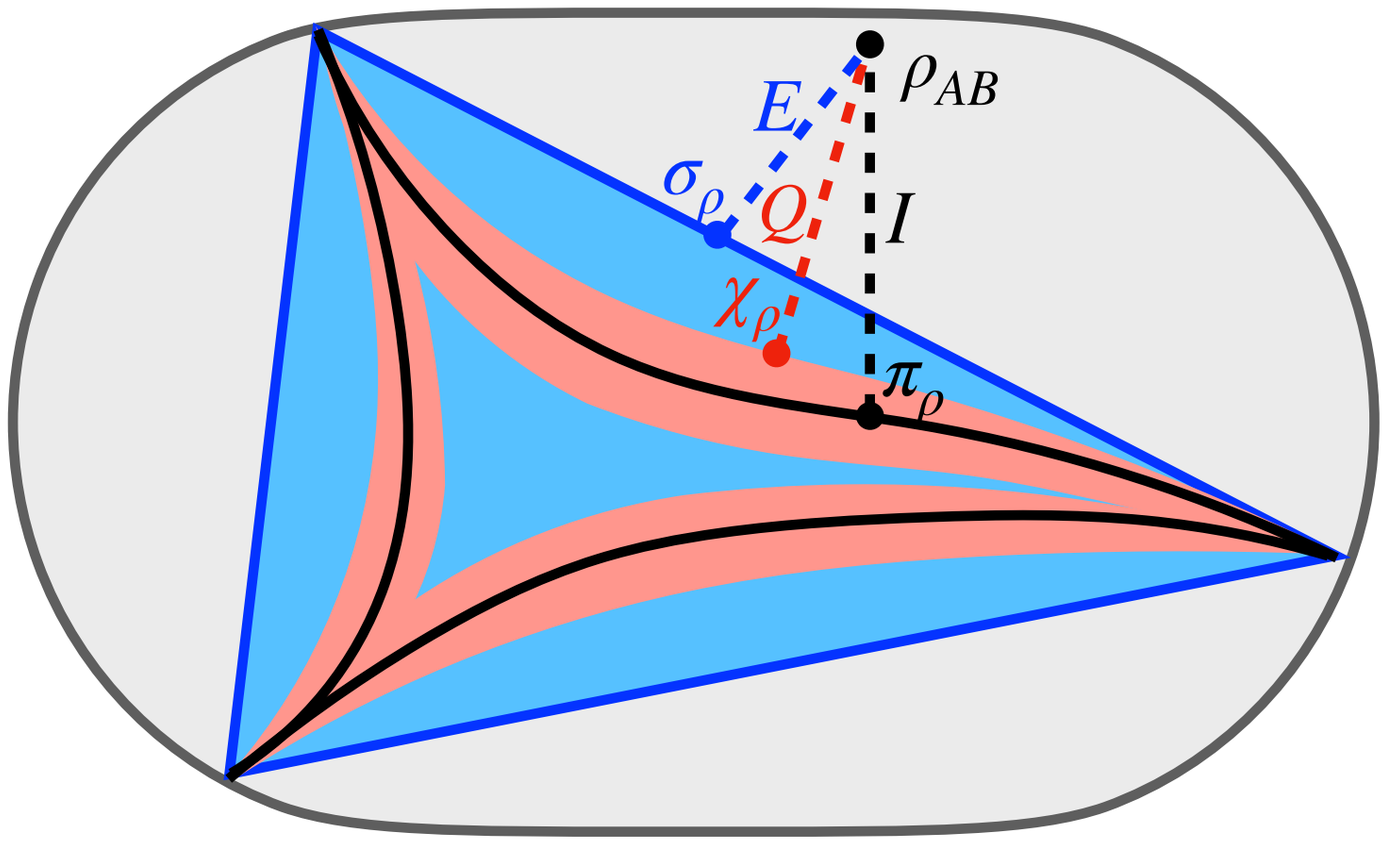

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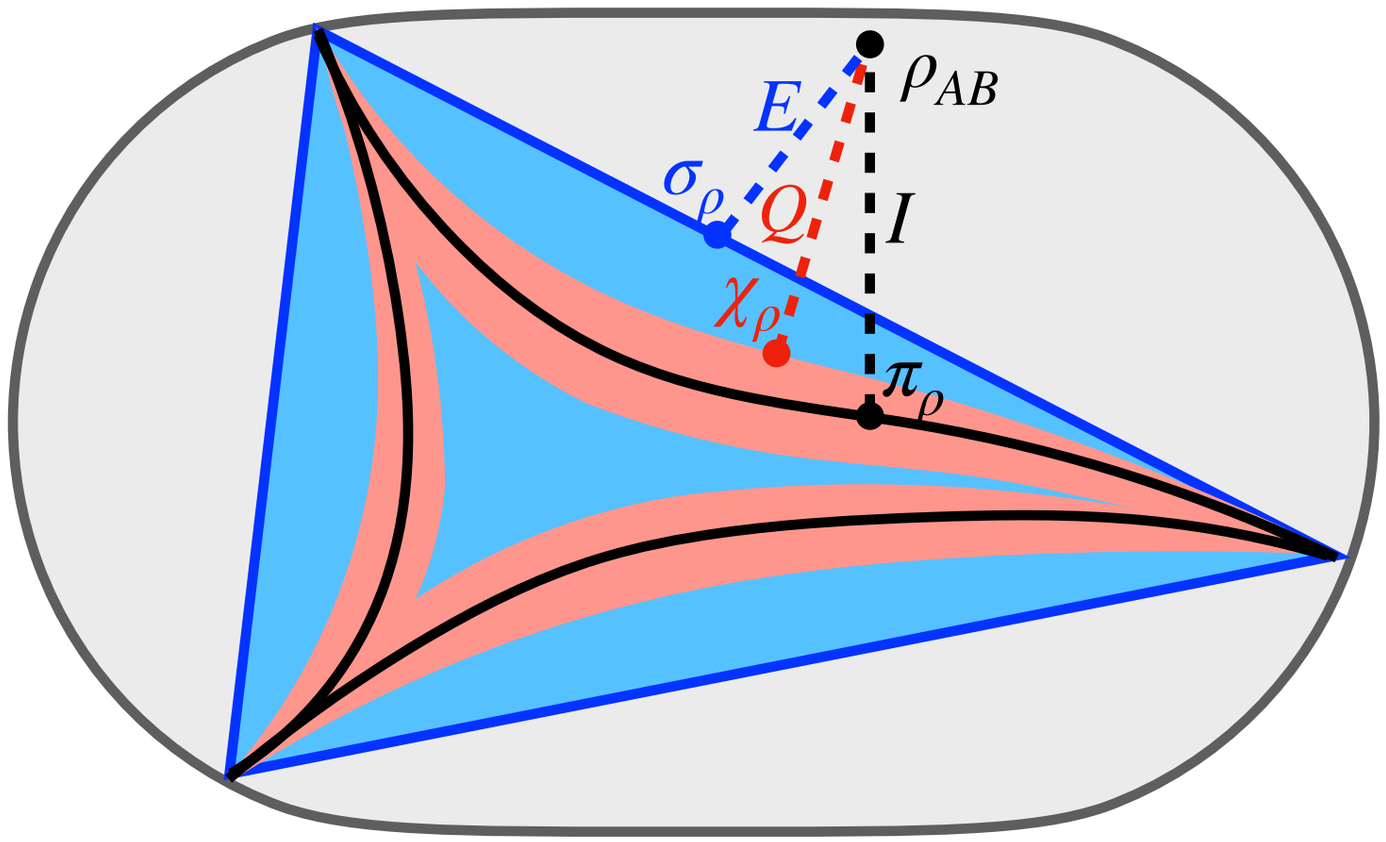

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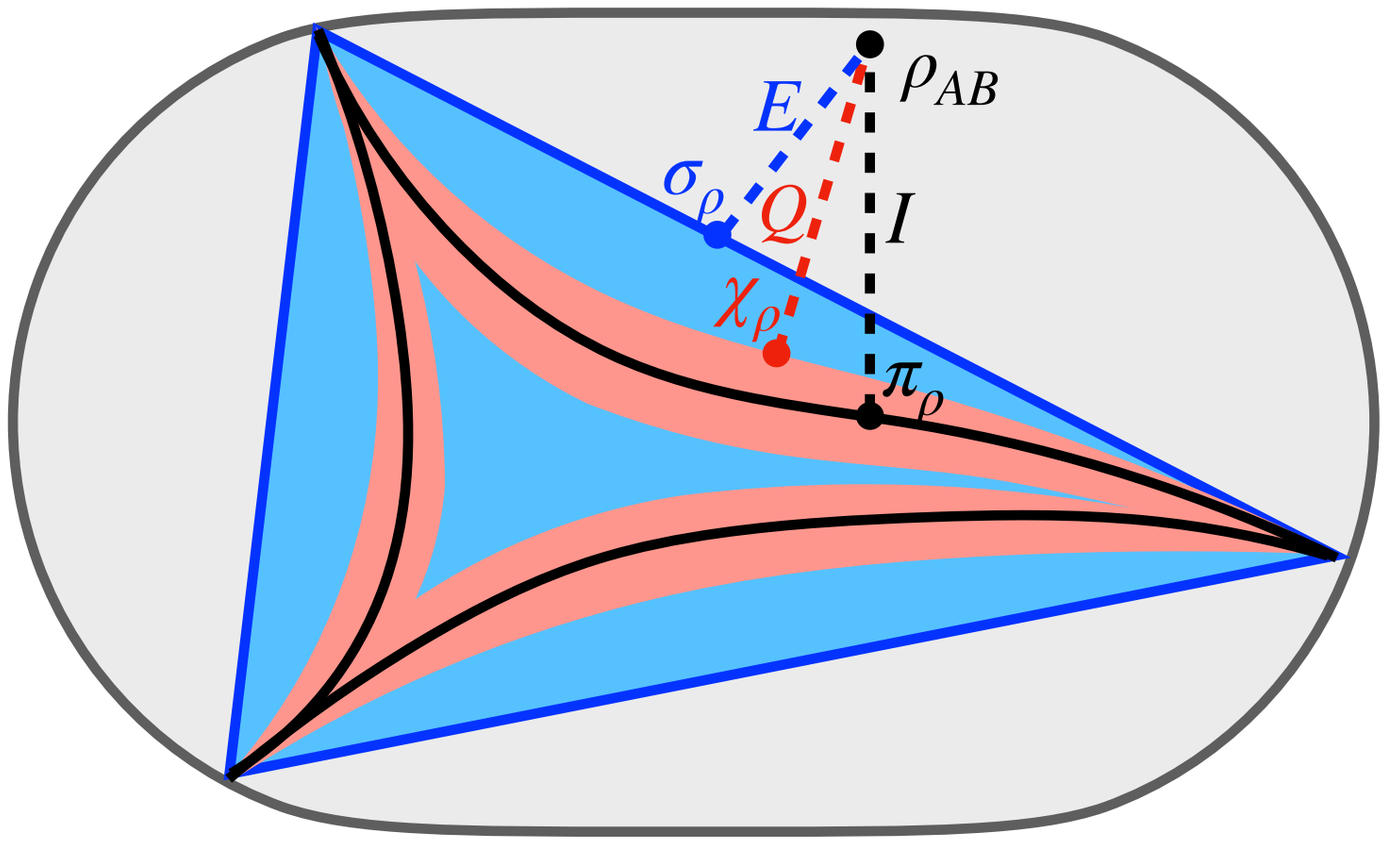

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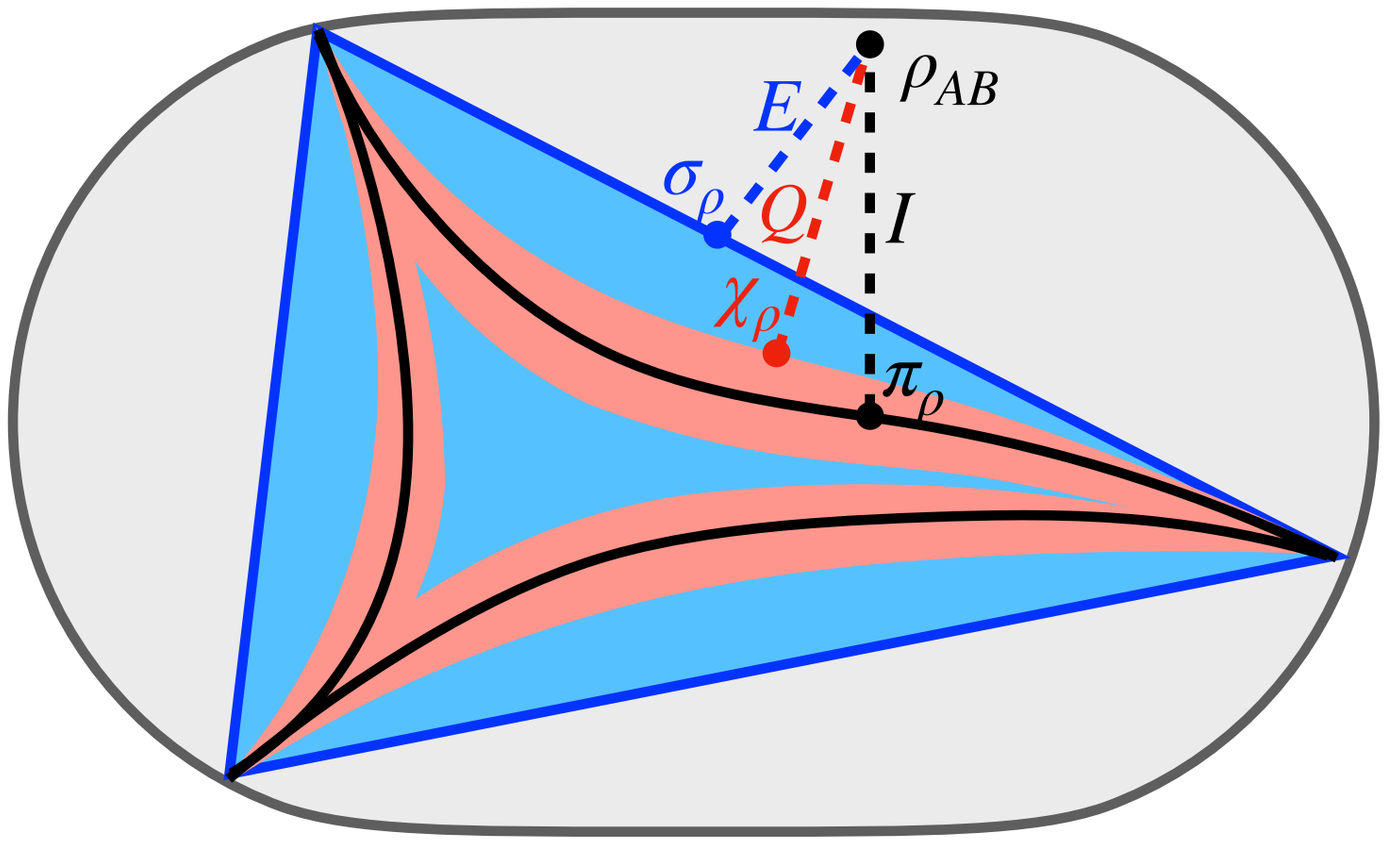

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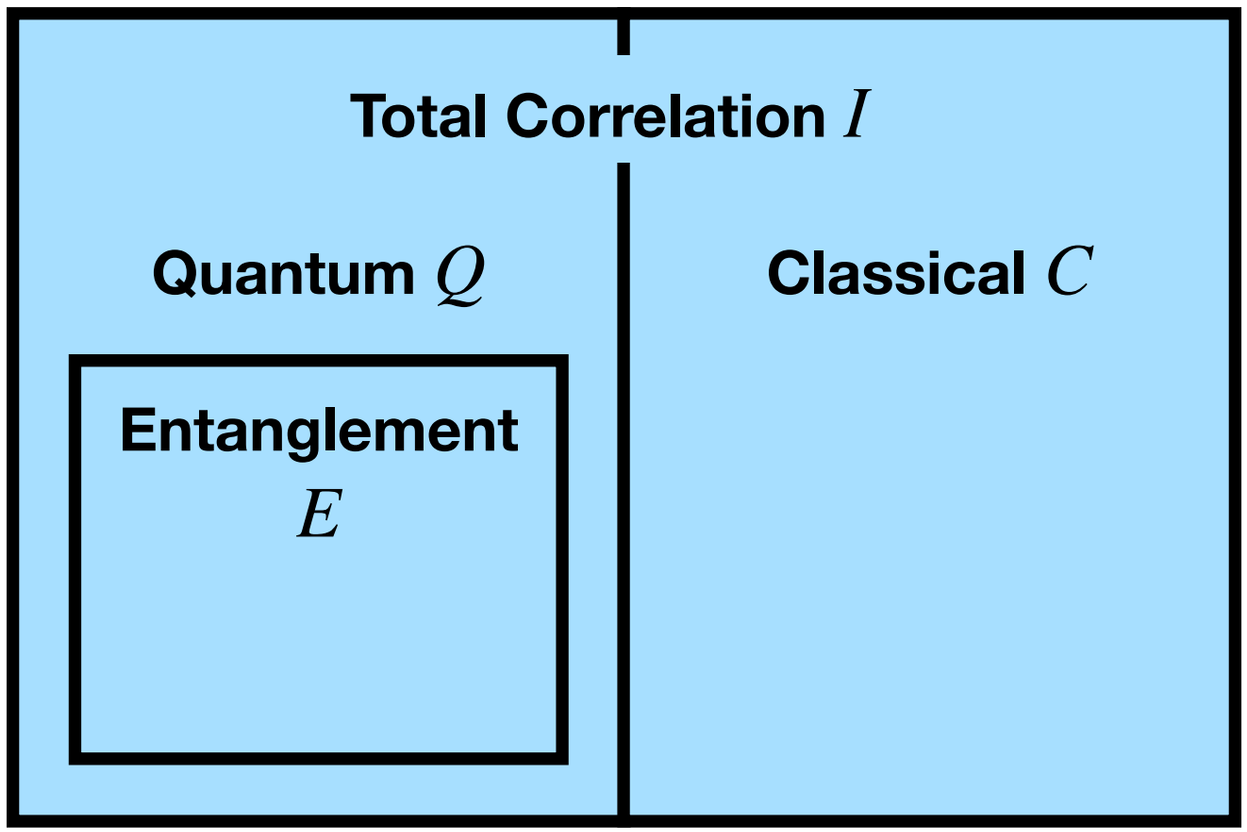
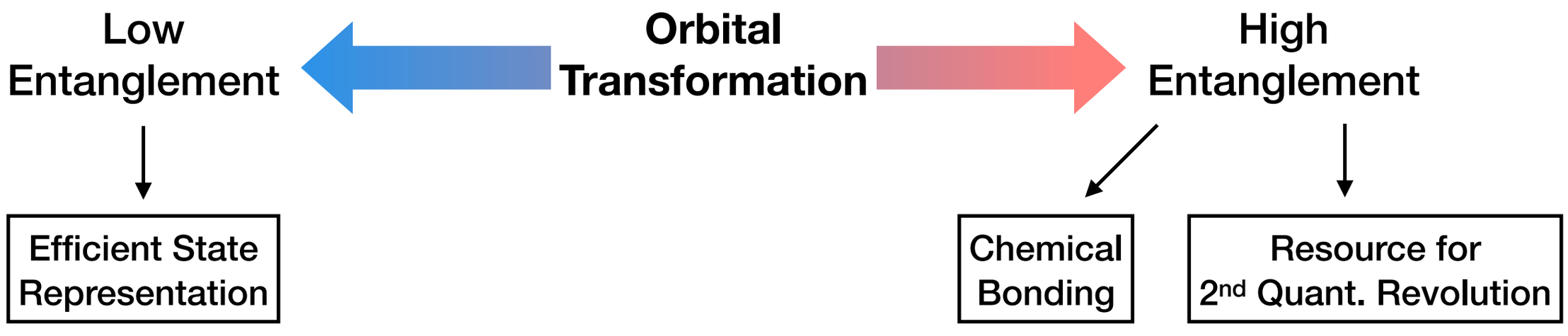
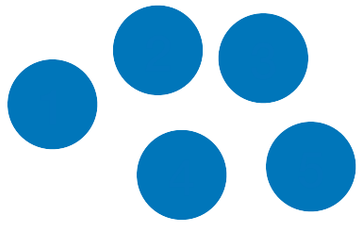


A Versatile Toolbox for QC and MBP



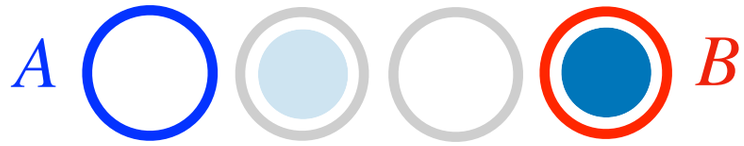
Fermionic Entanglement and Correlation

1st Quantisation



Particle Correlation

2nd Quantisation



Orbital Entanglement

Fermionic Entanglement and Correlation

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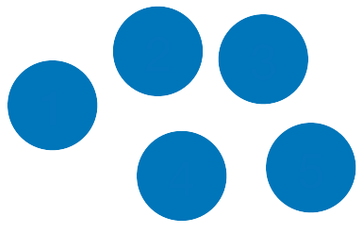

Particle Correlation

trace out particle

1pt-RDM $\gamma_{ij} = \langle f_i^\dagger f_j \rangle$

$C_p = S(\gamma) + S(1-\gamma)$

A. Gottlieb, N. Mauser, *Int. J. Quant. Inf.* 5.06: 815-827. (2007)

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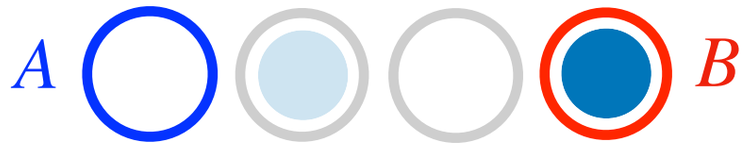

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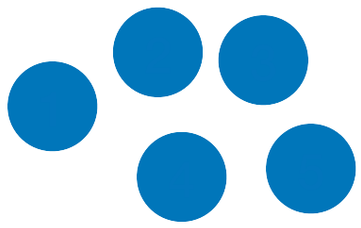

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- Basis independent
- Deviation from single Slater determinant
- Exact formula
- Not A vs B setting -> no apparent utility so far

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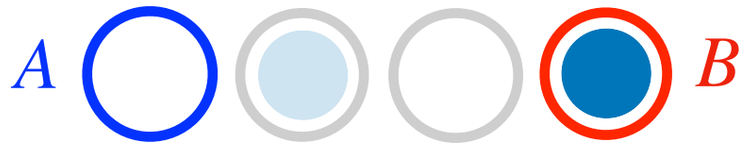

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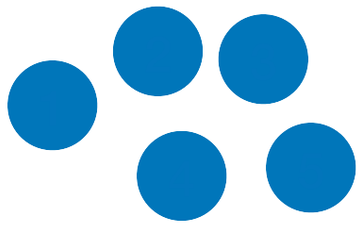

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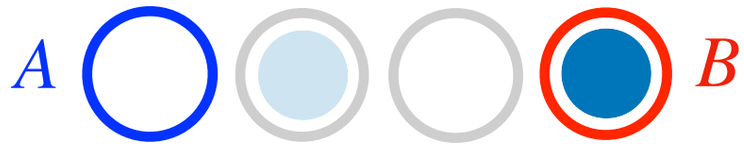

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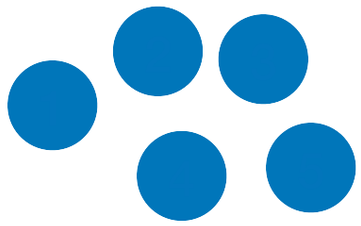

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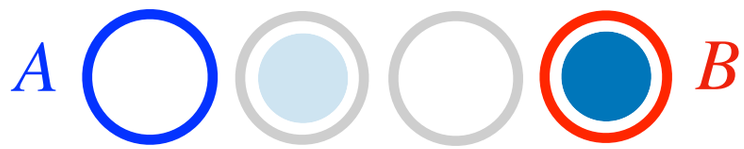

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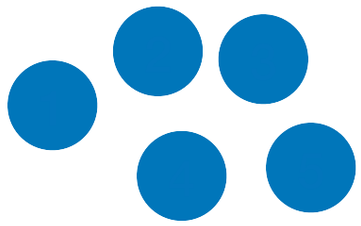

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Connection?

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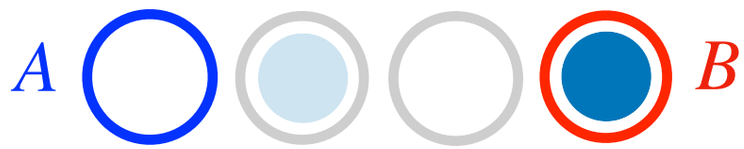

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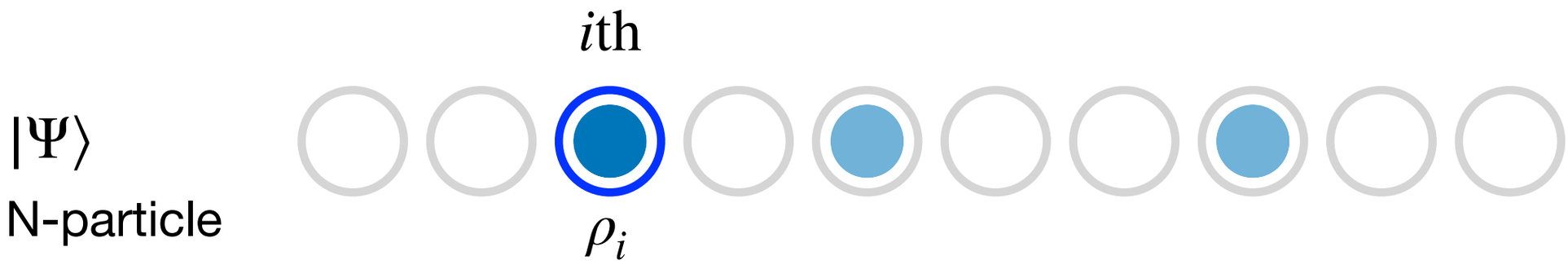
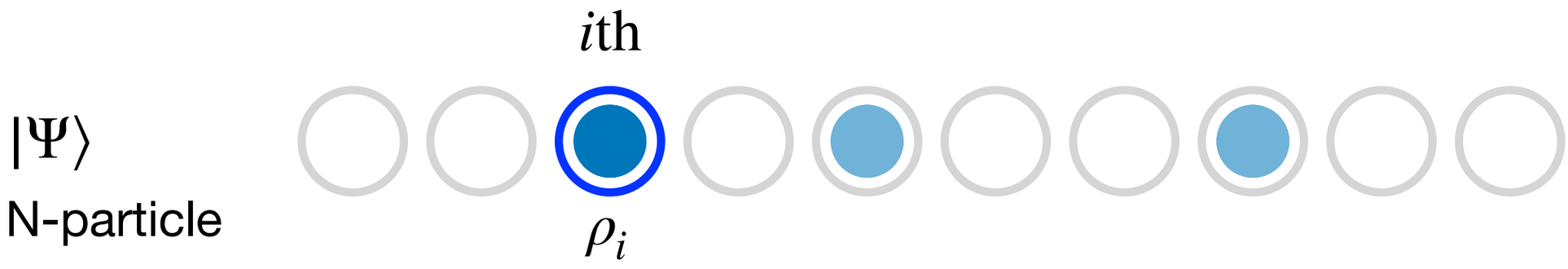
Particle correlation is minimal (spinless-)orbital entanglement



$S(\rho_i)$ — entanglement between $\{i\}$ and $\{i\}^c$

Particle correlation is minimal (spinless-)orbital entanglement



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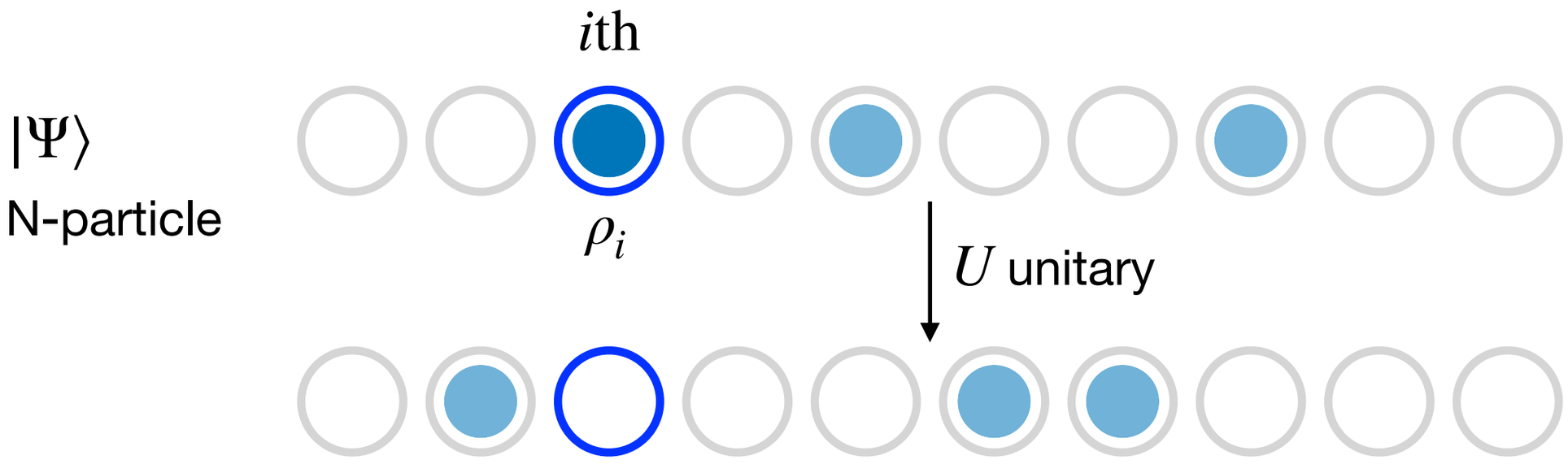

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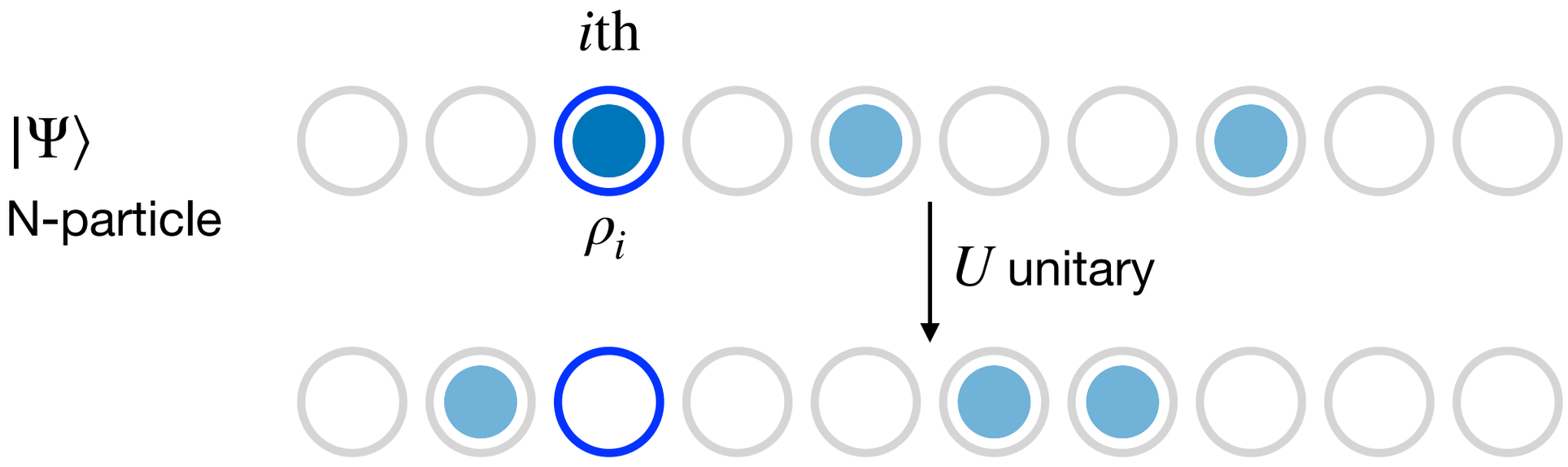
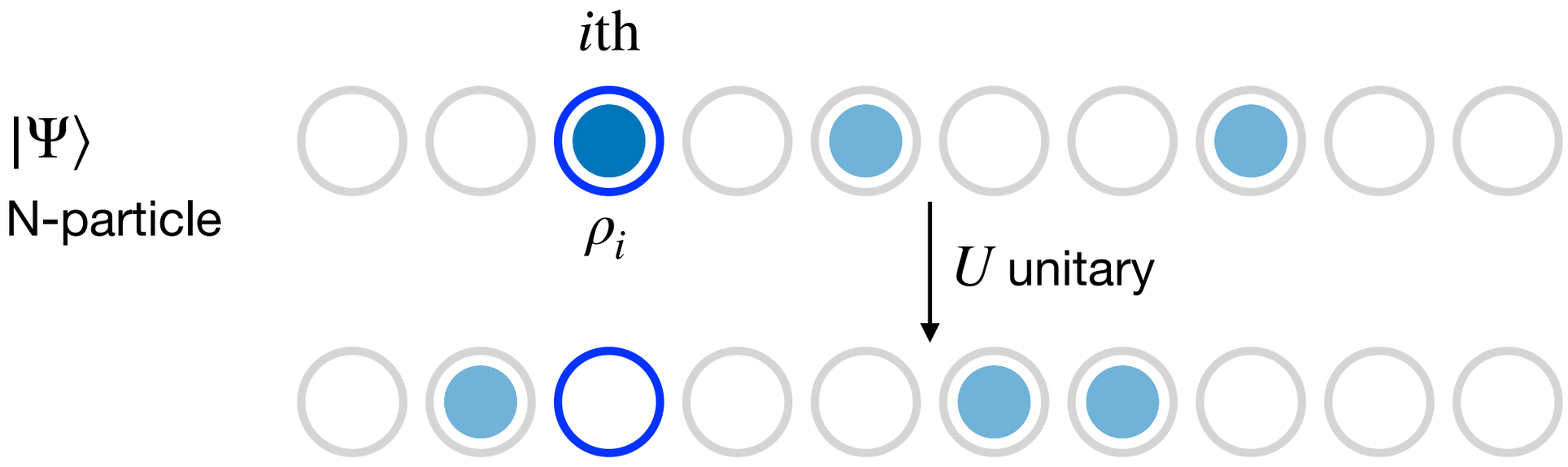


$S(\rho_i)$ — entanglement between $\{i\}$ and $\{i\}^c$

$\sum_i S(\rho_i)$ — covers all orbital entanglement (deviation from product state)

$\min_U \sum_i S(\rho_i)$ — minimal overall entanglement $= C_p \equiv S(\gamma) + S(1-\gamma)$

Particle correlation is minimal (spinless-)orbital entanglement



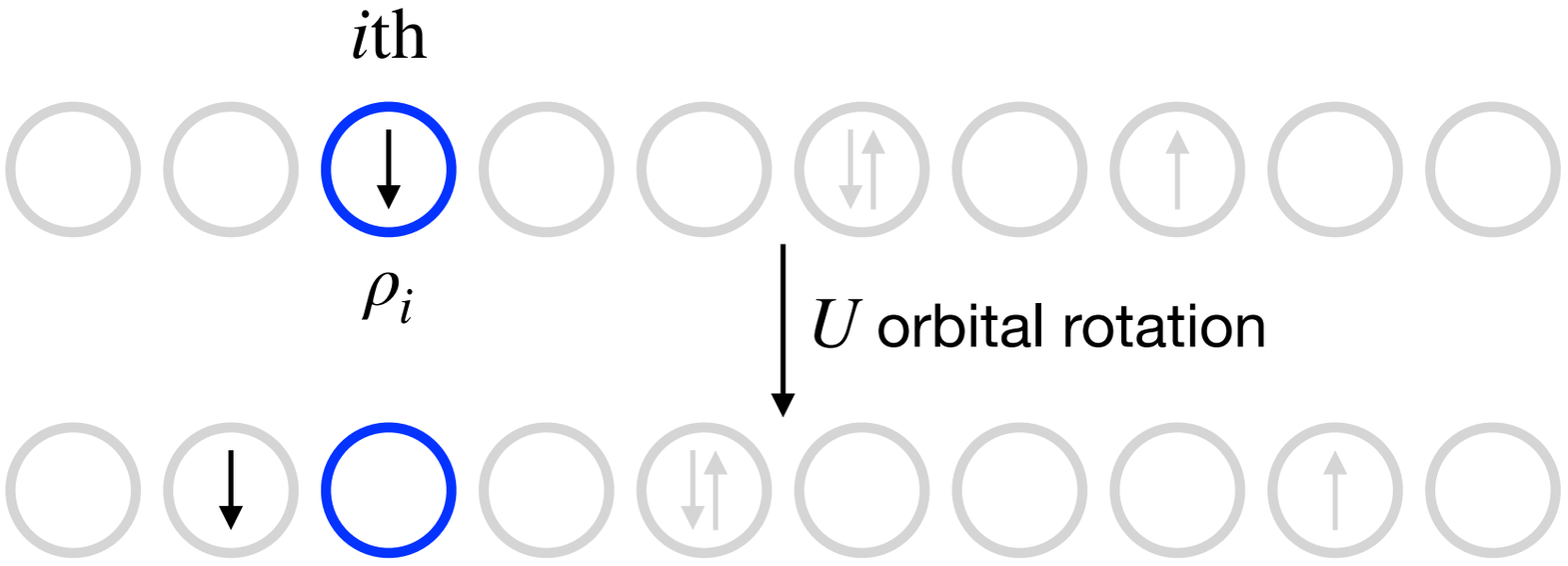
$S(\rho_i)$ — entanglement between $\{i\}$ and $\{i\}^c$

$\sum_i S(\rho_i)$ — covers all orbital entanglement (deviation from product state)

$\min_U \sum_i S(\rho_i)$ — minimal overall entanglement $= C_p \equiv S(\gamma) + S(1-\gamma)$

$$\rho_i = \begin{pmatrix} 1-n_i & 0 \\ 0 & n_i \end{pmatrix}$$ ← 1-particle quantities

Particle correlation bounds minimal orbital entanglement



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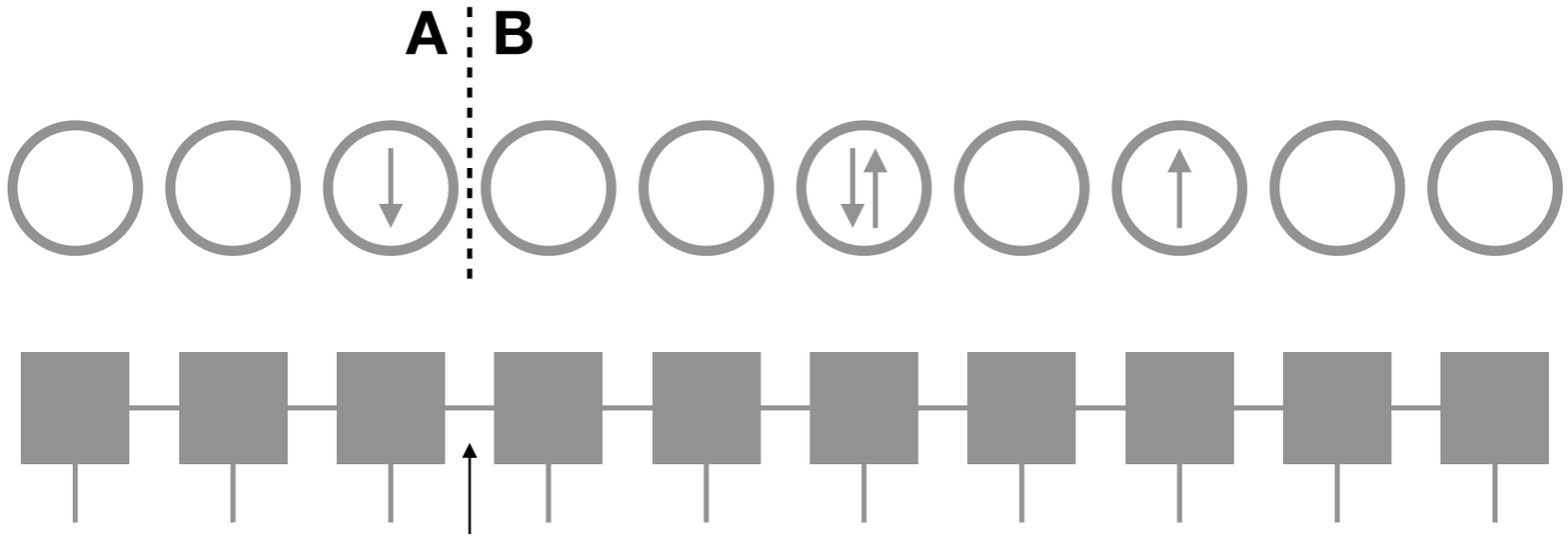
2-particle quantity

High cost of entanglement



MPS rep.

$$\log(D) \geq S(\rho_A)$$

Schuch, *et al.* (2008)
Phys. Rev. Lett. **100**, 030504

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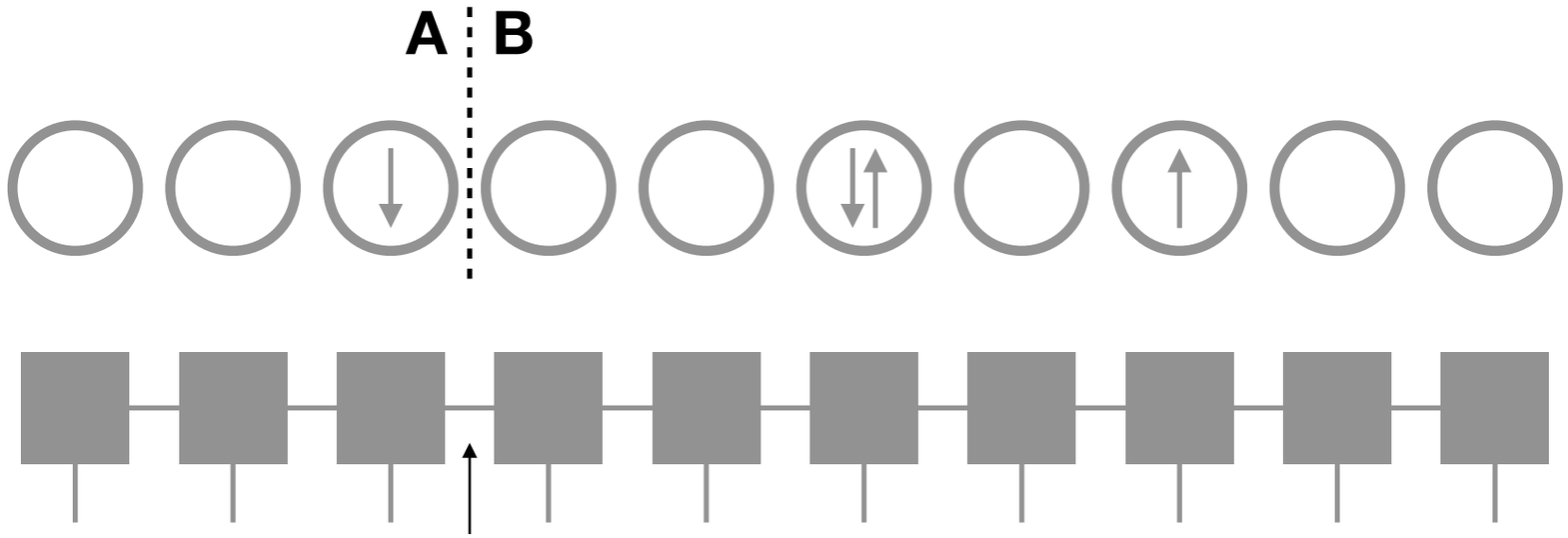

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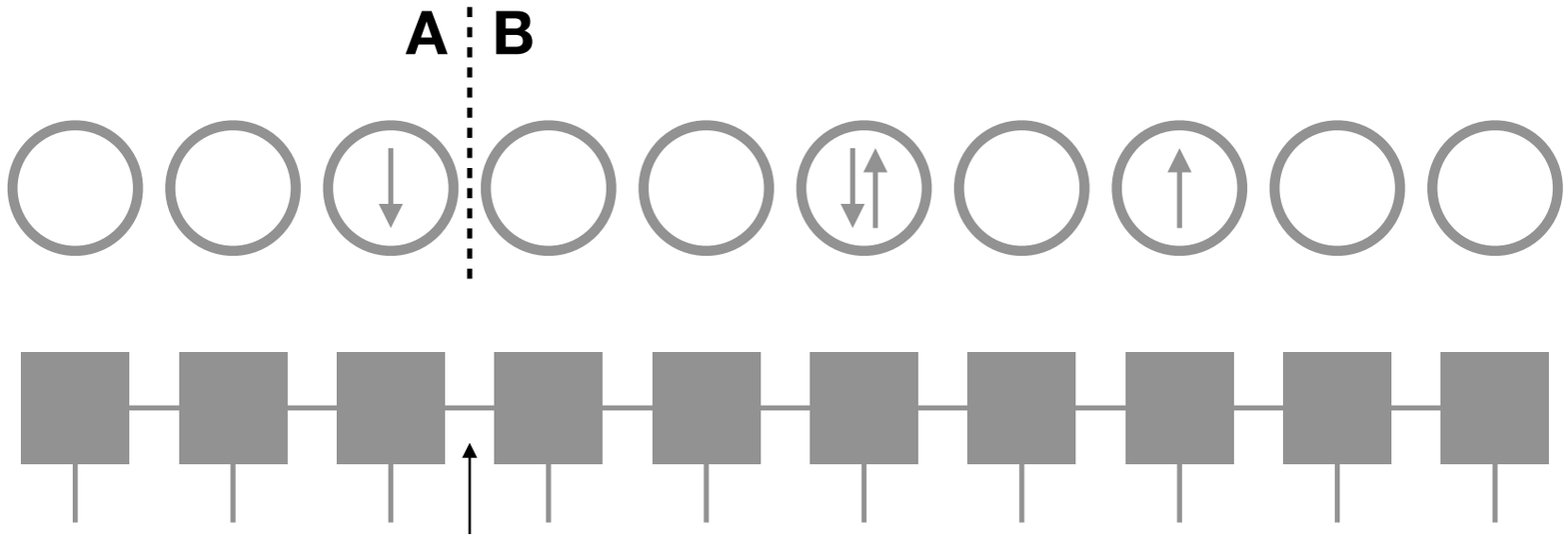

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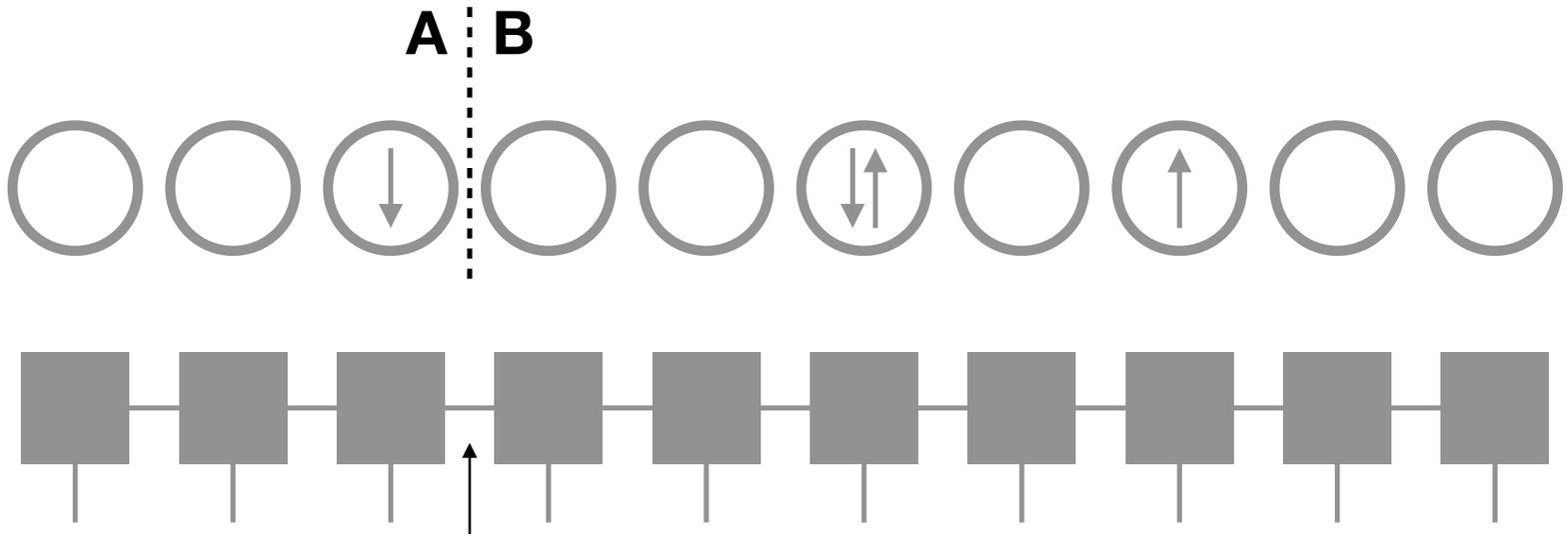
High cost of entanglement



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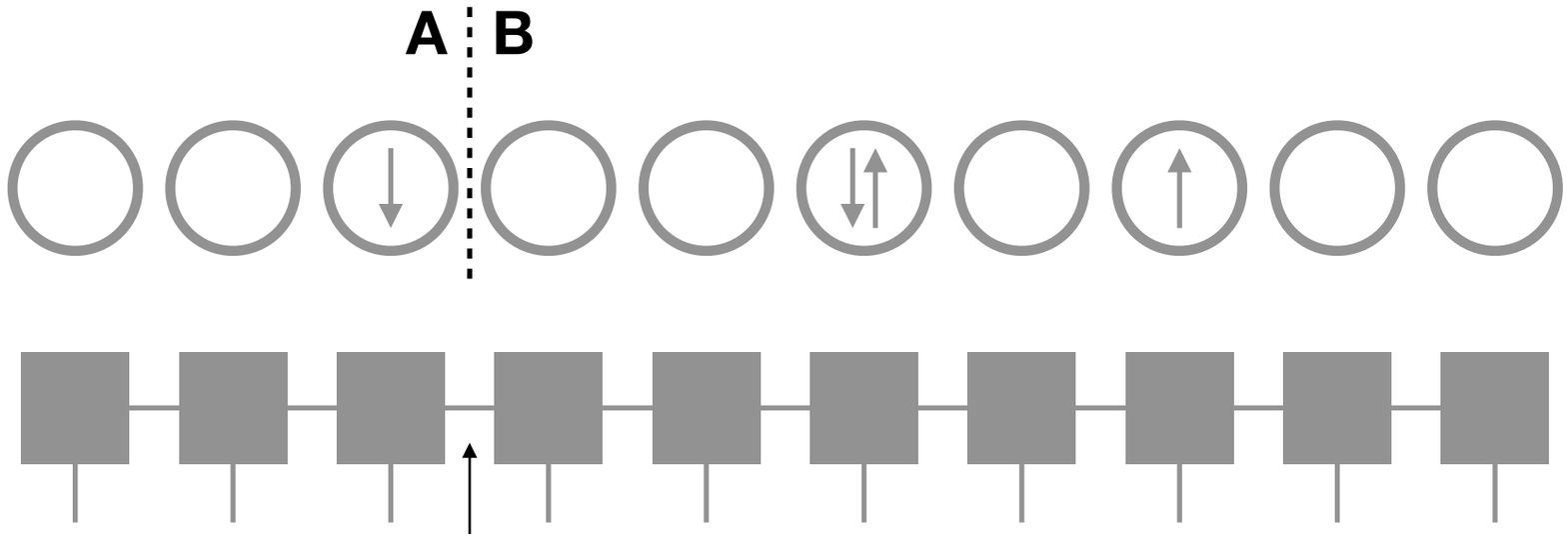

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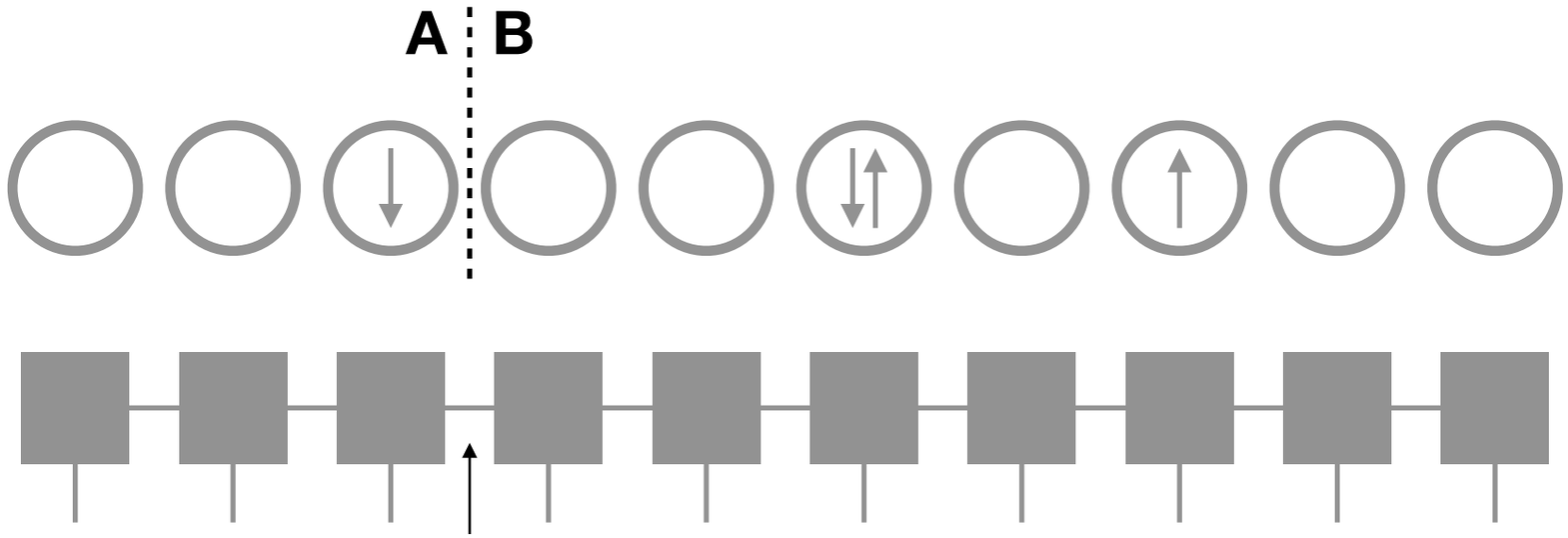
$$= \min_U \max_{A|B} \frac{1}{2} \left[\sum_i S(\rho_i) - I_A - I_B \right]$$

$I_{A/B} = \sum_{i \in A/B} S(\rho_i) - S(\rho_{A/B}) > 0$
correlation in block A/B

High cost of entanglement



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$$= \min_U \max_{A|B} \frac{1}{2}\left[\sum_i S(\rho_i) - I_A - I_B\right]$$

$$\leq \frac{1}{2}\min_U \sum_i S(\rho_i) \leq \frac{1}{2}C_p$$

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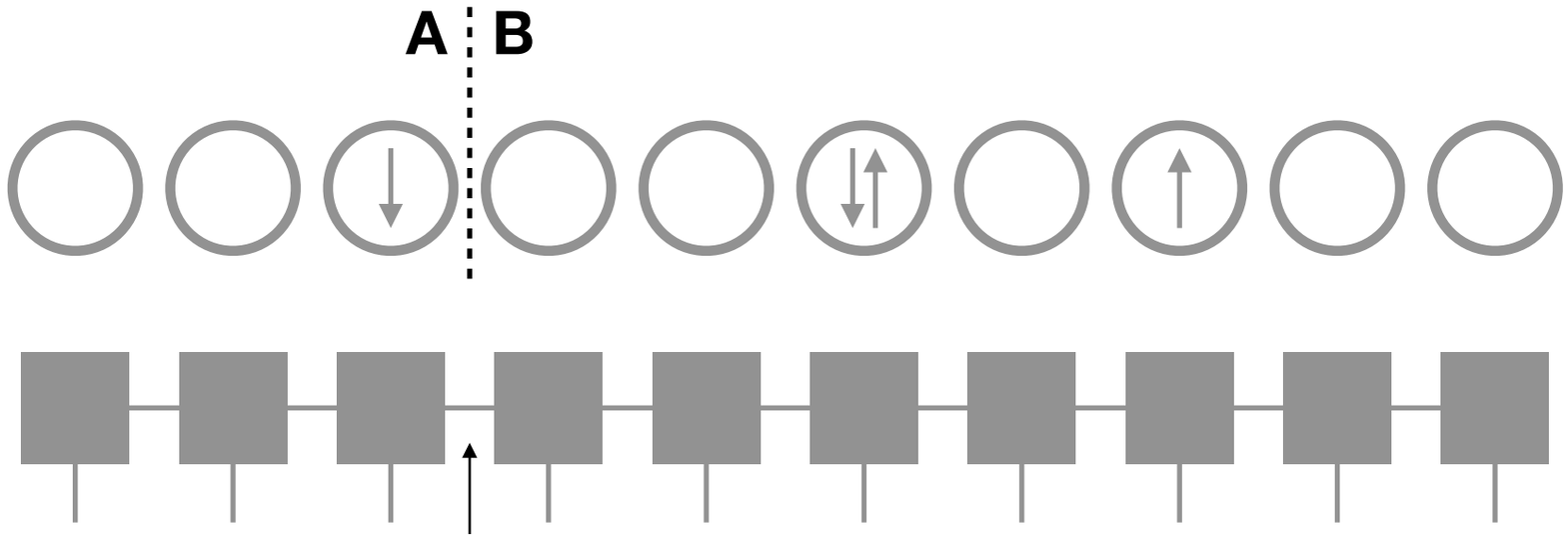

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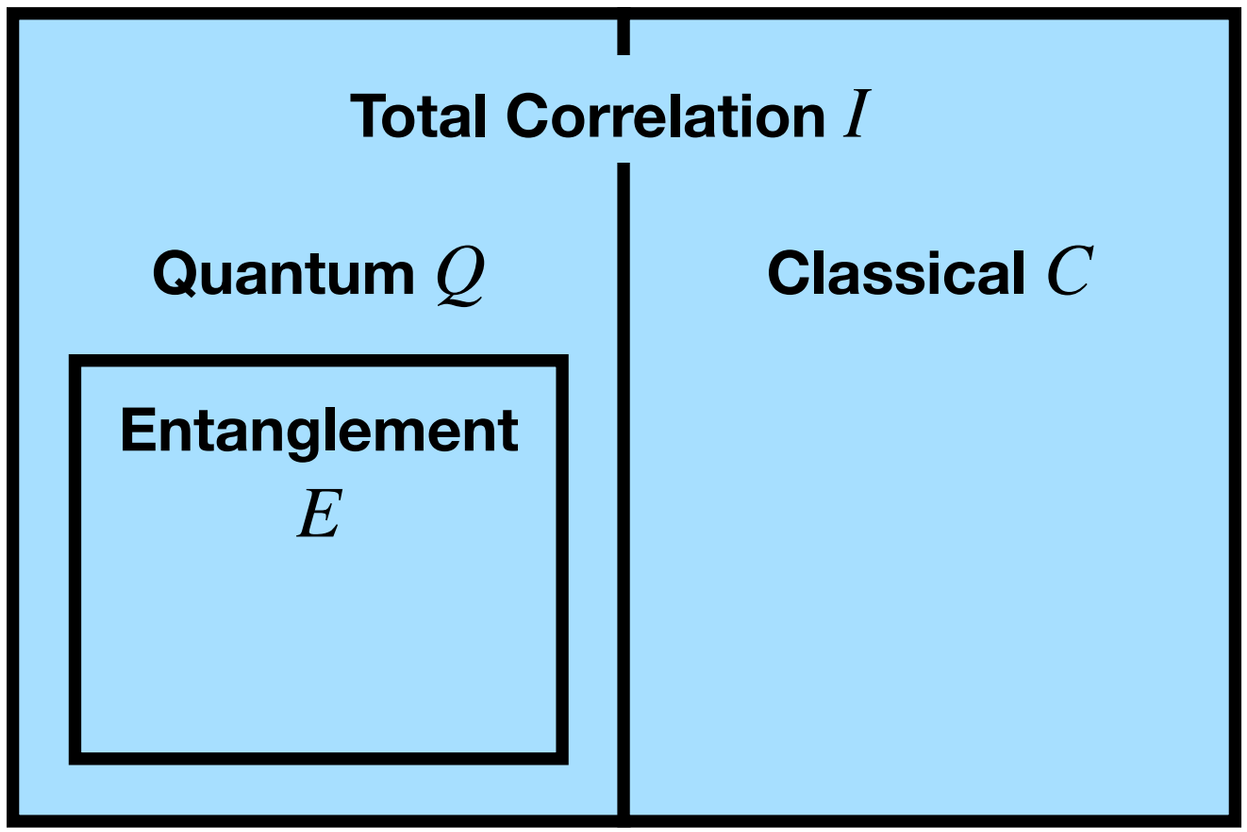
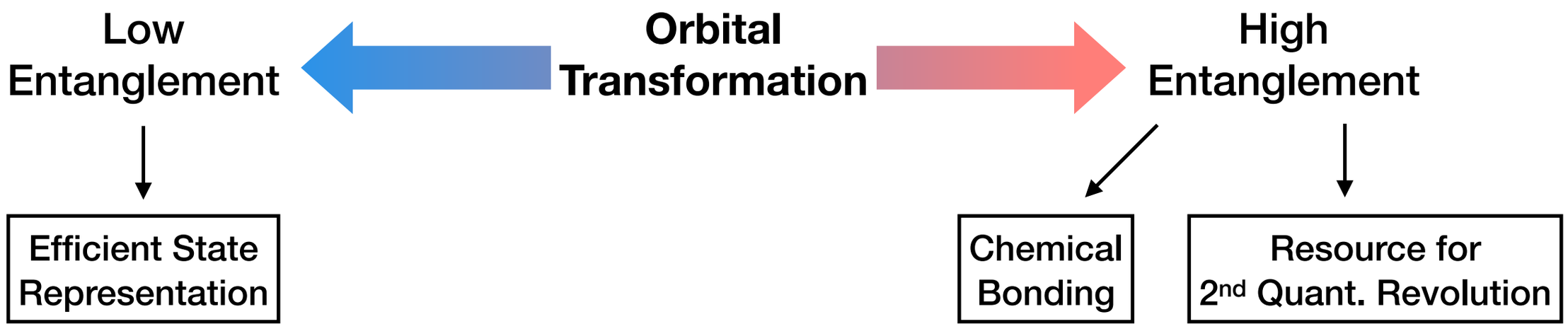
A lot of room for improvement still!



A Versatile Toolbox for QC and MBP



High reward of entanglement

JCTC Journal of Chemical Theory and Computation

Article

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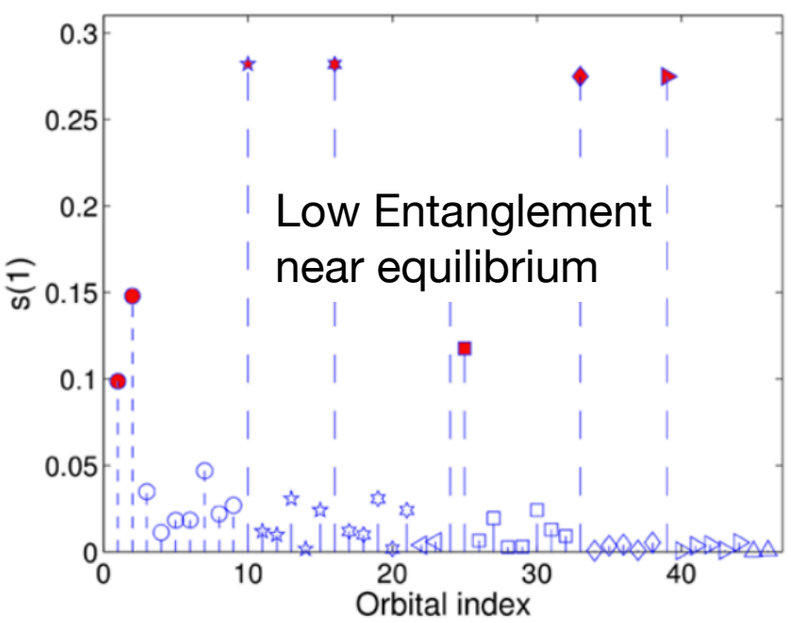
Orbital Entanglement in Bond-Formation Processes

Katharina Boguslawski,[†] Paweł Tecmer,[†] Gergely Barcza,[‡] Örs Legeza,*[,‡] and Markus Reiher*[,†]

[†]ETH Zürich, Laboratory of Physical Chemistry, Wolfgang-Pauli-Str. 10, CH-8093 Zürich, Switzerland

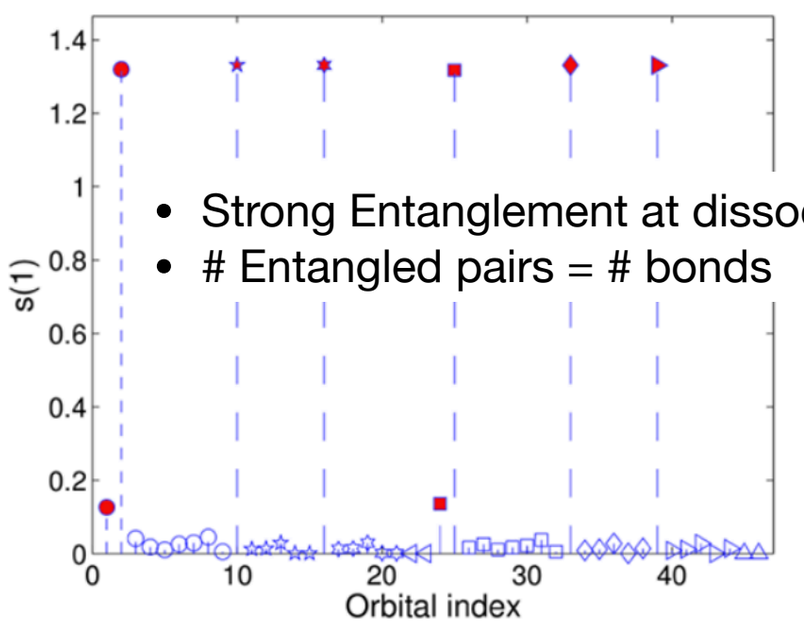
[‡]Strongly Correlated Systems "Lendület" Research Group, Wigner Research Center for Physics, H-1525 Budapest, Hungary

HF orbitals



Single orbital entropy

(a) $d_{\mathrm{NN}} = 1.12\text{Å}$



- Strong Entanglement at dissociation
- # Entangled pairs = # bonds

Single orbital entropy

(f) $d_{\mathrm{NN}} = 3.175\text{Å}$

dissociation

Quantifying bond orders

Quantifying bond orders

- Naïve Molecular Orbital Theory

$$\text{Bond Order} = \frac{N_{\text{bonding}} - N_{\text{anti-bonding}}}{2}$$

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  - Coulson's index
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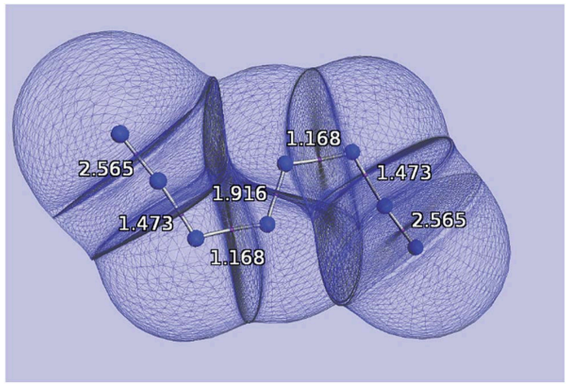
  - (De)localization index



Correlation of electron density between atomic regions

Quantifying bond orders

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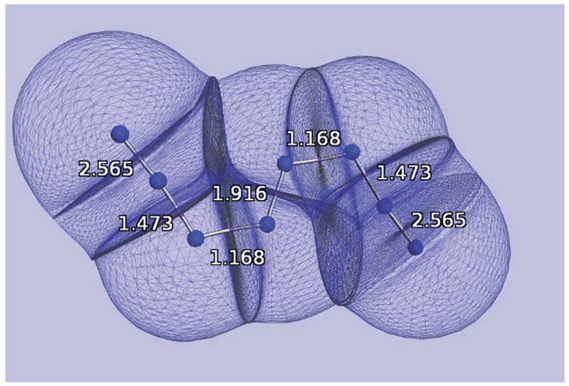

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To emphasize today's blurry state of affairs, the IUPAC's Gold Book introduces bond order as "*The electron population in the region between atoms A and B of a molecular entity at the expense of electron density in the immediate vicinity of the individual atomic centers*".[5] This definition leans more towards population analyses than towards counting shared electrons.

Outeiral et al., Chem. Sci., **9**, 5517 (2018)

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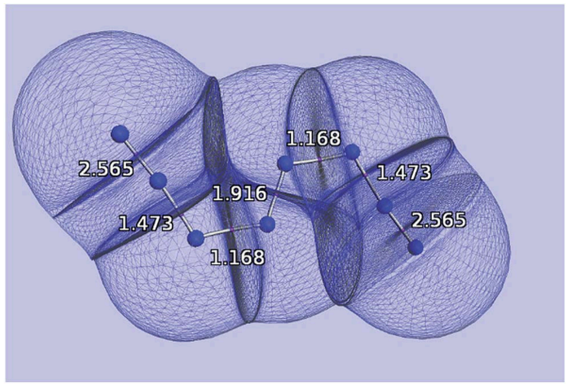

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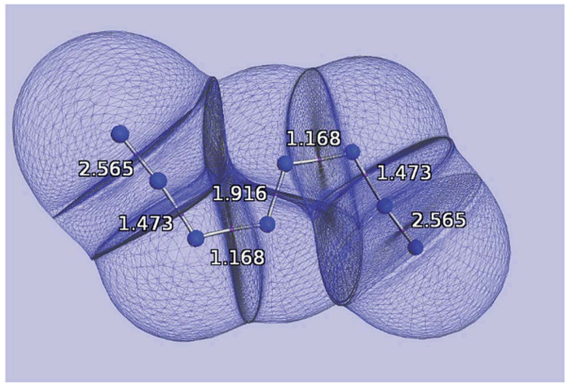

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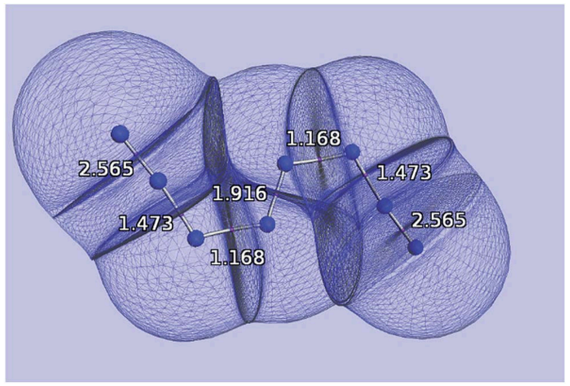

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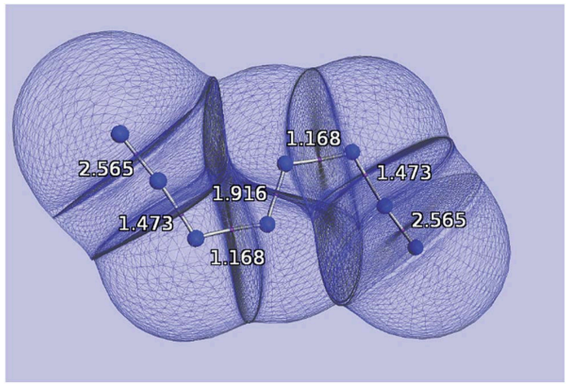

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Quantum Info Perspective

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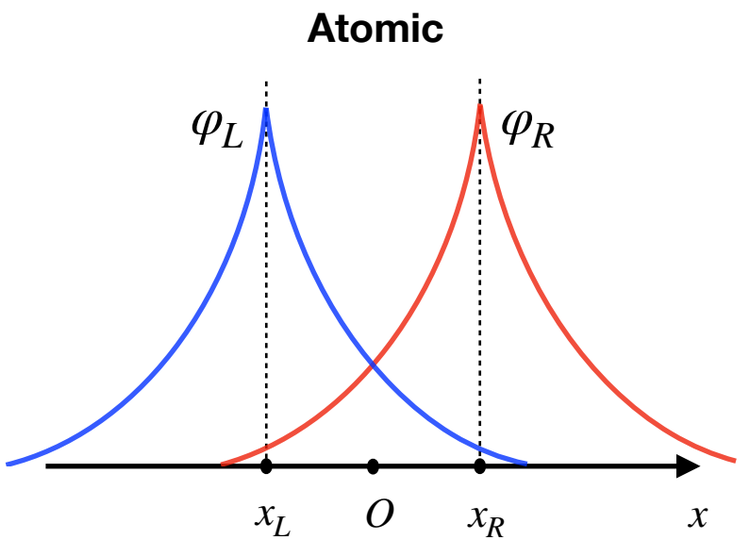
- Electron sharing between atoms -> Information sharing
- Identify orthogonal subsystems (localized orbitals) analogous to atomic spatial regions
- Working theory at equilibrium instead of dissociation (contrast to Boguslawski et al)

Single Covalent Bond



LD, S. Knecht, Z. Zimborás, C. Schilling, arxiv.org/abs/2205.15881 (2022).

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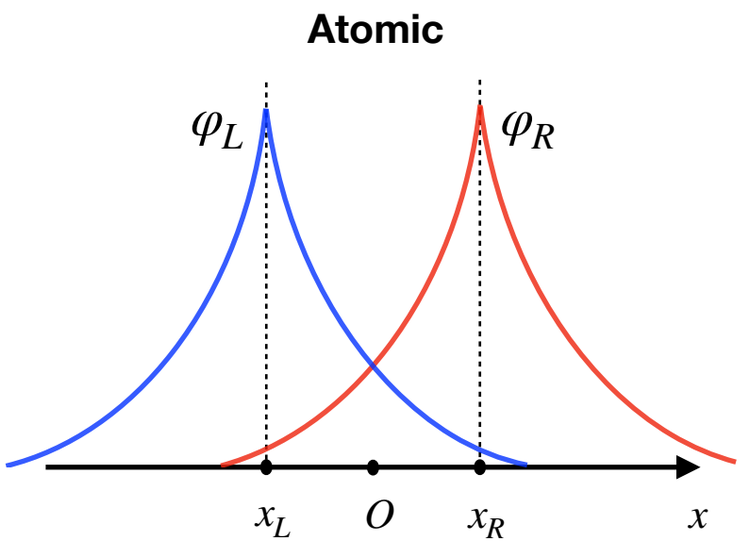

No subsystems

Non-orthogonal orbitals

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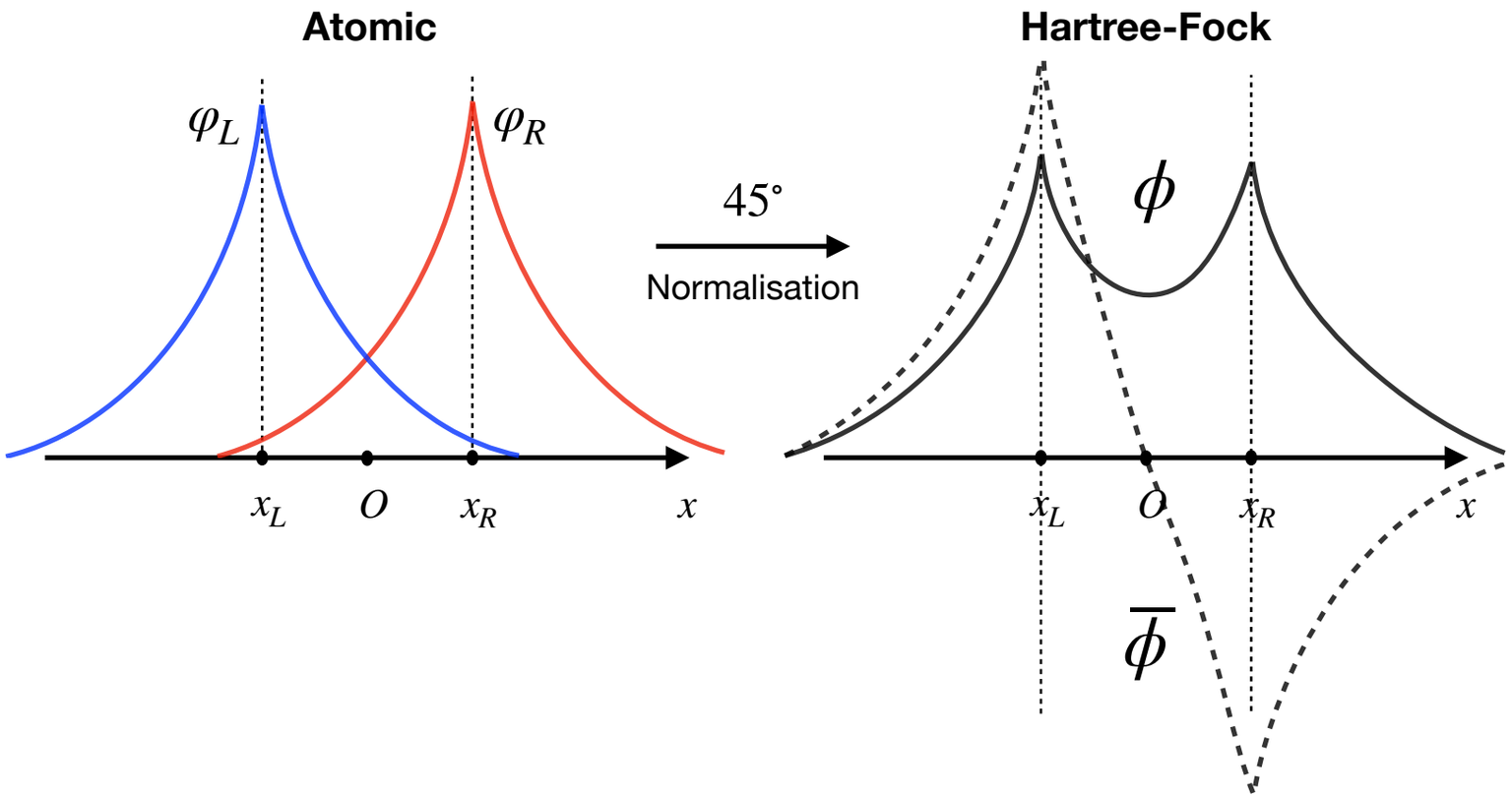

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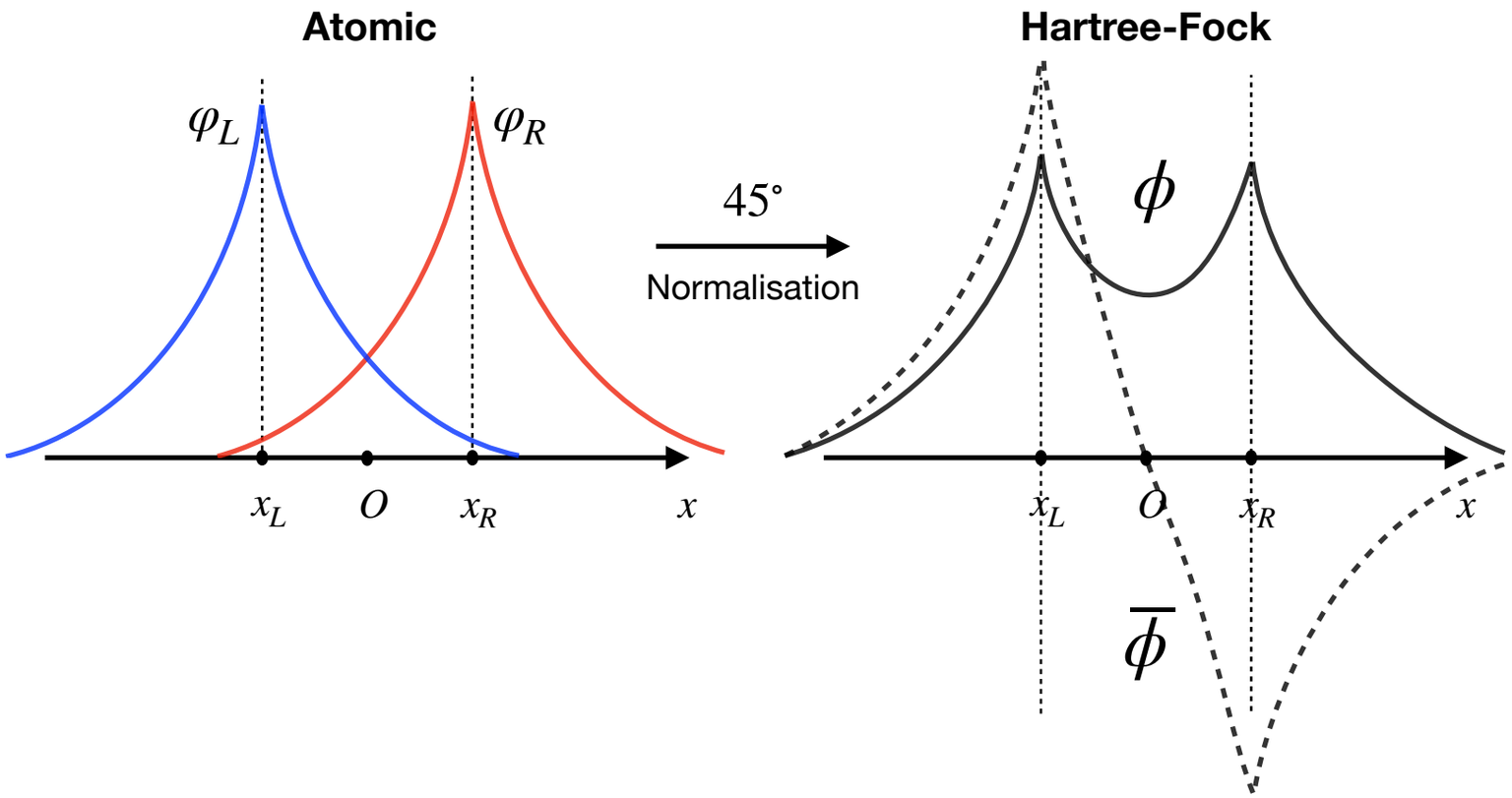

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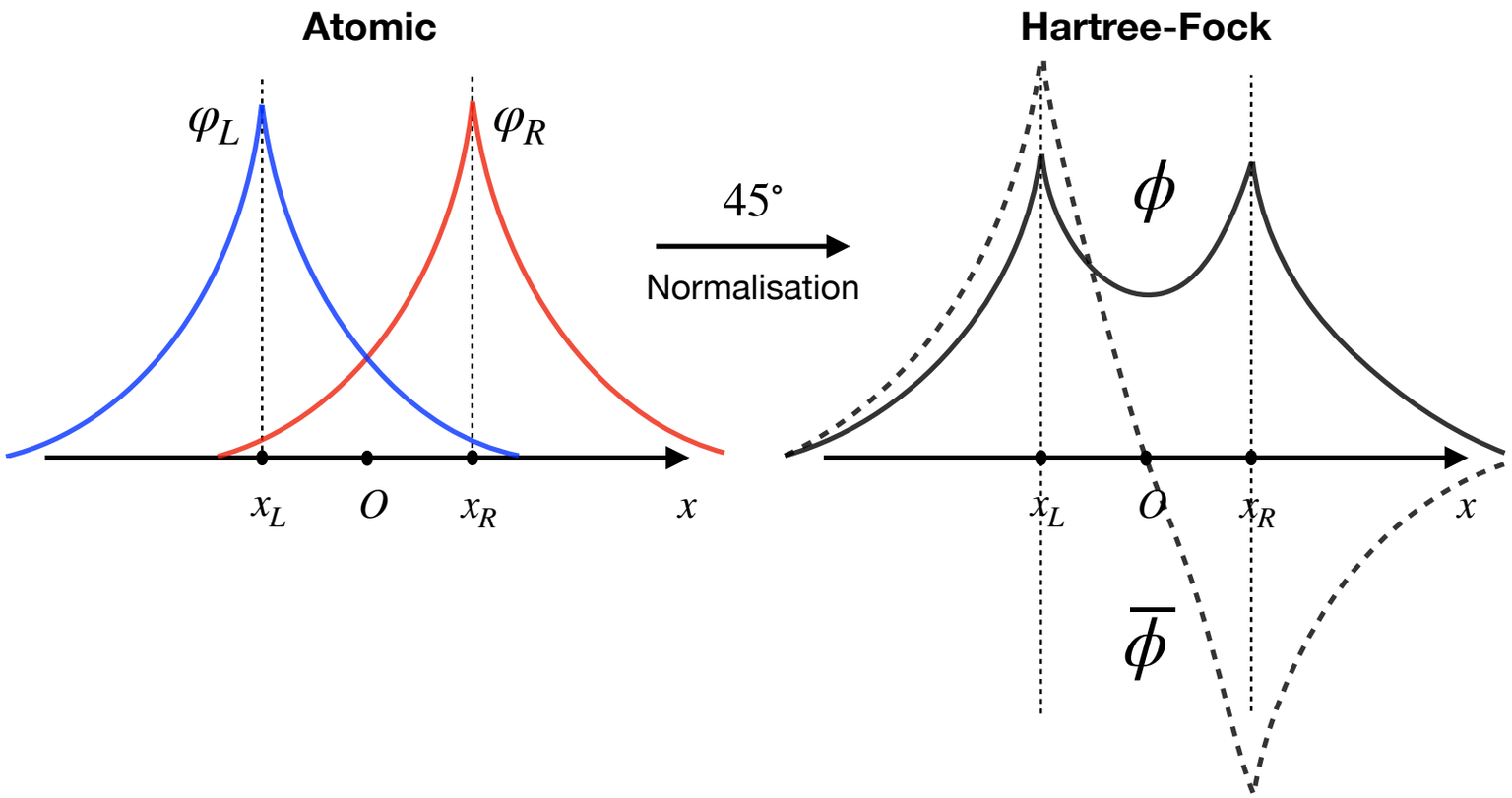

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No entanglement between ϕ and $\overline{\phi}$

$$|\Psi\rangle = |\uparrow\downarrow\rangle_{\phi} \otimes |\Omega\rangle_{\overline{\phi}}$$

$$E(|\Psi\rangle) = 0$$

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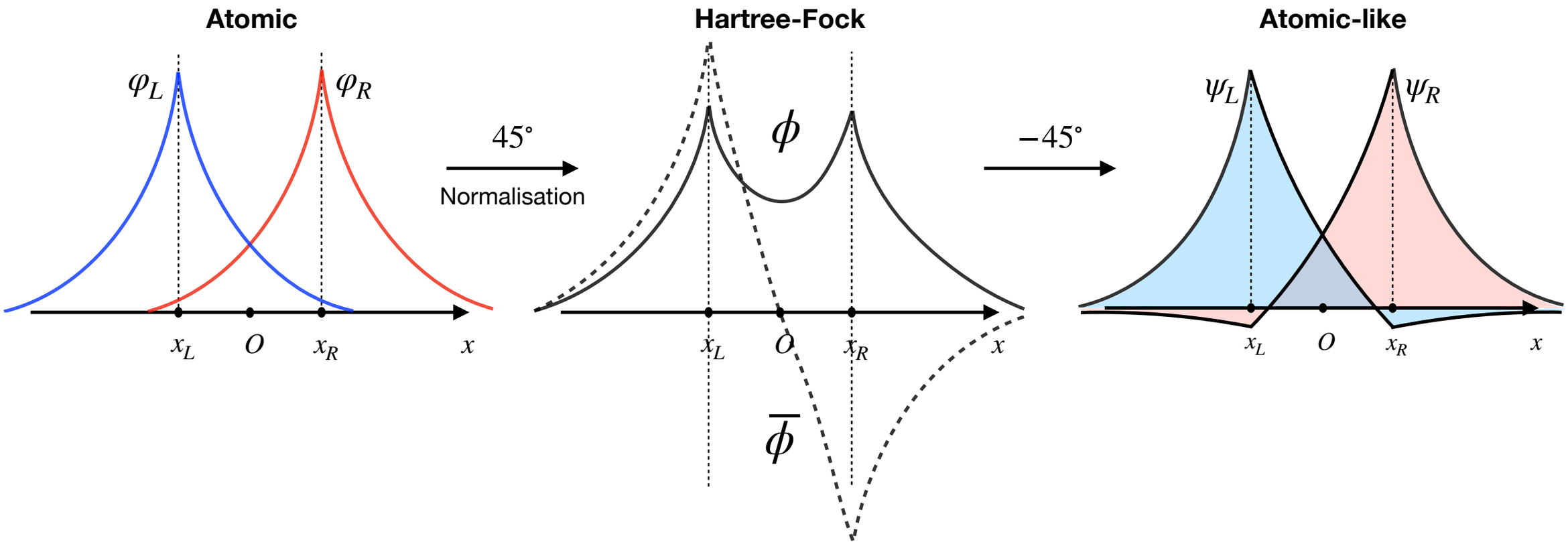

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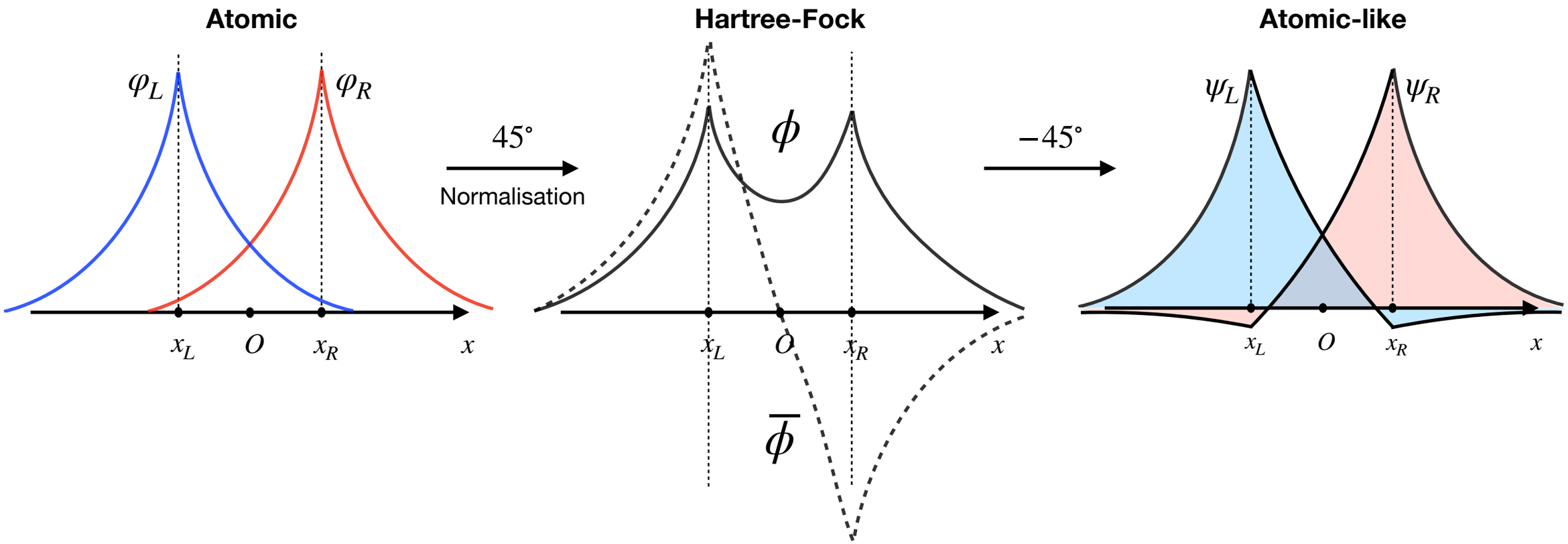

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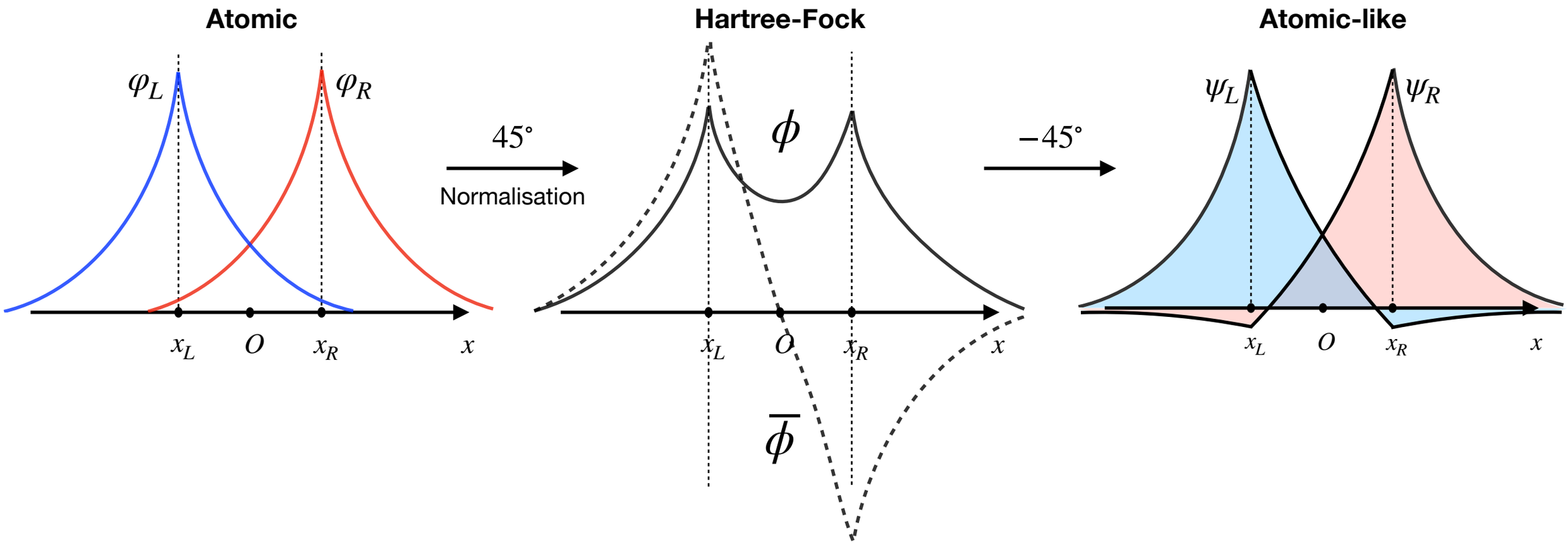

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$$E(|\Psi\rangle) = 0$$

Yes! subsystems

Yes! entanglement between ψ_L and ψ_R

$$|\Psi\rangle = |\uparrow\downarrow\rangle_{\psi_L} \otimes |\Omega\rangle_{\psi_R} + |\Omega\rangle_{\psi_L} \otimes |\uparrow\downarrow\rangle_{\psi_R} + |\uparrow\rangle_{\psi_L} \otimes |\downarrow\rangle_{\psi_R} - |\downarrow\rangle_{\psi_L} \otimes |\uparrow\rangle_{\psi_R}$$

$$E(|\Psi\rangle) = \ln(4)$$

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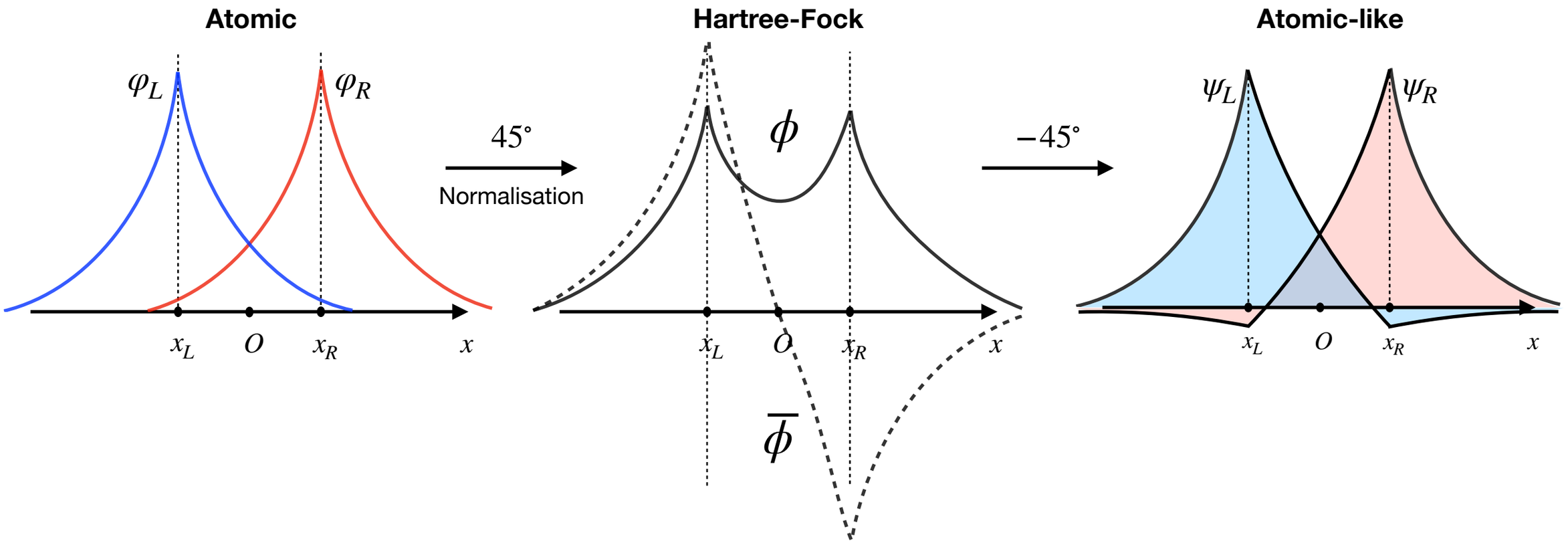
Single Covalent Bond



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Minimal Entanglement ⟶ **Maximal Entanglement**

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$$\text{Bond Order} = \frac{N_{\text{bonding}} - N_{\text{anti-bonding}}}{2}$$

Anti-bonding $\overline{\phi}$	—	—	↑	↑↓	
Bonding ϕ	↑	↑↓	↑↓	↑↓	
	$\lvert\Psi_1\rangle$	$\lvert\Psi_2\rangle$	$\lvert\Psi_3\rangle$	$\lvert\Psi_4\rangle$	
Bond Order	$\frac{1}{2}$	1	$\frac{1}{2}$	0	
E_{max}	$\ln(2)$	$2\ln(2)$	$\ln(2)$	0	Atomic-like
E_{min}	0	0	0	0	Hartree-Fock

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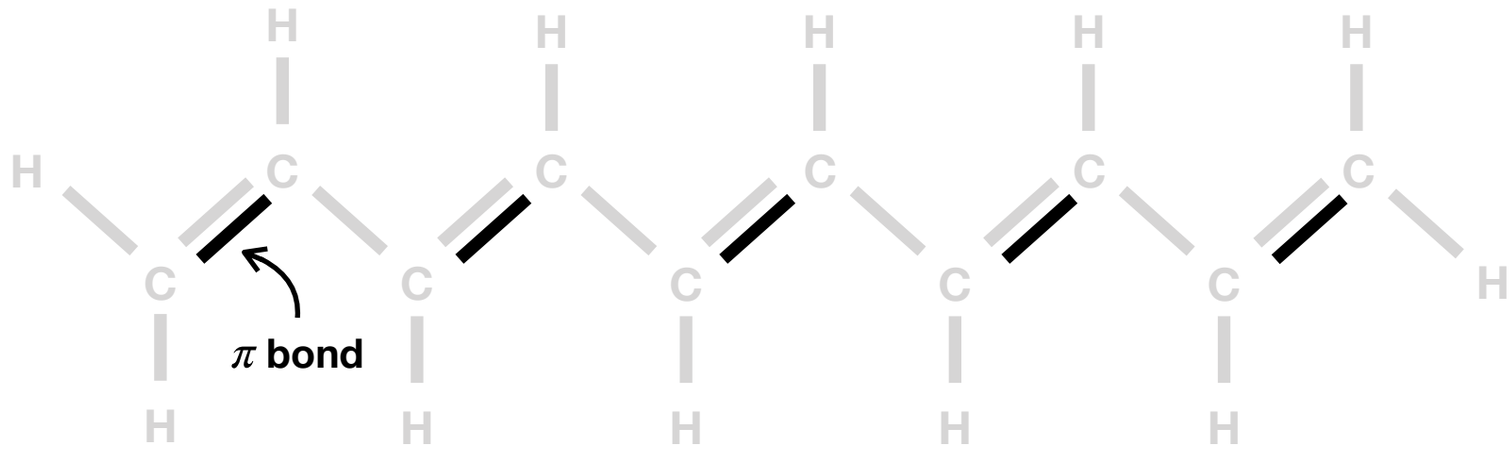
Multiple Bonds: Single Orbital Entanglement



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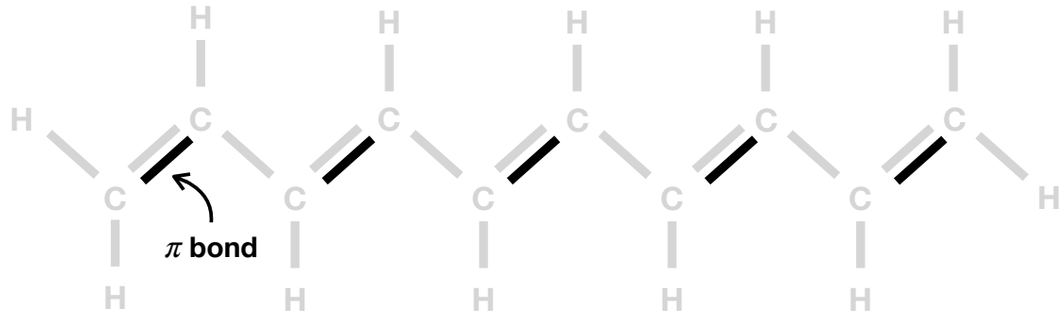

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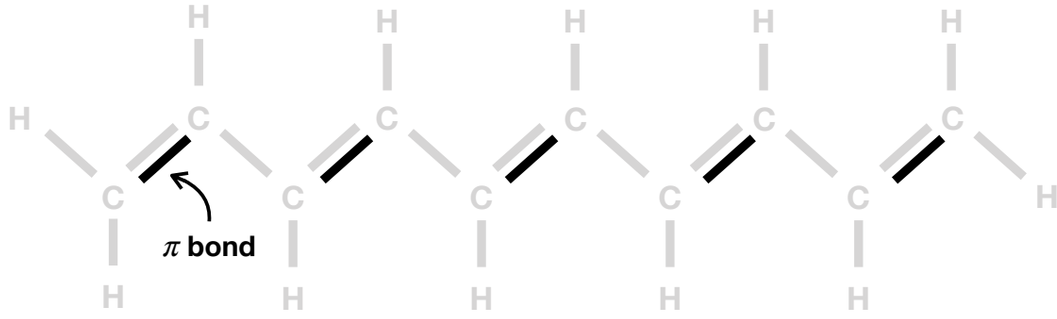

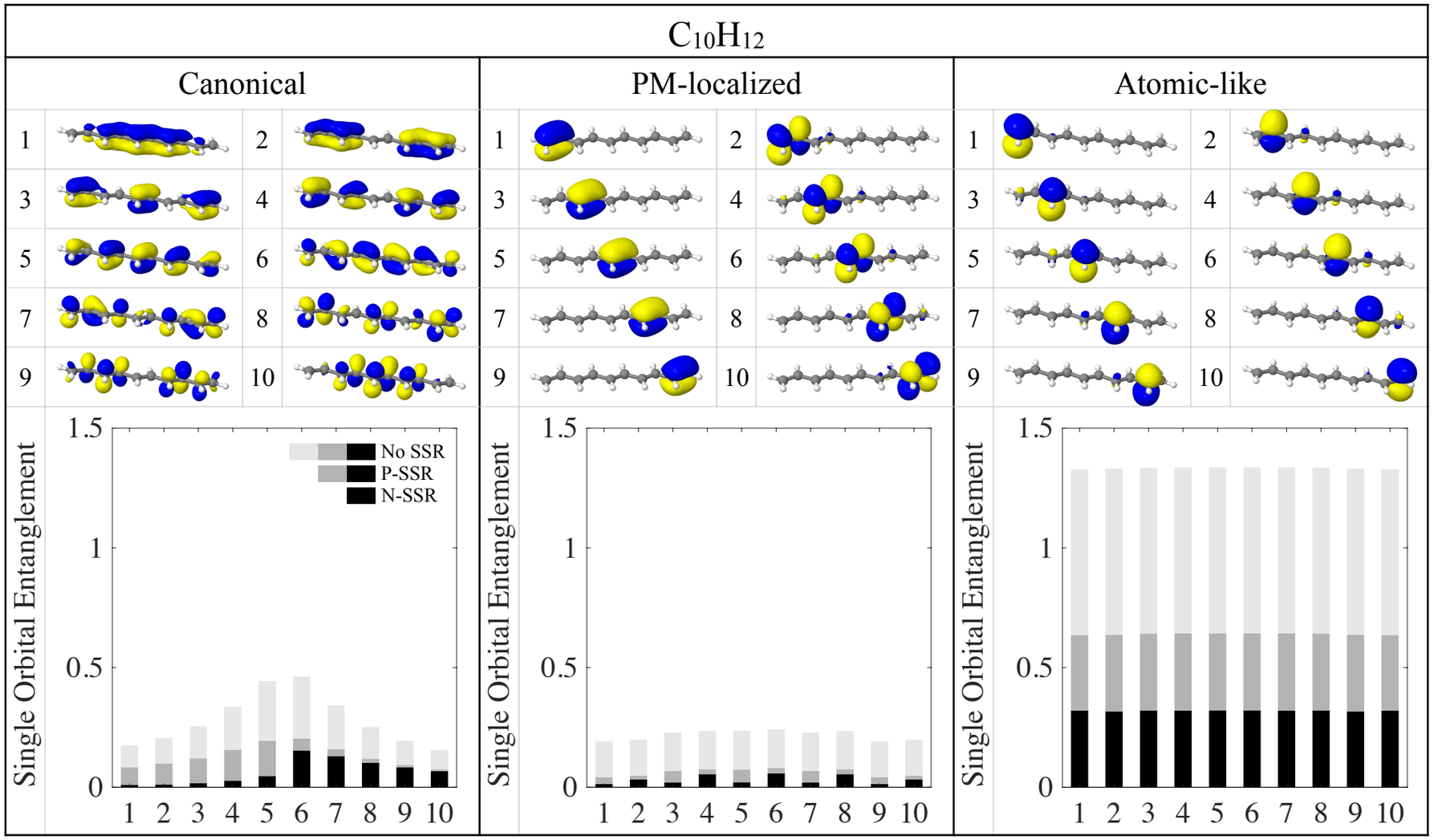

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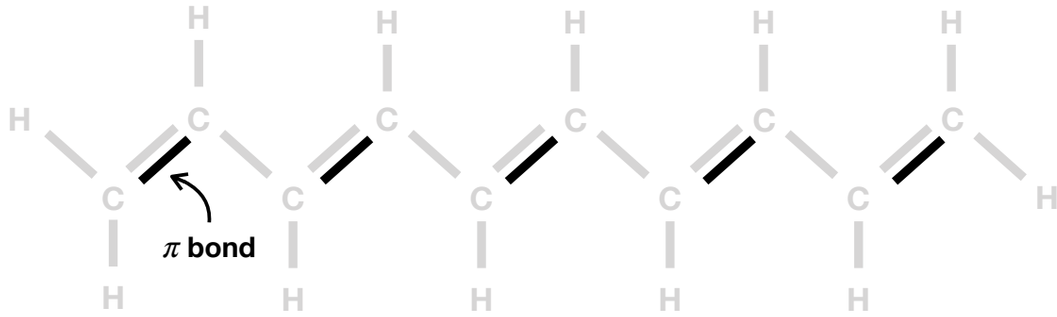

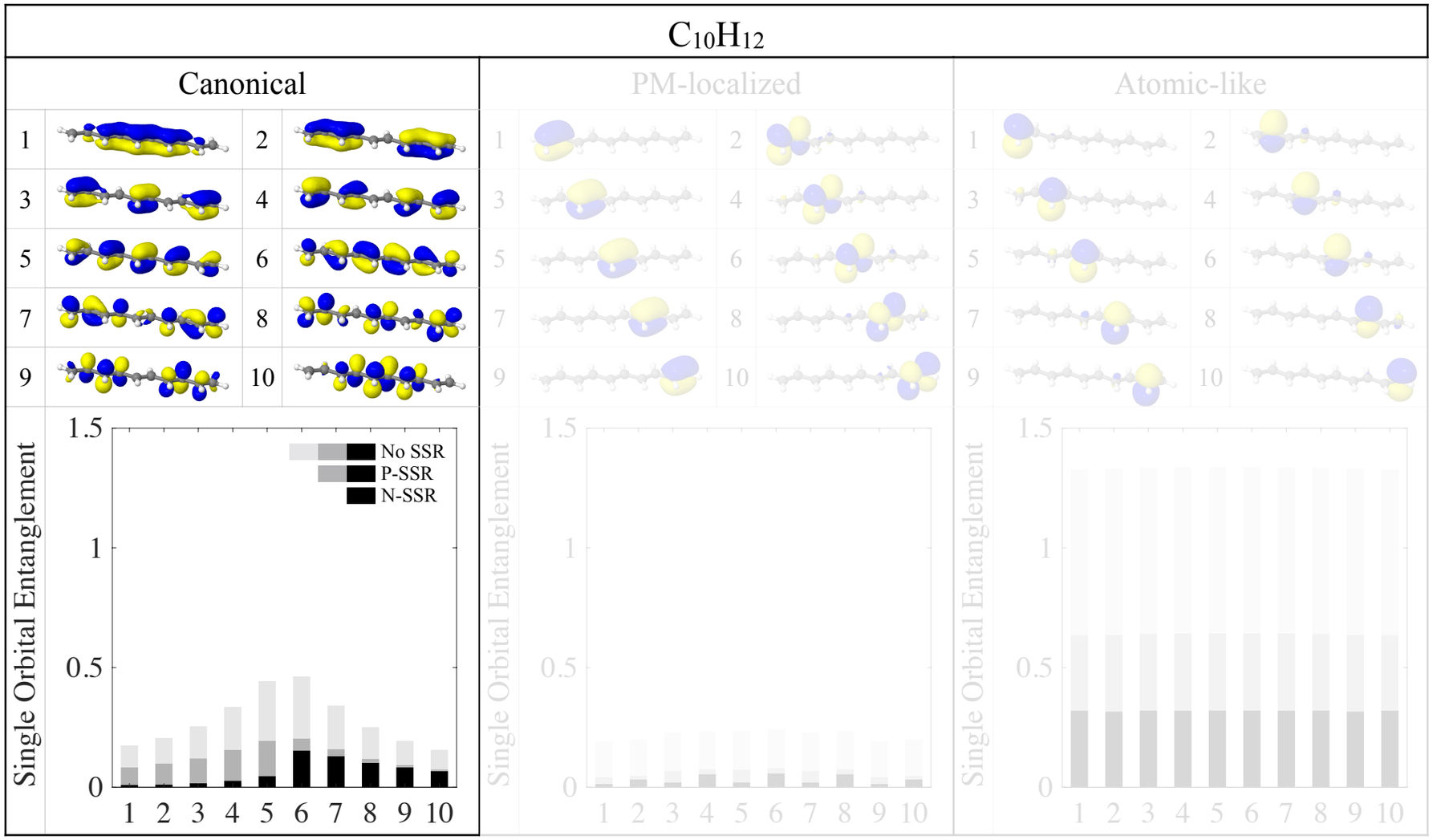

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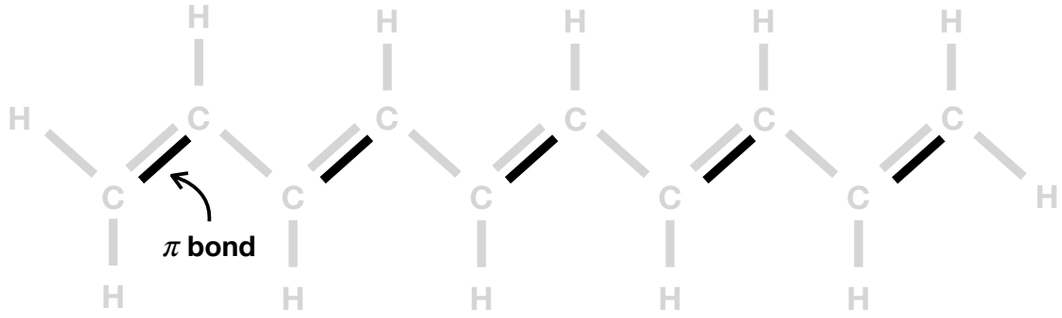

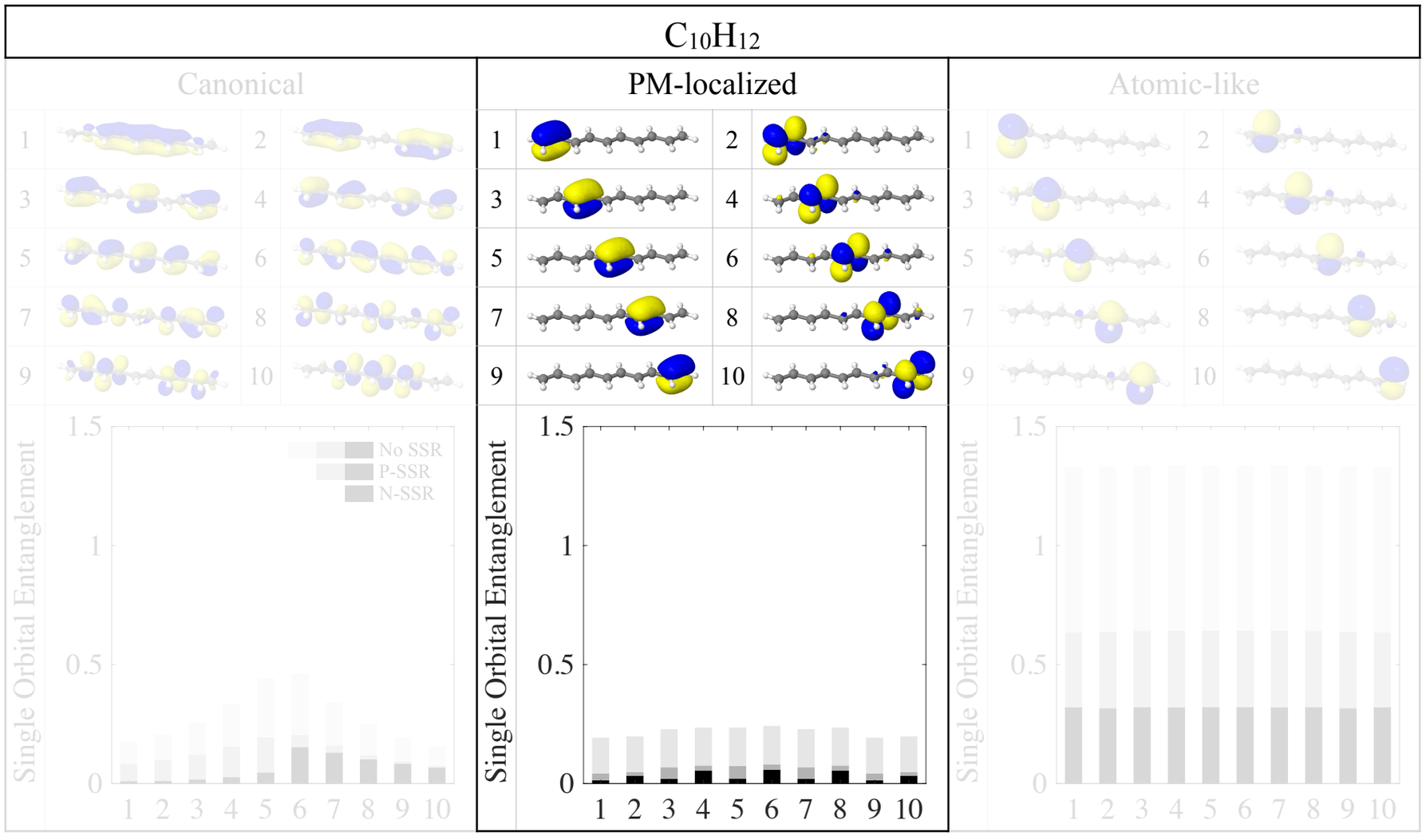

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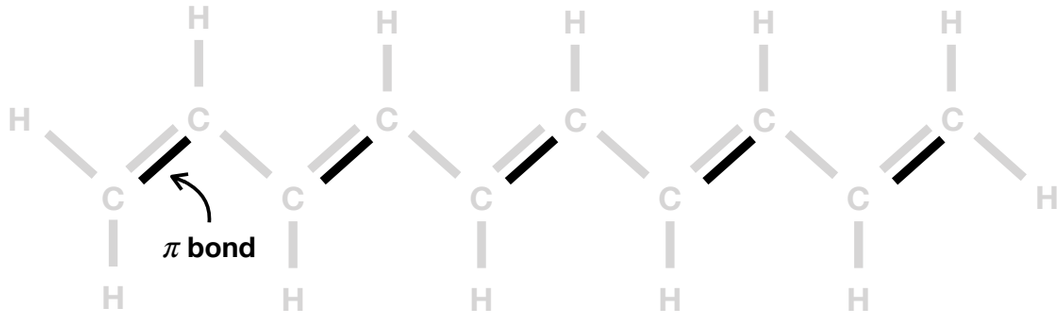

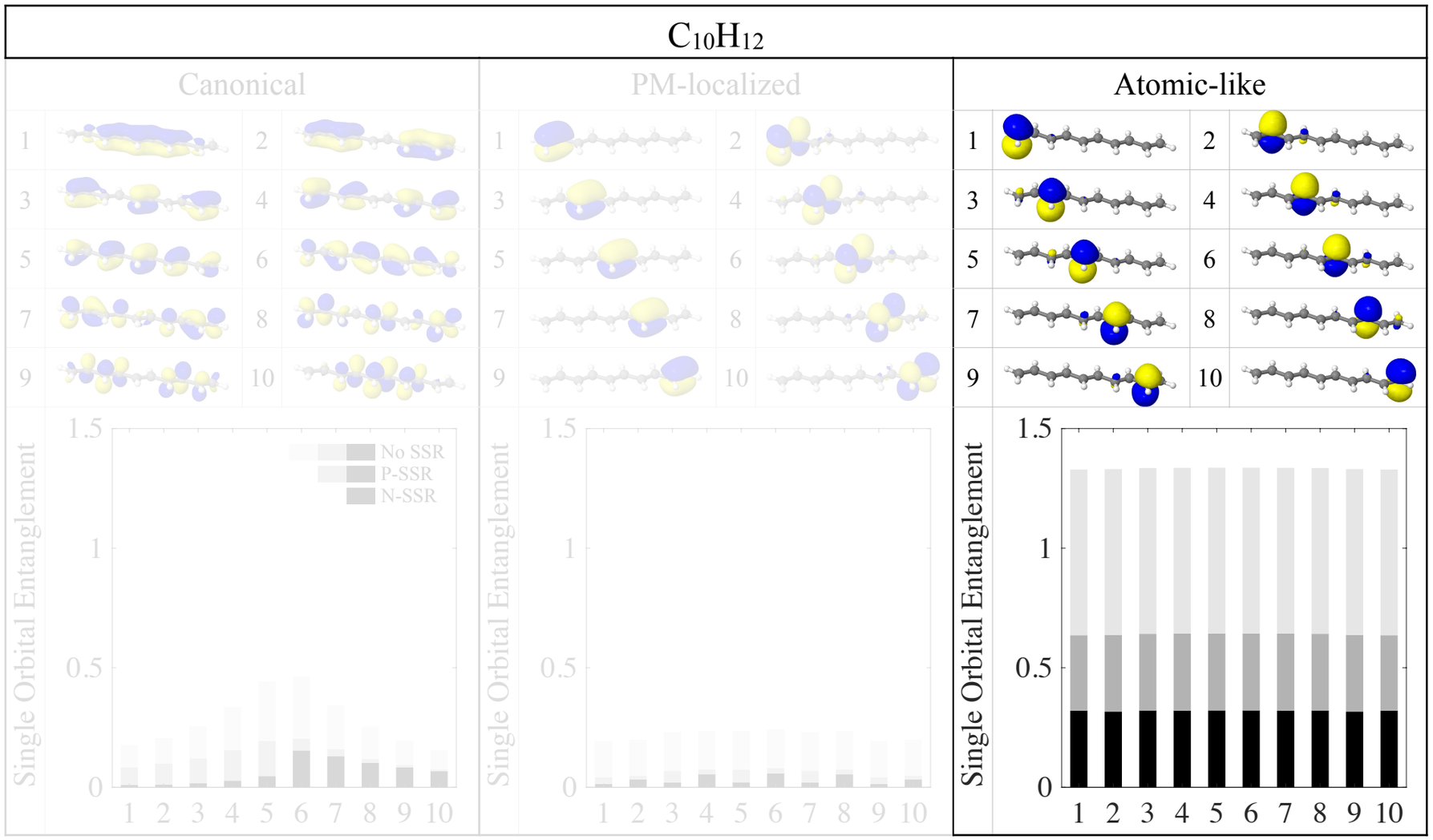

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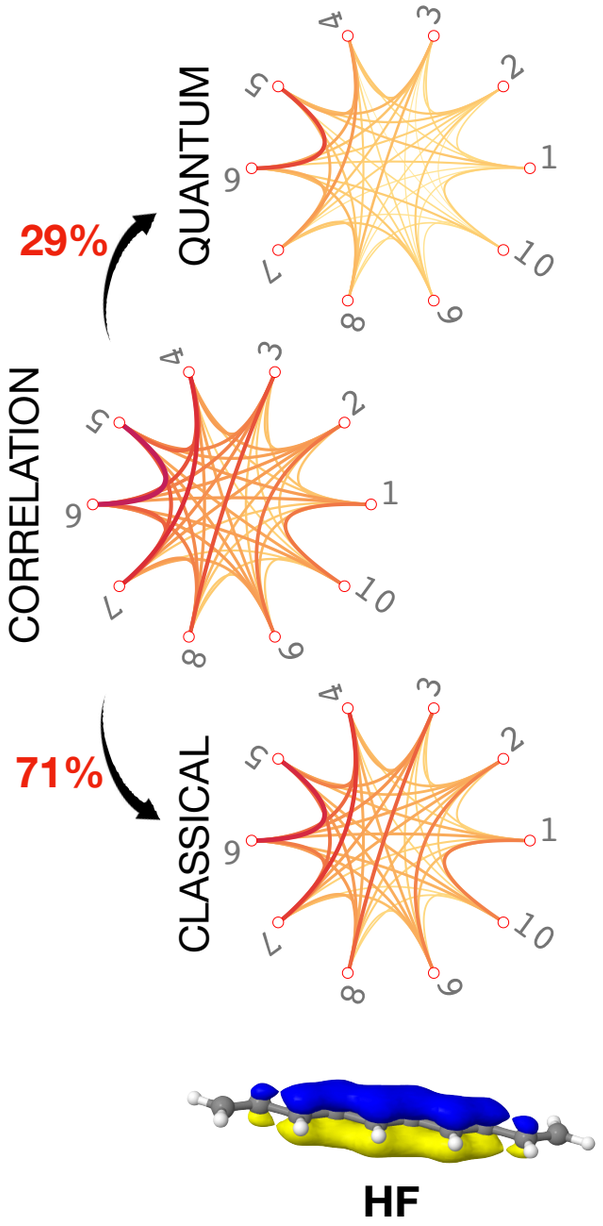
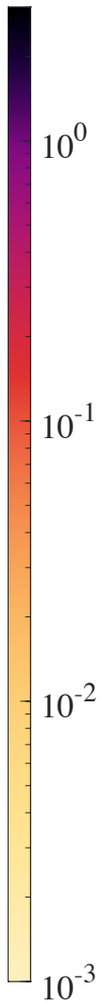
Multiple Bonds: Orbital-Orbital Correlation





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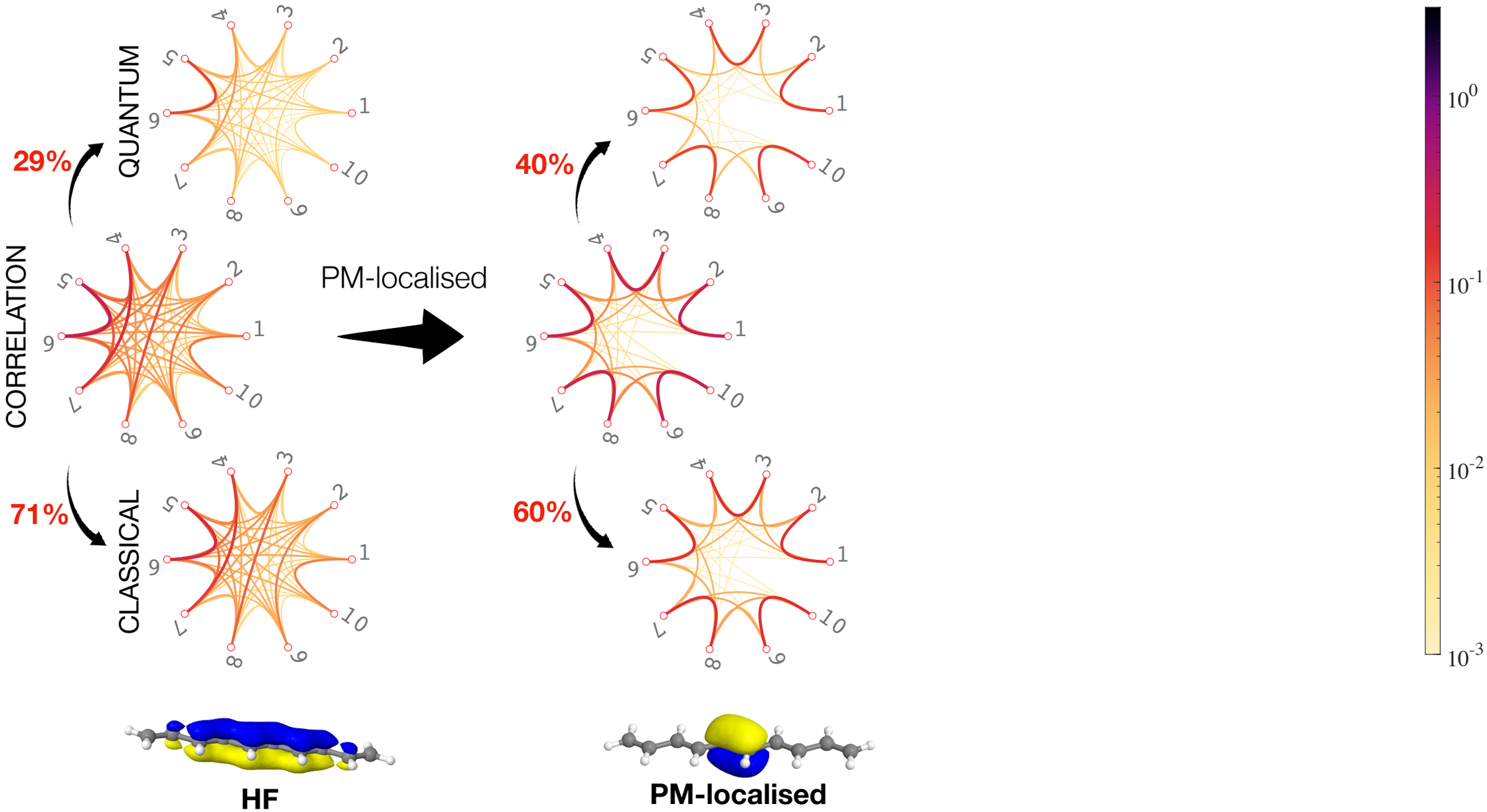

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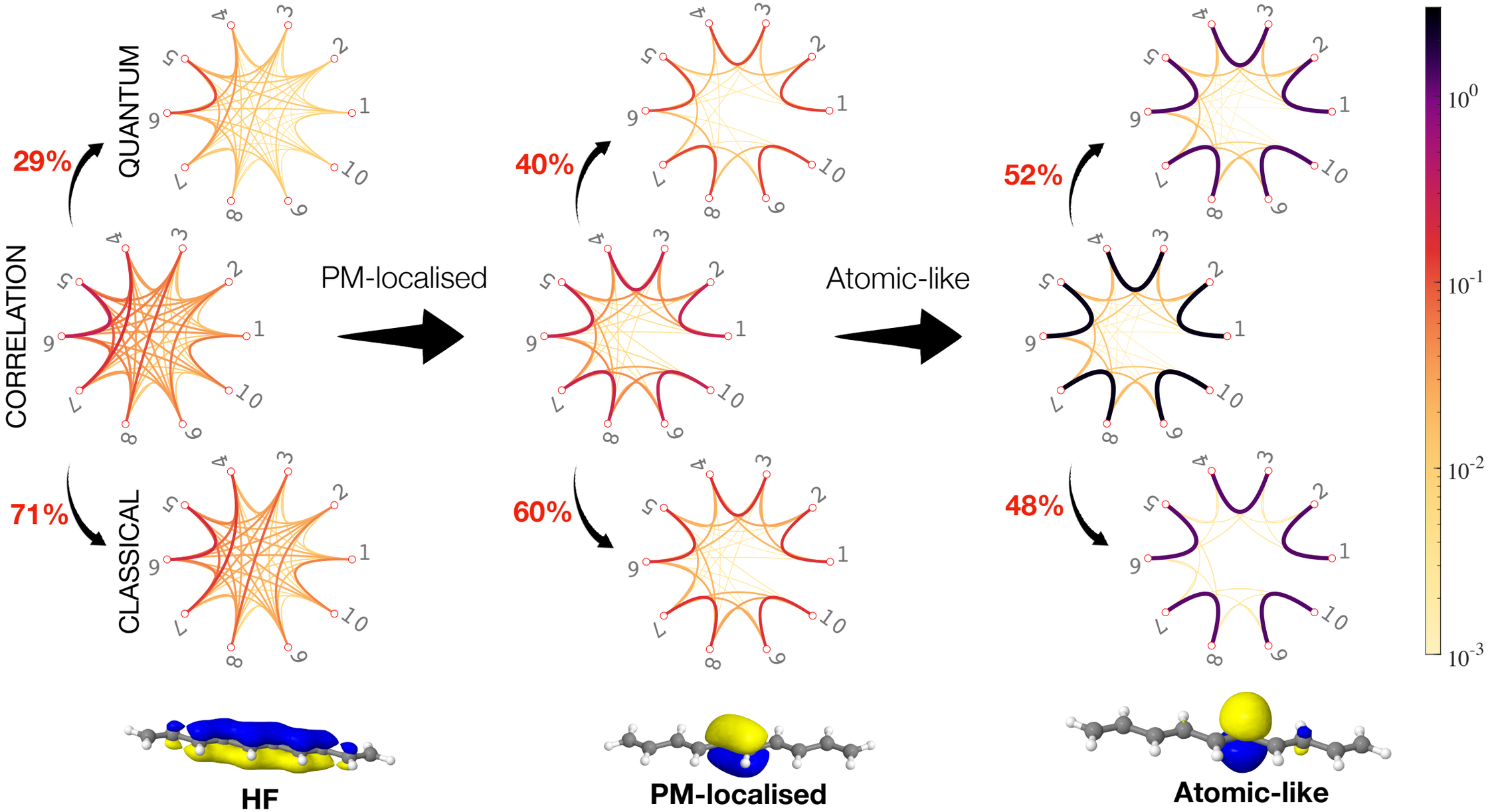

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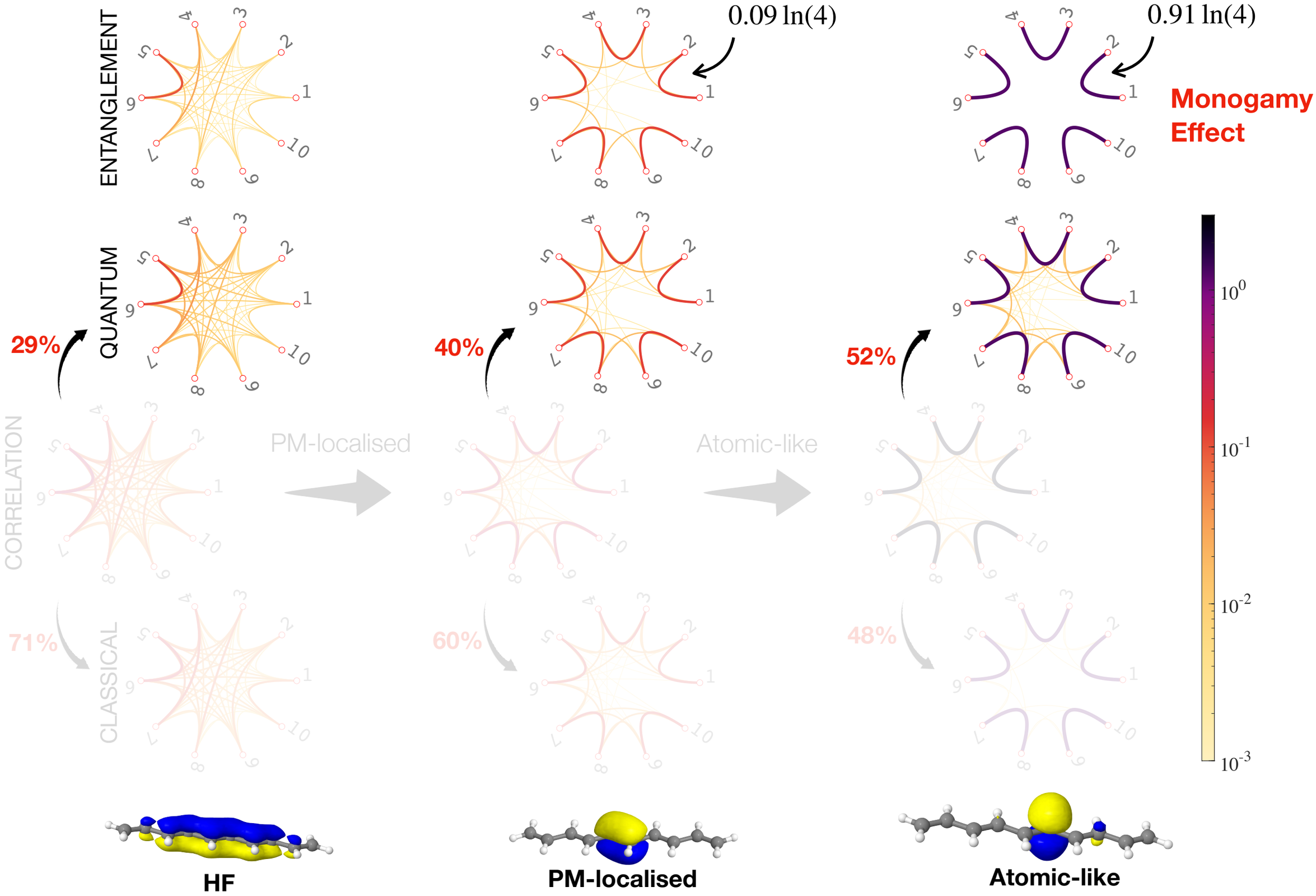

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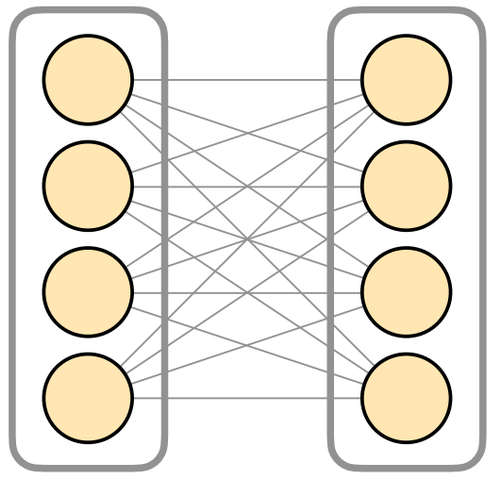
Orbital Localization Schemes and where to find them

- Localization criteria -> Not unique
- Spatial localization ≠> Maximum pairwise correlation
- Internal degrees of freedom in multi-orbital centers



Rotations within centers
do not change locality

DOES change correlation

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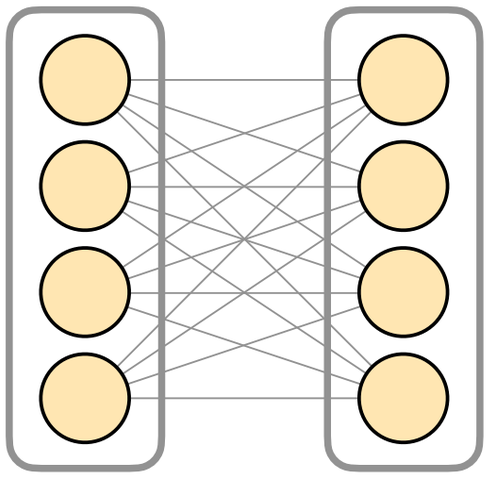
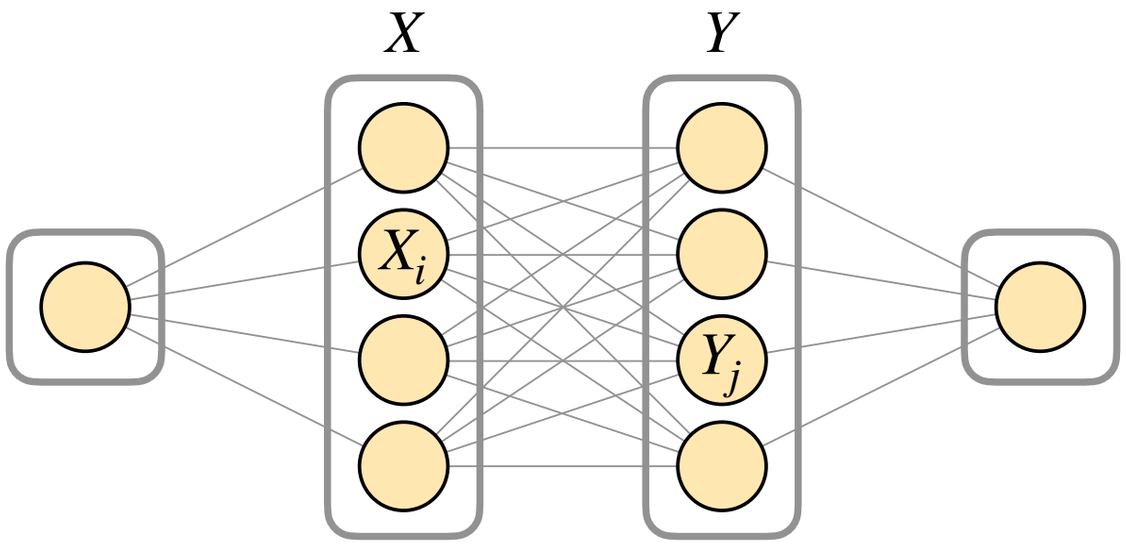


Rotations within centers
do not change locality

DOES change correlation

- Spatial locality alone is not enough for identifying valence orbitals

Correlation between multi-orbital atomic centers



LD, S. Knecht, C. Schilling, In Preparation.

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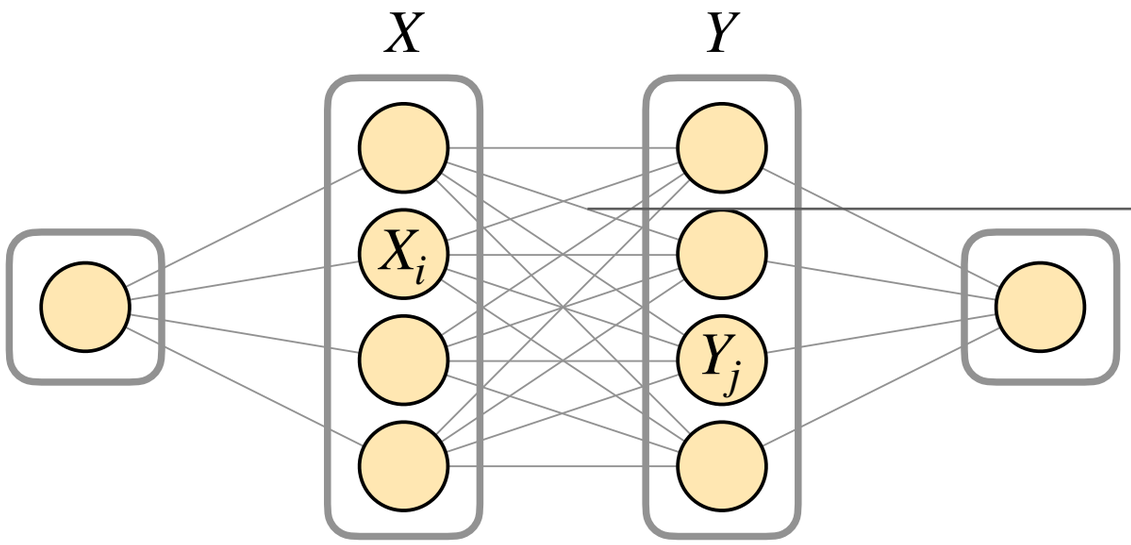
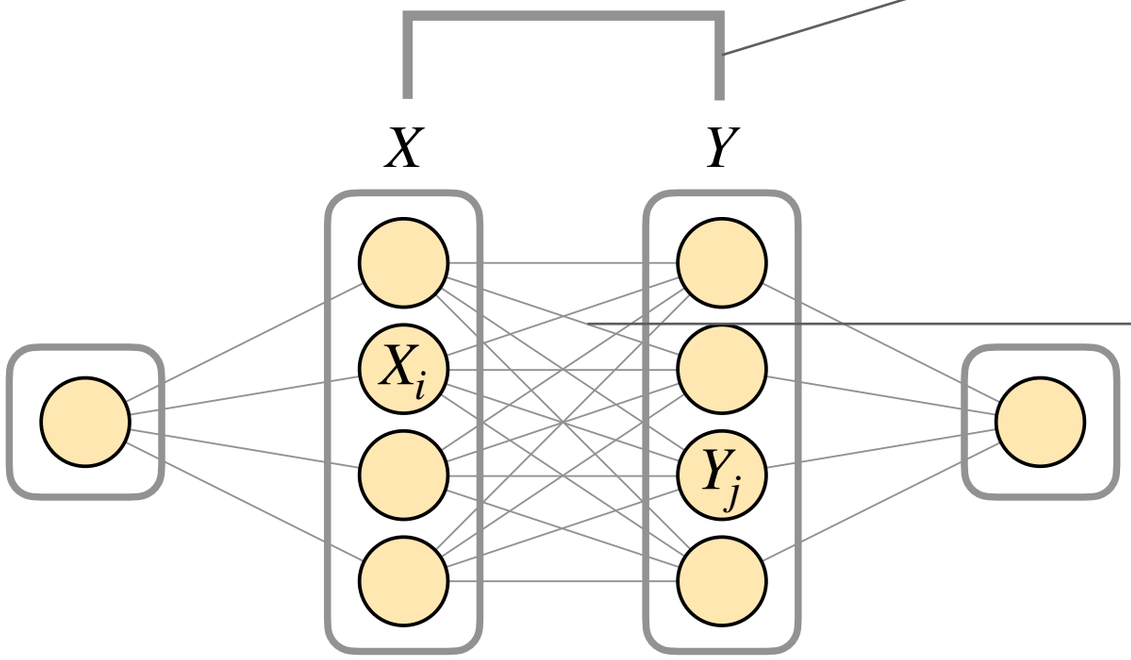


Pairwise Correlation

$$\mathrm{PC}(X, Y) = \sum_{i,j} I(\rho_{X_i, Y_j})$$

LD, S. Knecht, C. Schilling, In Preparation.

Correlation between multi-orbital atomic centers



Block Correlation

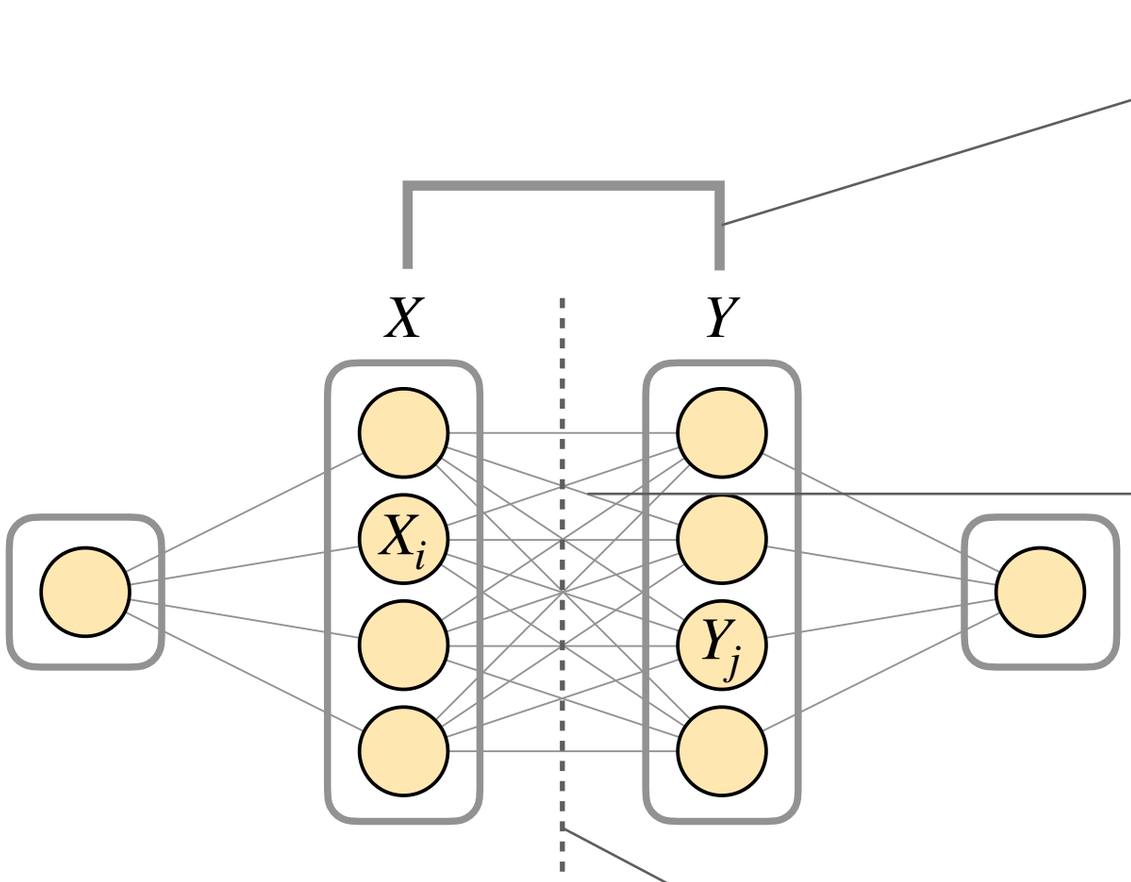
$$\mathrm{BC}(X, Y) = I(\rho_{X,Y})$$

Pairwise Correlation

$$\mathrm{PC}(X, Y) = \sum_{i,j} I(\rho_{X_i,Y_j})$$

LD, S. Knecht, C. Schilling, In Preparation.

Correlation between multi-orbital atomic centers



Block Correlation

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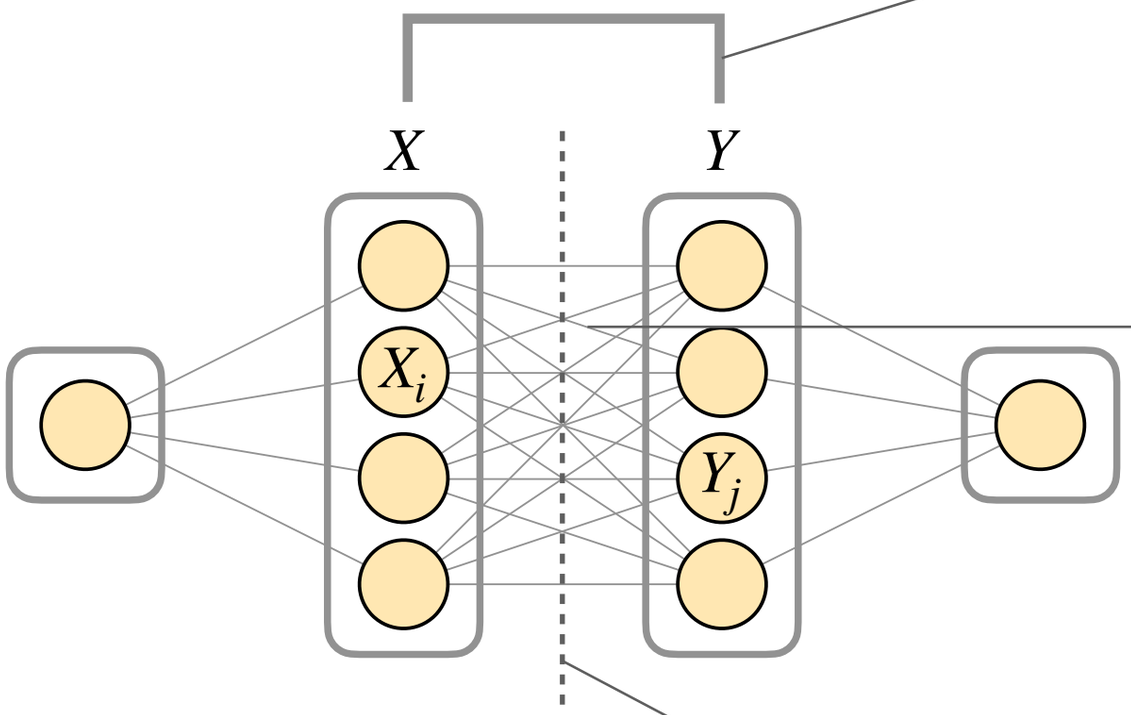
Bipartite Entanglement

LD, S. Knecht, C. Schilling, In Preparation.

Correlation between multi-orbital atomic centers



Block Correlation

$$\mathrm{BC}(X, Y) = I(\rho_{X,Y})$$

Pairwise Correlation

$$\mathrm{PC}(X, Y) = \sum_{i,j} I(\rho_{X_i,Y_j})$$

Objective function to maximize

$$\mathrm{PCS} = \sum_{\langle X,Y \rangle} \mathrm{PC}(X, Y)$$

Pairwise Correlation Sum

Bipartite Entanglement

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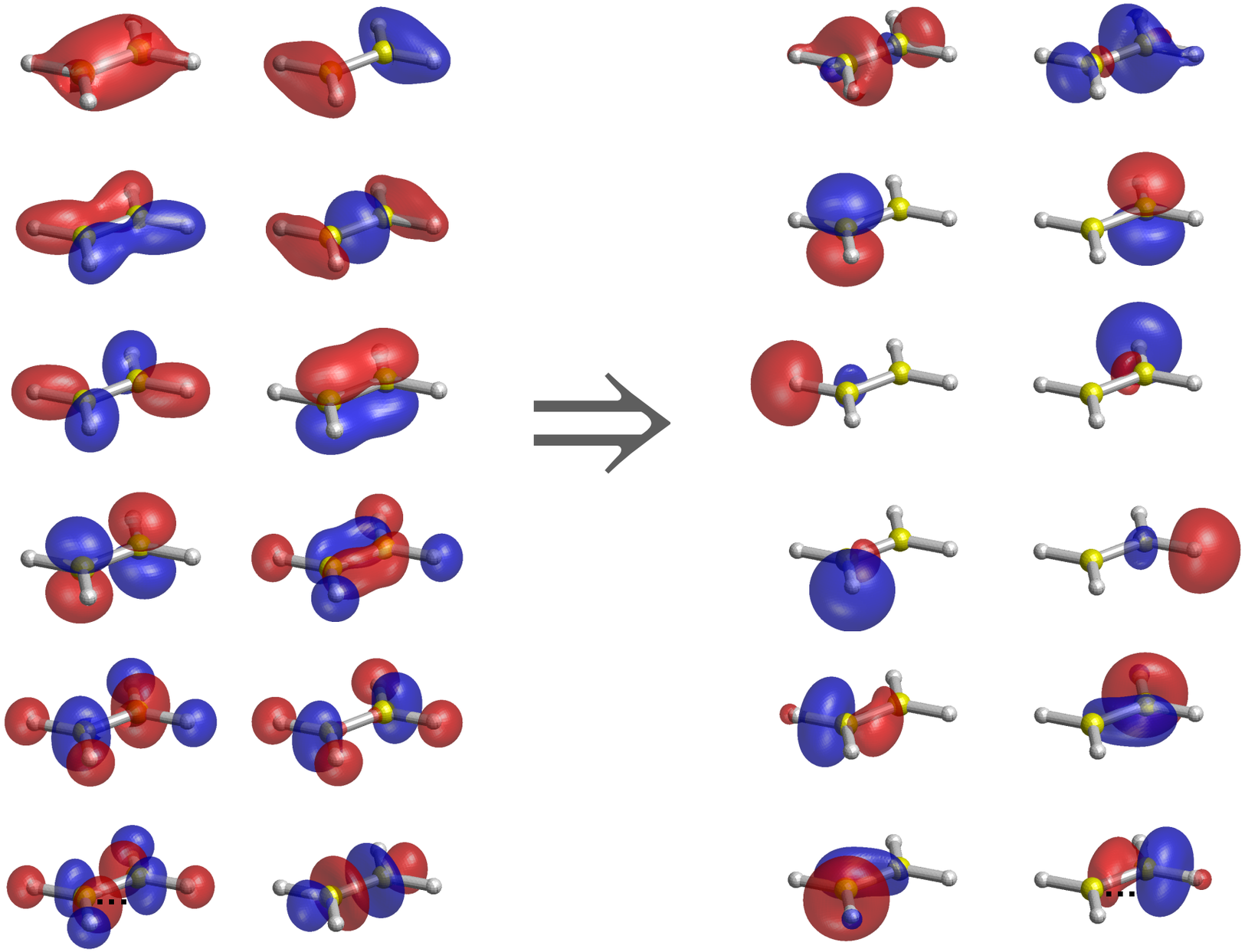
Canonical

Localized



Delocalised
Symmetric
Weakly Correlated
$N \approx 0, 2$ (anti)bonding

Localised
Symmetry-breaking
Strongly Correlated
$N \approx 1$ valence

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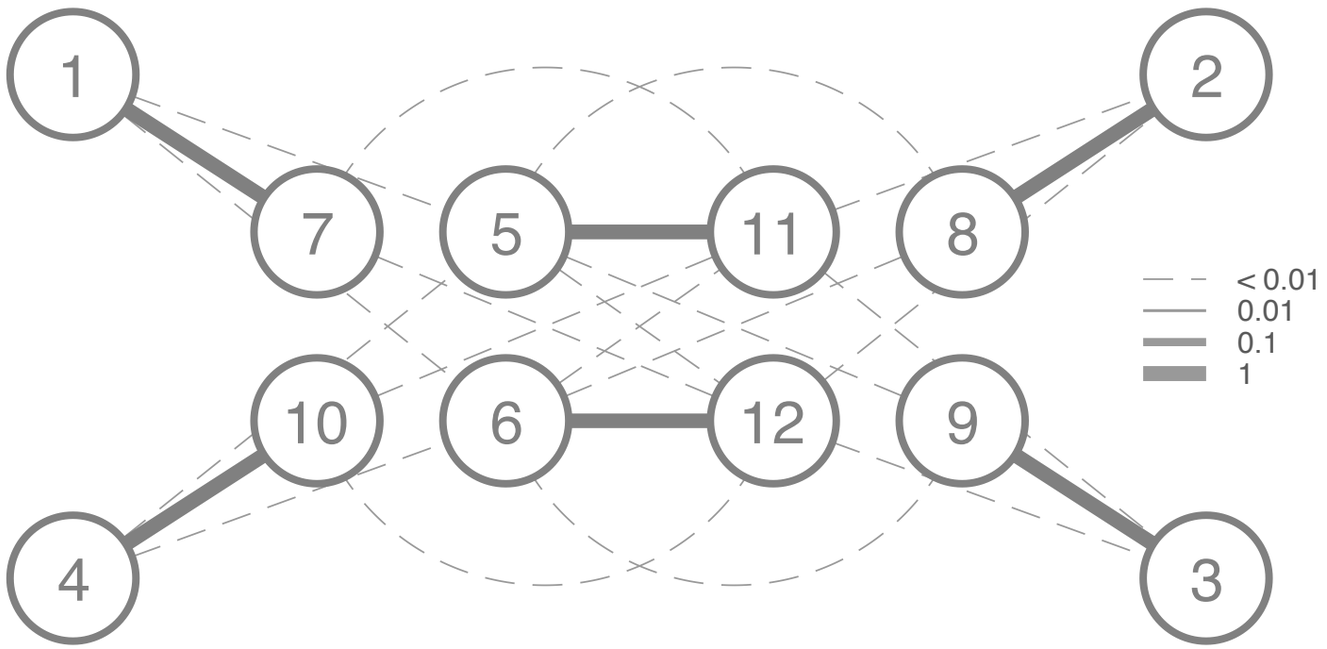

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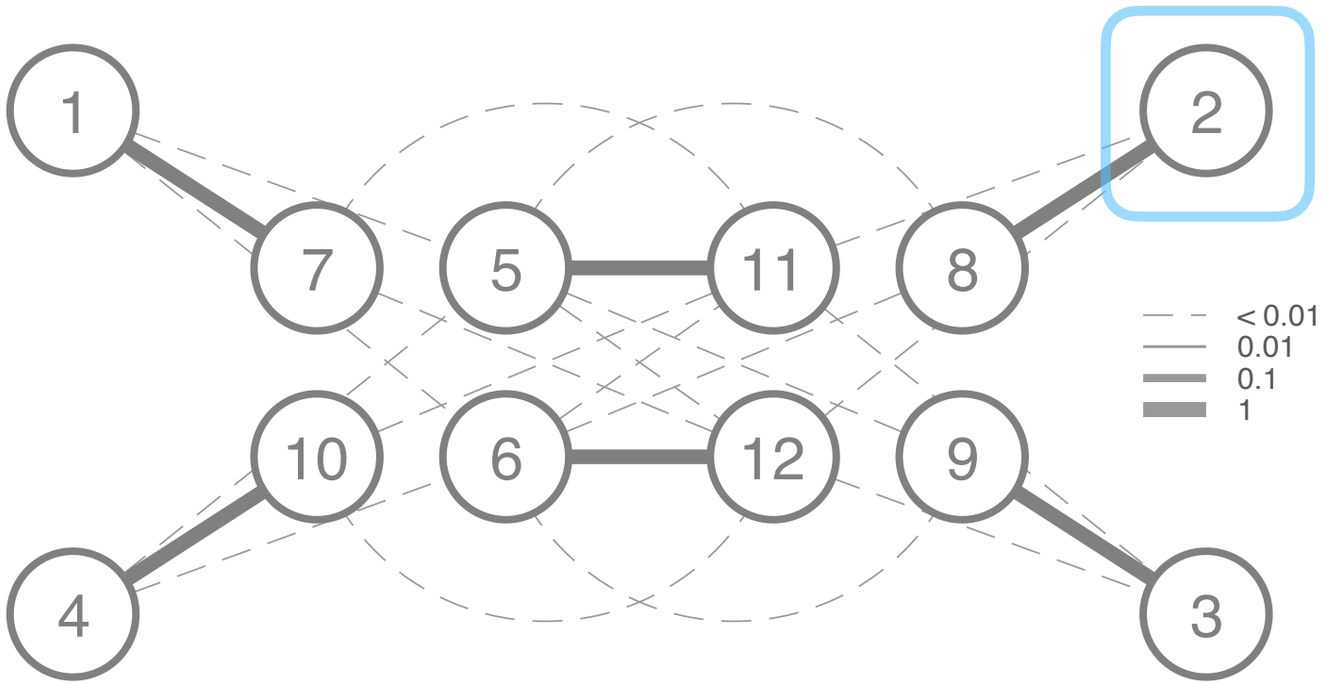
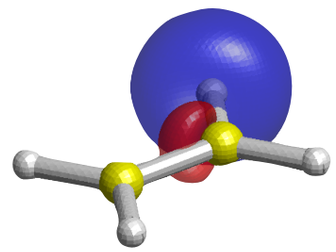


H-centered LMOs



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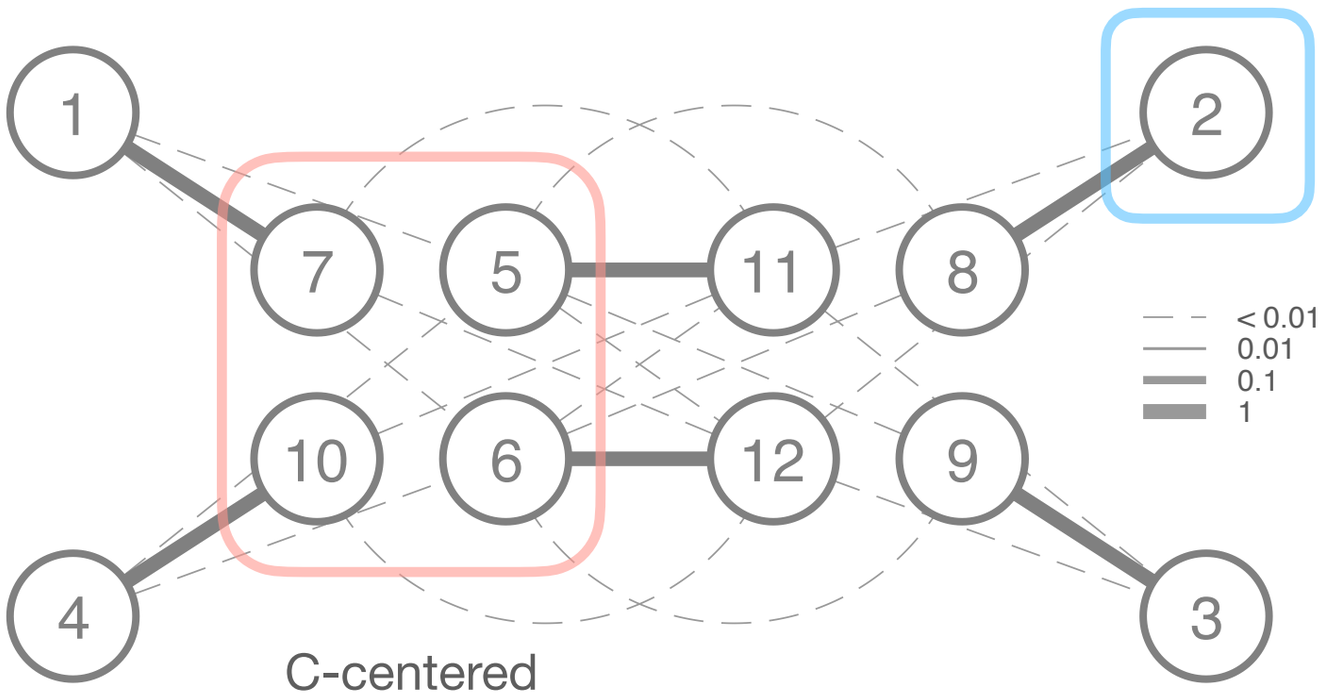

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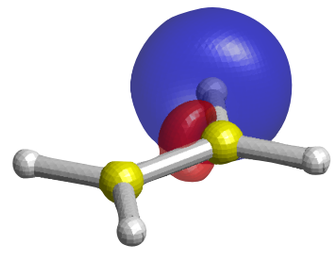
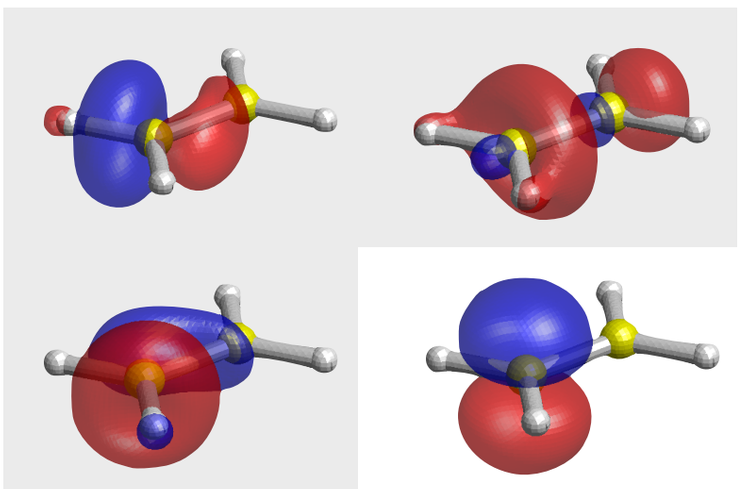


C-centered LMOs



sp2-hybrids

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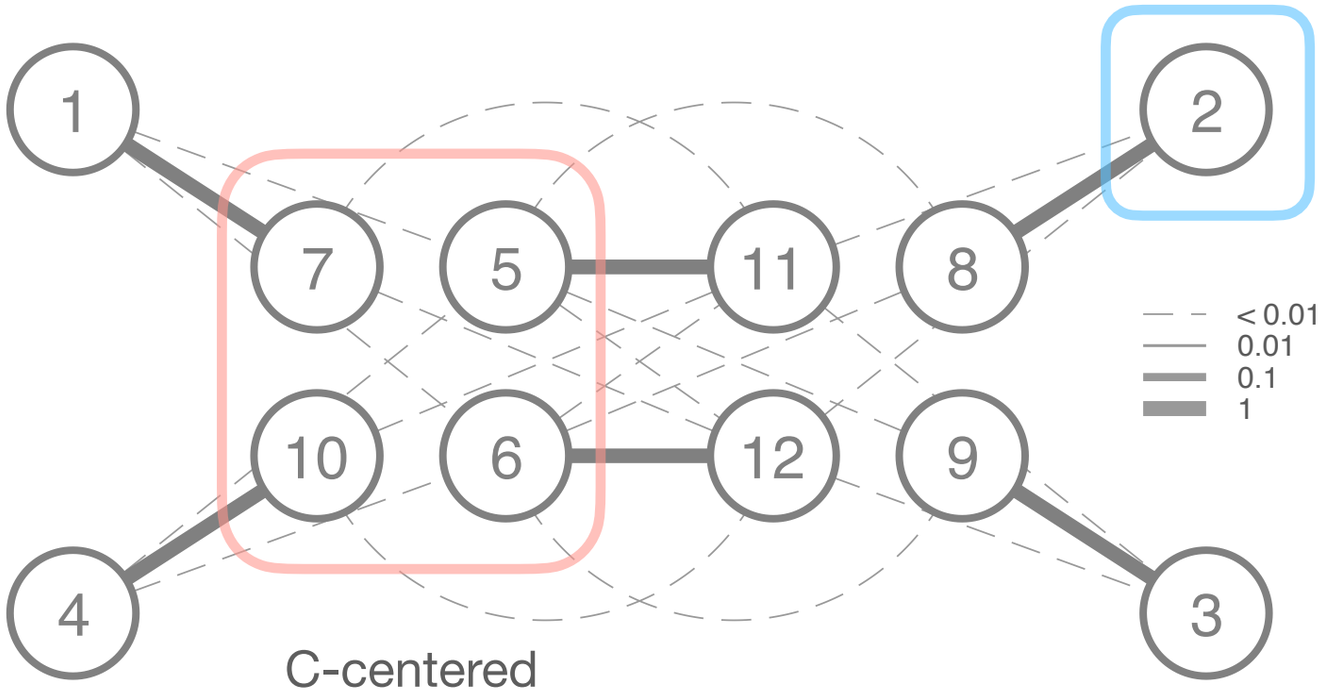

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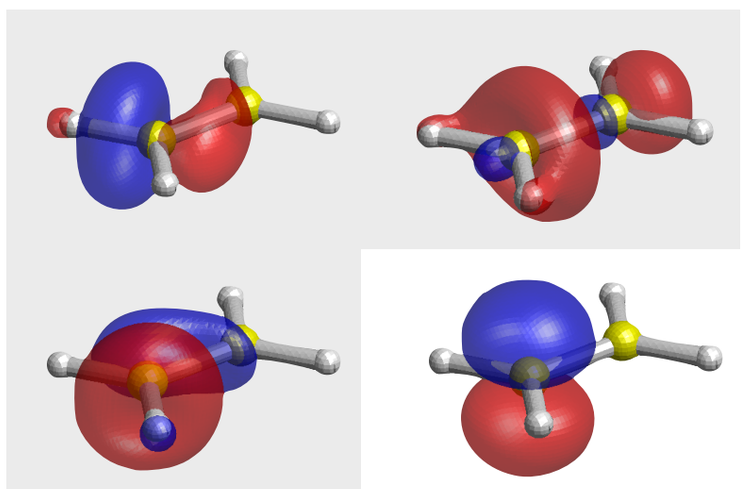

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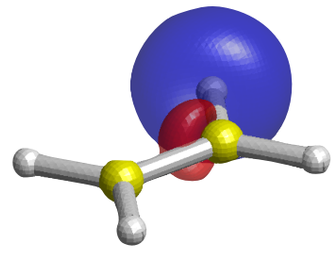

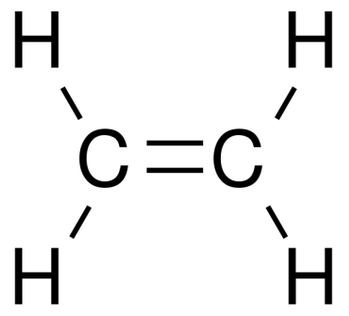

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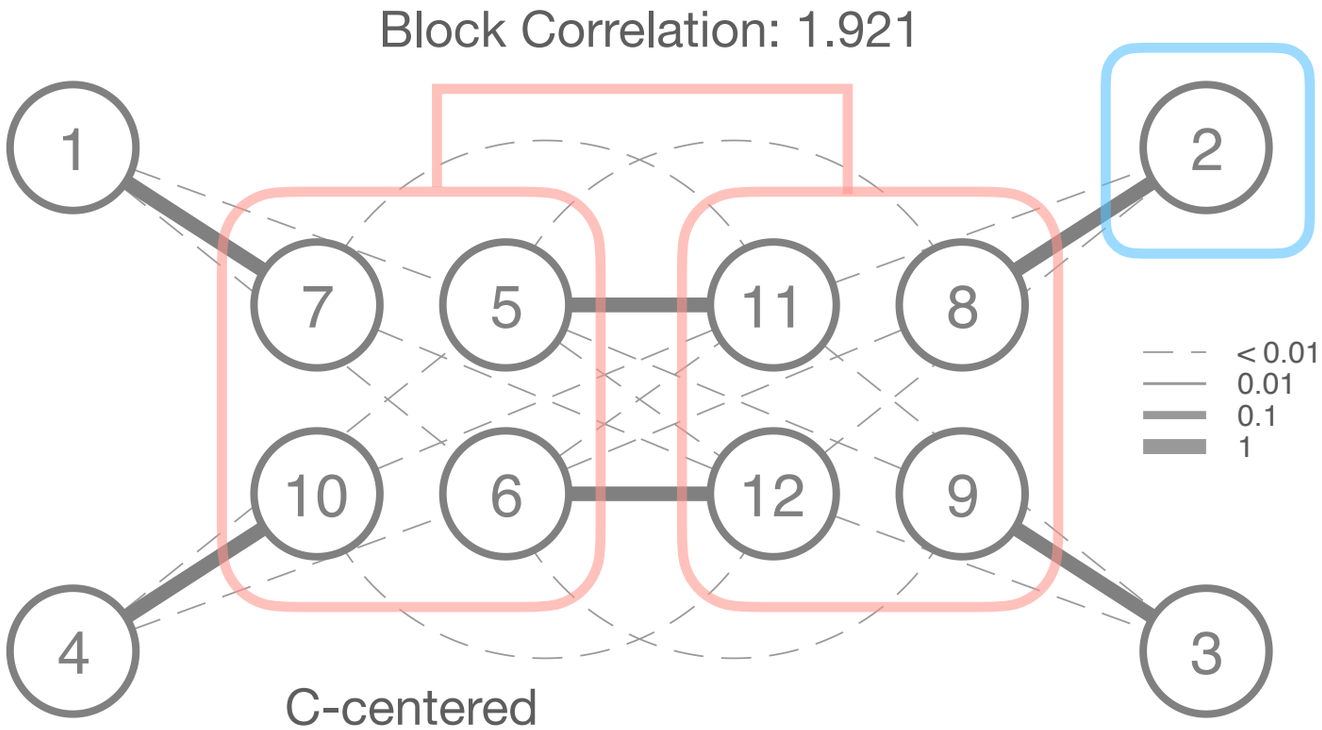

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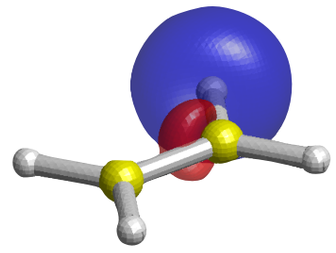

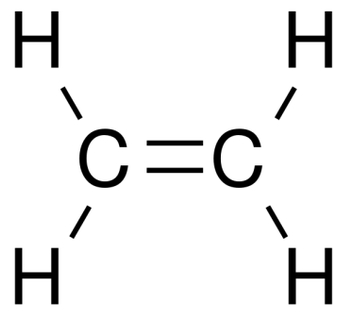

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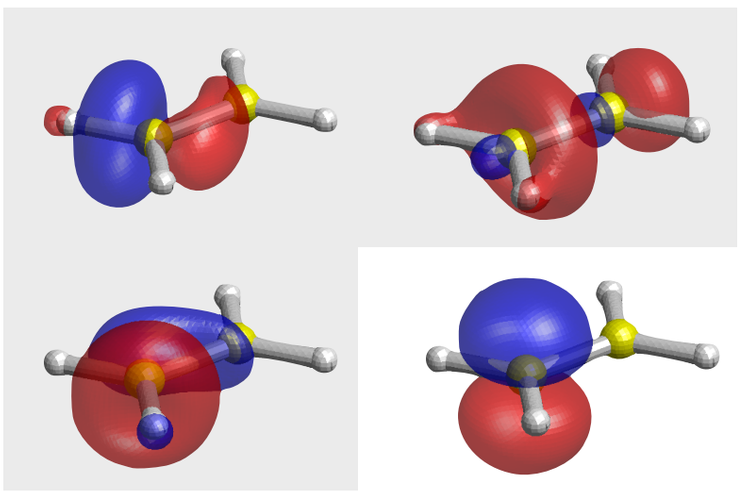

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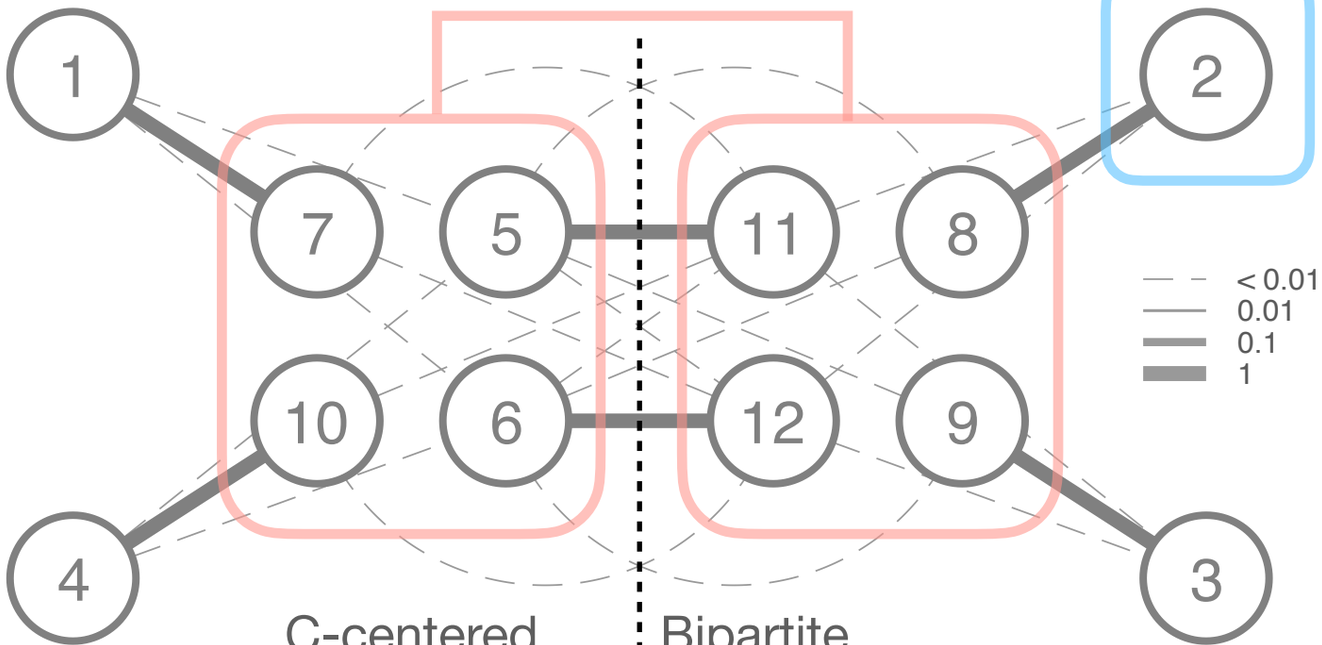

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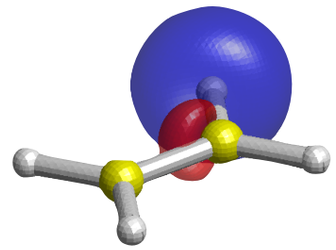

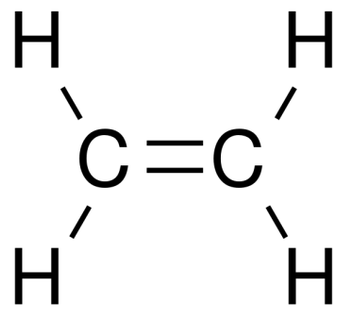

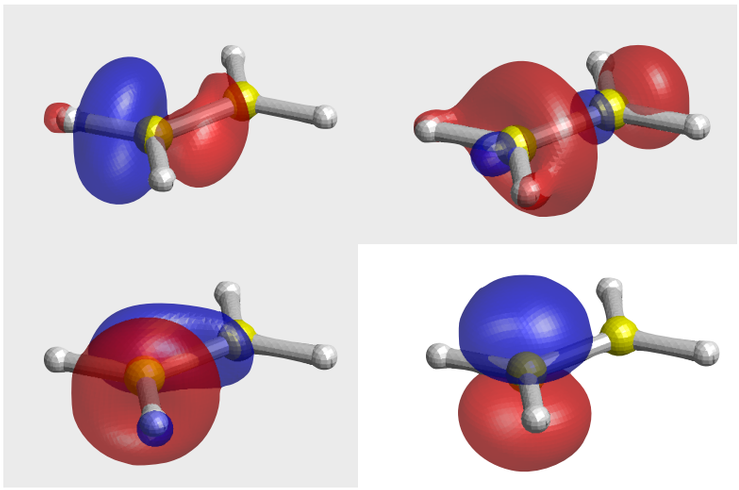

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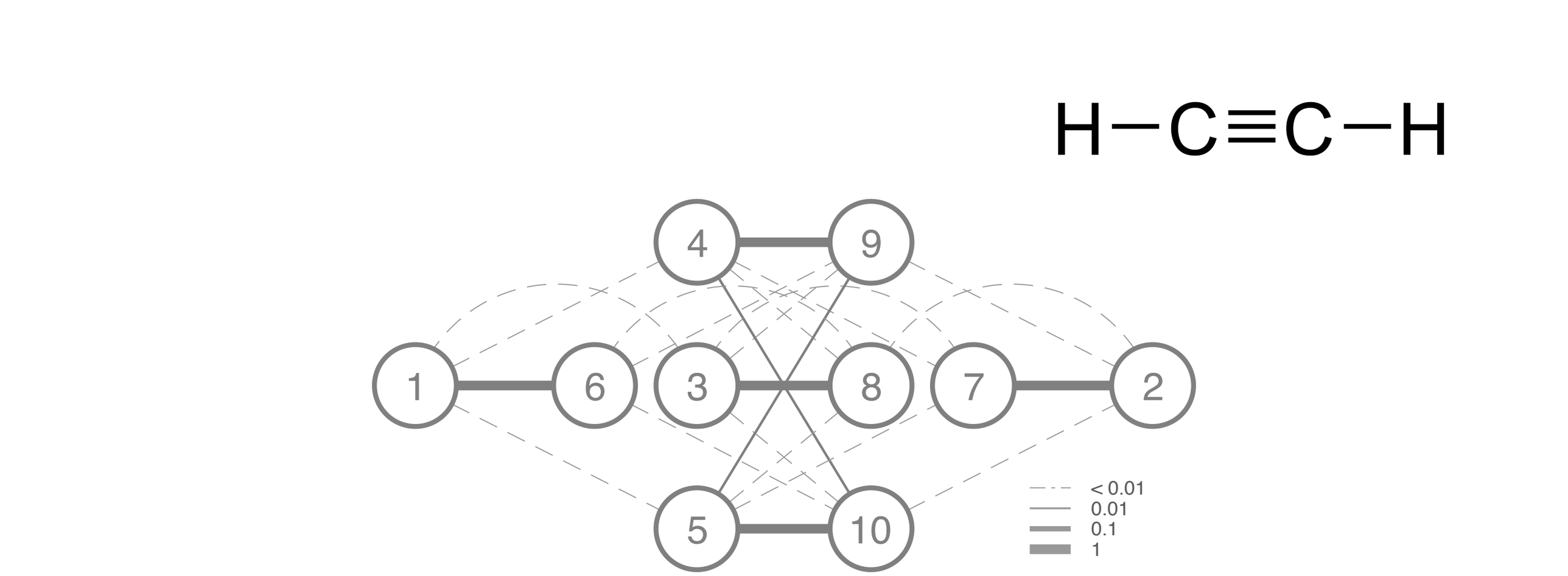

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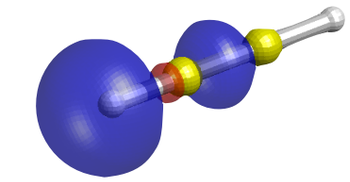
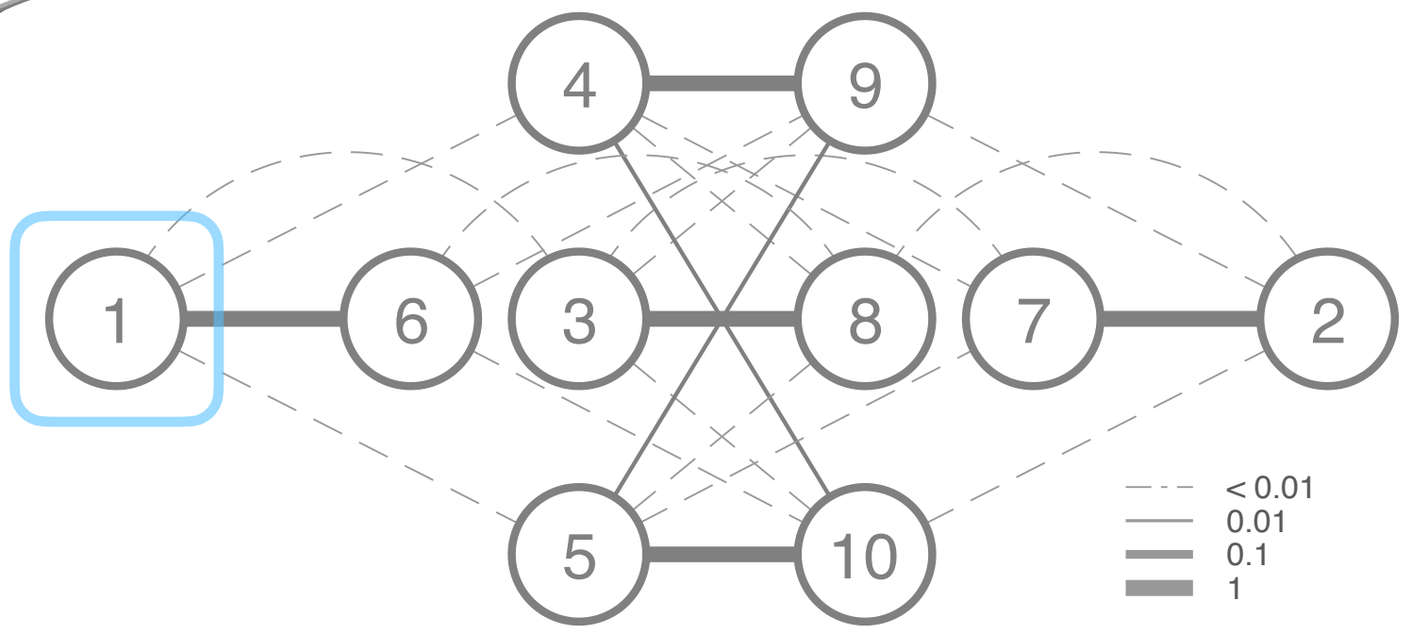


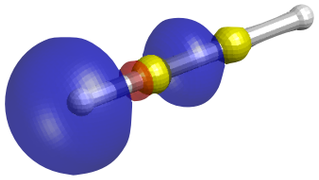
H-centered
LMOs



H−C≡C−H

LD, S. Knecht, C. Schilling, In Preparation.

$$H-C\equiv C-H$$



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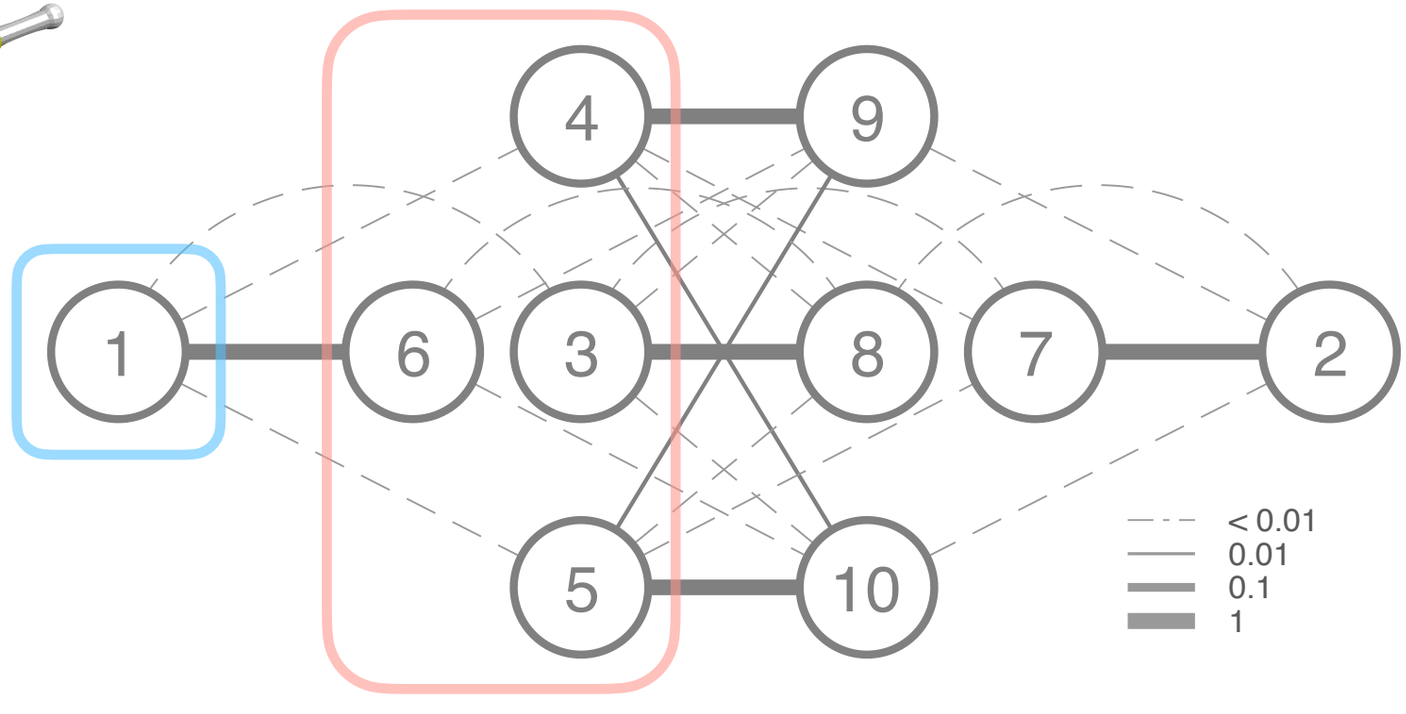
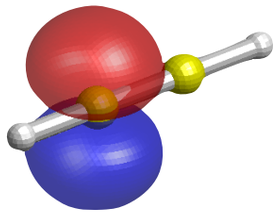
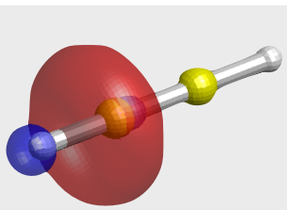
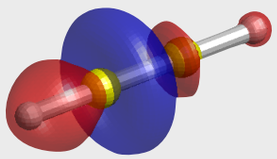
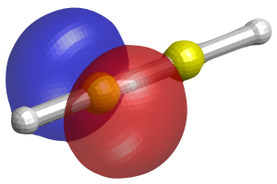




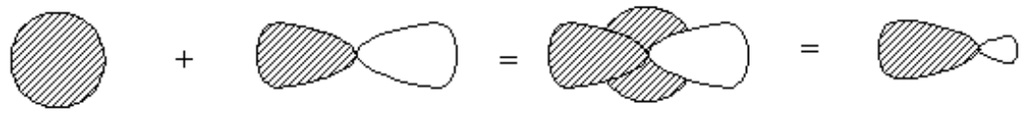
C-centered LMOs

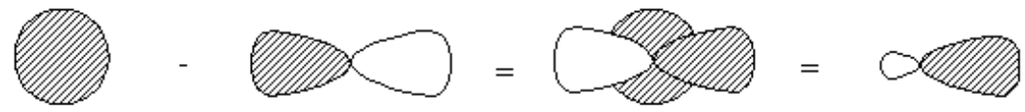






sp-hybrids





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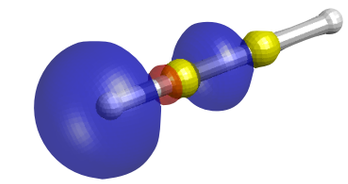
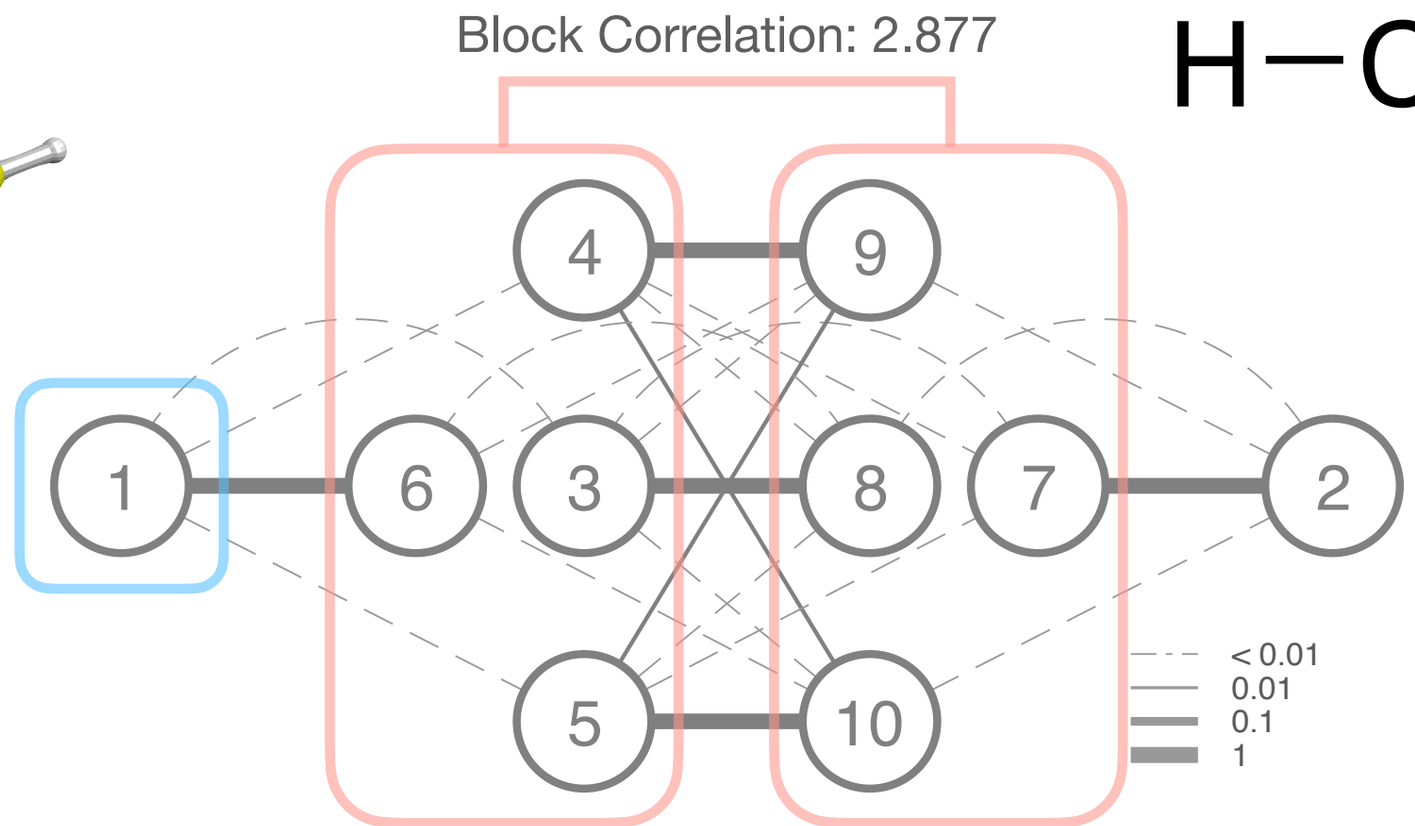
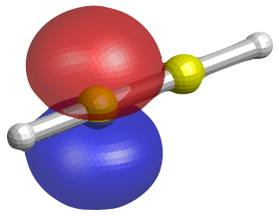


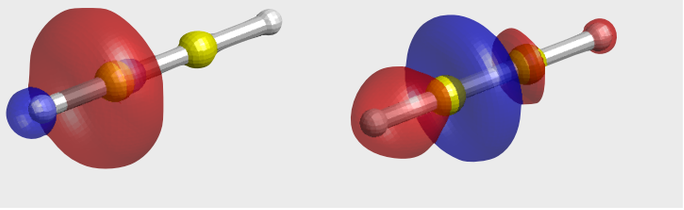
H-centered LMOs



$H-C\equiv C-H$



C-centered LMOs



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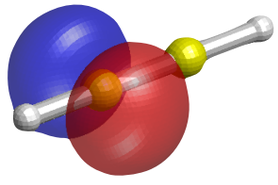

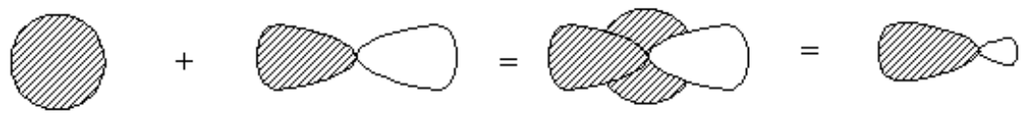

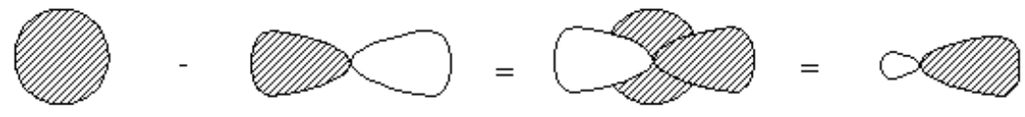

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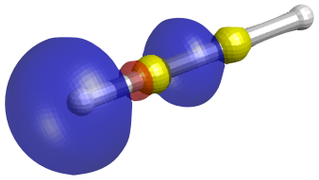
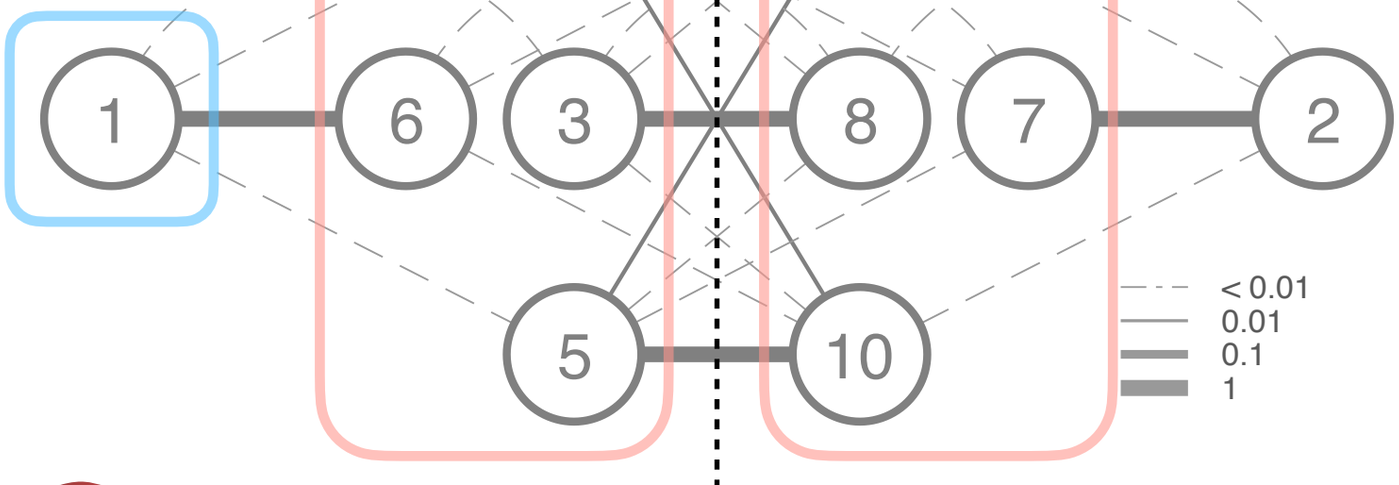
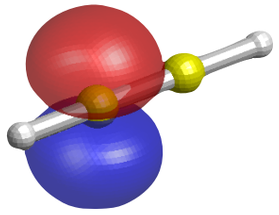
Block Correlation: 2.877

H−C≡C−H



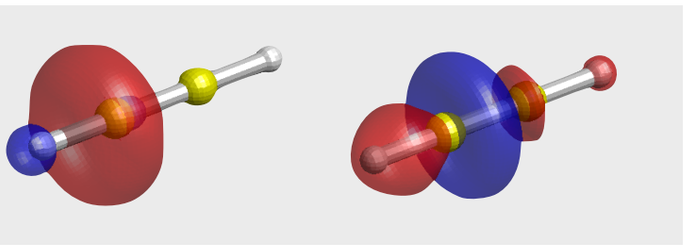
H-centered LMOs

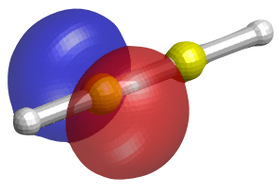




C-centered LMOs

Bipartite Entanglement: 2.938





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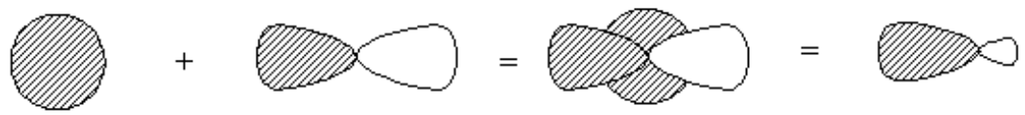
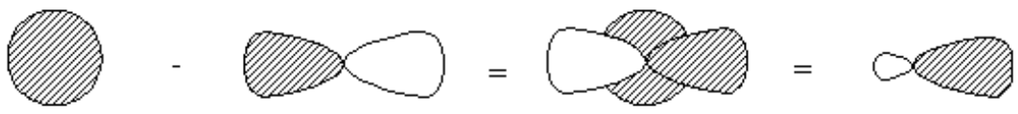
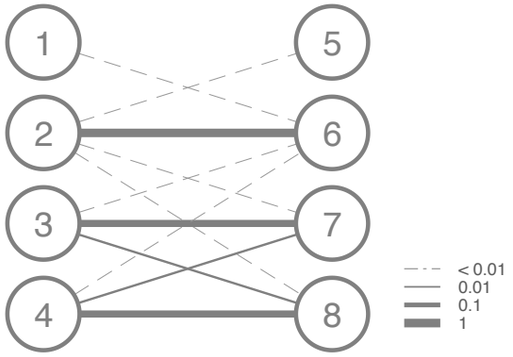




LD, S. Knecht, C. Schilling, In Preparation.



O_2		5	6	7	8
1		0.000	0.003	0.000	0.000
2		0.003	0.935	0.007	0.007
3		0.000	0.007	0.436	0.017
4		0.000	0.007	0.017	0.436

	O_2	N_2	C_2H_4	C_2H_2	C_2
BO(MO)	2	3	2	3	2
CAS(n_e,n_o)	(12,8)	(10,8)	(12,12)	(10,10)	(8,8)
Pairwise Corr. Sum	1.879	2.840	1.834	2.783	3.380
Block Corr.	1.924	2.928	1.920	2.877	3.532
Block Corr.(σ)	0.946	0.992	0.967	0.964	1.603
Block Corr.(π)	0.920	1.879	0.885	1.908	1.707
Bi. Ent.	1.924	2.928	1.969	2.938	3.532

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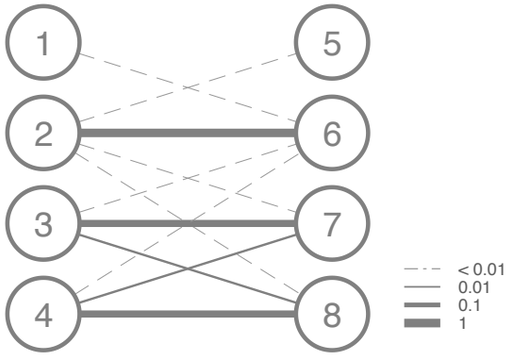

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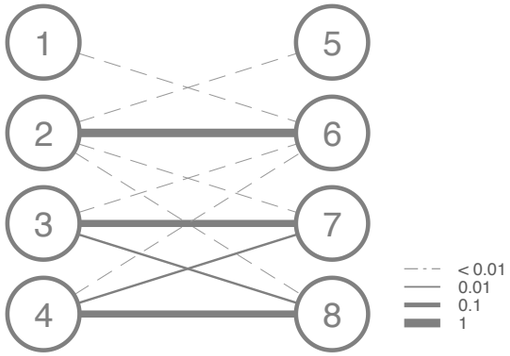

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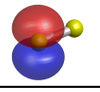
4		0.000	0.007	0.017	0.436

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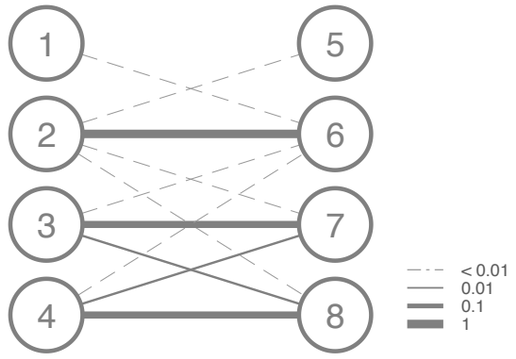

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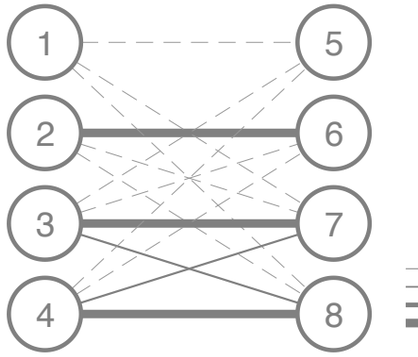

N_2		5	6	7	8
1		0.004	0.000	0.003	0.003
2		0.000	0.964	0.003	0.003
3		0.003	0.003	0.913	0.014
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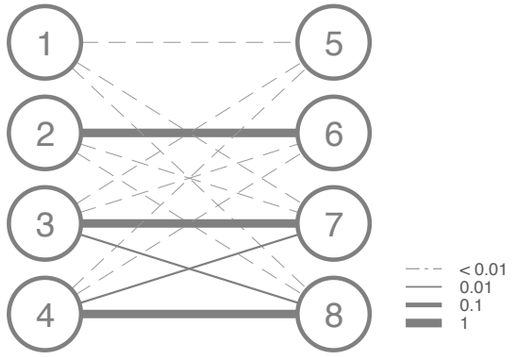

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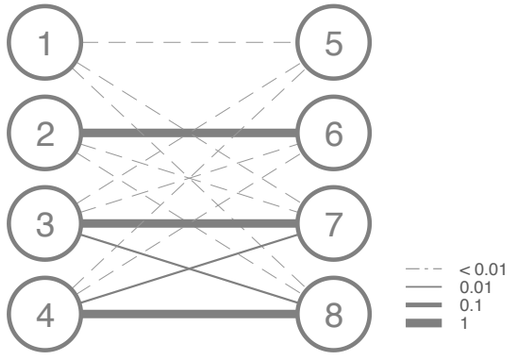

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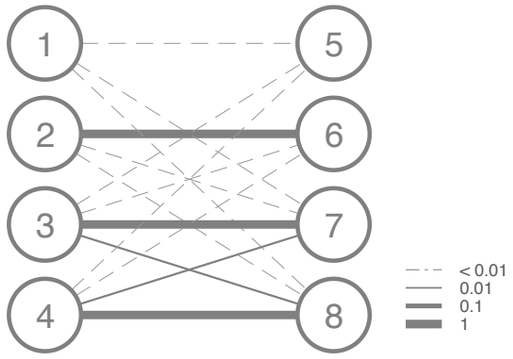

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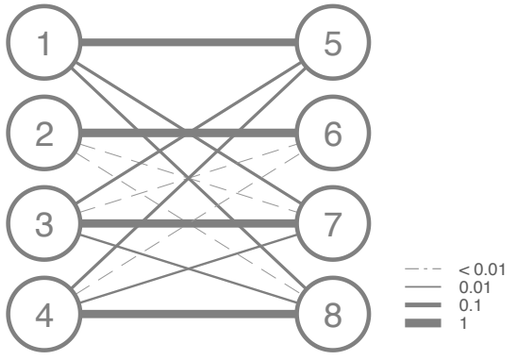

C_2		5	6	7	8
1		0.609	0.000	0.031	0.031
2		0.000	0.960	0.002	0.002
3		0.031	0.002	0.823	0.017
4		0.031	0.002	0.017	0.823

	O_2	N_2	C_2H_4	C_2H_2	C_2
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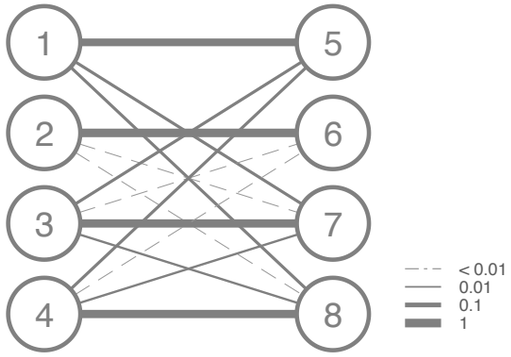

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3		0.031	0.002	0.823	0.017
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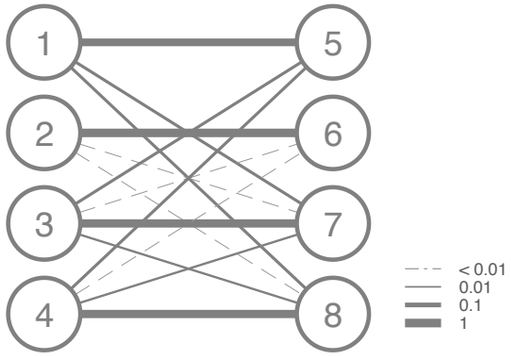
	O_2	N_2	C_2H_4	C_2H_2	C_2
BO(MO)	2	3	2	3	2
CAS(n_e,n_o)	(12,8)	(10,8)	(12,12)	(10,10)	(8,8)
Pairwise Corr. Sum	1.879	2.840	1.834	2.783	3.380
Block Corr.	1.924	2.928	1.920	2.877	3.532
Block Corr.(σ)	0.946	0.992	0.967	0.964	1.603
Block Corr.(π)	0.920	1.879	0.885	1.908	1.707
Bi. Ent.	1.924	2.928	1.969	2.938	3.532

TABLE I. Various correlation quantities as measures of bond order. For all molecules, the bipartite entanglement is calculated with respect to the left and right half separation of the molecule. For C_2H_4 and C_2H_2, the pairwise correlation sum and block correlation are calculated between the two carbon centers only. Correlation quantities are in unit of $4\ln(2)$, and the bipartite entanglement is in unit of $2\ln(2)$.



C_2		5	6	7	8
1		0.609	0.000	0.031	0.031
2		0.000	0.960	0.002	0.002
3		0.031	0.002	0.823	0.017
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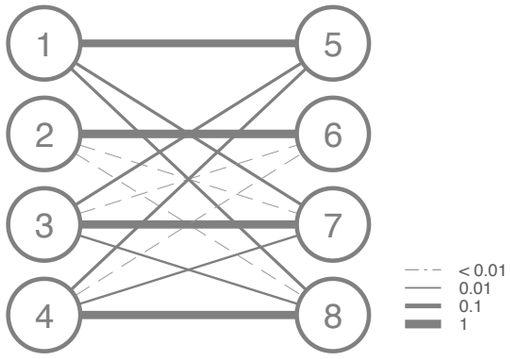

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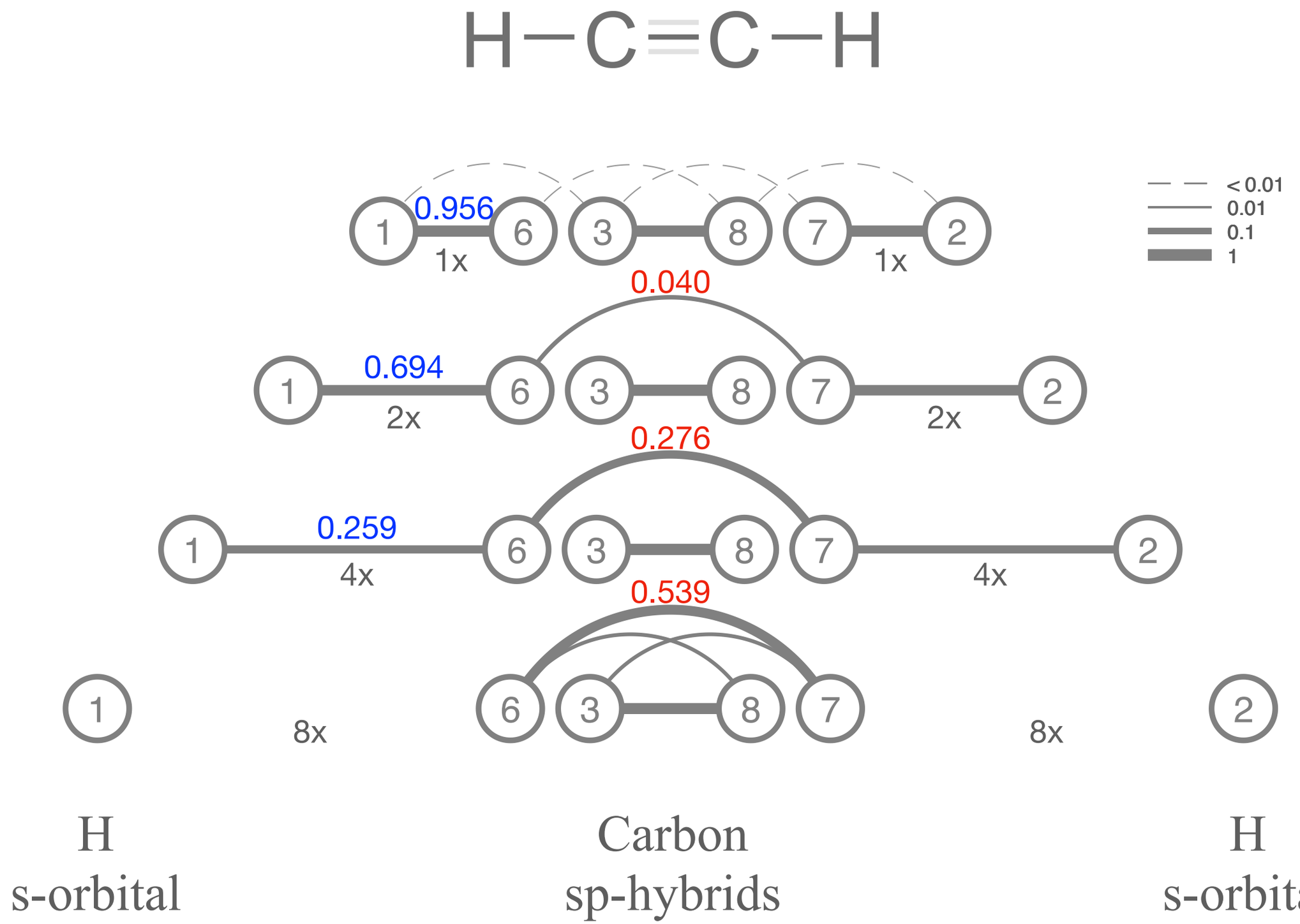
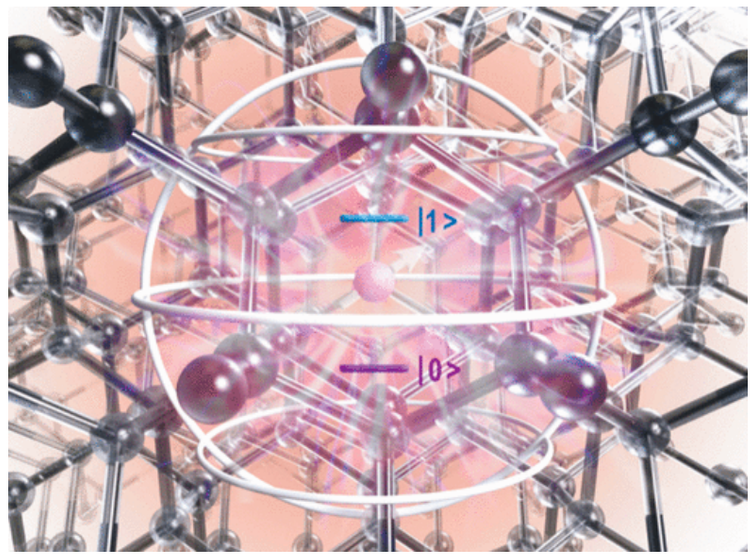


LD, S. Knecht, C. Schilling, In Preparation.

Summary

- Orbital entanglement is an estimator for computational cost
- Minimal orbital entanglement is bounded from above by particle correlation
- A single covalent bond corresponds to maximal orbital-orbital entanglement $E = \ln(4)$
- Maximizing correlation leads to localized valence orbitals
- Four pairs of strongly correlated valence orbitals in C_2

Outlooks



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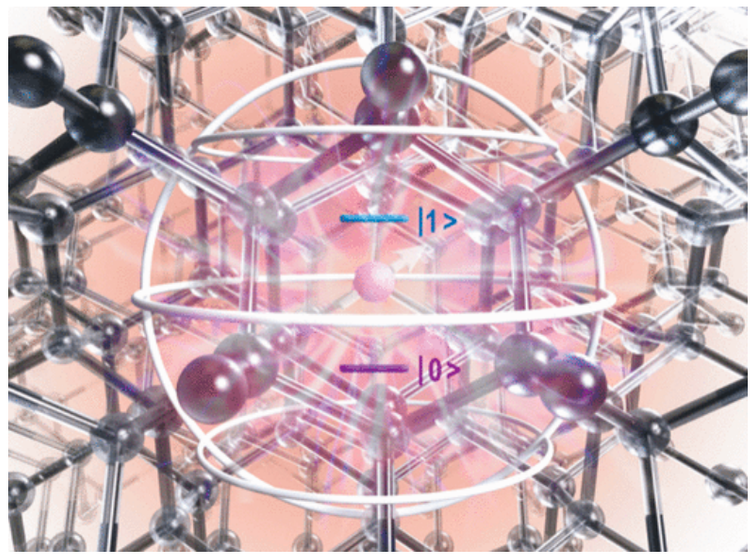
Outlooks

- Systematic comparison with existing bond order measures



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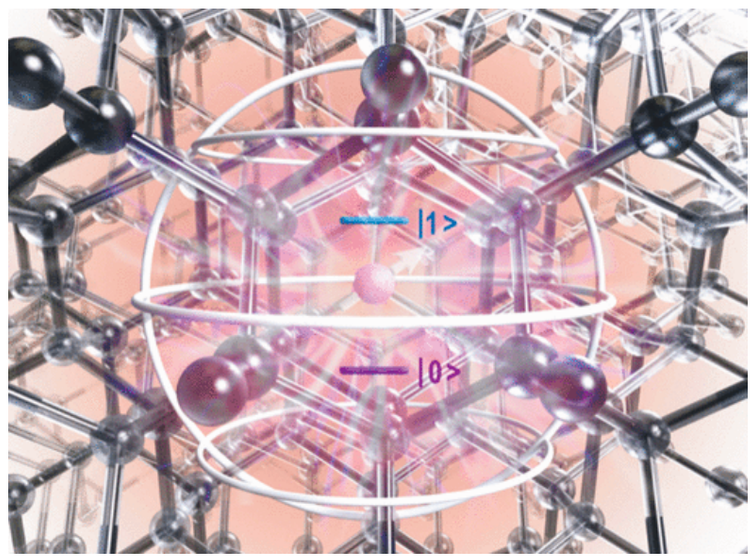
- Reduce computational cost for maximizing orbital correlation (high correlation = high computational cost)



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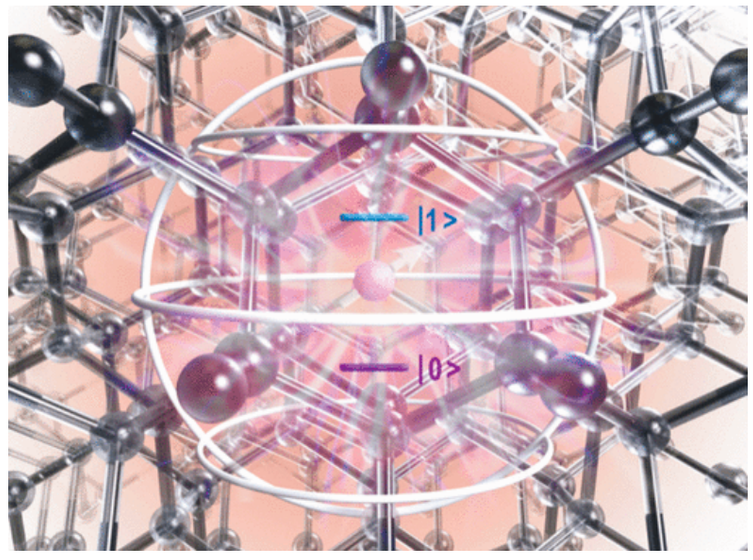
Outlooks

- Systematic comparison with existing bond order measures
- Reduce computational cost for maximizing orbital correlation (high correlation = high computational cost)
- Quantum embedding theory + correlation maximization -> large scale systems



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PhD and postdoc positions available!

Stefan Knecht
- Algorithmiq

Zoltán Zimborás
– Wigner Research Center for Physics

LD, S. Knecht, Z. Zimborás, C. Schilling, Quantum Correlations in Molecules: A Quantum Information Toolbox for Chemists, arxiv:2205.15881 (2022).

LD, Z. Zimborás, C. Schilling, Quantifying Electron Entanglement Faithfully, arXiv:2207.03377 (2022).