Orbital Entanglement and Correlation

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prominent entangled state
for bipartite system AB:

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left(|0\rangle \otimes |0\rangle + |1\rangle \otimes |1\rangle \right)$$

$$\rightarrow \rho_A = \frac{1}{2} \left(|0\rangle\langle 0| + |1\rangle\langle 1| \right)$$ mixed!

$$\Downarrow$$

$|\Psi\rangle$ entangled

Well, that's fine but …

… what is entanglement good for?

… how to define entanglement in systems of identical particles (e.g., electrons)?

… how to quantify it for total states that are not pure anymore, i.e., $|\Psi\rangle\langle\Psi| \to \rho$

[mixedness of $\rho_{A/B}$ could be due to mixedness of ρ rather than an indicator of entanglement] goal of this lecture:

answering all these questions
(in a rather comprehensive manner)

0) Physical relevance of entanglement

- in general: fascinating phenomenon
  $\rightarrow$ relevant for our understanding of physics

- provides important insights into behaviour and properties of quantum systems: quantum phase transitions, electronic structure, …

- Diagnostic tool for describing many-body quantum states
  $\rightarrow$ improving numerical methods

- Key resource for realizing quantum information processing tasks:
  - quantum cryptography
  - quantum teleportation
  - superdense coding
  - (possibly even) quantum computing

➡ operationally meaningful quantification of entanglement is essential!

Recent situation:

restriction to distinguish. particles (no electrons)

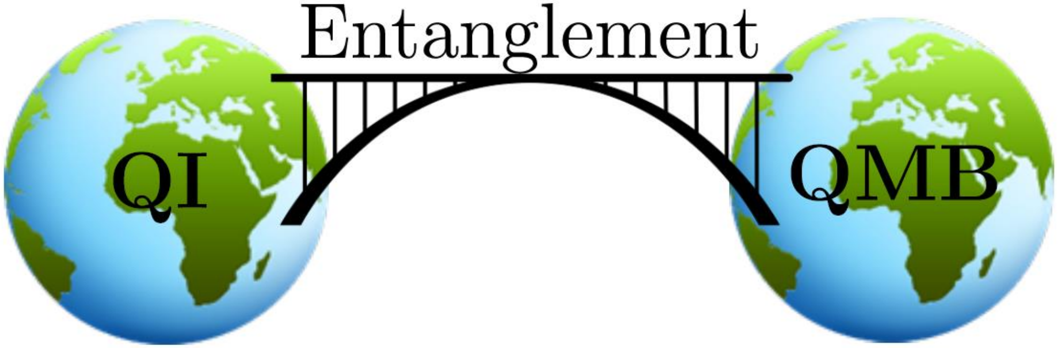
often rather abstract & mathematical

quantification often flawed

dubious application of QIT concepts in general (hype about entanglement)

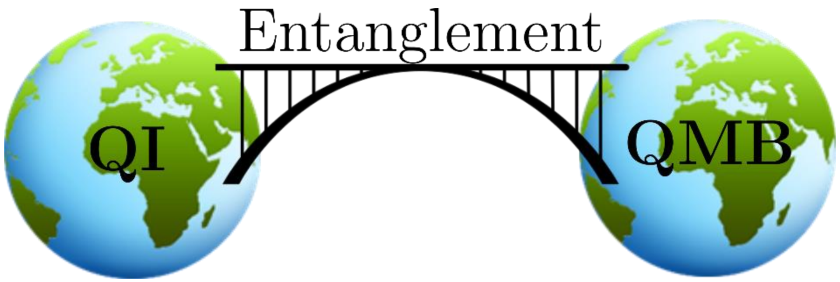
Our goal:

strengthening the connection between QI and QMB:



Timely!:

strengthening connection



serves

2nd quantum revolution:
controlling atoms & molecules $\rightarrow$ realizing QI taks

highlights

foundation for fermionic quantum correlation essential!

Outline

1) Quantum states and their geometry

2) Quantum information formalism

3) Application to fermions

4) Examples

1) Quantum states and their geometry

Simplest example: the qubit

system with a 2-dim. Hilbert space $\mathcal{H} \cong \mathbb{C}^2$

$\rightarrow$ pick orthonormal basis states: $|0\rangle, |1\rangle$

Hermitian matrices in $\mathbb{C}^{2\times 2}$: $\quad A = \frac{1}{2}\left(\alpha_0 \mathbb{1} + \vec{\alpha} \cdot \vec{\sigma}\right)$

with Pauli matrices:

$$\sigma_1 \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Remark: Dirac versus matrix representation

$$\hat{A} \equiv \sum_{\sigma,\tau=0,1} A_{\sigma\tau} |\sigma\rangle\langle\tau| \,, \quad A_{\sigma\tau} \equiv \langle\sigma|\hat{A}|\tau\rangle$$

inner product:

$$\langle \hat{A}, \hat{B} \rangle \equiv \mathrm{Tr}_{\mathcal{H}}[\hat{A}^\dagger \hat{B}] = \sum_{\sigma=0,1} \langle\sigma|\hat{A}^\dagger \hat{B}|\sigma\rangle = \sum_{\sigma,\tau=0,1} A^*_{\tau\sigma} B_{\sigma\tau}$$

density matrices:

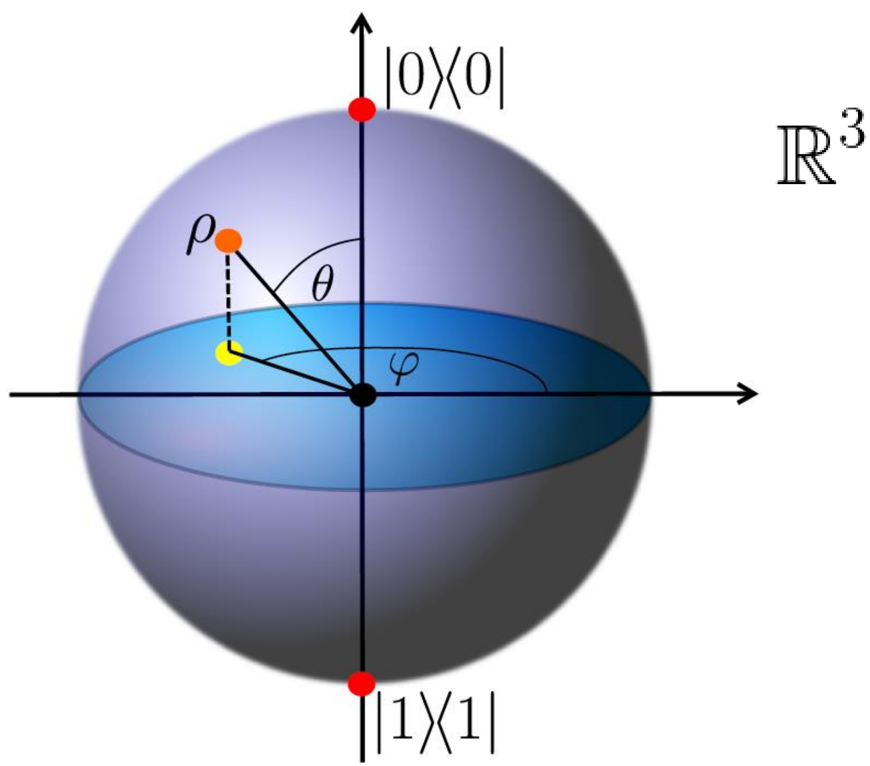
(Hermitian, positive semi-definite and trace-normalized to unity)

$$\rho = \frac{1}{2}\left(\mathbb{1} + \vec{\alpha}\cdot\vec{\sigma}\right)$$

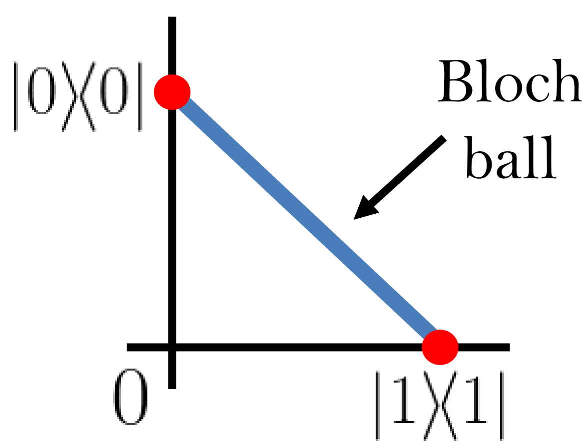
with $\vec{\alpha} \in \mathbb{R}^3, |\vec{\alpha}| \leq 1$

Bloch representation:

$\rho \leftrightarrow \vec{\alpha}$



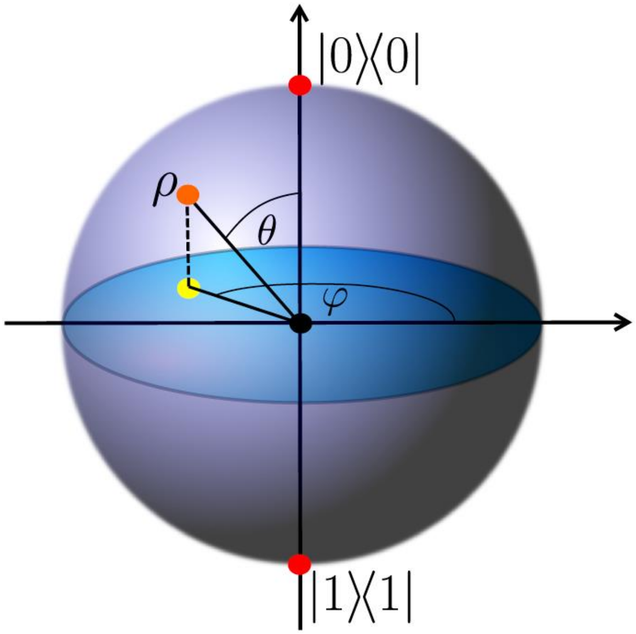
But wait: North & South pole aren't orthogonal !?



Exercise 2.3

Prove that for a qubit the following statements on density matrices ρ expressed as (5) are equivalent:

1. ρ lies on the boundary of the convex space of density matrices
2. $|\vec{\alpha}| = 1$
3. ρ is a projector, i.e., $\rho = \rho^2$
4. The spectrum (i.e., the set of eigenvalues) of ρ reads $\{0, 1\}$.



General case

system with a d-dim. Hilbert space $\mathcal{H}$

space of density operators (matrices):

$$\mathcal{D} \equiv \{\hat{\rho} : \mathcal{H} \xrightarrow{\text{linear}} \mathcal{H} \,|\, \hat{\rho}^\dagger = \hat{\rho} \,\wedge\, \hat{\rho} \geq 0 \,\wedge\, \mathrm{Tr}[\hat{\rho}] = 1\}$$

- $\mathcal{D}$ is convex
- extremal points: pure states, i.e., $\hat{\rho}^2 = \hat{\rho} \equiv |\Psi\rangle\langle\Psi|$
- inner product: $\langle \hat{A}, \hat{B} \rangle \equiv \mathrm{Tr}_{\mathcal{H}}[\hat{A}^\dagger \hat{B}]$

  $\rightarrow$ notion of geometry

2) Quantum information formalism

From now on we consider a multipartite (for simplicity bipartite) quantum system

total Hilbert space: $\mathcal{H}_{AB} \equiv \mathcal{H}_A \otimes \mathcal{H}_B$

total algebra of observables: $\mathcal{A}_{AB} \equiv \mathcal{A}_A \otimes \mathcal{A}_B$

notion of reduced states:

$$\begin{aligned}\langle \hat{A} \otimes \hat{1}_B \rangle_{\rho_{AB}} &= \mathrm{Tr}[\rho_{AB}(\hat{A} \otimes \hat{1}_B)] \\ &= \mathrm{Tr}_A[\rho_A \hat{A}] \quad , \ \forall \hat{A} \in \mathcal{A}_A\end{aligned}$$

defines $\rho_A \equiv \mathrm{Tr}_B[\rho_{AB}]$

Correlation function:

$$C_{\rho_{AB}}(\hat{A},\hat{B}) \equiv \langle \hat{A} \otimes \hat{B} \rangle_{\rho_{AB}} - \langle \hat{A} \rangle_{\rho_A} \langle \hat{B} \rangle_{\rho_B}$$

observation:

$$C_{\rho_{AB}}(\hat{A},\hat{B}) = 0 \;\;\not\Rightarrow\;\; C_{\rho_{AB}}(\hat{A}',\hat{B}') = 0,\;\; \forall \hat{A}',\hat{B}'$$

Definition 2.1 (Uncorrelated States) *Let $\mathcal{H}_{AB} \equiv \mathcal{H}_A \otimes \mathcal{H}_B$ be the Hilbert space and $\mathcal{A}_{AB} \equiv \mathcal{A}_A \otimes \mathcal{A}_B$ the algebra of observables of a bipartite system AB, with local Hilbert spaces $\mathcal{H}_{A/B}$ and local algebras $\mathcal{A}_{A/B}$. A state ρ_{AB} on $\mathcal{H}_{AB}$ is called uncorrelated, if and only if*

$$\langle \hat{A} \otimes \hat{B} \rangle_{\rho_{AB}} = \langle \hat{A} \rangle_{\rho_A} \langle \hat{B} \rangle_{\rho_B} \,, \tag{27}$$

for all local observables $\hat{A} \in \mathcal{A}_A$, $\hat{B} \in \mathcal{A}_B$. The set of uncorrelated states is denoted by $\mathcal{D}_0$ and states $\rho_{AB} \notin \mathcal{D}_0$ are said to be correlated.

measure of (total) correlation:

$$\begin{aligned} I(\rho_{AB}) &\equiv \min_{\sigma_{AB} \in \mathcal{D}_0} S(\rho_{AB} || \sigma_{AB}) \\ &= S(\rho_{AB} || \rho_A \otimes \rho_B) \,. \end{aligned}$$

with the quantum relative entropy:

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

Key result (universal bound on correlation function):

$$\boxed{C_{\rho_{AB}}(\hat{A},\hat{B}) \leq \sqrt{2\log(2)}\,\|\hat{A}\|_F\,\|\hat{B}\|_F\,\sqrt{I(\rho_{AB})}}$$

in particular, this implies

$$I(\rho_{AB}) = 0 \;\Rightarrow\; C_{\rho_{AB}}(\hat{A},\hat{B}) = 0,\;\forall \hat{A},\hat{B}$$

Key fact 2.1

Quantum information tools such as measures of different correlation types provide universal insights into the structure of multipartite quantum states. This means that they do not refer to any specific choice of observables but lead instead to statements (such as Eq. (31)) which are valid in general.

How about classical combinations (mixture) of uncorrelated states?

$$\rho_{AB} = \sum_i p_i \rho_A^{(i)} \otimes \rho_B^{(i)}$$

it is apparently correlated,

but is it also entangled?

No!

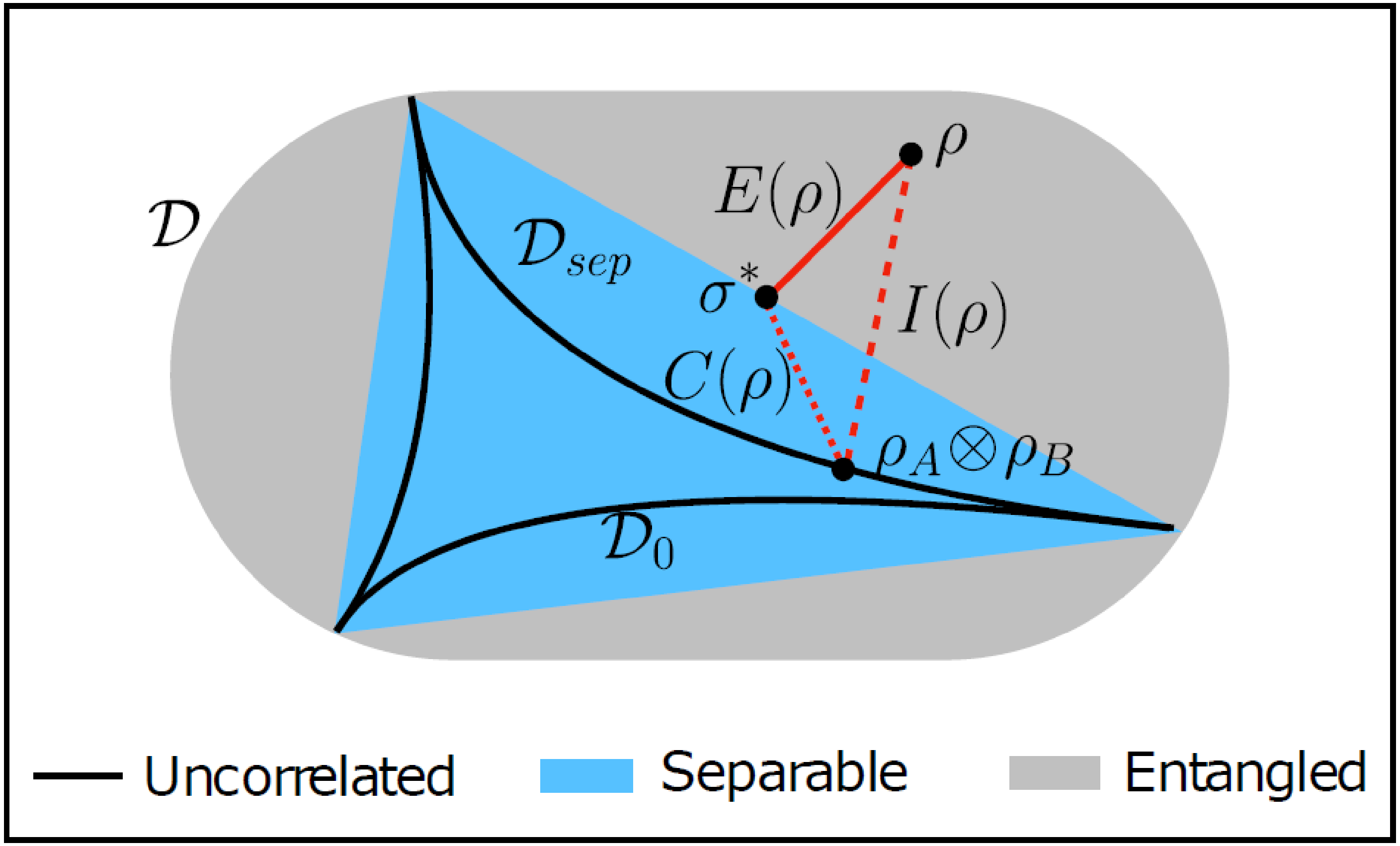
Definition 2.2 (Separable States) *A state ρ_{AB} is called separable/non-entangled if ρ_{AB} can be expressed as a convex linear combination ("classical mixture") of uncorrelated states, that is $\rho_{AB} \in \mathrm{Conv}(\mathcal{D}_0) \equiv \mathcal{D}_{sep}$. Otherwise a state is called entangled.*

measure of entanglement
(quantum relative entropy of entanglement):

$$E(\rho_{AB}) \equiv \min_{\sigma_{AB} \in \mathcal{D}_{sep}} S(\rho_{AB} || \sigma_{AB})$$

[Notoriously difficult to calculate!]

Complete geometric picture



3) Application to fermions

fermionic Hilbert space

- 1-particle Hilbert space $\mathcal{H}^{(1)}$
- N-fermion Hilbert space

$$\mathcal{H}^{(N)} \equiv \wedge^N[\mathcal{H}^{(1)}] = \mathcal{A}_N\left[\mathcal{H}^{(1)}\right]^{\otimes N}$$

- Fock space $\mathcal{F}(\mathcal{H}_1) = \bigoplus_{N=0}^{d} \wedge^N[\mathcal{H}^{(1)}]$

  - $|n_1, n_2, \ldots, n_d\rangle \equiv (f_1^\dagger)^{n_1}(f_2^\dagger)^{n_2}\cdots(f_d^\dagger)^{n_d}|\Omega\rangle$
  - $\{f_i^{(\dagger)}, f_j^{(\dagger)}\} = 0, \quad \{f_i^\dagger, f_j\} = \delta_{ij}$

Subsystems of fermionic systems (?)

$$\underbrace{\mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_1}_{N} \geq \boxed{\mathcal{H}_N \equiv \wedge^N[\mathcal{H}_1]} \leq \mathcal{F}[\mathcal{H}_1]$$

$$\cong \mathcal{F}[\mathcal{H}_1^{(L)}] \otimes \mathcal{F}[\mathcal{H}_1^{(R)}]$$

$\Downarrow$ $\Downarrow$

where is the tensor product?

particle correlation ☹

mode/orbital correlation

antisymmetry contributes

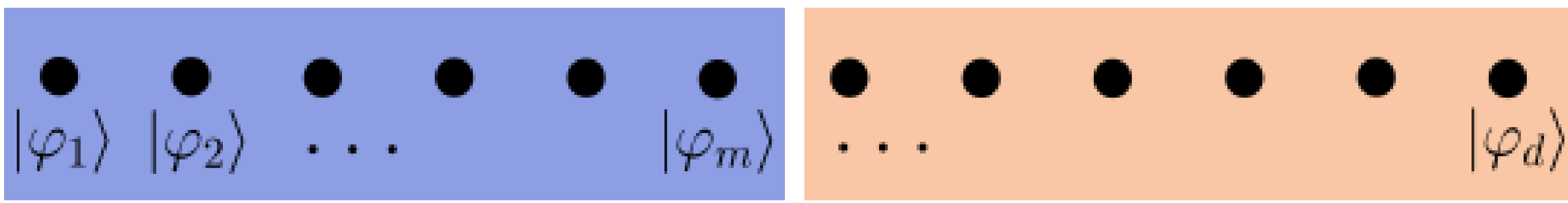
superselection rule for number parity would apply

$\Rightarrow$ unphysical

Tensor product in fermionic Fock space

$$\mathcal{F}_{AB} \equiv \mathcal{F}(\mathcal{H}_1) = \mathcal{F}(\mathcal{H}_1^{(A)}) \otimes \mathcal{F}(\mathcal{H}_1^{(B)}) \equiv \mathcal{F}_A \otimes \mathcal{F}_B$$

$$|n_1, \ldots, n_m, n_{m+1}, \ldots, n_d\rangle \mapsto |n_1, n_2, \ldots n_m\rangle_A \otimes |n_{m+1}, n_{m+2}, \ldots, n_d\rangle_B$$



in general:

$$\mathcal{H}_1 = \mathcal{H}_1^{(A)} \oplus \mathcal{H}_1^{(B)} \quad \Rightarrow \quad \mathcal{F}(\mathcal{H}_1) = \mathcal{F}(\mathcal{H}_1^{(A)}) \otimes \mathcal{F}(\mathcal{H}_1^{(B)})$$

caveat: number parity superselection rule

"nature does not allow one to mix even and odd particle number states"

algebra of observables $\mathcal{A} \neq \mathcal{B}(\mathcal{F})$

observables block-diagonal w.r.t. $\bigoplus_{N\,\mathrm{even}} \mathcal{H}_N$, $\bigoplus_{N\,\mathrm{odd}} \mathcal{H}_N$

stronger superselection rules possible:

- no creation of fermions: particle number SSR
- exp. limited set of measurements/operations

$\rightarrow \mathcal{A}$ smaller ($\rightarrow \mathcal{D}_0$ larger) indeed, just to recall:

Definition 2.1 (Uncorrelated States) *Let $\mathcal{H}_{AB} \equiv \mathcal{H}_A \otimes \mathcal{H}_B$ be the Hilbert space and $\mathcal{A}_{AB} \equiv \mathcal{A}_A \otimes \mathcal{A}_B$ the algebra of observables of a bipartite system AB, with local Hilbert spaces $\mathcal{H}_{A/B}$ and local algebras $\mathcal{A}_{A/B}$. A state ρ_{AB} on $\mathcal{H}_{AB}$ is called uncorrelated, if and only if*

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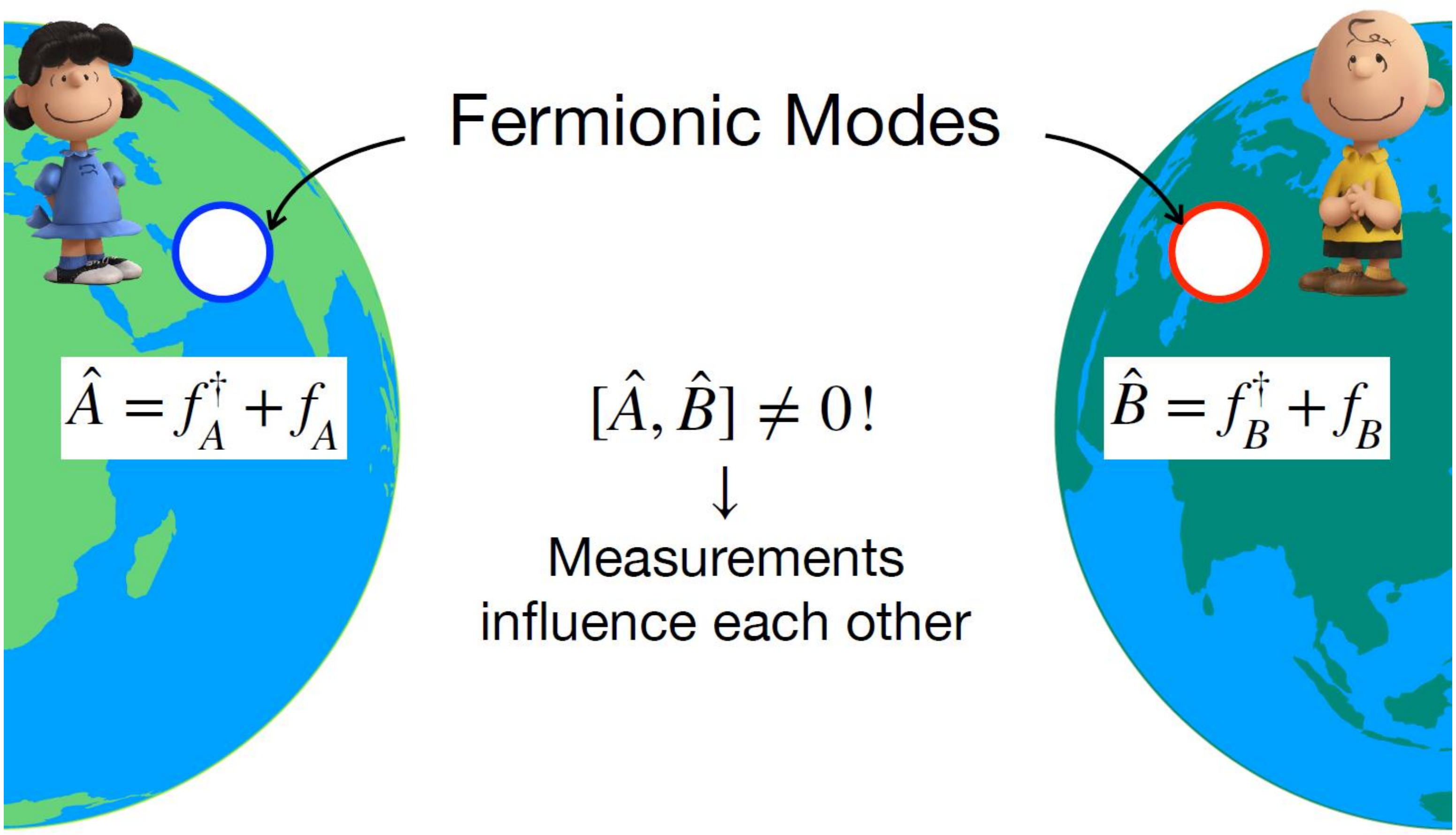
for all local observables $\hat{A} \in \mathcal{A}_A$, $\hat{B} \in \mathcal{A}_B$. The set of uncorrelated states is denoted by $\mathcal{D}_0$ and states $\rho_{AB} \notin \mathcal{D}_0$ are said to be correlated.

Key fact 2.2

Violation of the number parity superselection rule (P-SSR) would make superluminal signalling possible in contradiction to the laws of special relativity.



Key fact 2.3

Correlation and entanglement are relative concepts. They depend not only on the particular division of the total system into two (or more) subsystems but also on the underlying superselection rules (SSRs), which eventually defines the physical local algebras of observables $\mathcal{A}_{A/B}$ and the global algebra $\mathcal{A}_A \otimes \mathcal{A}_B$.

Key fact 2.4

By ignoring the fundamentally important SSRs, one may radically overestimate the true physical correlation and entanglement in a quantum state.

4) Examples

A single fermion

$$\text{state}\,|\Psi\rangle = \tfrac{1}{\sqrt{2}}(|L\rangle + |R\rangle)$$

mode correlation/entanglement:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|1, 0\rangle + |0, 1\rangle)$$

$L \quad R$

A single fermion

$$\text{state}\,|\Psi\rangle = \tfrac{1}{\sqrt{2}}(|L\rangle + |R\rangle)$$

mode correlation/entanglement:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|1,0\rangle + |0,1\rangle)$$

$$\Rightarrow\ \rho_L = \ \frac{1}{2}\left[|0\rangle_{L\,L}\langle 0| + |1\rangle_{L\,L}\langle 1|\right]$$

really correlated/entangled?

No!:

$$|\Psi\rangle\langle\Psi| = \frac{1}{2}[|1,0\rangle\langle 1,0|+|0,1\rangle\langle 0,1|+|1,0\rangle\langle 0,1|+|0,1\rangle\langle 1,0|]$$

$$|\Psi\rangle\langle\Psi|\Big|_{\mathcal{A}_A\otimes\mathcal{A}_B} = \frac{1}{2}\Big[|1,0\rangle\langle 1,0| + |0,1\rangle\langle 0,1|\Big]$$

$\Rightarrow$ $|\Psi\rangle\langle\Psi|$ is mode-corelated w.r.t. $L \leftrightarrow R$
but not mode-entangled

note:

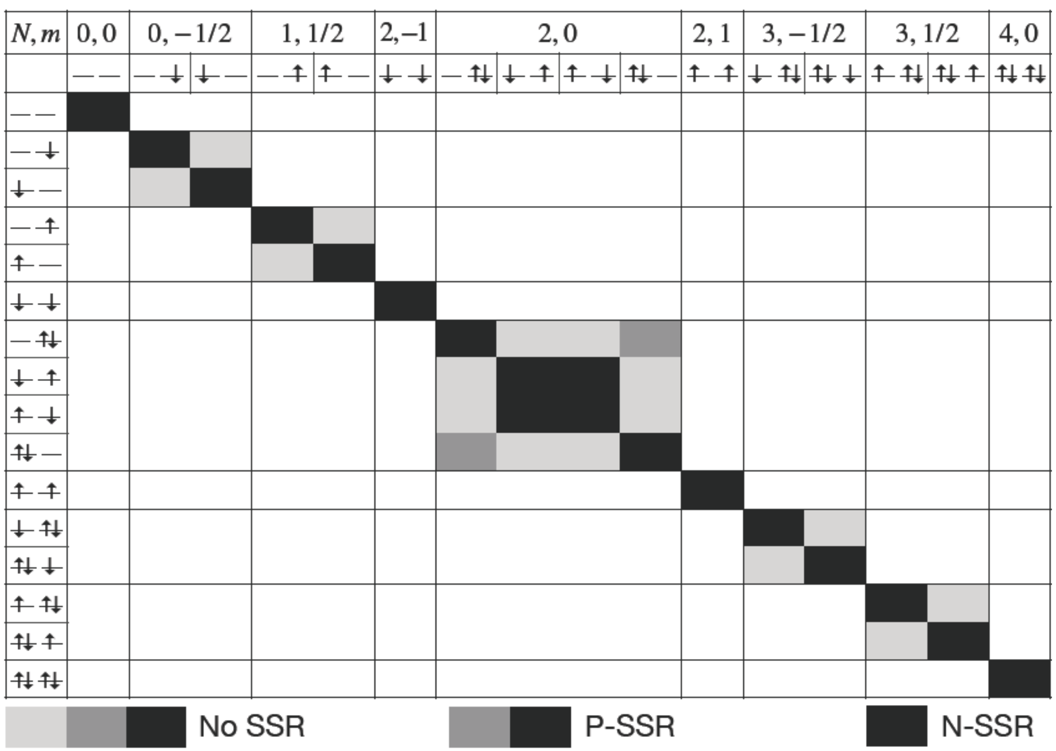
$\boxed{\text{(unnecessary) embedding of } \mathcal{H} \text{ and } \mathcal{A} \text{, respectively, can be quite misleading}}$

Orbital entanglement in molecules

two relevant partitions:

- orbital $i \leftrightarrow$ remaining orbitals
- orbital $i \leftrightarrow$ orbital j

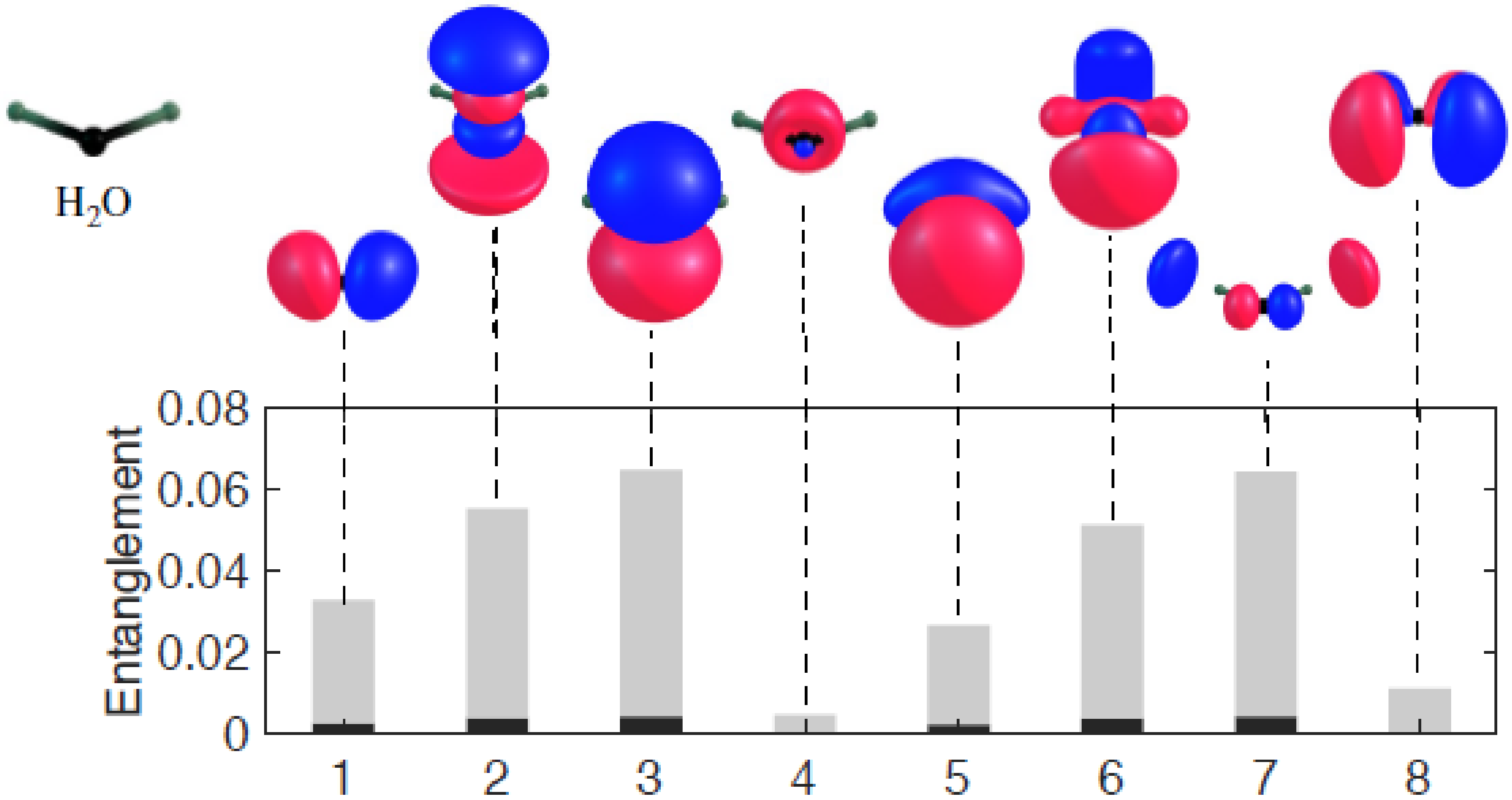
molecular ground state $|\Psi_N\rangle$



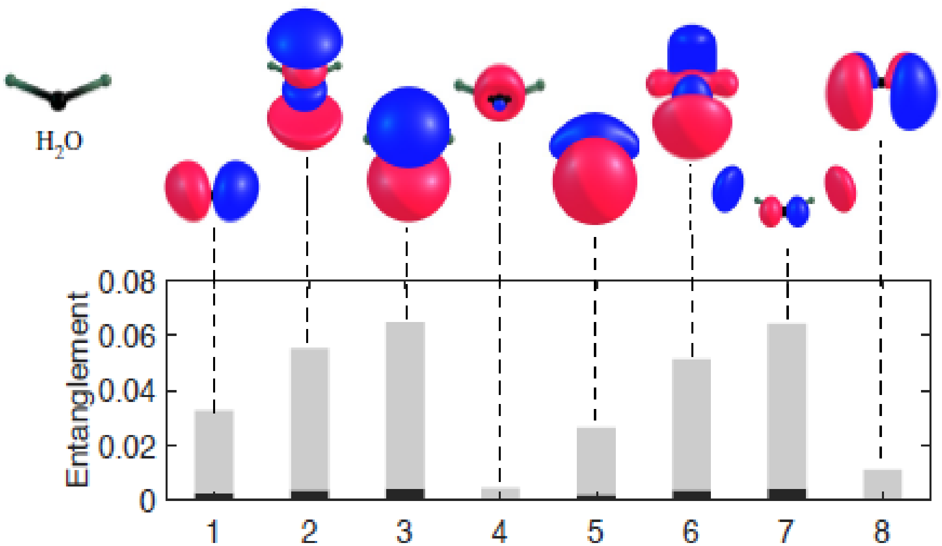
$$\rho_{ij}$$

$$\rho_i$$

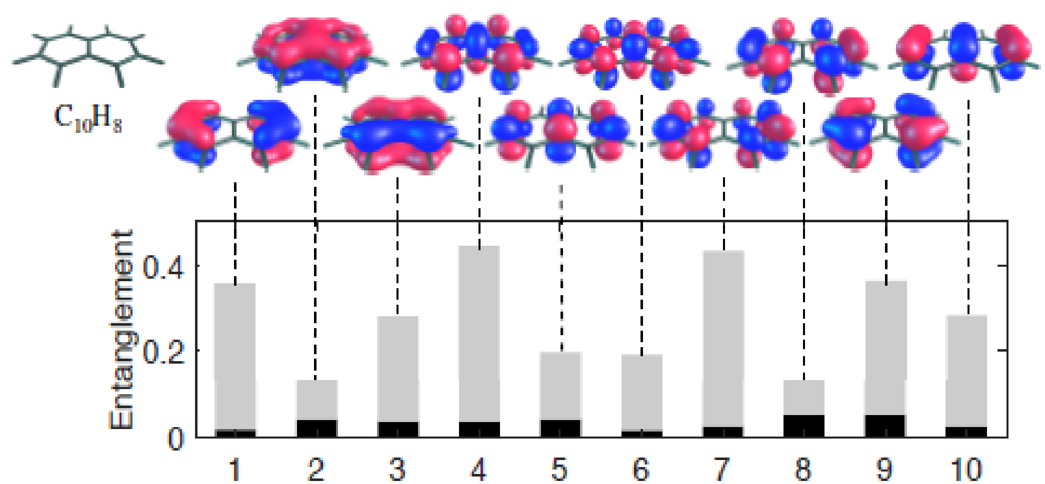
single-orbital entanglement/correlation:



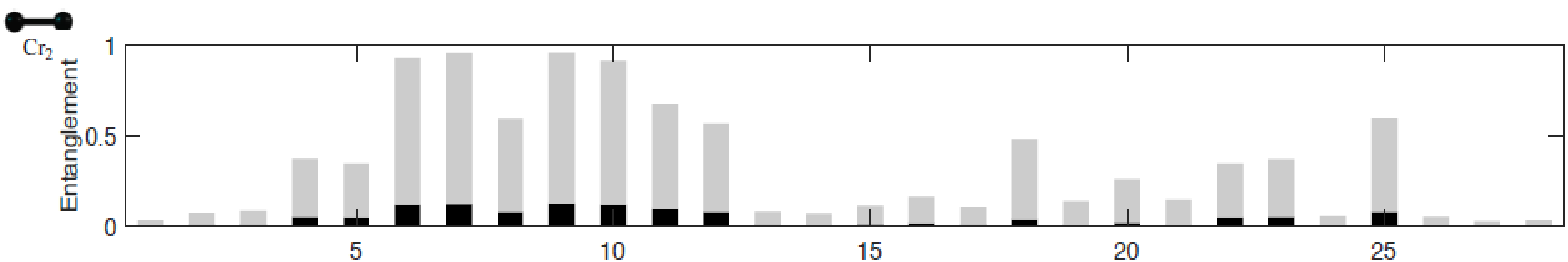
single-orbital entanglement/correlation:



No SSR	0.033	0.064	0.065	0.005	0.055	0.051	0.027	0.011
SSR	7%	7%	6%	5%	7%	7%	8%	4%



No SSR	0.376	0.170	0.310	0.451	0.240	0.235	0.441	0.155	0.383	0.313
SSR	12%	11%	12%	12%	12%	12%	12%	12%	12%	12%

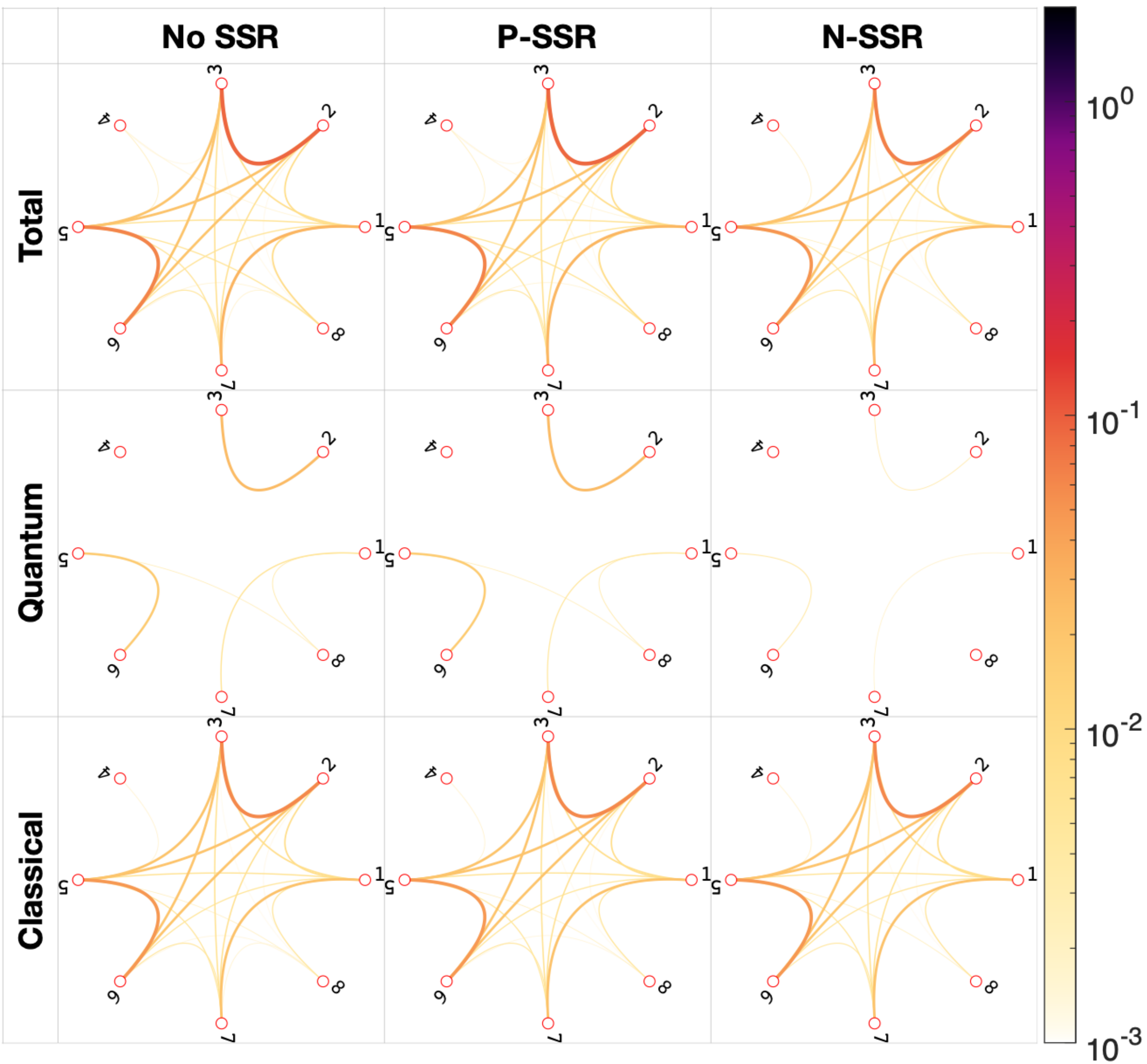


No SSR	0.035	0.075	0.087	0.372	0.347	0.925	0.956	0.592	0.958	0.912	0.673	0.566	0.083	0.071
SSR	10%	11%	11%	13%	14%	13%	13%	13%	13%	13%	14%	14%	11%	11%

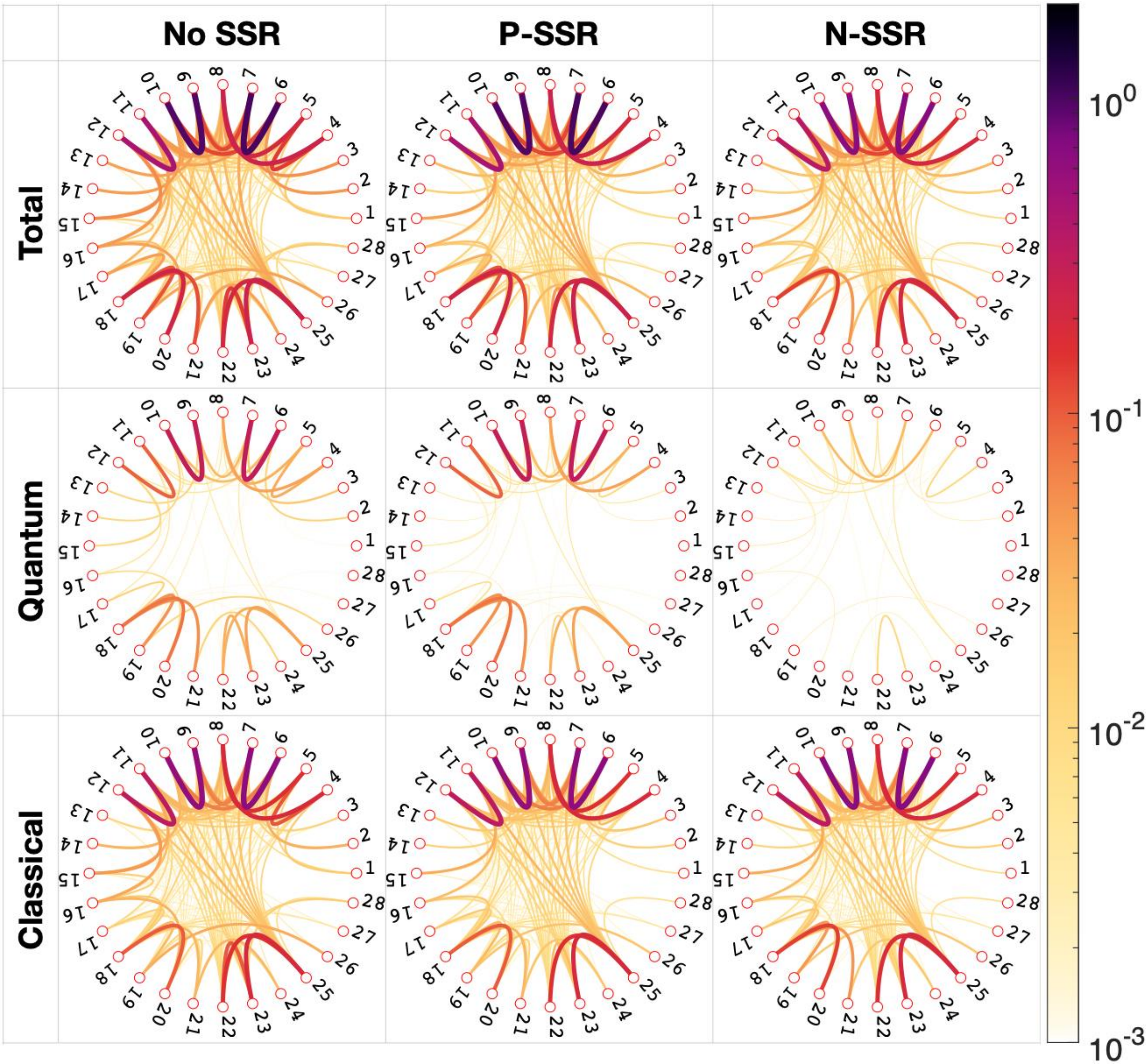
No SSR	0.111	0.161	0.104	0.481	0.138	0.260	0.148	0.347	0.368	0.056	0.593	0.053	0.029	0.034
SSR	12%	12%	10%	8%	5%	8%	5%	14%	14%	9%	14%	9%	9%	10%

orbital-orbital entanglement & correlation:

H_2O



Cr_2



Further reading

- Lecture notes/proceedings by Erik & Eva
- Extended lecture notes (soon on the arXiv)
- publications:

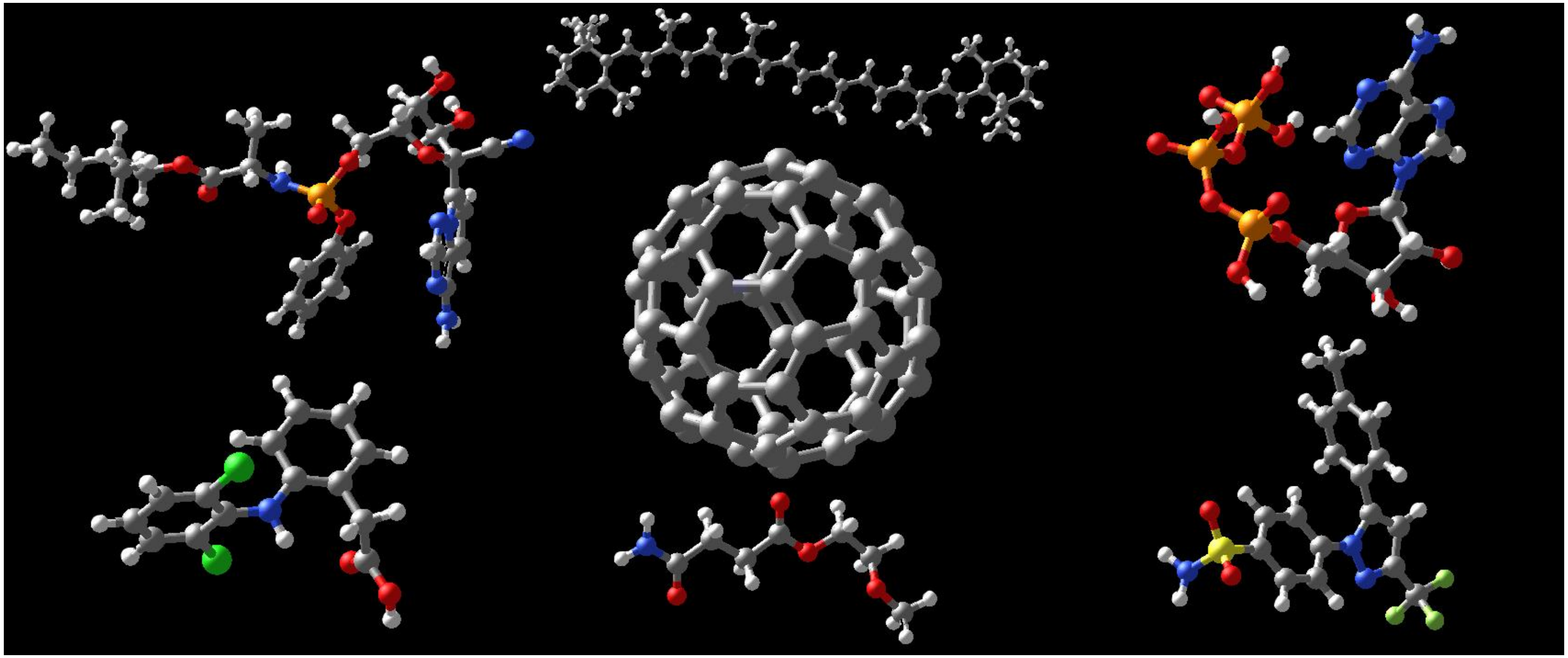
[L.Ding, **CS**, J. Chem. Theory Comput. 16, 4159 (2020)]

[L.Ding, S.Mardazad, S.Das, S.Szalay, U.Schollwöck, Z.Zimborás, **CS**, J. Chem. Theory Comput. 17, 79 (2021)]

+ forthcoming papers

International Symposium on Correlated Electrons
Symcorrel21

October 5th - 7th, 2021 (online)
Deadline: this week Friday!



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Thank you