9   Orbital Entanglement and Correlation

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1   Introduction

The development of quantum many-body physics has been strongly influenced in recent years by quantum information theory with a particular emphasis on the concept of entanglement. From a general point of view, entanglement is one of the most fascinating concepts of physics and there are at least three distinctive reasons for its significance in various fields of the quantum sciences:

(i) It provides important insights into the properties and behavior of quantum systems such as quantum phase transitions [1–3] and the formation/breaking of chemical bonds [4].

(ii) It serves as a diagnostic tool for the description of quantum many-body states. Hence, its rigorous quantification facilitates the development of more efficient descriptions of strongly interacting systems [5, 6]

(iii) It is an important resource used in the quantum information sciences for realizing, e.g., quantum cryptography [7, 8], superdense coding [9] and possibly even quantum computing [10].

In the more traditional fields such as condensed matter physics and quantum chemistry, however, point (iii) is not sufficiently well acknowledged. In particular, the quantification of entanglement and correlation is often flawed or at least operationally meaningless and the significance of the respective numbers for quantum information processing tasks is therefore unclear. This is due to the fact that the fundamental superselection rule ("nature does not allow one to superpose even and odd fermion number states") is erroneously ignored. In quantum information theory, however, entanglement is often studied in an abstract mathematical context, often decoupled from concrete physical systems. It is not unlikely that this huge separation between the worlds of quantum many-body physicists and quantum information theorists will have rather unpleasant consequences for the interface between those two fields. As a matter of fact, this interface is gaining a lot of relevance in recent years due to the ongoing second quantum revolution which may shape the 21st century as much as the first quantum revolution has shaped the 20th century: Individual quantum systems, such as atoms and molecules shall be controlled to a much greater extent than before to enable more powerful applications of quantum information. This apparently would necessitate a thorough understanding of entanglement and various other correlations types in the context of fermionic quantum systems both on a fundamental and an applied level. Due to the expected transformative impact of this second quantum revolution this challenging task can even be seen as a key strategic goal for the near-term future (see also the illustration in figure 1).

Accordingly, the main motivation of these lecture notes is to provide an introduction into the concept of entanglement and correlation in the context of fermionic quantum systems taking into account the needs of both quantum information scientists and quantum many-body physicists. For this, we recall and discuss on a more elementary level concepts that were already
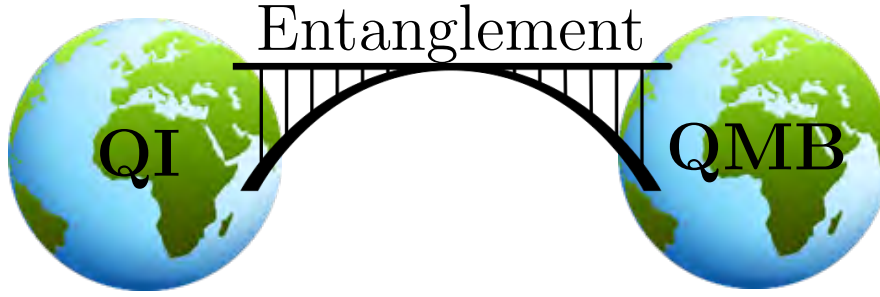
Fig. 1: *Strategic ambition for the quantum sciences: The connection between the worlds of quantum information (QI) and quantum many body physics (QMB) needs to be strengthened with a particular focus on entanglement as the unifying concept.*

presented in our recent articles [11, 12]. In section 2, we first recall the definition of entanglement and correlation in systems of *distinguishable* particles and then explain how those key concepts can be applied in the context of *identical* particles (mainly electrons). In particular, we explain the superselection rule and demonstrate that ignoring it would mean to violate fundamental laws of physics. Then, in section 3 we illustrate those concepts by applying them to smaller model systems which facilitate a fully analytical treatment. In section 4 we finally study more realistic systems (water, naphthalene and dichromium molecules) by exact numerical means and quantify the orbital correlation and its separation into quantum and classical parts.

2 Concept of correlation and entanglement

2.1 The quantum information theoretical formalism

The notion of correlation and entanglement plays a central role in quantum physics. In this section, we review those concepts and their quantification in the context of *distinguishable* subsystems as commonly studied in quantum information theory. We restrict ourselves to the most important case of bipartite settings and refer the reader to Refs. [13, 14] for an introduction into the concept of multipartite correlation and entanglement.

To introduce the concepts of entanglement and correlation, we first recall a few important aspects regarding quantum states and their geometry. Although it is illustrative to deal with wave functions, e.g., $\psi(\vec{r}, \sigma)$, as one can use them to construct probability clouds for atomic and molecular orbitals visualization, it is advantageous to adopt the representation-free formalism of density operators, acting on an underlying (for simplicity finite-dimensional) Hilbert space $\mathcal{H}$. This facilitates more direct and compact definitions of correlation and entanglement. As a matter of fact, both concepts refer solely to a decomposition of the system into two (or more) subsystems and do not depend on any possible choice of basis states for those subsystems. In this formalism, a quantum state is represented by a Hermitian operator ρ that is positive semi-definite (i.e., having non-negative eigenvalues) and trace-normalized to unity, $\mathrm{Tr}[\rho] = 1$, reflecting the probabilistic nature of quantum mechanics. For the following considerations it

will prove convenient to introduce and briefly discuss the set $\mathcal{D}$ of all density operators on a given finite-dimensional complex Hilbert space $\mathcal{H}$:

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

> **Exercise 2.1**
>
> Prove that in case of finite-dimensional complex Hilbert spaces $\mathcal{H}$ the Hermiticity of ρ is a direct mathematical consequence of its positive semi-definiteness (and therefore would not need to be imposed separately), i.e., show that $\rho \geq 0$ implies $\rho^\dagger = \rho$.

> **Exercise 2.2**
>
> Prove that the set $\mathcal{D}$ of density operators is convex.

Equipped with the common notion of density operators, we can now discuss the concept of expectation values of physical observables. The expectation value $\langle \hat{A} \rangle_\rho$ of an observable represented by a Hermitian operator $\hat{A}$ follows according to Born's rule as

$$\langle \hat{A} \rangle_\rho = \text{Tr}[\rho \hat{A}]. \tag{2}$$

The set of all Hermitian operators generated through multiplication gives rise to the algebra $\mathcal{B}(\mathcal{H})$ of all linear operators on $\mathcal{H}$. For the sake of mathematical elegance one typically refers to $\mathcal{B}(\mathcal{H})$ as the *algebra of observables* despite the fact that it contains also non-Hermitian operators. It is also worth noticing that — in contrast to $\mathcal{B}(\mathcal{H})$ — the real vector space of Hermitian operators on $\mathcal{H}$ does not exhibit any algebraic structure since this set is not closed under multiplication, i.e., the product of two Hermitian operators is not necessarily Hermitian anymore. While the expression (2) of the expectation value of an observable is one of the key concepts thought in any quantum mechanics course, a crucial observation is often left out. To be more specific, the compact form (2) reveals a more comprehensive and systematic notation of quantum states: A quantum state is a linear, positive semi-definite map $\langle \cdot \rangle_\rho$ from the algebra of observables to the complex numbers, normalized to unity $\langle \hat{1} \rangle_\rho = 1$. The density operator just defines this map according to (2). At first sight, this comment seems to be a bit pedantic and overly mathematical. Yet, this more comprehensive notion of quantum states will allow one to define the concept of reduced states in a rather straightforward manner (as we will see below) while in the concrete formalism based on density operators and wave functions several obstacles may arise. The latter often leads in practice to confusion and occasionally even to wrong expressions for the reduced density operators of subsystems.

> **Exercise 2.3**
>
> Let $\rho_1, \rho_2 \in \mathcal{D}$ be two density operators on the finite dimensional Hilbert space $\mathcal{H}$. Show that the following two statements are equivalent:
>
> 1. $\rho_1 = \rho_2$,
>
> 2. $\langle \hat{A} \rangle_{\rho_1} = \langle \hat{A} \rangle_{\rho_2}$, for all $\hat{A} \in \mathcal{B}(\mathcal{H})$.

Remark. The equivalence described in Exercise 2.3 is not valid anymore if the algebra $\mathcal{A}$ of observables is restricted, i.e., it does not contain all linear operators on the Hilbert space, $\mathcal{A} \subsetneq \mathcal{B}(\mathcal{H})$. As we will learn in the next section, this will be the case for fermionic quantum systems whose algebras of observables are restricted by the fundamental superselection rule to only those operators that are not altering the particle number parity.

To develop some intuition for the convex space of density operators and quantum states, respectively, we observe that the boundary of $\mathcal{D}$ is given by those $\rho \in \mathcal{D}$ which have at least one vanishing eigenvalue. In particular, the extreme points (those that cannot be written as a convex combination of others) are given by the pure states, $\rho \equiv |\Psi\rangle\langle\Psi|$. From a general point of view, the space $\mathcal{D}$ of quantum states could be interpreted as a subset of the Hermitian matrices with $\dim(\mathcal{H})$ many rows and columns. In that sense the space $\mathcal{D}$ can be equipped with a suitable metric. Examples include the distance metric based on the Frobenius norm, $d_F(\rho, \sigma) = \|\rho - \sigma\|_F \equiv \sqrt{\text{Tr}(\rho - \sigma)^2}$, or the Bures distance $d_B(\rho, \sigma) = \text{Tr}[\sqrt{\sqrt{\rho}\,\sigma\sqrt{\rho}}]^2$. For further details on the geometry of density matrices and respective metrics we refer the reader to Refs. [15–17].

One of the important conclusions from those geometric considerations is that the possible similarity of two density operators ρ, σ can be quantified in a universal way, i.e., without referring to a specific observable, despite the fact that ρ, σ do not carry any physical unit. In particular, whenever two quantum states are close to each other in the state space $\mathcal{D}$, their expectation values will be close to each other for any observable as well. This follows directly from the Cauchy-Schwarz inequality, $|\langle \hat{A}, \hat{B} \rangle| \leq \sqrt{|\langle \hat{A}, \hat{A} \rangle|}\sqrt{|\langle \hat{B}, \hat{B} \rangle|}$ applied to the Hilbert-Schmidt inner product, $\langle \hat{A}, \hat{B} \rangle \equiv \text{Tr}\hat{A}^\dagger \hat{B}$,

$$\left| \langle \hat{A} \rangle_\rho - \langle \hat{A} \rangle_\sigma \right| = \left| \text{Tr}\hat{A}(\rho - \sigma) \right| \leq \|\hat{A}\|_F \, d_F(\rho, \sigma). \tag{3}$$

To fully appreciate relation (3) let us recall that two quantum states with, e.g., the same energy can still differ in their expectation values of other relevant observables.

All considerations so far were just referring to the total system. The discussion of interesting physics refers, however, to a notion of subsystems. Let us consider in the following a quantum system which can be split into two subsystems A and B, occasionally also called Alice's and Bob's subsystem. In the common quantum information theoretical formalism those two subsystems are assumed to be distinguishable and its states are described by density operators ρ_{AB} on the total Hilbert space $\mathcal{H}_{AB} \equiv \mathcal{H}_A \otimes \mathcal{H}_B$, where $\mathcal{H}_{A/B}$ denotes the local Hilbert space of subsystem A/B. The underlying algebra $\mathcal{A}_{AB}$ of observables of the total system follows in the same way from the local algebras, $\mathcal{A}_{AB} \equiv \mathcal{A}_A \otimes \mathcal{A}_B$. The presence of a multipartite quantum system in particular allows us to introduce the important notion of reduced states corresponding to subsystems. To work this out, we consider a local measurement corresponding to $\hat{A} \in \mathcal{B}(\mathcal{H}_A)$. Its expectation value follows directly as

$$\langle \hat{A} \otimes \hat{1}_B \rangle_\rho = \text{Tr}\rho(\hat{A} \otimes \hat{1}_B). \tag{4}$$

Since such a measurement is essentially restricted to only Alice's subsystem, there exists a local description of the quantum state, with respect to which the expectation of any local operator $\hat{A}$

is the same as (4). This is the commonly used reduced density operator defined as

$$\rho_A \equiv \mathrm{Tr}_B \rho, \tag{5}$$

which satisfies

$$\langle \hat{A} \rangle_{\rho_A} = \langle \hat{A} \otimes \hat{1}_B \rangle_\rho, \quad \forall \hat{A} \in \mathcal{B}(\mathcal{H}_A). \tag{6}$$

It is exactly the content of Exercise 2.3 which proves the existence and uniqueness of this reduced density operator. In this context, it is also worth noticing that the more abstract notion of a quantum state as a linear map from the algebra of observables to the complex numbers would allow one to define on a mathematical level the reduced state in a particularly simple manner: The reduced state is given by the reduction of the total state to the subalgebra $\mathcal{A}_A \otimes \hat{1}$ (effectively $\mathcal{A}_A$). Then, by referring to the Riesz representation theorem, the existence of a corresponding density operator ρ_A follows directly.

> **Exercise 2.4**
>
> Calculate the reduced density operator ρ_A on the subsystem A of the two-qubit state
>
> $$|\Psi\rangle = \frac{1}{\sqrt{3}} |0\rangle_A \otimes |0\rangle_B + \frac{1}{\sqrt{3}} |1\rangle_A \otimes |0\rangle_B + \frac{1}{\sqrt{3}} |0\rangle_A \otimes |1\rangle_B.$$

To proceed, we notice that a particularly relevant class of observables in $\mathcal{A}_{AB}$ are the local ones, i.e, those of the form $\hat{A} \otimes \hat{B}$. As a matter of fact, they correspond to simultaneous measurements of $\hat{A}$ on subsystem A and $\hat{B}$ on subsystem B. To understand the relation between both subsystems, one would be interested in understanding how the respective measurements of both local measurements are correlated. As a matter of definition, they are uncorrelated if the expectation value of $\hat{A} \otimes \hat{B}$ factorizes,

$$
\begin{aligned}
\langle \hat{A} \otimes \hat{B} \rangle_{\rho_{AB}} &\equiv \mathrm{Tr}_{AB} \, \rho_{AB} \, \hat{A} \otimes \hat{B} \\
&= \mathrm{Tr}_{AB}[\rho_{AB} \, \hat{A} \otimes \hat{1}_B] \, \mathrm{Tr}_{AB}[\rho_{AB} \, \hat{1}_A \otimes \hat{B}] \\
&\equiv \mathrm{Tr}_A[\rho_A \, \hat{A}] \, \mathrm{Tr}_B[\rho_B \, \hat{B}] \equiv \langle \hat{A} \rangle_{\rho_A} \langle \hat{B} \rangle_{\rho_B}.
\end{aligned}
\tag{7}
$$

In the second line we introduced the identity operator $\hat{1}_{A/B} \in \mathcal{A}_{A/B}$ and the last line gives rise to the reduced density operators $\rho_{A/B} \equiv \mathrm{Tr}_{B/A} \rho_{AB}$ of subsystems A/B obtained by tracing out the complementary subsystem B/A. To quantify the correlation between the measurements of $\hat{A}$ and $\hat{B}$ one thus introduces the correlation function

$$C_{\rho_{AB}}(\hat{A}, \hat{B}) \equiv \langle \hat{A} \otimes \hat{B} \rangle_{\rho_{AB}} - \langle \hat{A} \rangle_{\rho_A} \langle \hat{B} \rangle_{\rho_B}. \tag{8}$$

Popular examples are the spin-spin or the density-density correlation functions, i.e., the local operators $\hat{A}$, $\hat{B}$ are given by some spin-component operator $\hat{S}_\tau(\vec{x})$ or the particle density operator $\hat{n}(\vec{x})$ at two different positions $\vec{x}_{A/B}$ in space.

The vanishing of the correlation function for a specific pair of observables $\hat{A}$, $\hat{B}$ does not imply by any means that the same will be the case for any other pair $\hat{A}'$, $\hat{B}'$ of local observables. A

prominent example would be the dissociated hydrogen state

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left(f_{L\uparrow}^\dagger f_{R\downarrow}^\dagger - f_{L\downarrow}^\dagger f_{R\uparrow}^\dagger \right)|\Omega\rangle\,, \tag{9}$$

where $f_{L/R\sigma}^\dagger$ denotes the fermionic creation operator for an electron at the left(L)/right(R) nucleus with spin σ, and $|\Omega\rangle$ the vacuum state. Its electron density-density correlation function between the left (L) and right (R) side vanishes in contrast to the respective spin-spin correlation functions. Inspired by this example, one would like to introduce a measure for the correlation between both subsystems without referring to a specific pair of local observables. One idea would be to determine an average of the correlation function $C_{\rho_{AB}}(\hat{A}, \hat{B})$ or its maximal possible value with respect to all possible choices of local observables $\hat{A}, \hat{B}$. At first sight, those two possible measures of total correlation seem to be very difficult (if not impossible) to calculate for a given ρ_{AB}. Yet, by referring to the geometric picture of density operators the introduction of a total correlation measure turns into a rather simple task. To explain this, we first define

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*

$$\langle \hat{A} \otimes \hat{B} \rangle_{\rho_{AB}} = \langle \hat{A} \rangle_{\rho_A} \langle \hat{B} \rangle_{\rho_B}, \tag{10}$$

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.

A comment is in order regarding the local algebras $\mathcal{A}_{A/B}$ that play a crucial role in definition 2.1. In the context of distinguishable subsystems one typically assumes that $\mathcal{A}_{A/B}$ comprises all Hermitian operators on the local space $\mathcal{H}_{A/B}$. As a consequence, a state ρ_{AB} is then uncorrelated if and only if it is a product state, $\rho_{AB} = \rho_A \otimes \rho_B$. This conclusion is, however, not true anymore if one would consider in definition 2.1 smaller subalgebras [18]. Actually, exactly this will be necessary in fermionic quantum systems due to the number parity superselection rule [19].

By referring to the geometric picture of density operators a measure for the total correlation between A and B follows naturally. It is given by the distance of ρ_{AB} to the set $\mathcal{D}_0$ of uncorrelated states (see also figure 2 for an illustration). In principle one could base such a measure on any possible distance-function. Yet, the notion of correlation and entanglement is formalized in quantum information theory by imposing plausible axioms defining valid measures, complemented by preferable features to guarantee an operational meaning [13, 14]. While further details on that subject matter would go beyond the scope of these lecture notes, we just would like to stress that the quantum relative entropy,

$$S(\rho||\sigma) = \operatorname{Tr} \rho \left(\log(\rho) - \log(\sigma) \right), \tag{11}$$

emerges as the preferable underlying function for a geometric correlation (and entanglement) measure (despite the fact that it is not a distance function in the strict mathematical sense) [20].

Besides its information theoretical meaning, the quantum relative entropy has additional appealing properties. For instance, it is invariant under unitary transformations,

$$S(\rho||\sigma) = S(U\rho U^\dagger || U\sigma U^\dagger) \tag{12}$$

and it is convex in both arguments. The total correlation measures follow as [21, 22]

$$I(\rho_{AB}) \equiv \min_{\sigma_{AB}\in\mathcal{D}_0} S(\rho_{AB}||\sigma_{AB}) = S(\rho_{AB}||\rho_A \otimes \rho_B). \tag{13}$$

Remarkably, the distinguished properties of the quantum relative entropy allow one to determine the minimizer $\sigma_{AB} \in \mathcal{D}_0$ of ρ_{AB}'s distance to $\mathcal{D}_0$ analytically. It follows as $\sigma_{AB} = \rho_A \otimes \rho_B$ and the correlation is nothing else than the quantum mutual information $I(\rho_{AB})$. The latter has a clear information theoretical meaning which emphasizes the significance of the total correlation measure (13). It quantifies the information content in the state ρ_{AB} which is not yet contained in the local states ρ_A, ρ_B.

Exercise 2.5

Prove that the following three definitions of the mutual information I are equivalent:

1. $I(\rho_{AB}) = S(\rho_A) + S(\rho_B) - S(\rho_{AB})$,

2. $I(\rho_{AB}) = S(\rho_{AB}||\rho_A \otimes \rho_B)$,

3. $I(\rho_{AB}) = \min_{\sigma_A,\sigma_B} S(\rho||\sigma_A \otimes \sigma_B)$.

We proceed by stating a crucial relation [23] between the total correlation (13) and individual correlation functions (8),

$$\frac{C_{\rho_{AB}}(\hat{A}, \hat{B})}{\|\hat{A}\|_F \|\hat{B}\|_F} \leq \sqrt{2\log(2)}\, \sqrt{I(\rho_{AB})}. \tag{14}$$

This means in particular that the correlation function of *any* two local observables $\hat{A}, \hat{B}$ is small whenever the quantum mutual information is small.

Exercise 2.6

Prove the crucial inequality (14). Hint: Combine (3) applied to the observable $\hat{A} \otimes \hat{B}$ with a well-known relation between the quantum relative entropy and the Frobenius norm (see, e.g., Theorem 10.6 in Ref. [24]).

A possibly large total correlation suggests that the accurate description of the total system AB requires significantly more computational effort than the one of both individual subsystems A, B (in case they were entirely decoupled). While this is rather unfortunate for a quantum chemist or a condensed matter theorist (they are interested in an accurate description of such systems) the opposite is true from a quantum informational point of view. To be more specific, primarily the quantum part of the total correlation represents an important resource for realizing quantum information processing tasks such as quantum cryptography [7, 8], superdense coding [9],

quantum teleportation [25] and possibly even quantum computing [10]. Typical protocols for realizing such fascinating tasks utilize so-called Bell pairs, i.e., maximally entangled pure state of two qubits (two-level quantum systems), e.g.,

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\rangle_A \otimes |\downarrow\rangle_B - |\downarrow\rangle_A \otimes |\uparrow\rangle_B\Big). \qquad (15)$$

It is thus one of the most important challenges to rigorously quantify the number of such Bell pairs that could be extracted from a given correlated quantum state ρ_{AB}. It is not hard to imagine that a correlated quantum state $\rho_{AB} = \sum_i p_i\, \rho_A^{(i)} \otimes \rho_B^{(i)}$ which is given as the *classical mixture* of uncorrelated states $\rho_A^{(i)} \otimes \rho_B^{(i)}$ does not offer any useful resource in that context: The system AB is found in uncorrelated states $\rho_A^{(i)} \otimes \rho_B^{(i)}$ yet there is a classical probabilistic uncertainty in which of them it will be in. To elaborate further on the quantification of entanglement one defines

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 of uncorrelated states, that is $\rho_{AB} \in \mathrm{Conv}(\mathcal{D}_0) \equiv \mathcal{D}_{sep}$. Otherwise a state is called entangled.*

Here, $\mathrm{Conv}(\cdot)$ stands for the convex hull and the term *separable* is frequently used in quantum information theory for denoting non-entangled states. In these lecture notes, we will use these two terms interchangeably.

In complete analogy to the concept of total correlation one has formulated plausible axioms for valid and operationally meaningful entanglement measures [13, 14]. By referring the reader to Ref. [22] for more details, it is again the geometric picture which leads to a prominent entanglement measure, the

$$E(\rho_{AB}) \equiv \min_{\sigma_{AB} \in \mathcal{D}_{sep}} S(\rho_{AB}||\sigma_{AB}). \qquad (16)$$

It measures in terms of the quantum relative entropy (11) the minimal distance of ρ_{AB} to the set $\mathcal{D}_{sep}$ of separable states. This and the general geometric picture is illustrated in figure 2. The set $\mathcal{D}_0$ of uncorrelated states (recall definition 2.1) is shown as a black curve. According to definition 2.2, its convex hull $\mathcal{D}_{sep} \equiv \mathrm{Conv}(\mathcal{D}_0)$ comprises all separable/non-entangled states while the remaining density operators (gray area) are entangled. The geometric correlation and entanglement measures are given by the closest distance from a general state $\rho \equiv \rho_{AB}$ to the sets $\mathcal{D}_0$ (red dashed) and $\mathcal{D}_{sep}$ (red), respectively. Since the uncorrelated states are in particular non-entangled, $\mathcal{D}_0 \subset \mathcal{D}_{sep}$, the entanglement can never exceed the total correlation,

$$I(\rho_{AB}) \geq E(\rho_{AB}). \qquad (17)$$

In contrast to the total correlation, there is no explicit analytical expression known for the relative entropy of entanglement in case of general mixed states and even its numerical calculation is typically quite demanding. That is quite different in case of pure states, $\rho_{AB} = |\Psi_{AB}\rangle\langle\Psi_{AB}|$, since (16) then simplifies to the entanglement entropy which is defined as the von Neumann entropy of the reduced density operators of subsystem A and B, respectively [26, 27],

$$E(|\Psi_{AB}\rangle\langle\Psi_{AB}|) = S(\rho_{A/B}) = -\mathrm{Tr}\, \rho_{A/B} \log(\rho_{A/B}). \qquad (18)$$
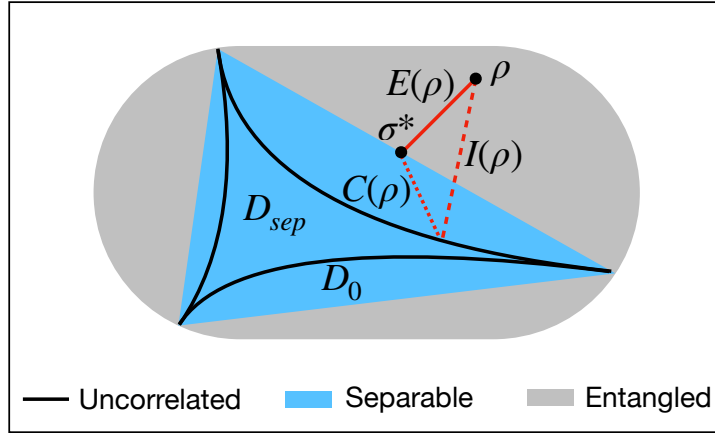
Fig. 2: *Schematic illustration of the space $\mathcal{D}$ of quantum states. Family $\mathcal{D}_0$ of uncorrelated states shown as thick black line and the separable states (its convex hull $\mathcal{D}_{sep}$) reside in the blue area. The grey area represents the entangled states and the red (dashed) line the geometric entanglement (classical correlation) measure $E(\rho)$ $(I(\rho))$. From a more heuristic point of view, one defines the classical correlation $C(\rho)$ as the quantum relative entropy between the closest separable and closest uncorrelated state.*

It is equivalent to calculate the entanglement entropy with either ρ_A or ρ_B, as they have the same eigenvalues in case of pure total states [28] and one has $E(|\Psi_{AB}\rangle\langle\Psi_{AB}|) = 0$ if and only if $|\Psi_{AB}\rangle$ factorizes. In that context, we also would like to recall that for mixed states ρ_{AB} the entanglement entropy (18) is obviously not a good measure for entanglement anymore since the mixedness of the reduced density operators $\rho_{A/B}$ could originate just from possible mixedness in ρ_{AB} (classical correlation).

Actually, knowing the closest separable state, the *classical correlation* of ρ can be quantified geometrically (see figure 2), namely as the distance from the closest separable state σ^* to the closest uncorrelated state $\rho_A \otimes \rho_B$ [29],

$$C(\rho) \equiv S(\sigma^*||\rho_A \otimes \rho_B). \tag{19}$$

We conclude this section with two crucial comments. The first one is concerned with the relation between the different types of correlation. In general, entanglement and classical correlation do not sum to the total correlation. This is because mixed quantum states typically contain quantum correlations beyond entanglement as it is concisely described by the concept of quantum discord [30]. Moreover, a known exact relation including quantum discord refers to an alternative definition of classical correlation which is more technical than our simple geometric one (see Eq. (19)) [30]. Due to its particular significance for quantum information tasks and for the sake of simplicity we focus in our lecture notes on entanglement, however, and refer to it occasionally as quantum correlation.

Last but not least, we would like to stress that for pure total states a remarkable operational meaning of the entanglement entropy (to the base 2) has been found [31, 26]: In the asymptotic limit of n identical two-qubit systems, each in the same pure quantum state shared between two parties A and B with an entanglement entropy S, the number m of maximally entangled

Bell pairs that can be extracted follows as $m = n\,S$. It is exactly this operational meaning of entanglement between distinguishable subsystems which raises some doubts about the common approach to entanglement and correlation in condensed matter physics and quantum chemistry: Applying some partial trace-like map to obtain some type of reduced density operator, possibly even not normalized to unity, and then plugging it into the formula for the von Neumann entropy does not necessarily mean to quantify correlation or entanglement.

2.2 Fermionic quantum systems

The concepts of entanglement and correlation, as reviewed in the previous section, refer to a well-defined separation of the total system into two (or more) distinguishable subsystems. In the simplest case, this separation emerges naturally from the physical structure of the total system, namely by referring to a possible spatial separation of two subsystems. In that case, it will be also easier to experimentally access both subsystems to eventually extract the entanglement from their joint quantum state. Nonetheless, the notion of bipartite correlation and entanglement is by no means unique for a given system since one just needs to identify some tensor product structure in the total system's Hilbert space, $\mathcal{H} \equiv \mathcal{H}_A \otimes \mathcal{H}_B$. In the most general approach, one even defines subsystems by choosing two commuting subalgebras $\mathcal{A}_A, \mathcal{A}_B$ of observables [18]. This also highlights the crucial fact that entanglement and correlation are relative concepts since they refer to a choice of subsystems/subalgebras of observables.

In case of identical fermions the identification of subsystems is not obvious at all. For instance, how could one decompose the underlying N-fermion Hilbert space $\mathcal{H}_N \equiv \wedge^N[\mathcal{H}_1]$ or the Fock space $\mathcal{F} \equiv \oplus_{N \geq 0} \mathcal{H}_N$? Actually, there exist two natural routes which look promising. The first one refers naturally to the 2nd quantized formalism and leads to a notion of *orbital* (sometimes also called mode or site) entanglement and correlation [32–34]. A second and more subtle route [11] which is not covered here is related more to first quantization and tries to define correlation and entanglement in the *particle* picture.

A natural tensor product structure emerges in the formalism of second quantization, facilitating a bipartition on the set of spin-orbitals. To explain this, let us fix a reference basis for the one-particle Hilbert space $\mathcal{H}_1$. We then introduce the corresponding fermionic creation ($f_i^\dagger$) and annihilation operators (f_j), fulfilling the fermionic commutation relations,

$$\{f_i^{(\dagger)}, f_j^{(\dagger)}\} = 0, \quad \{f_i^\dagger, f_j\} = \delta_{ij}. \tag{20}$$

In the quantum information community the one-particle reference states are often referred to as *modes*, or (lattice) sites by condensed matter physicists. Each spin-orbital or generally mode i can be either empty or occupied by a fermion. In this picture, the quantum states are naturally represented in the occupation number basis. The respective *configuration states*

$$|n_1, n_2, \ldots, n_d\rangle = (f_1^\dagger)^{n_1}(f_2^\dagger)^{n_2} \cdots (f_d^\dagger)^{n_d}|\Omega\rangle \tag{21}$$

with $n_1, n_2 \ldots, n_d \in \{0, 1\}$ form a basis for the underlying Fock space

$$\mathcal{F}(\mathcal{H}_1) = \bigoplus_{N=0}^{d} \wedge^N[\mathcal{H}^{(1)}]. \tag{22}$$

Bipartitions naturally arise as separations of the basis $\mathcal{B} = \{|\varphi_j\rangle\}_{j=1}^d$ of reference spin-orbitals into two disjoint subsets $\mathcal{B}_A = \{|\varphi_j\rangle\}_{j=1}^m$, $\mathcal{B}_B = \{|\varphi_j\rangle\}_{j=m+1}^d$. This in turn suggests a splitting of the configuration state according to

$$|n_1, \ldots, n_m, n_{m+1}, \ldots, n_d\rangle \mapsto |n_1, n_2, \ldots n_m\rangle_A \otimes |n_{m+1}, n_{m+2}, \ldots, n_d\rangle_B. \qquad (23)$$

The total Fock space $\mathcal{F}(\mathcal{H}_1)$ thus admits the tensor product structure

$$\mathcal{F}_{AB} \equiv \mathcal{F}(\mathcal{H}_1) = \mathcal{F}(\mathcal{H}_1^{(A)}) \otimes \mathcal{F}(\mathcal{H}_1^{(B)}) \equiv \mathcal{F}_A \otimes \mathcal{F}_B, \qquad (24)$$

with respect to the given ordering of the spin-orbitals, where $\mathcal{H}_1^{(A/B)}$ denotes the one-particle Hilbert space spanned by the first m and last $d-m$ spin-orbitals, respectively. Actually, any splitting of the one-particle Hilbert space into two complementary subspaces,

$$\mathcal{H}_1 = \mathcal{H}_1^{(A)} \oplus \mathcal{H}_1^{(B)}, \qquad (25)$$

induces a respective splitting (24) on the Fock space level.[1] Moreover, such a decomposition of the total Fock space into two factors allows us to introduce orbital reduced density operators $\rho_{A/B}$ for the respective orbital subsystem A/B. They are obtained by taking the partial trace of the total state ρ with respect to the complementary factor $\mathcal{F}_{B/A}$. Consequently, $\rho_{A/B}$ is defined as an operator on the local space $\mathcal{F}_{A/B}$ and in general does not have a definite particle number anymore.

It seems that we can now readily apply the common quantum information theoretical formalism referring to distinguishable subsystems. Yet there is one crucial obstacle. Not every Hermitian operator acting on a fermionic Fock space is a physical observable. For instance, nature does not allow one to coherently superpose even and odd fermion number states [19]. The significance of this *number parity superselection rule* (SSR) is rather obvious as it will be explained in the subsequent section since its violation would equivalently make superluminal signalling possible in contradiction to special relativity. The number parity SSR implies that the algebra of observables on any Fock space comprises only those operators which are block-diagonal with respect to the even and odd fermion number sectors, $\hat{A} = \hat{A}_{ee} + \hat{A}_{oo}$ [35].

2.3 Superselection rules

A key ingredient in the physics of fermionic systems is the so-called *parity superselection rule* (P-SSR). In its original form, P-SSR forbids coherent superpositions of even and odd fermion-numbers states. In a more modern version, P-SSR states that the operators belonging to physically measurable quantities must commute with the parity operator of the particle number. This means they have to be linear combinations of even degree monomials of the fermionic creation and annihilation operators. This in turn implies that a superposition of two pure states with even

---

[1] For the sake of mathematical rigor and conclusiveness, we would like to stress that the corresponding isomorphism $\mathcal{F}_{AB} \to \mathcal{F}_A \otimes \mathcal{F}_B$ is by no means unique. Yet, this changes when we take into account the parity superselection rule as discussed below.
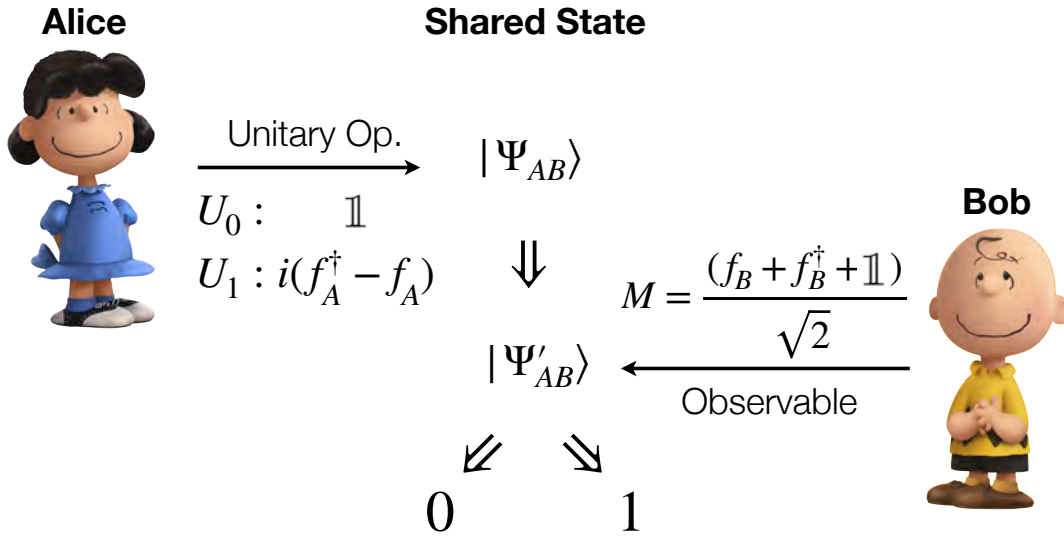
Fig. 3: *The protocol showing how superluminal signaling is possible when parity superselection rule is broken: Alice communicates the bit value $b \in \{0,1\}$ by applying the corresponding unitary U_b, Bob measures the observable M and obtains instantaneously that bit value, as explained in the text.*

and odd particle numbers cannot be distinguished from an incoherent classical mixture of those states, thus one recovers the original formulation as a consequence.

The idea that the laws of nature impose P-SSR on fermionic systems was originally derived based on group theoretical arguments [19, 36, 37]. However, the pertinence of P-SSR is also obvious from the fundamental fact that violation of P-SSR would lead to a violation of the no-signaling theorem, as we will explain in the following. The no-signaling theorem states that two spatially separated parties cannot communicate faster than the speed of light. To relate this fundamental law of physics to the P-SSR, let us assume that two distant parties Alice and Bob could violate the P-SSR. For our argument it is sufficient for Alice and Bob to have each access to one mode (e.g., an atomic spin-orbital). Their local Fock spaces are thus generated by the fermionic annihilation and creation operators $(f_A, f_A^\dagger)$ and $(f_B, f_B^\dagger)$, respectively. Assume now that they can share the state $|\psi\rangle_{AB} = \frac{1}{\sqrt{2}}(|0\rangle_A|0\rangle_B + |0\rangle_A|1\rangle_B)$, which is a superposition of odd and even number states. The procedure for Alice to communicate instantaneously one bit $b = 0, 1$ of classical information to Bob would be the following (see also figure 3): both of them synchronize the clocks in their labs, and they pre-decide to perform local operations at a particular time. If Alice wants to communicate 1, she does nothing (i.e., formally applies the unitary $U_1 = \mathbb{1}$), so $|\psi\rangle_{AB}$ remains unchanged; to communicate 0, Alice applies the unitary $U_0 = i(f_A^\dagger - f_A)$, and the state becomes $|\psi'\rangle_{AB} = \frac{i}{\sqrt{2}}(|1\rangle_A|0\rangle_B + |1\rangle_A|1\rangle_B)$. At the same instant Bob measures the observable $\frac{1}{2}(f_B + f_B^\dagger + \mathbb{1})$. One easily verifies that in both cases $b = 0, 1$ the outcome of that measurement is deterministic and will be nothing else than the value of b. Hence, this proposed procedure allows Alice to communicate instantaneously a bit b of information in contradiction to the no-signaling theorem and the laws of relativity.

> **Exercise 2.7**
>
> Recap various steps of the quantum protocol outlined above and calculate various intermediate quantum states to confirm that violation of the P-SSR would indeed make superluminal signalling possible.

Beside the parity superselection rule, it is often pertinent to consider superselection rules due to some experimental limitations. One such rule is the fermion *particle number superselection rule* (N-SSR). Measurable quantities obeying N-SSR must commute with the particle parity operators [36]. This, in the form of lepton number conservation, was once considered to be an exact symmetry of Nature. Recently, however, there have been indications that fundamental Majorana particles may exist which could lead to a violation of the N-SSR. Nevertheless, in a usual quantum chemistry set-up, we can safely regard N-SSR to hold. Indeed, the energies of common molecular systems are (in contrast to systems studied in high energy physics) sufficiently low to entirely suppress the emergence of electrons and other particles from vacuum fluctuations. In the following parts of the lecture notes we will in particular discuss the consequences of *both* superselection rules, but we assume that the N-SSR is the more relevant one in quantum chemistry.

Having established the fundamental importance of superselection rules, we will now elucidate how they affect our description of quantum states, and consequently change the physically accessible correlation and entanglement in a quantum state. Accordingly, the SSRs will have important consequences for the realization of quantum information processing tasks.

In the following, we will explain on a more abstract level superselection rules by referring to the concept of local symmetries and present a general scheme for taking them into account. The examples provided in Section 3 will then demonstrate those general concepts on a more elementary level by applying them to the particle number and number parity symmetry for electronic quantum systems. From a general point of view, SSRs are restrictions on local algebras of observables, resulting in physical algebras $\mathcal{A}_A$ and $\mathcal{A}_B$. If the SSR is related to some locally conserved quantity $Q_{A/B}$, then local operators must also preserve this quantity. That is, all local observables satisfy

$$\mathcal{A}_{A/B} \ni \mathcal{O}_{A/B} = \sum_q P_q \, \mathcal{O}_{A/B} P_q, \tag{26}$$

where q ranges over all possible value of $Q_{A/B}$ and P_q's are projectors onto the eigensubspaces, i.e., $\mathcal{O}_{A/B}$ are block diagonal in any eigenbasis of $Q_{A/B}$. It follows that different SSRs will lead to drastically different $\mathcal{A}_{A/B}$. The fact that we cannot physically implement every mathematical operator changes the accessibility of quantum states. The fully accessible states are called the physical states, and they satisfy

$$\rho = \sum_{q,q'} P_q \otimes P_{q'} \, \rho \, P_q \otimes P_{q'}, \tag{27}$$

or equivalently

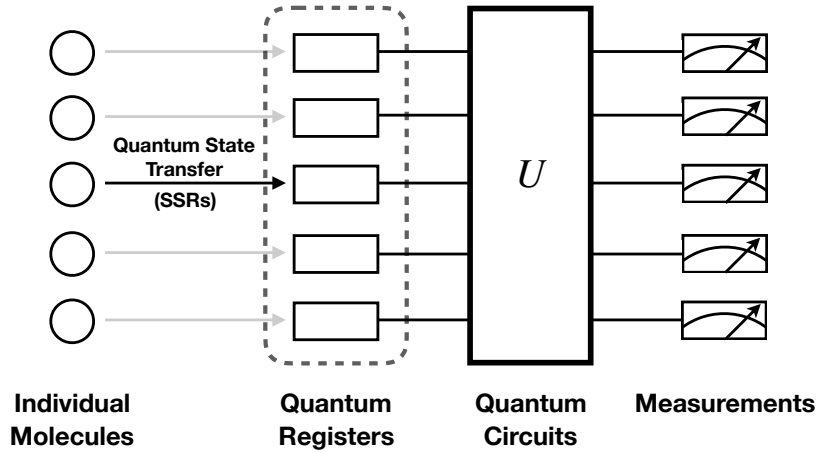$$\left[\rho, \, Q_{A/B} \right] = 0. \tag{28}$$

Fig. 4: *Schematic protocol for utilizing entanglement from molecular systems (see text for more details).*

For a general state ρ which does not satisfy (28), we can obtain its physical part by the following projection

$$\rho^{\mathrm{Q}} \equiv \sum_{q,q'} P_q \otimes P_{q'} \, \rho \, P_q \otimes P_{q'}. \tag{29}$$

The physical state ρ^{Q} gives the same expectation value as ρ for all *physical* observables. Therefore we can define a new class of uncorrelated states to be the ones with uncorrelated physical parts with respect to the physical algebra:

$$\mathcal{D}_0^{\mathrm{Q\text{-}SSR}} = \left\{ \rho \,\middle|\, \langle \mathcal{O}_A \otimes \mathcal{O}_B \rangle_\rho = \langle \mathcal{O}_A \rangle_{\rho_A} \langle \mathcal{O}_B \rangle_{\rho_B} \; \forall \mathcal{O}_A \in \mathcal{A}_A, \mathcal{O}_B \in \mathcal{A}_B \right\}. \tag{30}$$

It is clear that the new set of uncorrelated states includes the one of the distinguishable setting, i.e., $\mathcal{D}_0 \subseteq \mathcal{D}_0^{\mathrm{Q\text{-}SSR}}$. Consequently also more states are deemed separable. Relating to figure 2, both the correlation and entanglement measure become smaller in the presence of an SSR. There are two key messages here. First of all, 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 SSRs, which eventually defines the physical local algebras of observables $\mathcal{A}_{A/B}$ and the global algebra $\mathcal{A}_A \otimes \mathcal{A}_B$. Secondly, by ignoring the fundamentally important SSRs, one may radically overestimate the amount of physical correlation and entanglement in a quantum state.

One of the biggest motivations for correctly identifying the amount of physical correlation and entanglement in a quantum state is its value for information processing tasks. An operationally meaningful quantification of entanglement does not only reveal non-local properties of a quantum state, but should also measure the amount of resource that can be extracted for performing various quantum information tasks mentioned in section 1. In figure 4 we illustrate the schematic protocol for utilizing entanglement from molecular systems. The quantum states of individual molecules are transferred to SSR-free quantum registers through local measurements and classical communication. A quantum circuit represented by a unitary gate U in figure 4 then acts on these quantum register states to perform computations. Finally, the end results of the computation are retrieved with carefully designed measurements. The key step that limits

the extraction of entanglement is the transferring of the quantum state, which is constrained by the underlying SSR [38]. What remains on the quantum registers after the transfer are the *physical* parts defined in Eq. (29). From this perspective, the Q-SSR-constrained total correlation, entanglement, and classical correlation of a single system in a state ρ follow as

$$
\begin{aligned}
I^{\text{Q-SSR}}(\rho) &= I(\rho^{\text{Q}}), \\
E^{\text{Q-SSR}}(\rho) &= E(\rho^{\text{Q}}), \\
C^{\text{Q-SSR}}(\rho) &= C(\rho^{\text{Q}}).
\end{aligned}
\tag{31}
$$

All quantum information theoretical concepts discussed so far are applicable to any *arbitrary* orthonormal basis of $D \geq 2$ spin orbitals. In particular, they then refer to any *arbitrary* separation of them into subsystems A and B defined by spin-orbitals $\{|\varphi_j\rangle\}_{j=1}^{D_A}$ and $\{|\varphi_j\rangle\}_{j=D_A+1}^{D}$, respectively. As far as the description of electronic structure is concerned, there are two particularly relevant separations. To explain them, let us first observe that the underlying one-particle Hilbert space. $\mathcal{H}^{(1)}$ consists of orbital and spin degrees of freedom, i.e., $\mathcal{H}^{(1)} \equiv \mathcal{H}_l^{(1)} \otimes \mathcal{H}_s^{(1)}$, where $\dim(\mathcal{H}_l^{(1)}) \equiv d$, $\dim(\mathcal{H}_s^{(1)}) \equiv 2$ and $\dim(\mathcal{H}^{(1)}) \equiv D = 2d$. The first partition picks one orbital $|\chi\rangle \in \mathcal{H}_l^{(1)}$ and then defines subsystem A through the two spin-orbitals $|\chi\rangle \otimes |\sigma\rangle$, $\sigma = \uparrow, \downarrow$. Subsystem B follows accordingly and comprises the remaining $D-2$ spin-orbitals. The corresponding measures for entanglement and correlation can be referred to as single-orbital entanglement and correlation. As we will show in section 3.1, the fact that the total N-electron ground state of a molecular system is pure drastically simplifies the respective measures and in particular leads to closed formulas. The second more elaborated separation quantifies entanglement and correlation between two orbitals $|\chi_i\rangle, |\chi_j\rangle \in \mathcal{H}_l^{(1)}$. This means to first trace out the complementary $D-4$ spin-orbitals to obtain a two-orbital reduced density matrix $\rho_{i,j}$ which is "living" on a sixteen-dimensional Fock space as illustrated in figure 5. Then, one applies to this new "total state" $\rho_{i,j}$ the formalism of bipartite entanglement and correlation for the separation $i \leftrightarrow j$ (see also the subsequent section).

Finally, let us also illustrate how the SSRs are implemented in the calculation of pairwise orbital entanglement. According to the previous comments, particularly Eq. (29), we just need to replace $\rho_{i,j}$ by its physical part $\rho_{i,j}^{\text{Q}}$. For the case of P-SSR and N-SSR this is illustrated in figure 5. $\rho_{i,j}^{\text{P}}$ is obtained by cutting out all light gray parts and $\rho_{i,j}^{\text{N}}$ follows after removing two additional entries (gray).

To avoid confusion, we recall that the quantum state on the algebra of observables based on two orbitals i, j is described by the full 2RDM $\rho_{i,j}$, including the gray and light gray entries as well. Yet, if we ask about the true physical correlation and entanglement between orbitals i and j this means to restrict in a first step the quantum state to the subalgebra

$$
\mathcal{A}_i \otimes \mathcal{A}_j \subsetneq \mathcal{A}_{i,j} \,.
\tag{32}
$$

Indeed, $\mathcal{A}_i \otimes \mathcal{A}_j$ is smaller than the full two-orbital algebra $\mathcal{A}_{i,j}$ because of the Q-SSR which is applied for the former on both single-orbital algebras individually. Just to illustrate this in more concrete terms, we observe for instance that the operator $f_{i\sigma}^\dagger f_{j\tau}$ belongs to $\mathcal{A}_{i,j}$ but not to $\mathcal{A}_i \otimes \mathcal{A}_j$, neither for P-SSR nor N-SSR, since $f_{i\sigma}^\dagger$ and $f_{j\tau}$ change locally the number parity.
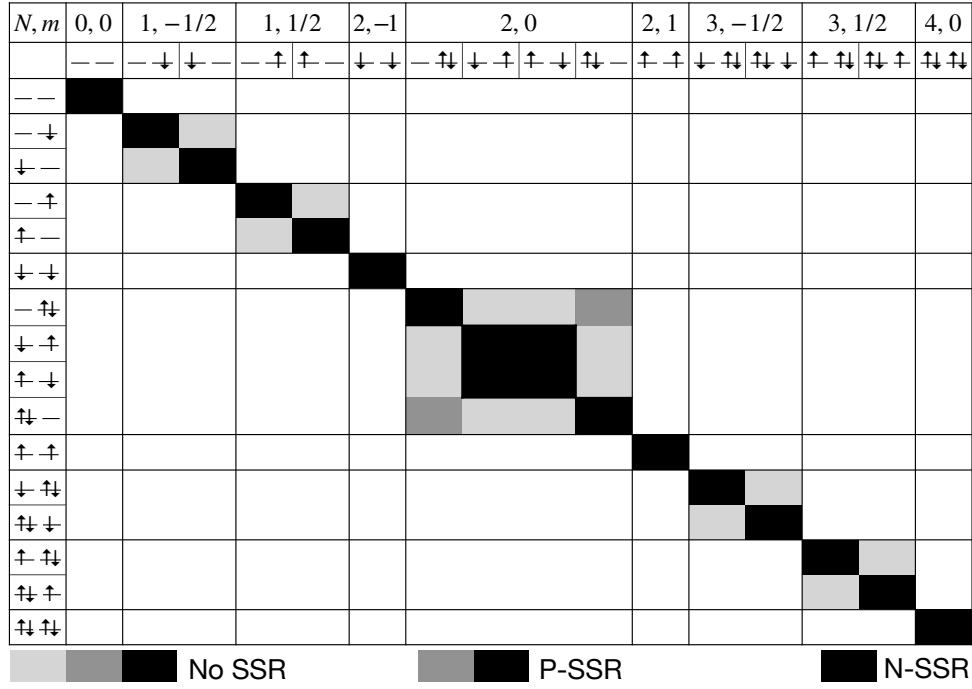
N,m	0,0	1,−1/2		1,1/2		2,−1	2,0				2,1	3,−1/2		3,1/2		4,0
	— —	— ↓	↓ —	— ↑	↑ —	↓ ↓	— ↑↓	↓ ↑	↑ ↓	↑↓ —	↑ ↑	↓ ↑↓	↑↓ ↓	↑ ↑↓	↑↓ ↑	↑↓ ↑↓
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No SSR   P-SSR   N-SSR

Fig. 5: *Illustration of two-orbital reduced density matrix $\rho_{i,j}$ and its superselected variants $\rho_{i,j}^{Q}$, $Q = N, P$. Most entries vanish due to spin and particle symmetry (white). According to (29) the P-SSR sets light gray entries to zero while N-SSR removes in addition two entries (gray).*

3 Analytic treatment

3.1 Closed formulas for entanglement and correlation

We first look at the single-orbital total correlation and entanglement and assume a pure quantum state $\rho = |\Psi\rangle\langle\Psi|$ for the total N-electron system (typically it will be the ground state or an excited state of a molecular system). The one-orbital reduced density matrix associated with the orbital $|\chi_j\rangle$ is obtained by tracing out all remaining orbitals [34]

$$\rho_j = \mathrm{Tr}_{\backslash\{j\}}[|\Psi\rangle\langle\Psi|]. \tag{33}$$

We reiterate that the partial trace $\mathrm{Tr}_{\backslash\{j\}}[\cdot]$ does not mean to trace out particles but instead refers to the tensor product in the second quantization, i.e., it exploits the structure $\mathcal{F} = \mathcal{F}_j \otimes \mathcal{F}_{\backslash\{j\}}$. From a practical point of view, the non-vanishing entries of the single-orbital reduced density matrix can be determined by calculating expectation values of $|\Psi\rangle$ involving only fermionic creation and annihilation operators referring to orbital $|\chi_j\rangle$. For more details we refer the reader to Refs. [39,40,34]. Due to the fixed particle number and the spin symmetry of $|\Psi\rangle$ the one-orbital reduced density matrix will be always diagonal in the local reference basis $\{|\Omega\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\}$ of orbital $|\chi_j\rangle$:

$$\rho_j = \begin{pmatrix} p_1 & 0 & 0 & 0 \\ 0 & p_2 & 0 & 0 \\ 0 & 0 & p_3 & 0 \\ 0 & 0 & 0 & p_4 \end{pmatrix}. \tag{34}$$

By referring to the so-called Schmidt decomposition, the total state then takes the form

$$|\Psi\rangle = \sqrt{p_1}|\Omega\rangle \otimes |\Psi_{N,M}\rangle + \sqrt{p_2}|\uparrow\rangle \otimes |\Psi_{N-1,M-\frac{1}{2}}\rangle \tag{35}$$
$$+ \sqrt{p_3}|\downarrow\rangle \otimes |\Psi_{N-1,M+\frac{1}{2}}\rangle + \sqrt{p_4}|\uparrow\downarrow\rangle \otimes |\Psi_{N-2,M}\rangle,$$

where $|\Psi_{n,m}\rangle$ is a quantum state with particle number n and magnetization m of the complementary subsystem comprising the remaining $D-2$ spin-orbitals. Now we can readily determine the physical part ρ^Q in the presence of P-SSR or N-SSR. In the absence of SSRs, the single-orbital entanglement of $|\Psi\rangle$ is simply given by the von Neumann entropy of ρ_j, and the single-orbital total correlation is simply twice the entanglement,

$$E(|\Psi\rangle\langle\Psi|) = S(\rho_j) = -\sum_{i=1}^{4} p_i \ln(p_i).$$
$$I(|\Psi\rangle\langle\Psi|) = 2E(|\Psi\rangle\langle\Psi|). \tag{36}$$

In the case of Q-SSR, we need to consider the physical part ρ^Q of $\rho = |\Psi\rangle\langle\Psi|$, which is no longer a pure state. Consequently the single-orbital entanglement cannot be quantified by the von Neumann entropy of ρ_j anymore. Instead we have to invoke the geometric picture in figure 2. We first calculate the physical states with respect to P-SSR and N-SSR according to (29), and then their correlation and entanglement are quantified using (13) and (16). Remarkably, despite the fact that ρ^Q is not a pure state anymore the single-orbital correlation and entanglement under P-SSR and N-SSR still involves the spectrum of ρ_j only:

$$I(\rho^P) = (p_1 + p_4)\ln(p_1 + p_4) + (p_2 + p_3)\ln(p_2 + p_3)$$
$$- 2(p_1\ln(p_1) + p_2\ln(p_2) + p_3\ln(p_3) + p_4\ln(p_4)),$$
$$I(\rho^N) = p_1\ln(p_1) + (p_2 + p_3)\ln(p_2 + p_3) + p_4\ln(p_4)$$
$$- 2(p_1\ln(p_1) + p_2\ln(p_2) + p_3\ln(p_3) + p_4\ln(p_4)), \tag{37}$$
$$E(\rho^P) = (p_1 + p_4)\ln(p_1 + p_4) + (p_2 + p_3)\ln(p_2 + p_3)$$
$$- p_1\ln(p_1) - p_2\ln(p_2) - p_3\ln(p_3) - p_4\ln(p_4),$$
$$E(\rho^N) = (p_2 + p_3)\ln(p_2 + p_3) - p_2\ln(p_2) - p_3\ln(p_3).$$

In particular, this implies immediately for both SSRs (Q=P,N)

$$I^{\text{Q-SSR}}(\rho) = E^{\text{Q-SSR}}(\rho) + E(\rho). \tag{38}$$

For the case of no SSR, this is consistent with Eq. (36).

As already explained in the previous section, the second particularly relevant partitioning of the total system leads to a notion of orbital-orbital correlation and entanglement. It is fully described by the two-orbital reduced density matrix associated with orbital $|\chi_i\rangle$ and $|\chi_j\rangle$

$$\rho_{i,j} = \text{Tr}_{\setminus\{i,j\}}[|\Psi\rangle\langle\Psi|]. \tag{39}$$

For the specific case of a total system consisting of just two orbitals, the only two-orbital "reduced" density operator is given by the total (pure) state. Consequently, the orbital-orbital

correlation and entanglement thus coincide with the single-orbital ones and the above results (36), (37) immediately apply. Due to the electron interaction, the two-orbital reduced density matrices $\rho_{i,j}$ of *general* systems are, however, not pure anymore. This makes the calculation of orbital-orbital entanglement and classical correlation highly non-trivial: According to the definition of the relative entropy of entanglement (16) one needs to minimize the distance between $\rho_{i,j}$ and $\sigma_{i,j} \in \mathcal{D}_{sep}$ which *a priori* involves 255 parameters. Yet, $\rho_{i,j}$ inherits particle and spin symmetries from the molecular ground state $\rho = |\Psi\rangle\langle\Psi|$ which changes the general situation drastically. As a consequence almost all of its entries vanish as it is shown in figure 5 (see also Refs. [39]). Based on elaborated ideas the respective minimization (16) can be simplified accordingly by transferring those symmetries to $\mathcal{D}_{sep}$ [41,42]. The latter simplification eventually allows us to calculate below the entanglement between $|\chi_1\rangle, |\chi_2\rangle \in \mathcal{H}_l^{(1)}$ for any $\rho_{i,j}$.

In the following, we will illustrate those concepts in the form of several analytical examples.

3.2   Single electron state

At first glance it might seem somewhat bizarre to examine the correlation and entanglement in a system with only one particle. However, the reader shall bear in mind that the separation into subsystems is not referring to particles but *orbitals*. The total Fock space $\mathcal{F}$ in our case of two orbitals ($|1\rangle, |2\rangle$) has indeed a natural tensor product structure between the Fock spaces of the first and second orbital, i.e., $\mathcal{F} = \mathcal{F}_1 \otimes \mathcal{F}_2$. Therefore the notion of correlation and entanglement between two physically distinct orbitals is entirely legitimate even in the case of one single electron.

In the following we consider the specific one-electron state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(f_{1\uparrow}^\dagger + f_{2\uparrow}^\dagger)|\Omega\rangle \equiv \frac{|\uparrow\rangle \otimes |\Omega_2\rangle + |\Omega_1\rangle \otimes |\uparrow\rangle}{\sqrt{2}}. \tag{40}$$

Here, $f_{j\sigma}^\dagger$ denotes the fermionic creation operator for the spin-orbital $|j\sigma\rangle$, $j = 1, 2, \sigma = \uparrow, \downarrow$ and $|\Omega\rangle$ and $|\Omega_{1/2}\rangle$ the global and local vacuum states, respectively. If the SSRs are ignored, state (40) is certainly entangled. Yet, as we will show now this entanglement is artificial since it disappears when the P-SSR is taken into account. To prove this, recall that the P-SSR physical part of ρ is obtained by projecting onto fixed local parity sectors

$$\rho^P = \sum_{\tau,\tau'=\text{odd, even}} P_\tau \otimes P_{\tau'} \rho P_\tau \otimes P_{\tau'} = \frac{1}{2}|\Omega_1\rangle\langle\Omega_1| \otimes |\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\uparrow\rangle\langle\uparrow| \otimes |\Omega_2\rangle\langle\Omega_2|, \tag{41}$$

which is correlated but not entangled. Indeed, it is a classical mixture of two uncorrelated states. For the sake of completeness, we would like to stress that for single electron states there is no difference between P-SSR and N-SSR. In particular for the state (40) we find

$$\rho^N = \sum_{m,n=0}^{2} P_m \otimes P_n \, \rho \, P_m \otimes P_n$$

$$= \frac{1}{2}|\Omega_1\rangle\langle\Omega_1| \otimes |\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\uparrow\rangle\langle\uparrow| \otimes |\Omega_2\rangle\langle\Omega_2| = \rho^P. \tag{42}$$

	No SSR	P-SSR	N-SSR
Total	$2\ln(2)$	$\ln(2)$	$\ln(2)$
Quantum	$\ln(2)$	0	0
Classical	$0.208\ln(2)$	$\ln(2)$	$\ln(2)$

Table 1: *Total, quantum and classical correlation between the two orbitals in the one-electron state $|\Psi\rangle$ in (40), for the case without SSR, with P-SSR and with N-SSR.*

We present in table 1 the orbital total correlation ("Total"), entanglement ("Quantum") and classical correlation ("Classical") between $|1\rangle$ and $|2\rangle$ contained in state (40) which can easily be calculated based on the physical states (41), (42).

The number 0.208 in table 1 is the constant $\ln(4/3)/2$. When P-SSR or N-SSR is present (they are equivalent in the case of only one electron), all entanglement is wiped out and all correlation is classical, as it is shown by the second and third column. This striking example shows that one can never extract any entanglement from a single one-electron quantum state even if it appears at first sight as being entangled.

> **Exercise 3.1**
>
> Recalculate various entries of table 1.

> **Exercise 3.2**
>
> Building up on Exercise 3.1, explain why single electron quantum states are never P-SSR or N-SSR entangled (i.e., for any dimension of the underlying one-particle Hilbert space $\mathcal{H}^{(1)}$ and any splitting (25)).

3.3 Dissociated hydrogen

Having studied the orbital-orbital correlation and entanglement in a one-electron state, we now add a second electron to our two-orbital system. As an example, we consider the ground state of the hydrogen molecule in the dissociation limit. The two orbital system now consists of the $1s$ orbital at each nucleus (both orthonormal as we assume almost infinite separation) and the ground state follows as

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(f_{1\uparrow}^\dagger f_{2\downarrow}^\dagger - f_{1\downarrow}^\dagger f_{2\uparrow}^\dagger)|\Omega\rangle. \tag{43}$$

In table 2 we list the total correlation, entanglement and classical correlation between $|1\rangle$ and $|2\rangle$. When no SSR is considered, all three types of correlation equal those of the one-electron state in table 1. However, in contrast to the latter, the ground state $|\Psi\rangle$ of the dissociated hydrogen molecule is already a physical state, with respect to both P-SSR and N-SSR. From (43) we infer that $|\Psi\rangle$ is a pure state with definite local parities (odd, odd) and definite local particle numbers $(1, 1)$. The projection (29) therefore does not change the state $|\Psi\rangle\langle\Psi|$ and thus all three types of correlation are unaffected by P-SSR and N-SSR according to (31).

	No SSR	P-SSR	N-SSR
Total	$2\ln(2)$	$2\ln(2)$	$2\ln(2)$
Quantum	$\ln(2)$	$\ln(2)$	$\ln(2)$
Classical	$0.208\ln(2)$	$0.208\ln(2)$	$0.208\ln(2)$

Table 2: *Total, quantum and classical correlation between both orbitals $|1\rangle, |2\rangle$ in the dissociated hydrogen ground state $|\Psi\rangle$ in (43), for the case without SSR, with P-SSR and N-SSR.*

Exercise 3.3

Recalculate various entries of table 2.

3.4 Hubbard dimer

The dissociated hydrogen molecule described in the previous section is a very special case with a definite local particle number (and of course, parity). If we consider intermediate bond length, however, different local particle number or parity sectors will start to mix, and hence the behavior of the orbital correlation and entanglement will be more interesting. To elaborate on this, we turn to an elementary model system. The Hamiltonian of this Hubbard dimer which comprises two sites reads

$$H = -t \sum_{\sigma=\uparrow,\downarrow} f_{1\sigma}^\dagger f_{2\sigma} + \text{H.c.} + U \sum_{j=1,2} \hat{n}_{j\uparrow}\hat{n}_{j\downarrow}, \tag{44}$$

where $f_{j\sigma}^{(\dagger)}$ are annihilation (creation) operators associated with a spin σ electron on site $j = 1, 2$. It is worth recalling that small hopping rates t correspond to larger inter-nuclei separations. The repulsive potential U penalizes any doubly occupied site, effectively describing the Coulomb repulsion of two electrons in the same $1s$ orbital. Exploiting the symmetries of (44) one easily determines the ground state of the Hubbard dimer

$$|\Psi\rangle = \frac{a}{\sqrt{2}}\left(f_{1\uparrow}^\dagger f_{2\downarrow}^\dagger - f_{1\downarrow}^\dagger f_{2\uparrow}^\dagger\right)|\Omega\rangle + \frac{b}{\sqrt{2}}\left(f_{1\uparrow}^\dagger f_{1\downarrow}^\dagger - f_{2\downarrow}^\dagger f_{2\uparrow}^\dagger\right)|\Omega\rangle, \tag{45}$$

where

$$a = \sqrt{\frac{W + \frac{U}{2}}{2W}}, \quad b = \frac{2t}{\sqrt{2W\left(W + \frac{U}{2}\right)}}, \quad W = \sqrt{\frac{U^2}{4} + 4t^2}. \tag{46}$$

The orbital-orbital total correlation I, entanglement E and classical correlation C in the ground state (45) are plotted in figure 6, for the case without SSR, with P-SSR and N-SSR [11], as a function of the parameter t/U. In this special case of just two orbitals in total and a pure state, the single-orbital and orbital-orbital correlation and entanglement coincide.

In the case without any SSR, the orbital-orbital entanglement E (red solid) is exactly half of the total correlation I. For finite t/U, i.e., when $b > 0$ in (45), P-SSR and N-SSR drastically reduce
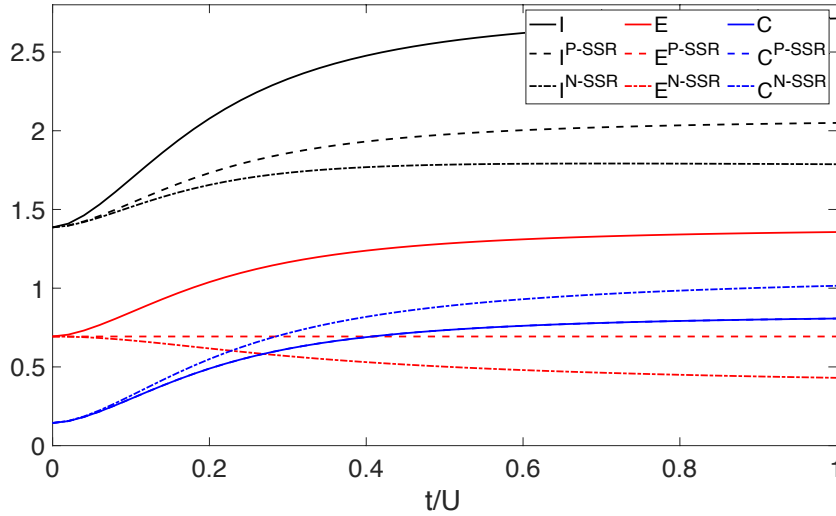
Fig. 6: *Total correlation I (black), entanglement E (red) and classical correlation C (blue) between both sites for the ground state of the Hubbard dimer* (44) *as functions of the ratio t/U. The curves for C and $C^{P\text{-}SSR}$ coincide.*

the orbital-orbital total correlation and entanglement, as is shown by the curves corresponding to $I^{\text{P-SSR}}$ (black dashed), $I^{\text{N-SSR}}$ (black dot-dashed), $E^{\text{P-SSR}}$ (red dashed) and $E^{\text{N-SSR}}$ (red dot-dashed). N-SSR being the stronger rule, reduces correlation and entanglement the most. However, when we take $t/U \to 0$, corresponding to the dissociation limit, the effect of P-SSR and N-SSR disappears. This is due to the vanishing coefficient b in (45) in the dissociation limit, which results in a ground state that is physical in the presence of both P-SSR and N-SSR, as it has already been pointed out in section 3.3.

In the weak coupling limit, $U \to 0$, the Hamiltonian (44) reduces to the hopping Hamiltonian. Since the latter is a one-particle operator it is a particularly simple task to understand the form of its ground state: Both electrons just occupy (in different spin states) the energetically lower one-particle state $1/\sqrt{2}\big(|L\rangle + |R\rangle\big)$. This is nothing else than the bonding orbital which maximizes relative to the antibonding orbital $1/\sqrt{2}\big(|L\rangle - |R\rangle\big)$ the electron density between both nuclei/sites. The corresponding ground state therefore reads

$$|\Psi(U{=}0)\rangle = \frac{1}{2}\Big(f_{1\uparrow}^{\dagger}f_{1\downarrow}^{\dagger} + f_{1\uparrow}^{\dagger}f_{2\downarrow}^{\dagger} + f_{2\uparrow}^{\dagger}f_{1\downarrow}^{\dagger} + f_{2\uparrow}^{\dagger}f_{2\downarrow}^{\dagger}\Big)|\Omega\rangle \,. \tag{47}$$

Exercise 3.4

Calculate for the state (47) all nine correlation quantities (in analogy to Table 2) and verify their correctness by comparison with the numerical results presented in Figure 6.

All these previous elementary examples already reveal the drastic effect of SSRs on orbital correlation and entanglement. In the following section we will apply the quantum information theoretical concepts to systems with more orbitals.

4 Numerical application to molecular ground states

In this section we investigate the correlation and entanglement in the ground states of molecules. We consider exemplarily three chemical systems, the water molecule H_2O, naphthalene $C_{10}H_8$ and the chromium dimer Cr_2, each containing different levels of correlation. Accurate ground states are found by using the density matrix renormalization group (DMRG) method as outlined in the following section 4.1. The single-orbital and orbital-orbital correlation and entanglement are studied in sections 4.2 and 4.3 with respect to two sets of orbitals, the Hartree Fock molecular orbitals and the so-called natural orbitals. To avoid any confusion, it is worth noticing that the choice of orbitals with respect to which those quantities are eventually calculated is made only *after* having obtained a good approximation of the molecule's quantum state. Only for illustrative purposes we will choose in the following for this the Hartree-Fock orbitals which at the same time already play some role in the calculation of the ground state. Hence, in complete analogy to expectation values of more conventional observables, the orbital entanglement and correlation depend on both the molecule's quantum state $|\Psi\rangle$ and the choice of orbitals. Yet, they do not depend on the numerical method that is used to obtain the concrete quantum state $|\Psi\rangle$.

4.1 Computational details

In order to find a ground state, and from it compute the required orbital reduced density matrices, we start with a preceding Hartree-Fock calculation to establish the molecular orbitals. For our post-Hartree-Fock DMRG calculation we construct an active space consisting of the most relevant molecular orbitals and compute integral elements with the one- and two-particle Hamiltonian T and V, respectively. Those respective integral elements define the electronic Hamiltonian at hand by referring to second quantization

$$H = \sum_{ij\sigma} T_{ij}\, f_{i\sigma}^\dagger f_{j\sigma} + \sum_{ijkl\sigma\tau} V_{ijkl}\, f_{i\sigma}^\dagger f_{j\tau}^\dagger f_{k\tau} f_{l\sigma}\,. \tag{48}$$

For our DMRG calculations we do not fix any molecular symmetries. Yet, the total particle number and the z-component of the total spin are always assumed to be conserved, with the latter one always fixed to be zero. Furthermore, we did not employ exceedingly large active spaces for two reasons. First, the ground states are almost exactly found. Second, for the purpose of demonstration, our findings do not qualitatively hinge on the tiny improvement found by resorting to larger active spaces. In particular, the reduction in correlation and entanglement due to the regularly ignored superselection rules turns out to exceed by several orders of magnitude the truncation error of our active spaces.

To obtain for each ground state $|\Psi\rangle$ the required one- (ρ_j) and two-orbital reduced density matrices ($\rho_{i,j}$) we trace all orbitals except one and two, respectively (recall Eqs. (33), (39)).
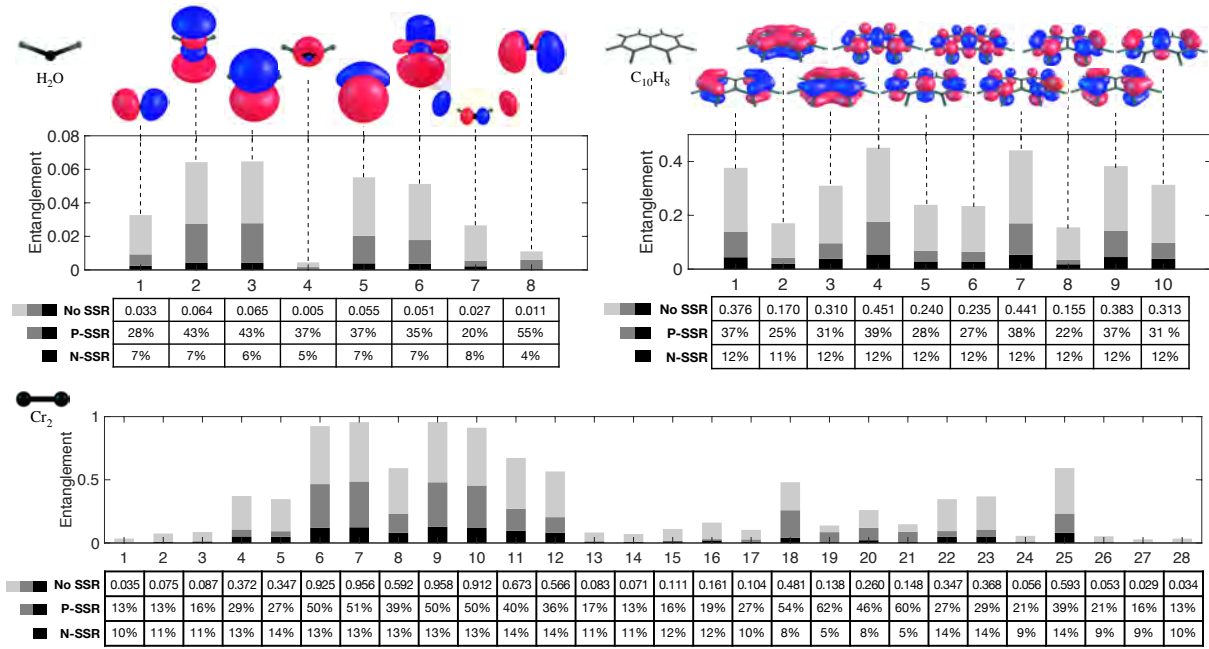
	No SSR	0.033	0.064	0.065	0.005	0.055	0.051	0.027	0.011
	P-SSR	28%	43%	43%	37%	37%	35%	20%	55%
	N-SSR	7%	7%	6%	5%	7%	7%	8%	4%

	No SSR	0.376	0.170	0.310	0.451	0.240	0.235	0.441	0.155	0.383	0.313
	P-SSR	37%	25%	31%	39%	28%	27%	38%	22%	37%	31 %
	N-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	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
	P-SSR	13%	13%	16%	29%	27%	50%	51%	39%	50%	50%	40%	36%	17%	13%	16%	19%	27%	54%	62%	46%	60%	27%	29%	21%	39%	21%	16%	13%
	N-SSR	10%	11%	11%	13%	14%	13%	13%	13%	13%	13%	14%	14%	11%	11%	12%	12%	10%	8%	5%	8%	5%	14%	14%	9%	14%	9%	9%	10%

Fig. 7: *Single-orbital entanglement of the Hartree-Fock molecular orbitals (as visualized) in the ground states of H_2O, $C_{10}H_8$ and Cr_2 for the three cases of no, P- and N-SSR. Exact values of entanglement and the remaining entanglement in terms of percentage of the No SSR case in the presence of P-SSR and N-SSR are listed in the table below each plot.*

4.2 Single-orbital entanglement and correlation

After having obtained the ground states of the desired molecules, we can now explore single-orbital correlation and entanglement by applying the respective formulas from section 3.1. Since the states ρ at hand are all *pure* states, the single-orbital total correlation without any SSR is always exactly twice the single-orbital entanglement, as stated in (36). When P-SSR or N-SSR is taken into account, the respective physical states ρ^P and ρ^N are no longer pure, but in general mixtures of fixed parity or particle number states. However, in the form of Eq. (38) there still exists an exact relation between total correlation and entanglement in the presence of SSRs. Because of this, we focus in this section on the entanglement.

In figure 7 we plotted the single-orbital entanglement in the ground state of the H_2O, $C_{10}H_8$ and Cr_2, respectively, for the case without SSR, with P-SSR and with N-SSR, using the analytic formulas (36) and (37). Below each figure we listed the exact values of single-orbital entanglement in the absence of SSRs, and also the remaining entanglement in the presence of P-SSR and N-SSR, in percentage. All these results refer here and in the following to the Hartree-Fock molecular orbitals which are for the sake of completeness also visualized for H_2O and $C_{10}H_8$.

Generally speaking, the single-orbital entanglement of Hartree-Fock orbitals is quite small compared to the one of *atomic* orbitals in a bond (see sections 3.3 and 3.4), particularly for H_2O and $C_{10}H_8$. This confirms that the Hartree-Fock orbitals give rise to a much more local structure than that the atomic orbitals and in that sense define a much better starting point for high precision ground state methods. Comparing the three systems, the water molecule contains the

weakest single-orbital entanglement, less than 10^{-1} for all eight orbitals, whereas the strongest single-orbital entanglement in naphthalene and the chromium dimer have the values 0.451 and 0.958, respectively. This already emphasizes the different levels of correlation in those systems. Yet, it is worth noticing that any type of orbital entanglement and correlation (e.g., single- or two-orbital entanglement) strongly depends on the chosen reference basis. Even for a configuration state (21) one could find large orbital entanglement and correlation if one referred to orbitals which differ a lot from the natural orbitals.

From a quantum information perspective, the effect of SSRs on the single-orbital entanglement is drastic. The presence of P-SSR and N-SSR considerably reduces the amount of physical entanglement. According to the accompanying tables in figure 7, P-SSR eliminates at least 45% of it and occasionally even up to 87%. Taking into account the more relevant N-SSR eliminates between 86% and 96%. Intriguingly, the entanglement hierarchy, however, remains almost intact. That is, if one orbital is more entangled with the rest than another orbital, the same will likely hold in the presence of P-SSR and N-SSR. It is also worth noting that even the stronger N-SSR does never wipe out the entire entanglement, which we shall see below can happen in the context of orbital-orbital entanglement.

From a quantum chemistry point of view, in figure 7 the single-orbital entanglement varies significantly from orbital to orbital. In particular, some orbitals are barely correlated with the others. Since we have chosen our active spaces systematically by taking into account various Hartree-Fock orbitals energetically closest to the Fermi level, this is a good indicator that our actives spaces were large enough to cover most of the correlation contained in the three molecules. On the other hand, if most orbitals were strongly entangled, the respective active space probably would have been too small. This is also the reason why the single-orbital correlation could help to automate the selection of active orbital spaces in quantum chemistry, as has been suggested and worked out in Refs. [43, 44]. Our refined analytic results (36) and (37) demonstrated in figure 7 are able to identify exactly the quantum part of the total correlation while also taking into account the important superselection rules. These additional facets make precise the usage of quantum information theoretic concepts in the context of quantum chemistry, and may offer new perspectives into the selection of active space.

4.3 Orbital-orbital entanglement and correlation

To provide more detailed insights into the correlation and entanglement structure of molecular ground states, we also study the pairwise correlation and entanglement between two orbitals. This can be done in general in three steps:

1. Obtain the two-orbital reduced density matrix $\rho_{i,j}$ by tracing out all orbital degrees of freedom but orbital i and j as described in (39).

2. Apply the suitable projection to obtain the physical part $\rho_{i,j}^{Q}$ of $\rho_{i,j}$ under Q-SSR, as explained in section 2.3.

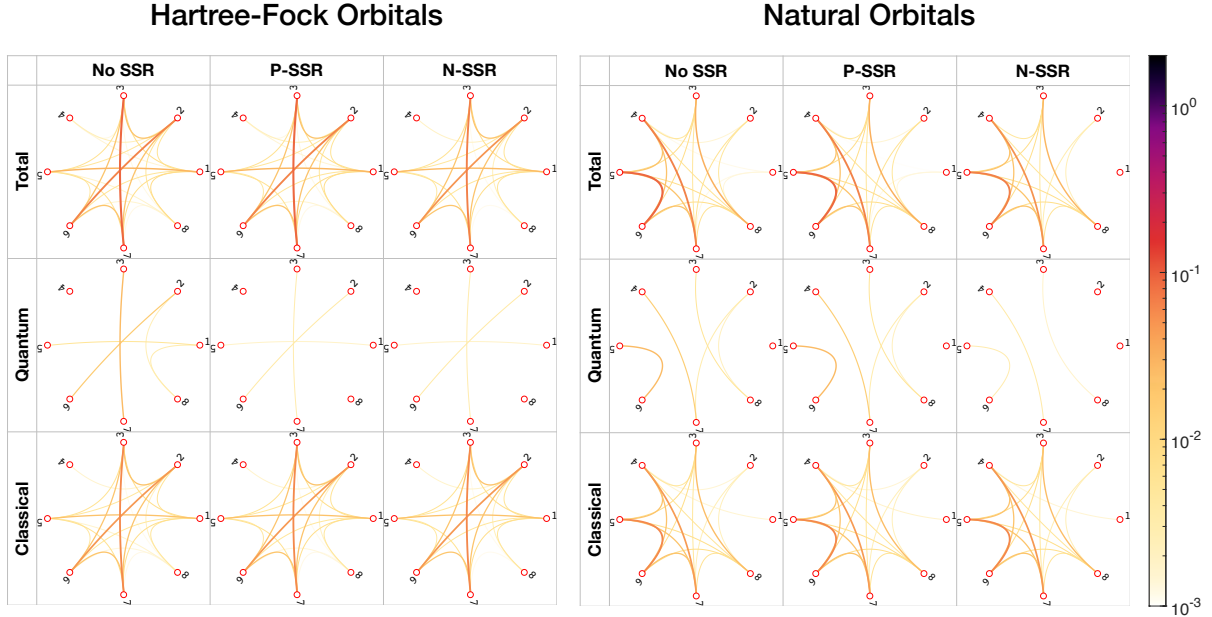3. Calculate the correlation and entanglement between the two orbitals using (31).

Fig. 8: *Total correlation, entanglement ("Quantum") and classical correlation between any two Hartree-Fock (left) and natural (right) orbitals in the ground state of H_2O for the case with no, P- and N-SSR.*

It is worth recalling that the two-orbital reduced density matrices $\rho_{i,j}$ are typically highly mixed, which is due to the coupling between different Hartree-Fock orbitals in the Hamiltonian (48). The total correlation for a mixed state, measured by the distance to the closest uncorrelated state (13), can always be calculated analytically, as it coincides with the quantum mutual information (13). However, the entanglement quantified as the distance to the closest separable state (16) is immensely difficult to obtain by analytic means due to two reasons. One is the challenge imposed by the high dimensionality, even if we are interested in the entanglement between just two orbitals. The respective total system in that case has a Hilbert space isomorphic to $\mathbb{C}^4 \otimes \mathbb{C}^4$ (see also figure 5). A generic density matrix is then described by $16 \times 16 - 1 = 255$ real-valued parameters. In order to find the closest separable state to a two-orbital state $\rho_{i,j}$, one already needs to navigate through 255 parameters. The second difficulty lies in the complexity of the boundary of the set of separable states $\mathcal{D}_{sep}$. So far exact criteria for separability known are only for Hilbert spaces with dimensions up to 2×3 [45, 46]. In some cases when the total state exhibits many symmetries, the closest separable state for the two-orbital reduced state can still be found analytically [42]. In general, however, one has no choice but to resort to a combination of analytic tools and numerical methods, which is here the case.

The quantities calculated are the total correlation, entanglement and classical correlation between two Hartree-Fock orbitals, for the case without SSR, with P-SSR and with N-SSR. All those nine quantities are calculate for all pairwise combinations of orbitals, for the ground states of all three molecules introduced in section 4.1. Since each ground state is a singlet with a fixed electron number, any two-orbital reduced state $\rho_{i,j}$ is also symmetric with respect to the total two-orbital spin, magnetization and particle number [42]. Using the symmetry argument [41],
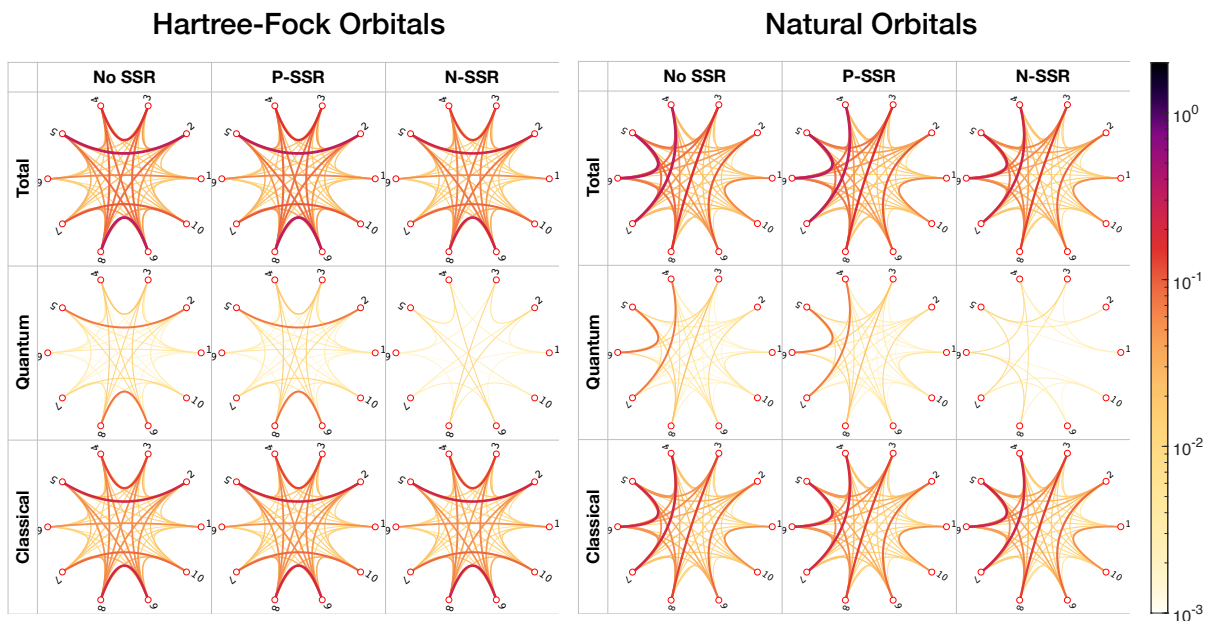
Fig. 9: *Total correlation, entanglement ("Quantum") and classical correlation between any two Hartree-Fock (left) and natural (right) orbitals in the ground state of $C_{10}H_8$ for the case with no, P- and N-SSR.*

the closest separable state $\sigma_{i,j}^*$ is block diagonal in the simultaneous eigenbasis of the respective two-orbital spin and particle number operators (as also illustrated in figure 5). In the case of N-SSR, the projections used for calculating the physical state further increase the symmetry of $\sigma_{i,j}^*$, which eventually allows us to determine it analytically [42]. For the case without SSR and with P-SSR, we developed an algorithm based on semidefinite programming to find the closest separable state and calculate the entanglement in an numerically exact way [42].

In figure 8, 9 and 10 we present the different types of correlation of the ground state of H_2O constructed with 8 orbitals, $C_{10}H_8$ with 10 orbitals and Cr_2 with 28 orbitals, respectively.

There are several important messages to get across. First of all, similar to the results for the single-orbital entanglement, the water molecule contains the weakest orbital-orbital correlation, and the chromium dimer the strongest. Most importantly, our comprehensive analysis then reveals that the quantum part of the total correlation plays only a minor role. In fact, the orbital-orbital entanglement is usually one order of magnitude smaller than the total correlation, and the molecular structure is thus dominated by classical correlation. This key result of the analysis emphasizes that the quantum mutual information (13) is not a suitable tool for quantifying orbital entanglement, as it leads to a gross overestimation. From a general point of view, our findings raise questions about the significance of entanglement in chemical bonding and quantum chemistry in general.

Similar to the single-orbital entanglement, SSRs also have a drastic effect on the orbital-orbital entanglement, yet in a qualitatively different way. In the molecular systems we considered, P-SSR preserved almost all of the orbital-orbital entanglement, whereas in the case of N-SSR, almost no orbital-orbital entanglement is left, and consequently almost all orbital-orbital corre-
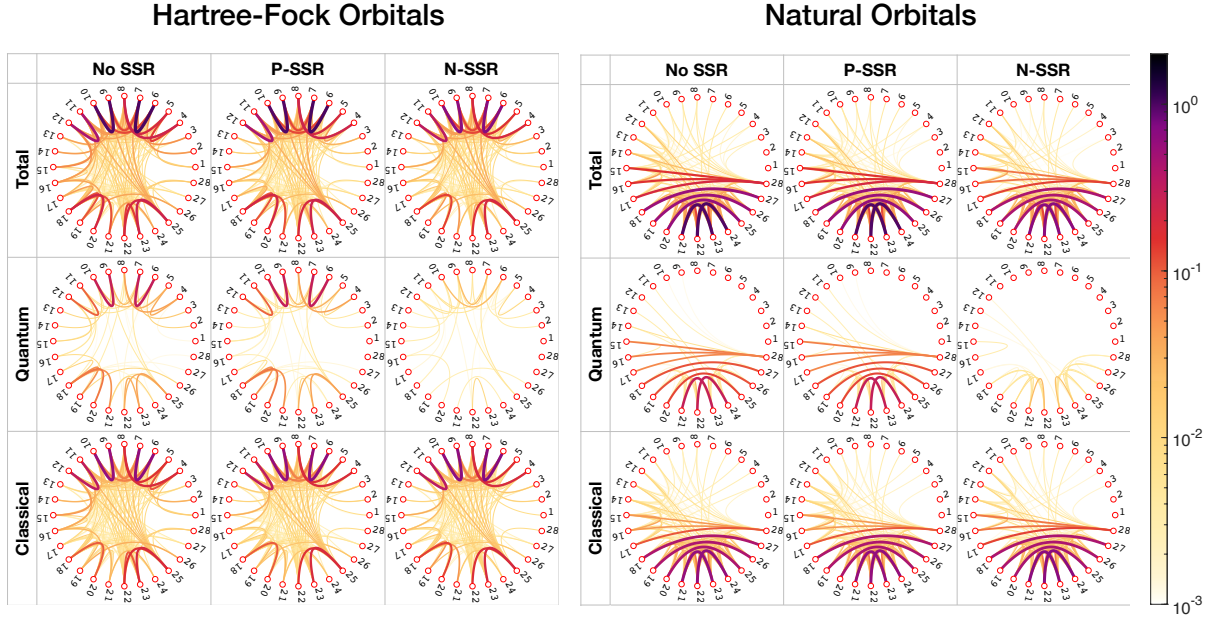
Fig. 10: *Total correlation, entanglement ("Quantum") and classical correlation between any two Hartree-Fock (left) and natural (right) orbitals in the ground state of Cr_2 for the case with no, P- and N-SSR.*

lation is classical. Furthermore, in some instances even the *entire* orbital-orbital entanglement is destroyed by the N-SSR. Referring to figure 5, this indicates that most of the contribution to orbital-orbital correlation and entanglement comes from superposing $f_{i\downarrow}^\dagger f_{i\uparrow}^\dagger |\Omega\rangle$ and $f_{j\downarrow}^\dagger f_{j\uparrow}^\dagger |\Omega\rangle$, which are marked as the dark grey blocks. These states describe either empty or doubly occupied orbitals. In fact, in all three molecules, single excitations are highly suppressed in any of the molecular orbitals we consider. This is qualitatively different to the analysis of a single bond in section 3.3 which was referring to *localized atomic* orbitals, each singly occupied. In agreement with valence bonding theory, this observation confirms that two-orbital correlation and entanglement are suitable tools for describing bonding orders only if they are applied to localized atomic orbitals.

Lastly we would like to compare the correlation patterns of the Hartree-Fock orbitals with those of the natural orbitals (see Figure 8, 9 and 10). To recap, the natural orbitals are the eigenstates of the orbital one-particle reduced matrix

$$\gamma_{i,j}^{(l)} \equiv \sum_{\sigma=\uparrow,\downarrow} \langle \Psi | f_{j\sigma}^\dagger f_{i\sigma} | \Psi \rangle . \tag{49}$$

The natural orbitals inherit the ordering of the natural orbital occupation numbers (eigenvalues of $\rho^{(l)}$) which are arranged decreasingly. Previous observations regarding the correlation patterns with respect to the Hartree-Fock orbitals is still present. Entanglement takes up only a small fraction of the total correlation, and the presence of SSRs drastically reduce the entanglement. In contrast to the more scrambled pattern of the Hartree-Fock orbitals, however, an additional pairing structure emerges among the natural orbitals. To be more precise, orbitals in the neighbourhood of the Fermi level are strongly correlated but they share this entanglement

only within pairs. After all, these pairs are symmetrical relative to the Fermi level. This suggests a potential simplified description of the ground state in the natural orbital basis. At the same time, the qualitative difference between the correlation patterns of the two sets of orbitals demonstrates again that correlation and entanglement are relative concepts.

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