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Sufficient Condition for the Openness of a Many-electron Quantum System from the Violation of a Generalized Pauli Exclusion Principle

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Information about the interaction of a many-electron quantum system with its environment, we show, is encoded within the one-electron density matrix (1-RDM). While the 1-RDM from an ensemble many-electron quantum system must obey the Pauli exclusion principle, the 1-RDM must obey additional constraints known as *generalized Pauli conditions* when it corresponds to a closed system describable by a single wave function. By examining the 1-RDM's violation of these generalized Pauli conditions, we obtain a sufficient condition at the level of a single electron for a many-electron quantum system's openness. In an application to exciton dynamics in photosynthetic light harvesting we show that the interaction of the system with the environment (quantum noise) relaxes significant constraints imposed on the exciton dynamics by the generalized Pauli conditions. This relaxation provides a geometric (kinematic) interpretation for the role of noise in enhancing exciton transport in quantum systems.

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The Pauli exclusion principle requires that the occupations of the orbitals lie between zero and one. These Pauli conditions hold for one-electron reduced density matrices (1-RDMs) from both open and closed quantum systems [1, 2]. More than 40 years ago, it was recognized that there are additional conditions on the 1-RDM for closed quantum systems [3, 4]. Recently, these additional constraints, known as *generalized Pauli conditions*, have been systematically derived for arbitrary numbers of electrons and orbitals [5, 6] and applied to closed, time-independent systems such as atoms and molecules [7–11].

In this Communication we use the violation of the generalized Pauli conditions to quantify the interaction of a quantum system with its environment. The violation, we show, provides a *sufficient condition for the openness of any many-electron quantum system that is computable from knowledge of only the 1-RDM*. In principle, the 1-RDM can be computed from experiment [12], computation [13–20], or any combination of experiment and computation. Here we demonstrate this condition through calculations of exciton dynamics in photosynthetic light harvesting. The results show that environmental noise relaxes significant constraints imposed on the exciton dynamics by a closed quantum system, providing a geometric interpretation for the role of noise in enhancing exciton transport. The sufficient condition, computable from only the 1-RDM, is potentially applicable to a wide variety of open many-electron quantum systems.

Integrating the N -electron density matrix over all electrons save one generates the one-electron reduced density matrix (1-RDM), which gives the probability of finding one electron for all possible configurations of the other $N - 1$ electrons [1]. The eigenfunctions of the 1-RDM are known as the natural orbitals ϕ_i , and its eigenvalues are known as the natural orbital occupation numbers

n_i [21]. The generalized Pauli conditions, also known as *pure N -representability conditions* can be written as linear inequalities on the ordered set of natural orbital occupation numbers n_i . For 3 electrons in 6 spin orbitals these conditions are

$$n_1 + n_6 = n_2 + n_5 = n_3 + n_4 = 1 \quad (1)$$

$$n_5 + n_6 - n_4 \geq 0, \quad (2)$$

where $n_i \geq n_{i+1}$ [3, 5]. The union of the inequalities (and equalities) forms a convex set (polytope). The occupation numbers n_i are ordered from highest to lowest because in the absence of ordering the occupation numbers form a non-convex set. Sets of orbital occupation numbers $\{n_i\}$ that lie either inside or on the boundary of the polytope are compatible with at least one closed (or pure) 3-electron quantum system, but sets of orbital occupation numbers $\{n_i\}$ that lie outside the polytope are only compatible with an open (or ensemble) 3-electron quantum system. Consequently, the violation of the above generalized Pauli conditions provides a sufficient, although not necessary condition, for the openness of a 3-electron quantum system.

Generalization of the above results to N electrons provides the solution to the *pure N -representability* problem of the 1-RDM [5]:

Theorem 1: For N electrons in r orbitals a diagonal, eigenvalue-ordered 1-RDM 1D , constrained to trace to N , is derivable from the integration of at least one *pure N -electron* density matrix (pure N -representable) if and if ${}^1D \in P_{(N,r)}^1$ where $P_{(N,r)}^1$ is the convex polytope whose facets are defined by Pauli and generalized Pauli conditions.

Proof: The proof is given by Klatchko in Ref. [5].

Similarly, the solution of the ensemble N -representability problem for the 1-RDM [2] can be summarized as follows:

Theorem 2: For N electrons in r orbitals a diagonal, eigenvalue-ordered 1-RDMs 1D , constrained to trace

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to N , is derivable from the integration of at least one *ensemble* N -electron density matrix (ensemble N -representable) if and if ${}^1D \in E_{(N,r)}^1$ where $E_{(N,r)}^1$ is the convex polytope whose facets are defined by Pauli conditions.

Proof: The proof is given by Coleman in Ref. [2].

We present a corollary to these two theorems for open N -electron quantum systems. Because the N -representability of an RDM is invariant to unitary transformations of the orbitals, this corollary can be applied to an arbitrary non-diagonal 1-RDM by its unitary transformation to a diagonal eigenvalue-order 1-RDM [2]:

Corollary: If ${}^1D \in E_{(N,r)}^1 \setminus P_{(N,r)}^1$, then the 1-RDM is only derivable by integration from an ensemble (open) N -electron density matrix.

Proof: The set inclusion ${}^1D \in E_{(N,r)}^1 \setminus P_{(N,r)}^1$ implies from Theorems 1 and 2 that the 1-RDM is ensemble N -representable but not pure N -representable.

To use the generalized Pauli conditions to quantify a quantum system's interaction with its environment, we introduce a Euclidean metric δ to compute the shortest distance of a given set of orbital occupation numbers to the boundary of the convex polytope of pure N -representable occupation numbers. Occupation numbers are pure N -representable if and only if they represent at least one pure N -electron quantum system. We will refer to δ as the *pure distance*. For a system of 3 electrons in 6 orbitals we compute the δ by solving the following constrained optimization by sequential quadratic programming [22]:

$$\delta(t) = \sigma \min_{\vec{p} \in \mathbb{R}^6} \|\vec{n} - \vec{p}\| \quad (3)$$

$$\text{such that } p_{i+1} \leq p_i \text{ for all } i, \quad (4)$$

$$\sum_i p_i = 3, \quad (5)$$

$$0 \leq p_i \leq 1 \text{ for all } i, \quad (6)$$

$$p_i + p_{7-i} = 1 \text{ for all } i, \quad (7)$$

$$p_4 - p_5 - p_6 = 0. \quad (8)$$

Eqs. (4) and (5) represent the ordering and trace conditions, respectively. Eq. (6) contains the Pauli exclusion principle for each of the occupation numbers. Finally, Eqs. (7) and (8) express the generalized Pauli conditions for a system of three electrons in six orbitals. \mathbb{R}^6 is the space of real vectors of length six. The symbol σ is chosen as either +1 or -1 to denote whether the distance to the boundary is from a set of occupation numbers *inside* the polytope or *outside* the polytope, respectively.

We demonstrate the use of the generalized Pauli conditions for open, time-dependent systems by applying them to exciton transport in photosynthetic light harvesting where environmental interactions play an important role [23–28]. In particular, we look at the three chromophore subsystem of the Fenna-Matthews-Olson (FMO) complex which has been shown to have a quantum efficiency similar to that of the full seven chromophore network [26]. Each chromophore is modeled

as a single electron with access to two states, ground and excited. We model the time evolution of the exciton density matrix of the N -electron system ${}^N D$ by the quantum Liouville equation

$$\frac{d}{dt} {}^N D = -\frac{i}{\hbar} [\hat{H}, {}^N D] + \hat{L} ({}^N D), \quad (9)$$

in which the Lindblad operator \hat{L} given in Ref. [26] accounts for environmental interactions including dephasing, dissipation, and transfer of the exciton to the sink. The site and coupling energies of the chromophores that define the effective Hamiltonian as well as the rate parameters for dissipation, dephasing and sink transfer are taken from previous work [23, 26–28].

At time $t = 0$ a photon excites the electron of chromophore 1 (or site 1), producing an exciton that travels the network, oscillating between sites 1 and 2, and eventually exits the FMO complex by entering the reaction center (sink). The nature of the Hamiltonian constrains the number of excitations in the system to one [23]. As seen in previous work [23–25], because chromophores 1 and 2 have similar energies, the exciton oscillates between these sites; furthermore, the coherences decay in time due to environmental effects with the excitation gradually exiting the system as it returns to its ground-state configuration.

The degree to which the system interacts with its environment can be examined from the idempotency of the N -electron (exciton) exciton density matrix:

$$\gamma(t) = \left[\text{Tr}({}^N D(t)) - \text{Tr}({}^N D(t)^2) \right]. \quad (10)$$

The $\gamma(t)$ is nonzero if and only if the quantum system is open. While $\gamma(t)$ provides a definitive answer to whether the system is open, it requires knowledge of the N -electron (exciton) density matrix. The N -electron density matrix can be readily computed for some model quantum systems, but its cost for many realistic quantum systems scales exponentially with system size.

Table 1 shows the 1-electron and N -electron indicators of environmental effects, the pure distance $\delta(t)$ and the idempotency criterion $\gamma(t)$, in the presence and the absence of environmental interactions. At $t = 0$, just after the first chromophore is excited, the three-chromophore network is in a pure (closed) state. In the absence of environmental effects the system remains inside the pure set for all time t . In fact, its spectrum of occupation numbers lies on the boundary of the set except when strong correlation due to degeneracy in the populations of sites 1 and 2 pushes the occupation spectrum inside the set. In the presence of environmental effects the system becomes open (ensemble) for $t > 0$ which is reflected in both the *nonzero* idempotency $\gamma(t)$ and the *negative* pure distance $\delta(t)$. At 500 fs, for example, the idempotency γ is positive with a value of 0.6603 and the pure distance δ is negative with a value of -0.1454. By 10 ps, when the N -electron density matrix begins to regain idempotency with γ decreasing to 0.0089, δ shows that the spectrum of

TABLE I. The 1-electron and N -electron indicators of environmental effects, the pure distance $\delta(t)$ and the idempotency criterion $\gamma(t)$, are shown in the presence and the absence of environmental interactions. In the presence of environmental effects the system becomes open (ensemble) for $t > 0$ which is reflected in both the *nonzero* idempotency $\gamma(t)$ and the *negative* pure distance $\delta(t)$.

Time (fs)	Idempotency criterion $\gamma(t)$		Pure distance $\delta(t)$	
	No Bath	Bath	No Bath	Bath
0	1×10^{-15}	0.0000	1×10^{-15}	0.0000
100	1×10^{-15}	0.3777	1×10^{-15}	-0.0231
200	1×10^{-15}	0.5408	1×10^{-15}	-0.0695
300	1×10^{-15}	0.6107	1×10^{-15}	-0.1139
400	1×10^{-15}	0.6405	1×10^{-15}	-0.1515
500	1×10^{-15}	0.6603	1×10^{-15}	-0.1454
1000	1×10^{-15}	0.6712	1×10^{-15}	-0.0072
10000	1×10^{-15}	0.0089	1×10^{-15}	0.0003

natural occupation numbers reenters the polytope of pure 1-RDMs with $\delta = 0.0003$. Importantly, δ can be positive for nonzero γ because the negative pure distance δ is a sufficient but not a necessary condition for openness.

Figure 1 compares the pure distance $\delta(t)$ as a time-dependent indicator of the openness of a quantum system for both closed (no bath) and open (with bath) quantum systems for times in the range 0-3 ps. In the closed system the pure distance is always nonnegative, and in the open system the pure distance is frequently negative. An important feature of Fig. 1 is that positive spikes in pure distance, representing the movement of occupation numbers inside the polytope, occur at times when the entanglement between sites 1 and 2 is maximal. This coincidence demonstrates the interplay between openness and entanglement [29, 30]. The openness of quantum systems (namely, its interaction with the environment) is typically evident in the occupation numbers of the 1-RDM, but when a quantum system is strongly entangled, the evidence of openness in the 1-RDM disappears. Higher RDMs are required in such cases to obtain a certificate for the openness of the system. Systems with greater entanglement between homogeneous components, previous results indicate, require greater environmental noise for maximal efficiency [31]. The present results indicate that in systems that are strongly correlated or entangled greater noise is required to force the 1-RDM to explore the larger set of occupation numbers associated with open quantum systems.

The system's trajectory in population space (the space of natural occupation numbers) provides a dynamical map of quantum information as it flows through the system, which can be analyzed for openness with the generalized Pauli conditions. In Fig. 2, we see the trajectory with femtosecond resolution for the duration of 10 ps for (a) closed and (b) open systems. Each axis represents the population in the excited states of one of the three chromophores (sites). Even though there are 6 occupation numbers, only three of them are unique since on each

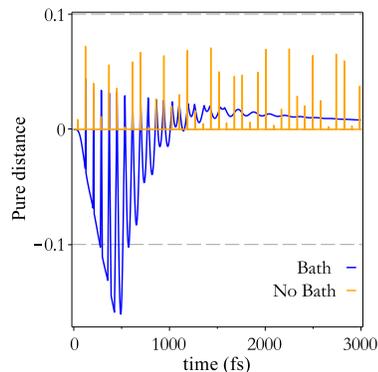


FIG. 1. (Color online) The pure distance $\delta(t)$ is compared for closed and open quantum systems for a time range of 0-3 ps. In the closed system the pure distance is always nonnegative, and in the open system the pure distance is frequently negative. An important feature is that positive spikes in pure distance, representing the movement of occupation numbers inside the polytope, coincide with the times when sites 1 and 2 are maximally entangled.

chromophore the occupation numbers of the orbital pairs are constrained by the exciton Hamiltonian to sum to one. The trajectory in time starts with the excitation at site 1, denoted in the figure by the big green (dark gray) sphere at the coordinate (1,0,0). Points along the trajectory are color coded in green (dark grey) and orange (light grey) to denote points that lie *inside* and *outside* of the polytope of pure occupation numbers, respectively. The closed system in (a) remains pure (closed) throughout its trajectory (note that all points on the trajectory are green); the exciton in (a) oscillates between sites 1 and 2, never reaching the reaction center. When environmental noise is added through dissipation, dephasing, and sink terms, we observe in (b) that the quantum system moves immediately from a closed 1-RDM (green or dark grey) to an open 1-RDM (orange or light grey).

The trajectory of occupation numbers provides a visual demonstration of how environmental noise facilitates the transport of the exciton to site 3 from which it can enter the sink. Environmental noise, it has been observed, can enhance exciton transport in a quantum system [23–25]. Typically, the enhancement is characterized by the dynamics of the quantum system. The pure and ensemble sets of the 1-RDM provide a kinematic, rather than a dynamic, interpretation of the enhancement. From the 1-RDM perspective we observe that the role of the noise is to increase the size of the set of 1-RDMs that is accessible to the quantum system. The enlargement of the set of 1-RDMs arises from the violation of the generalized Pauli conditions in the presence of environmental interactions. Importantly, the change in set size is kinematic, and yet it facilitates the dynamic transfer of exciton population through the system to the sink.

Understanding the degree to which a quantum system interacts with its environment is critical because this in-

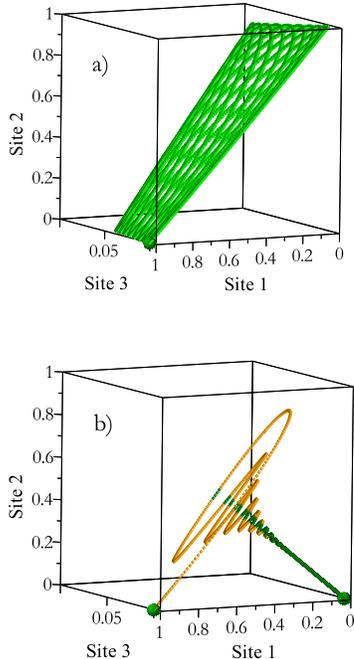


FIG. 2. (Color online) The system's trajectory in the exciton population space is shown for (a) closed and (b) open systems. Points along the trajectory are color coded in green (dark grey) and orange (light grey) to denote points that lie *inside* and *outside* of polytope of pure (closed) occupation numbers, respectively. While the closed system in (a) remains pure (closed) throughout its trajectory, the open system explores a larger space of occupation numbers than the closed system as it relaxes to its ground state.

teraction can significantly influence its energies and properties. The openness of a quantum system can be computed through its N -electron density matrix. Determination of the N -electron density matrix by either theory or experiment, however, is challenging and difficult because the matrix scales exponentially with the system size [1, 32]. In this Communication we have shown that the openness of a quantum system is encoded directly in the 1-RDM. Unlike the N -electron density matrix the 1-RDM scales as a polynomial in the number of electrons in the quantum system. While for an open system the occupation numbers of the 1-RDM are bounded by zero and one by the well-known Pauli exclusion principle [2, 33],

for a closed system the occupation numbers of the 1-RDM are bounded by a more stringent set of inequalities known as generalized Pauli conditions [3–5]. Importantly, these generalized conditions significantly restrict the physically realistic occupation numbers for closed quantum systems beyond the usual Pauli conditions. By studying their violation for an open quantum system, we are able to ascertain the openness of a quantum system from the 1-RDM alone. The generalized Pauli conditions become more numerous and complicated for $N > 3$, and further work is needed to make their application more practical. Although we use the Euclidean metric to define the distance to the boundary of $P_{(N,r)}^1$ [34], we could also employ other metrics such as the trace distance or the Bures metric, which is related to quantum fidelity [35].

The role of environmental interactions or quantum noise is to relax the generalized Pauli conditions, allowing the quantum system to explore a much larger set of trajectories in the natural-orbital occupation numbers. Traditionally, noise is viewed in terms of its effect on the dynamics of the system [23–26]. The present work, however, shows that there is also a fundamental kinematic interpretation in terms of the geometry of the 1-RDM sets [34]. As seen in the application to photosynthetic light harvesting, the noise expands the set of allowable 1-RDMs from its pure N -representable set to its ensemble N -representable set [1, 18], which significantly expands the set of trajectories in orbital occupations by which the exciton can move through the chromophore network and thereby allows the exciton to travel efficiently to the reaction center for its conversion to chemical energy. The sufficient condition encoded in the 1-RDM for an open quantum system provides physical insight through its orbital occupations into the ramifications of environment interactions and openness in quantum mechanics. Experimentally, it may be possible to apply generalized Pauli conditions to probe the system-bath interactions in a variety of physical and chemical systems. The present work represents a step towards a broader use of the 1-RDM and its occupation numbers in the study of the interaction of open quantum systems with their environments.

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