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# Communication: Satisfying fermionic statistics in the modeling of open time-dependent quantum systems with one-electron reduced density matrices

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For an open, time-dependent quantum system, Lindblad derived the most general modification of the quantum Liouville equation in the Markovian approximation that models environmental effects while preserving the non-negativity of the system's density matrix. While Lindblad's modification is correct for $N$-electron density matrices, solution of the Liouville equation with a Lindblad operator causes the one-electron reduced density matrix (1-RDM) to violate the Pauli exclusion principle. Consequently, after a short time, the 1-RDM is not representable by an ensemble $N$-electron density matrix (not ensemble $N$-representable). In this communication, we derive the necessary and sufficient constraints on the Lindbladian matrix within the Lindblad operator to ensure that the 1-RDM remains $N$-representable for all time. The theory is illustrated by considering the relaxation of an excitation in several molecules $F_2$, $N_2$, CO, and $BeH_2$ subject to environmental noise. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4906942]

## I. INTRODUCTION

Open time-dependent quantum systems are important to understanding a range of chemical phenomena from molecules in solvent or protein environments to materials embedded in a larger-scale structure.[1–3] The influence of the environment on a system's energy can be as significant or even more significant than the influence of electron correlation. The evolution of the closed quantum system is governed by the quantum Liouville equation, also known as the von Neumann equation.[4,5] For an open quantum system, Lindblad derived the most general modification of the quantum Liouville equation in the Markovian approximation that models environmental effects while preserving the non-negativity of the probability distribution (or more specifically, the positive semidefiniteness of the system's density matrix).[6–9]

While Lindblad's operator is correct for $N$-electron density matrices, the operator has been observed to cause significant violation of the Pauli exclusion principle in the time evolution of the 1-electron reduced density matrix (1-RDM).[10] As discussed in Refs. 10–12, the preservation of the fermionic statistics of the 1-RDM in an open, time-dependent system, even with an interaction-free Hamiltonian, is a non-trivial problem. Despite previous difficulties, the generalization of the Lindblad operator to preserve fermionic statistics is critical to the accurate treatment of environmental effects in the time evolution of effective one-electron theories such as the time-dependent Hartree-Fock and density functional theories. Constraining the 1-RDM to obey the Pauli exclusion principle, which requires the eigenvalues of the 1-RDM to lie between 0 and 1, is equivalent to constraining the 1-RDM to be *ensemble $N$-representable*, that is, representable by at least one ensemble $N$-electron density matrix.[13,14] In this communication, we derive the necessary and sufficient constraints on the Lindbladian matrix within the Lindblad operator to ensure that the 1-RDM remains ensemble $N$-representable throughout its time evolution, which is equivalent to its obeying the Pauli exclusion principle for all time. The theory is illustrated by considering the relaxation of an excitation in several molecules, $F_2$, $N_2$, CO, and $BeH_2$, subject to environmental noise.

## II. THEORY

### A. Fermion conditions on Lindbladian matrices

An open, time-dependent quantum system of $N$-electrons can be described by the time dependent $N$-electron density matrix $D$ governed by the quantum Liouville equation[4]

$$\frac{dD}{dt} = -i[H,D] + L(D,C) \tag{1}$$

with a Lindblad term $L(D,C)$ added to account for the interaction of the $N$-electron system with its environment[6]

$$L(D,C) = CDC^{\dagger} - \frac{1}{2}\{C^{\dagger}C,D\}. \tag{2}$$

Importantly, the Lindblad term treats the interaction of the system with the environment while keeping the $N$-electron density matrix positive semidefinite at each time, that is,

$$D \geq 0. \tag{3}$$

A matrix is *positive semidefinite* if and only if all of its eigenvalues are non-negative. Collectively, this semidefinite constraint on the matrix and additional constraints that the matrix be (i) Hermitian, (ii) normalized, and (iii) antisymmetric

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[a)] Electronic mail: damazz@uchicago.edu in the exchange of its particles ensure that it is an $N$-particle density matrix with fermion statistics.[13]

Although the above formalism is exact, it is often computationally expensive to propagate the $N$-electron density matrix as a function of time with the Liouville equation. One mean-field-like approximation is to replace (i) the $N$-electron Hamiltonian with its explicit two-body electron-electron interactions by an interaction-free Hamiltonian and (ii) the $N$-electron density matrix with its explicit treatment of electron correlation by a 1-RDM. The simplest derivation of this approximation is to generalize the one-electron Liouville equation

$$\frac{d\,{}^1D}{dt} = -i[{}^1H,{}^1D] + L({}^1D,{}^1C), \tag{4}$$

where ${}^1D$ is the 1-RDM, ${}^1H$ is the one-body interaction-free Hamiltonian, and ${}^1C$ is the one-body Lindblad matrix. If we set $\mathrm{Tr}({}^1D) = N$, then Eq. (4) can describe not only a one-electron system when $N = 1$ but also an ensemble of $N$ non-interacting one-electron systems when $N > 1$. As in the $N$-electron case, the structure of the Lindblad term in Eq. (2) ensures that the 1-RDM remains positive semidefinite for all time.

Unlike the $N$-electron density matrix, however, the 1-RDM has additional constraints to ensure that it represents an ensemble $N$-electron density matrix, known as *$N$-representability conditions*.[13,15] In addition to the non-negativity of the 1-RDM, it is also necessary for the one-hole RDM ${}^1Q$ to be positive semidefinite. Therefore, in addition to being (i) Hermitian and (ii) normalized to $N$, the 1-RDM must also satisfy two linear matrix inequalities

$${}^1D \geq 0, \tag{5}$$

$${}^1Q \geq 0. \tag{6}$$

Coleman showed that these conditions on the 1-RDM are necessary and sufficient ensemble $N$-representability conditions.[13] Furthermore, they are equivalent to the well-known Pauli principle that the occupation numbers of the 1-RDM must lie between zero and one.

While the Lindblad term by construction is known to keep the 1-RDM positive semidefinite for all time,[6–9] it is necessary to explore the effect of the Lindblad term on the requisite positive semidefiniteness of the one-hole RDM. To address this question, we substitute the expression for the one-particle RDM in terms of the one-hole RDM

$${}^1D = {}^1I - {}^1Q \tag{7}$$

into the Liouville equation with the Lindblad term in Eq. (4). Because the one-particle identity matrix ${}^1I$ is time-independent and commutes with the Hamiltonian, the non-dissipative portion of Eq. (4) simplifies forthwith, and we obtain

$$\frac{d\,{}^1Q}{dt} = -i[{}^1H,{}^1Q] - L({}^1I - {}^1Q, C). \tag{8}$$

Now, we consider the Lindblad term as a functional of ${}^1I - {}^1Q$,

$$L({}^1I - {}^1Q,{}^1C) = -L({}^1Q,{}^1C) + [{}^1C,{}^1C^\dagger]. \tag{9}$$

From Eq. (9), it can be seen that to obtain an equation analogous to Eq. (4) for the one-hole RDM, an added restriction must be imposed on the Lindbladian matrix ${}^1C$. Specifically, for the 1-hole RDM to evolve according to the Liouville equation with a Lindblad operator, it is necessary and sufficient that the second term in Eq. (4) vanishes. If $[{}^1C,{}^1C^\dagger] = 0$, then Liouville equation for the one-hole RDM can be expressed as

$$\frac{d\,{}^1Q}{dt} = -i[{}^1H,{}^1Q] + L({}^1Q,{}^1C), \tag{10}$$

which is the hole analogue of Eq. (4). Just as in the case of the 1-electron RDM, this equation keeps the one-hole RDM positive semidefinite for all time. We have proven that the time evolution of the one-particle RDM by Eq. (4) keeps both the one-particle RDM and the one-hole RDM positive semidefinite for all time under the condition that the Lindbladian matrix ${}^1C$ commutes with its adjoint. Therefore, *constraining the Lindbladian matrix ${}^1C$ such as its commutator with its adjoint vanishes causes the 1-fermion RDM solution of the quantum Liouville equation to satisfy the Pauli exclusion principle for all time* (that is, remain $N$-representable for all time). For the commutator to vanish, the ${}^1C$ matrix can be constrained to be Hermitian $S$, anti-Hermitian $A$, or a sum of Hermitian and anti-Hermitian matrices $S + A$, where $SA = 0$. This restricted class of ${}^1C$ includes the generators of Gaussian semigroups.

### B. Fermion conditions on multiple Lindbladian matrices

Considering the case where there are numerous dissipation channels represented by multiple Lindbladian matrices, we can use Eq. (4) as a starting point to generalize the theory of Sec. II A. Taking the summation of the Lindblad terms over $m$ channels yields

$$\frac{d\,{}^1D}{dt} = -i[{}^1H,{}^1D] + \sum_{i=1}^{m} L({}^1D,{}^1C_i). \tag{11}$$

By the same method as previously presented, an analogous equation can be derived for the 1-hole RDM

$$\frac{d\,{}^1Q}{dt} = -i[{}^1H,{}^1Q] + \sum_{i=1}^{m} L({}^1Q,{}^1C_i). \tag{12}$$

Once again, to have Eq. (12) hold true to preserve the fermionic character of the system, each Lindbladian matrix ${}^1C_i$ must satisfy

$$[{}^1C_i,{}^1C_i^\dagger] = 0. \tag{13}$$

Constraining each of the Lindbladian matrices ${}^1C_i$ to be either Hermitian or anti-Hermitian is sufficient for the 1-fermion RDM solution of the quantum Liouville equation to satisfy the Pauli exclusion principle and remain $N$-representable for all time.

A specific, physically important example of Lindbladian matrices that satisfy the above requirement is the case where each Lindbladian matrix ${}^1C_i$ is a rank-one projection matrix

$${}^1C_i = \gamma_i v_i v_i^\dagger. \tag{14}$$

If $m$ is chosen to equal the number $r$ of one-electron orbitals and each $v_i$ is a vector representing the $i$th orbital, then

TABLE I. The first 8 occupation numbers of $F_2$, $N_2$, and CO are presented at 0.0 fs where they have their time-independent Hartree-Fock values and at 2.0 fs after evolution of the Liouville equation in the presence of environmental noise. When the Lindbladian matrix ${}^1C$ is selected to be Hermitian, the occupation numbers remain between 0 and 1 including those not shown. In contrast, when the Lindbladian matrix ${}^1C$ is selected to be non-Hermitian, the highest occupation numbers increase in value to violate the Pauli exclusion principle dramatically by 2 fs.

| | $F_2$ | | | $N_2$ | | | CO | | |
|---|---|---|---|---|---|---|---|---|---|
| | | t = 2.0 fs | | | t = 2.0 fs | | | t = 2.0 fs | |
| Occupation number | t = 0 | ${}^1C={}^1C^\dagger$ | ${}^1C\neq{}^1C^\dagger$ | t = 0 | ${}^1C={}^1C^\dagger$ | ${}^1C\neq{}^1C^\dagger$ | t = 0 | ${}^1C={}^1C^\dagger$ | ${}^1C\neq{}^1C^\dagger$ |
| 1 | 1 | 0.9934 | 3.6364 | 1 | 0.8654 | 5.4281 | 1 | 0.8655 | 3.1680 |
| 2 | 1 | 0.9235 | 3.6364 | 1 | 0.7666 | 5.4281 | 1 | 0.7677 | 3.1680 |
| 3 | 1 | 0.9234 | 2.3821 | 1 | 0.7620 | 0.7771 | 1 | 0.7637 | 1.6463 |
| 4 | 1 | 0.9211 | 2.3821 | 1 | 0.7584 | 0.7771 | 1 | 0.7601 | 1.6463 |
| 5 | 1 | 0.9202 | 1.6387 | 1 | 0.7539 | 0.3329 | 1 | 0.7586 | 1.2508 |
| 6 | 1 | 0.9138 | 1.6387 | 1 | 0.7499 | 0.3329 | 1 | 0.7566 | 1.2508 |
| 7 | 1 | 0.9113 | 0.5483 | 1 | 0.7466 | 0.1778 | 1 | 0.7519 | 0.4827 |
| 8 | 1 | 0.9105 | 0.5483 | 1 | 0.7196 | 0.1778 | 1 | 0.7218 | 0.4827 |

each ${}^1C_i$ represents the interaction of the *i*th orbital of the system with the environment with $\gamma_i$ controlling the degree of the interaction. If we further restrict the number $m$ of channels to the $N$ occupied orbitals, then we recover the form of the Lindbladian matrix presented by Pershin *et al.*[10] The present work shows that the rank-one Lindbladian matrices in Ref. 10 are a special case of the more general arbitrary-rank Hermitian Lindbladian matrices that preserve the fermionic statistics of the 1-RDM for all time. Even within the rank-one approximation, generalizing the number of Lindbladian channels from the $N$ occupied orbitals to the $r$ occupied and unoccupied (virtual) orbitals provides additional flexibility for modeling the interaction of the system with the environment that maintains particle-hole symmetry.[20,21]

## III. APPLICATIONS

To illustrate, we consider the time evolution of 4 molecules $N_2$, CO, $F_2$, and $BeH_2$ initialized to their first excited states. For each molecule, the effective one-electron Hamiltonian is constructed at the Hartree-Fock level of theory. Hartree-Fock calculations were performed in the Dunning-Hay double-zeta basis set[16] with the quantum chemistry package GAMESS.[17] For each molecule, the time evolution was performed with both a Hermitian ${}^1C$ matrix and a non-Hermitian ${}^1C$ matrix. The elements of the ${}^1C$ matrix were generated with the random number generator in the computer algebra system Maple.[18] The time propagation of the 1-RDM was performed by solving the Liouville equation with a fourth-fifth order Runge-Kutta method for solving initial-value differential equations.[19]

Table I presents the first 8 occupation numbers of $F_2$, $N_2$, and CO at 0.0 fs as well as at 2.0 fs. At 0.0 fs, the occupation numbers are those from solving the time-independent Hartree-Fock approximation to the Schrödinger equation. When the Lindbladian matrix ${}^1C$ is selected to be Hermitian, the interaction of each electronic system with an environment causes the occupations to change from 1 and 0 for the occupied and unoccupied orbitals, respectively, to values between 0 and 1 at 2 fs. In contrast, when the Lindbladian matrix ${}^1C$ is selected to be non-Hermitian, the highest occupation numbers increase in value to violate the Pauli exclusion principle dramatically by 2 fs.

Figure 1 shows the twelve occupation numbers of $BeH_2$ as functions of time using (a) a Hermitian and (b) a non-Hermitian Lindbladian matrix ${}^1C$. With a Hermitian matrix

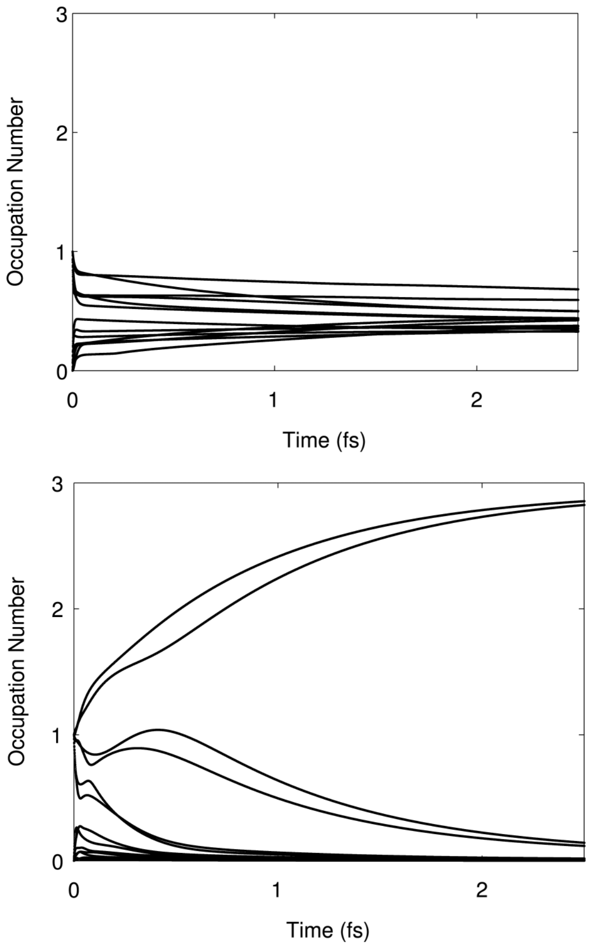

FIG. 1. The twelve occupation numbers of $BeH_2$ are shown as functions of time using (a) a Hermitian and (b) a non-Hermitian Lindbladian matrix ${}^1C$. With a Hermitian matrix ${}^1C$, the occupation numbers lie between 0 and 1 in accordance with the Pauli exclusion principle, but with a non-Hermitian ${}^1C$ matrix, the occupation numbers dramatically exceed 1 as the electrons in $BeH_2$ assume bosonic character.

$^1C$, the occupation numbers lie between 0 and 1 in accordance with the Pauli exclusion principle, but with a non-Hermitian $^1C$ matrix, the occupation numbers dramatically exceed 1 as the electrons in $BeH_2$ assume bosonic character. The non-Hermitian matrix $^1C$ has the ability to convert a system obeying fermionic statistics to a system obeying only bosonic statistics.

## IV. DISCUSSION AND CONCLUSIONS

Addition of the Lindblad operator to the quantum Liouville equation provides the most general time evolution within the Markovian approximation that preserves the non-negativity of the $N$-electron density matrix.[6–8] The most common use of the quantum Liouville equation in many-electron quantum systems, however, is to evolve a RDM such as the one-electron RDM according to an effective one-electron Hamiltonian. In this case, Lindblad's derivation is not complete because additional constraints, known as $N$-representability conditions, are necessary to ensure that a RDM represents at least one ensemble $N$-electron system.[13–15] The breakdown of fermionic statistics (in other words, the violation of the Pauli exclusion principle) has been observed in Ref. 10 for the time evolution of the 1-RDM subject to the Lindblad operator. A generalization of the Lindblad operator to preserve fermion statistics is necessary for treating environmental effects such as noise and dissipation in the time evolution of effective one-electron theories (i.e., in the time-dependent Hartree-Fock and density functional theories).

In this communication, a general constraint on the Lindblad operator was derived to ensure that the 1-RDM generated by the quantum Liouville equation satisfies the Pauli exclusion principle for all time. Specifically, we showed that if the Lindbladian matrix is constrained to commute with its adjoint, then the 1-RDM satisfies the Pauli exclusion principle at all times, meaning that during the time evolution, its eigenvalues always lie in the interval [0,1]. We formally derived this result by showing that if the Lindbladian matrix commutes with its adjoint, then the Lindblad operator preserves the non-negativity of both the one-particle RDM $^1D$ and the one-hole RDM $^1Q$, that is, $^1D \geq 0$ and $^1Q \geq 0$, which imply the Pauli exclusion principle. We also generalized the results to the addition of multiple Lindblad operators to the quantum Liouville equation. In that case, it is necessary to constrain each Lindbladian matrix to commute with its adjoint. A sufficient condition for the dynamics to obey fermionic statistics is to constrain the Lindbladian matrix to be either Hermitian or anti-Hermitian.

The present generalization of Lindblad operator provides a general framework for incorporating environmental effects, especially dephasing and dissipation, into the time evolution of 1-RDMs within effective one-electron theories. Our generalization reduces to Pershin *et al.*'s earlier work,[10] if we introduce a rank-one Lindbladian matrix for controlling the interaction of each occupied orbital with the environment. Within a rank-one model of the Lindbladian matrices, we recommend including bath channels for both the occupied and unoccupied orbitals as a more realistic approximation that obeys particle-hole symmetry.[20,21] $N$-representable approximations to the Lindblad operator may be especially important within the framework of time-dependent density functional theories that incorporate environmental noise.

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