Spin density matrix of a two-electron system. I. General theory and exact master equations

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We consider a scenario where interacting electrons confined in quantum dots (QDs) are either too close to be resolved, or we do not wish to apply measurements that resolve them. Then, the physical observable is an electron spin only and the system state is fully described by the spin density matrix. Accounting for the spatial degrees of freedom, we examine to what extent a Hamiltonian description of the spin-only degrees of freedom is valid. We show that as long as there is no coupling between singlet and triplet states, this is indeed the case, but when there is such a coupling, there are open systems effects, i.e., the dynamics is nonunitary even without interaction with a true bath. Our primary focus is an investigation of nonunitary effects, based on exact master equations we derive for the spin density matrix in the Lindblad and time-convolutionless forms, and the implications for quantum computation. In particular, we demonstrate that the Heisenberg interaction does not affect the unitary part (apart from a Lamb shift) but does affect the nonunitary contributions to the time evolution of the spin density matrix. In a sequel paper, we present a detailed analysis of an example system of two quantum dots, including spin-orbit effects.

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I. INTRODUCTION

In many quantum computation proposals, the spin of a localized particle, e.g., an electron or nuclear spin, is a natural carrier of quantum information—a qubit—which can be effectively protected and/or processed to achieve a computational task. The ability to govern the spin state via controllable interactions is a key ingredient underlying several proposed scalable quantum computer architectures in semiconductor nanostructures where the spin of an electron localized in a quantum dot (QD) or by a donor atom serves as a single qubit.[1–11] It is a typical assumption that a single electron is trapped in each individual QD and an electron spin can unambiguously be assigned to a QD. Using the spin degree of freedom of electrons trapped in QDs (rather than their charge) for information processing is of special interest since spins have comparatively long coherence times in semiconductor nanostructures.[12–15]

In this work, we revisit a rather fundamental issue. In essence, we ask: "what is a spin?" To clarify this question (which is not meant in the sense of the relativistic origin of spin, as our work is essentially nonrelativistic but includes relativistic corrections such as spin-orbit interaction), we distinguish between the notion of a *pure spin* and a *pseudospin*.

Let us start with pseudospins, a notion which applies to the majority of studies utilizing spins for quantum information processing. In order to ascribe a spin to a local site, such as a QD, one defines the electron spin operator as a bilinear combination of electron annihilation and creation Fermi operators, c_{As} and $c_{As}^{\dagger}$, in a localized orbital ϕ_A (s is a spin index and A is the QD index),

$$s_A^{\alpha} = \frac{1}{2} \sum_{ss'=1}^{2} c_{As}^{\dagger} (\sigma_{\alpha})_{ss'} c_{As'}, \quad \alpha = x,y,z \tag{1}$$

(see, e.g., Appendix A in Ref. 16). Then, the operators $\{s_A^{\alpha}\}_{\alpha}$ obey the usual su(2) commutation rules. Equation (1) implies implicit dependence of the spin operators on coordinate degrees of freedom and allows one to ascribe a spin to a QD. We call a spin defined by Eq. (1) a pseudospin, meaning that it carries some coordinate dependence. It is important to note that the Heisenberg exchange interaction arises only between pseudospins. This is a consequence of the coordinate dependence of pseudospins. Indeed, the Heisenberg exchange interaction constant J_H is electrostatic in nature, i.e., it derives from the Coulomb interaction.[16]

As opposed to a pseudospin, we define a pure spin as a spin that does not have any coordinate dependence. This is the usual definition of a spin operator via the Pauli matrices $\vec{\sigma}=(\sigma_x,\sigma_y,\sigma_z)$,[17] which do not depend on coordinates. Considering the spin degrees of freedom as carriers of quantum information, the spatial degrees of freedom must, in principle, be irrelevant for the storage of quantum information. From the quantum information point of view, it does not matter in what orbital state an electron is if one neglects possibly small spin-orbit interaction effects. Although it is not possible, physically, to divide the system into purely spin and spatial parts [as the "spin" physics is embedded in space], we would like, in a succinct description of spin dynamics, to eliminate irrelevant information. However, rather than ignoring the coordinate dependence, we follow the standard procedure of open quantum systems[18] and trace over the coordinates, leaving us with a *spin density matrix* as the primary object of investigation. Our motivation for investigating such a pure-spin model is a scenario where interacting and confined electrons either are too close to be resolved, or one does not wish to apply measurements that resolve them. Then, the physical observable is an electron spin only (one cannot unambiguously ascribe a spin to a site such as a QD) and the system state is fully described by the spin density matrix.

For simplicity of analysis, we consider a prototype system of two interacting electrons trapped in two sites A and B and

separated by the distance r_{AB}. One of our first findings is that the Heisenberg interaction, except for the Lamb energy shift, leaves the unitary part of the pure-spin dynamics invariant. This means that the pure-spin setting is inappropriate for any of the multitude of approaches to quantum computation and decoherence control which rely on enacting quantum logic gates via control of (sometimes only) Heisenberg interactions.[1–11,19–40] In these cases, one must be able to *resolve spins*, as in the pseudospin setting. After developing the appropriate formalism, we turn to a comparison of pure and pseudospin dynamics, in particular, spin-orbit effects.

In the case of pure spins, we are particularly interested in finding the conditions under which their dynamics is unitary (effectively closed system) or nonunitary (open system). We show that as long as there is no coupling between singlet and triplet states, the dynamics is unitary (i.e., a Hamiltonian description of the spin-only degrees of freedom is valid), but with the singlet-triplet state coupling, there are open systems effects, i.e., the dynamics is nonunitary already due to the orbital degrees of freedom, even without coupling to a true bath. To exhibit these effects, we derive several master equations for the spin density matrix and analyze their implications for quantum computation. Our central results are contained in Eqs. (49) and (94). Equation (49) is a Lindblad-like master equation for the pure-spin dynamics, which clearly exhibits the nonunitary nature of this dynamics (it does not, however, invoke a Markovian approximation). Equation (94) does the same within the time-convolutionless approach.

This paper is the first in a series of two. In this paper (Part I), we develop a variety of general models for pure-spin open system dynamics. Specifically, in Sec. II, the operator sum representation for the spin density matrix is derived, while the Lindblad-type and time-convolutionless (TCL) master equations are considered, respectively, in Secs. III and IV. We conclude Part I with a discussion in Sec. V.

In Part II,[41] we highlight the differences and relationship between pseudospin and pure-spin models and provide a concrete illustration in terms of a system of two quantum dots trapping one electron each. In particular, we present calculation results demonstrating non-unitary effects in the pure-spin model due to both external magnetic field inhomogeneity and spin-orbit interaction.

Atomic units, $\hbar=e=m_e=1$, $1/c\simeq 1/137$, are used throughout the paper unless otherwise stated.

II. OPERATOR-SUM REPRESENTATION

A. Hamiltonian

The total two-electron system Hamiltonian has the generic form

$$\hat{H}=\hat{h}_1+\hat{h}_2+w_{12}. \tag{2}$$

Here, $\hat{h}_i$, $i=1,2$ is a one-electron Pauli Hamiltonian which includes spin-dependent terms,

$$\hat{h}_i=\frac{1}{2m^*}\left(\vec{p}_i+\frac{1}{c}\vec{A}(\vec{r}_i,t)\right)^2+V_{\mathrm{Tr}}(\vec{r}_i,t)+\vec{B}(\vec{r}_i,t)\cdot\vec{s}_i, \tag{3}$$

where m^* is the effective electron mass in the medium, $(\vec{r}_i,\vec{p}_i)$ are the electrons' position and momentum operators, $\vec{A}(\vec{r}_i,t)$ and $V_{\mathrm{Tr}}(\vec{r}_i,t)$ are, respectively, the vector potential and the trapping potential, which has two minima at sites $\vec{r}_A$ and $\vec{r}_B$ where the electrons are localized. The magnetic fields

$$\vec{B}(\vec{r}_i,t)=\vec{B}_{\mathrm{ex}}(\vec{r}_i,t)+\vec{B}_{\mathrm{so}}(\vec{r}_i,\vec{p}_i,t) \tag{4}$$

are due to the external (possibly spatially inhomogeneous) magnetic field $\vec{B}_{\mathrm{ex}}$ and the spin-orbit interaction field $\vec{B}_{\mathrm{so}}$ which can usually considered to be a small perturbation; $\vec{s}_i=\frac{1}{2}\vec{\sigma}_i$ is the spin vector of Pauli matrices (here, we included the gyromagnetic factor g_e and Bohr magneton μ_B in the definition of the magnetic fields so that magnetic fields are measured in energy units). The two-electron interaction term

$$w_{12}=V_{\mathrm{ee}}(r_{12})+V_{\mathrm{dip}}(\vec{s}_1,\vec{s}_2,\vec{r}_{12}) \tag{5}$$

consists of the interelectron electrostatic interaction potential $V_{\mathrm{ee}}(r_{12})=1/(\varepsilon r_{12})$, where ε is the dielectric constant of the medium, with $\varepsilon=1$ in vacuum, and the spin-spin magnetic dipole interaction,[42]

$$V_{\mathrm{dip}}=1.45\ \mathrm{meV}\left(\frac{\vec{s}_1\cdot\vec{s}_2 r_{12}^2-3(\vec{s}_1\cdot\vec{r}_{12})(\vec{s}_2\cdot\vec{r}_{12})}{r_{12}^5}-\frac{8\pi}{3}\vec{s}_1\cdot\vec{s}_2\delta(\vec{r}_{12})\right), \tag{6}$$

which contains a term inversely proportional to the cube of interelectron distance r_{12}, and the contact term proportional to the δ function [coordinates and spins in Eq. (6) are measured in a.u.).

B. Basis states

If the system described by the Hamiltonian [Eq. (2)] can be considered as a closed system that does not interact with its environment, then dynamics of the state Ψ_{tot} is governed fully by the corresponding Schrödinger equation. The state $\Psi_{\mathrm{tot}}(\vec{r},\sigma,t)$ depends both on the electrons' spatial coordinates $\vec{r}\equiv(\vec{r}_1,\vec{r}_2)$ and the spin variables $\sigma\equiv(\sigma_1,\sigma_2)$. Within the ground-state approximation, which consists of neglecting excited states, we assume that an electron can be trapped in two ground "molecular-type" orbital states ϕ_A and ϕ_B with energies ε_A and ε_B, respectively; ϕ_A and ϕ_B are orthonormal states obtained in the same trapping potential: $\hat{h}_c\phi_{A,B}=\varepsilon_{A,B}\phi_{A,B}$, where $\hat{h}_c$ is the coordinate part of Eq. (3). Here, our notation $\phi_{A,B}$ indicates that the state is assumed to be predominantly localized near the site $\vec{r}_{A,B}$. We do not assume *a priori* any symmetry of the trapping potential. With two up and down spin states $\chi_{\uparrow,\downarrow}(\sigma)$ $\left(s_z\chi_{\uparrow,\downarrow}=\pm\frac{1}{2}\chi_{\uparrow,\downarrow}\right)$, the one-electron basis comprises four states: $\phi_A(\vec{r}_i)\chi_{\uparrow,\downarrow}(\sigma_i)$ and $\phi_B(\vec{r}_i)\chi_{\uparrow,\downarrow}(\sigma_i)$. The corresponding two-electron basis set is defined by Slater determinants.[17]

The singlet subspace,

$$\Phi_{si}=f_{si}(\vec{r})\chi_s(\sigma),\quad i=1,2,3, \tag{7}$$

where two-electron symmetric orbitals,

$$f_{s1}(\vec{r}) = \frac{1}{\sqrt{2}}[\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) + \phi_A(\vec{r}_2)\phi_B(\vec{r}_1)],$$

$$f_{s2}(\vec{r}) = \phi_A(\vec{r}_1)\phi_A(\vec{r}_2), \quad f_{s3}(\vec{r}) = \phi_B(\vec{r}_1)\phi_B(\vec{r}_2),$$

represent the states of single and double occupancies, respectively, and the antisymmetric singlet spin function,

$$\chi_s = \frac{1}{\sqrt{2}}[\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) - \chi_\uparrow(\sigma_2)\chi_\downarrow(\sigma_1)],$$

describes the spin state with total spin $S=0$ and magnetic spin projection number $M_S=0$.

The triplet subspace,

$$\Phi_{ti} = f_t(\vec{r})\chi_{ti}(\sigma), \quad i = 1,2,3, \tag{8}$$

where a two-electron antisymmetric orbital,

$$f_t(\vec{r}) = \frac{1}{\sqrt{2}}[\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) - \phi_A(\vec{r}_2)\phi_B(\vec{r}_1)],$$

and the triplet symmetric spin states,

$$\chi_{t1} = \chi_\uparrow(\sigma_1)\chi_\uparrow(\sigma_2),$$

$$\chi_{t2} = \frac{1}{\sqrt{2}}[\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) + \chi_\uparrow(\sigma_2)\chi_\downarrow(\sigma_1)],$$

$$\chi_{t3} = \chi_\downarrow(\sigma_1)\chi_\downarrow(\sigma_2),$$

describe spin states with $S=1$ and $M_S=1,0,-1$, respectively.

Note that the six basis functions Φ_{si} and Φ_{ti} in Eqs. (7) and (8) are orthonormal, as are their orbital and spin functions,

$$\langle f_{si}|f_{sj}\rangle = \delta_{ij}, \quad \langle f_{si}|f_t\rangle = 0,$$

$$\langle \chi_{ti}|\chi_{tj}\rangle = \delta_{ij}, \quad \langle \chi_{ti}|\chi_s\rangle = 0. \tag{9}$$

In the above basis set, we have

$$\Psi_{\text{tot}}(t) = \sum_{i=1}^{3} [a_{si}(t)\Phi_{si} + a_{ti}(t)\Phi_{ti}], \tag{10}$$

where the expansion coefficients are solutions of the Schrödinger equation,

$$i|\dot{a}_s\rangle = H^{ss}|a_s\rangle + H^{st}|a_t\rangle,$$

$$i|\dot{a}_t\rangle = H^{ts}|a_s\rangle + H^{tt}|a_t\rangle, \tag{11}$$

where the column vectors $|a_s\rangle=(a_{s1},a_{s2},a_{s3})^T$ and $|a_t\rangle=(a_{t1},a_{t2},a_{t3})^T$ are vectors of singlet and triplet amplitudes, and

$$H^{ss}_{ij} = \langle\Phi_{si}|\hat{H}|\Phi_{sj}\rangle, \quad H^{st}_{ij} = \langle\Phi_{si}|\hat{H}|\Phi_{tj}\rangle,$$

$$H^{ts}_{ij} = \langle\Phi_{ti}|\hat{H}|\Phi_{sj}\rangle, \quad H^{tt}_{ij} = \langle\Phi_{ti}|\hat{H}|\Phi_{tj}\rangle,$$

$$H^{ss\dagger} = H^{ss}, \quad H^{tt\dagger} = H^{tt}, \quad H^{st\dagger} = H^{ts} \tag{12}$$

are correspondingly singlet-singlet, singlet-triplet, triplet-singlet, and triplet-triplet subspace interaction Hamiltonians. We note that within the Heitler-London approximation,[43] one neglects the double occupancy states contribution in expansion (10).

C. Spin density matrix

By analogy with the theory of open quantum systems, one can formally consider the spin subsystem as a "system," while the orbital degrees of freedom belong to the "bath." Then, the total Hamiltonian [Eq. (2)] governs the evolution of this "system+bath," with the system Hamiltonian being the Zeeman interaction term with a space-independent magnetic field (this term may be absent), the spin-independent terms describing the bath, and the spin-dependent terms (which depend both on spin and coordinate variables) describing the interaction between system and bath.

A description of the open system in terms of a completely positive (CP) map will result if (but not only if[44]) we assume that system (S) and bath (B) are initially decoupled, so that the total initial density matrix $\rho_{\text{tot}}(t=0)=|\Psi_{\text{tot}}(0)\rangle\langle\Psi_{\text{tot}}(0)|$ is a tensor product of the system and bath density matrices [$\rho(0)$ and $\rho_B(0)$, respectively], with $\rho(0)$ being defined on the whole system subspace. The system dynamics is described by the *spin density matrix*,

$$\rho(0) \mapsto \rho(t) = \text{Tr}_B\{U(t)[\rho(0)\otimes\rho_B(0)]U^\dagger(t)\}. \tag{13}$$

Here, Tr_B is the partial trace over the coordinates ("bath") and the time-evolution operator is

$$U(t) = T_{\leftarrow}\exp\left(-i\int_0^t d\tau\hat{H}(\tau)\right), \tag{14}$$

where $\hat{T}_{\leftarrow}$ is a chronological time-ordering operator.

Now we come to an important observation: it follows from Eqs. (7) and (8) that the spin and orbital degrees of freedom in $|\Psi_{\text{tot}}(0)\rangle$ [Eq. (10)] are factorized only if the state belongs to either the singlet or the triplet subspace, but not to a superposition of both. Therefore, the total initial density matrix cannot be represented in a tensor product form if the initial state contains both singlet and triplet parts. In order to understand the case of a CP map description, we next consider these two cases.

1. Singlet initial state

In this case, $|a_t(0)\rangle=0$, and the total density matrix state takes the form

$$\rho_{\text{tot}}(0) = \rho(0)\otimes\sum_{ij} a_{si}(0)a^*_{sj}(0)|f_{si}\rangle\langle f_{sj}|,$$

where $\rho(0)=\mathbf{S}$ with $\mathbf{S}=|\chi_s\rangle\langle\chi_s|$ being the projection operator on the singlet subspace, and $\langle a_s(0)|a_s(0)\rangle=1$. With this initial state, Eq. (13) can be rewritten similarly to a CP map in the operator sum representation as[18,45,46]

$$\rho(t) = \sum_{i=1}^{3}\mathbf{A}_{si}(t)\rho(0)\mathbf{A}^\dagger_{si}(t) + \mathbf{A}_t(t)\rho(0)\mathbf{A}^\dagger_t(t), \tag{15}$$

where the Kraus operators $\{\mathbf{A}_{si},\mathbf{A}_t\}$ expressed in terms of the $a_{s,t}(t)$ coefficients are

$$\mathbf{A}_{si}(t) = a_{si}(t)\mathbf{S}, \quad \mathbf{A}_t(t) = \sum_{i=1}^{3} a_{ti}(t)\mathbf{K}_i^\dagger, \tag{16}$$

with

$$\mathbf{K}_i = |\chi_s\rangle\langle\chi_{ti}| \tag{17}$$

being operators coupling the triplet and singlet subspaces. Note that the Kraus operators depend on initial conditions via the dependence of $|a_s(t)\rangle$ and $|a_t(t)\rangle$ on the initial amplitudes $|a_s(0)\rangle$. This implies that Eq. (15) does in fact *not* represent a CP map—more on this below in Sec. II D. The first term in Eq. (15), containing the sum over i, and the second one describe, respectively, the singlet and triplet states contributions to $\rho(t)$.

Using the normalization condition for the a's—$\langle a_s(t)|a_s(t)\rangle + \langle a_t(t)|a_t(t)\rangle = 1$—one derives the normalization condition,

$$\sum_{i=1}^{3} \mathbf{A}_{si}^\dagger \mathbf{A}_{si} + \mathbf{A}_t^\dagger \mathbf{A}_t = \mathbf{S}, \tag{18}$$

which guarantees preservation of the trace of ρ in the case of a singlet initial state.

2. Triplet initial state

Similarly, in the triplet case, the initial state is specified by

$$\rho_{\text{tot}}(0) = \rho(0) \otimes |f_t\rangle\langle f_t|,$$

where

$$\rho(0) = \sum_{ij} a_{ti}(0)a_{tj}^*(0)\mathbf{T}_{ij}, \tag{19}$$

with

$$\mathbf{T}_{ij} = |\chi_{ti}\rangle\langle\chi_{tj}| \tag{20}$$

being coupling operators between triplet states, and $\langle a_t(0)|a_t(0)\rangle = 1$. Then, the operator sum representation is exactly the same as Eq. (15) but the Kraus operators $\{\mathbf{A}_{si}, \mathbf{A}_t\}$ are defined differently as

$$\mathbf{A}_{si}(t) = \sum_{j=1}^{3} U_{ij}^{st}(t)\mathbf{K}_j, \quad \mathbf{A}_t(t) = \sum_{i,j=1}^{3} U_{ij}^{tt}(t)\mathbf{T}_{ij}, \tag{21}$$

where the evolution operator matrix elements are defined as solutions of the differential matrix equation,

$$i\dot{U} = HU,$$

$$U(0) = I,$$

$$U = \begin{pmatrix} U^{ss} & U^{st} \\ U^{ts} & U^{tt} \end{pmatrix}, \quad H = \begin{pmatrix} H^{ss} & H^{st} \\ H^{ts} & H^{tt} \end{pmatrix}. \tag{22}$$

Here, I is the 6×6 identity matrix. Notice the difference between the singlet and triplet cases in the definition of the Kraus operators. Namely, the triplet Kraus operators do not depend on the initial conditions, unlike the singlet case. The initial triplet amplitude dependence is present only in $\rho(0)$. Nevertheless, even in the triplet case, we do not obtain a CP map since there is a dependence of the Kraus operators on the domain (in this case, on the subspace of triplet states).

The normalization condition changes to

$$\sum_{i=1}^{3} \mathbf{A}_{si}^\dagger \mathbf{A}_{si} + \mathbf{A}_t^\dagger \mathbf{A}_t = \mathbf{T}, \tag{23}$$

where $\mathbf{T} = \text{Tr}\,\mathbf{T}_{ij} = \Sigma_i \mathbf{T}_{ii}$ is the projection operator on triplet subspace.

3. Mixed initial state

Although a mixed initial state, which contains both singlet and triplet parts, cannot be represented in a product form, a slight modification of Kraus operators in Eq. (16) according to

$$\mathbf{A}_{si}^{(m)}(t) = \mathbf{A}_{si}(t)/\langle a_s(0)|a_s(0)\rangle^{1/2},$$

$$\mathbf{A}_t^{(m)}(t) = \mathbf{A}_t(t)/\langle a_s(0)|a_s(0)\rangle^{1/2} \tag{24}$$

will provide the operator sum representation [Eq. (15)] for the mixed initial state. The normalization condition [Eq. (18)] is accordingly renormalized so that the right-hand side is divided by $\langle a_s(0)|a_s(0)\rangle$. If $\langle a_s(0)|a_s(0)\rangle = 1$, the mixed case formulas go over into the singlet ones.

D. Analysis

Note that in spite of having assumed a factorized initial state in the singlet and triplet cases, the operator sum representation [Eq. (15)] is *not* completely positive.[18] This is because the singlet and triplet Kraus operators [Eqs. (16) and (21)] depend on which initial state (singlet or triplet) is chosen. This happens since in the general case, when the initial spin density matrix $\rho(0)$ contains both singlet and triplet parts, it is not possible physically to realize such a state in the product form $\rho(0)\otimes|f\rangle\langle f|$, with $|f\rangle$ being a reference coordinate wavefunction, in the total Hilbert space. In this case, $|f\rangle$ would be simultaneously symmetric and antisymmetric with respect to permutations of coordinates, which can be realized only if $f \equiv 0$. Therefore, it not possible to obtain Kraus operators independent of $\rho(0)$ in the general mixed case. The Kraus operators in Eq. (24) do depend on $\rho(0)$. There is no contradiction to the Kraus representation theorem,[18,45,46] which states that a map $\rho(0) \to \rho(t)$ has the Kraus representation if and only if it is linear, completely positive, and trace preserving, because there is a subtle difference between the Kraus representation of a map and the Kraus representation of a state under the action of a map. The Kraus operators describing the Kraus representation of a map are independent of the state $\rho(0)$, while the Kraus operators describing the Kraus representation of a state $\rho(0)$ under the action of a map may be dependent on the initial state.[47]

III. LINDBLAD-TYPE MASTER EQUATION

While the operator sum representation [Eq. (15)] can, in principle, be used to investigate spin dynamics, it is not clear

how to separate out the unitary evolution of the (spin) system from the possibly nonunitary one, which results from the system-bath coupling. The reason is that, in general, each Kraus operator will contain a contribution from both the unitary and the nonunitary components of the evolution. In Ref. 48, a general procedure was devised to derive from the operator sum representation a CP Markovian master equation, where unitary and nonunitary terms could be identified. The Markovian part of the derivation was based on a coarse-graining procedure. Here, we use a similar formal approach, based on explicit expressions for the spin density matrix, but avoid the coarse graining step since we are not interested in the Markovian limit.

Using Eq. (16) for the Kraus operators, the operator sum representation Eq. (15) can be reduced to

$$\rho(t) = \langle a_s(t)|a_s(t)\rangle \mathbf{S} + \sum_{ij=1}^{3} (|a_t(t)\rangle\langle a_t(t)|)_{ij}\mathbf{T}_{ij}. \tag{25}$$

It is straightforward to check that in the general mixed case where both triplet and singlet components are present in the initial state [Eq. (25)] holds true. After some algebraic manipulation, one can transform the time derivative of Eq. (25) into

$$\frac{\partial \rho}{\partial t} = -i[\mathbf{H}^{tt}, \rho] + \mathcal{L}_{ts}[a_s(t), a_t(t)], \tag{26}$$

where

$$\mathbf{H}^{tt} = \sum_{ij=1}^{3} H_{ij}^{tt}\mathbf{T}_{ij}, \tag{27}$$

and

$$\mathcal{L}_{ts} = i\left(\mathrm{Tr}(G)\mathbf{S} - \sum_{ij=1}^{3} G_{ij}\mathbf{T}_{ij}\right),$$

$$G_{ij} = F_{ij} - F_{ij}^{\dagger}, \quad F_{ij} = (H^{ts}|a_s(t)\rangle\langle a_t(t)|)_{ij}. \tag{28}$$

In the derivation of Eq. (26), we have used Eq. (11). Clearly, if $H^{ts} \equiv 0$ (no singlet-triplet coupling), then $\mathcal{L}_{ts} \equiv 0$ and Eq. (26) describes unitary evolution.

Since the orthogonal projection operators $\mathbf{S}$ and $\mathbf{T}$ commute with ρ, Eq. (26) is invariant under the transformation

$$\mathbf{H}^{tt} \mapsto \mathbf{H}^{tt} + E_s(t)\mathbf{S} + E_t(t)\mathbf{T}, \tag{29}$$

where $E_s(t)$ and $E_t(t)$ are any functions of time. In the limit $H^{ts} \equiv 0$, $\mathbf{H}^{tt}$ represents an effective spin Hamiltonian. The Hamiltonian [Eq. (29)] is clearly Hermitian if $E_s(t)$ and $E_t(t)$ are real functions.

A procedure to obtain the effective spin Hamiltonian was proposed in Refs. 32–34, based on a comparison of the two expectation values,

$$\langle \Psi_{\mathrm{tot}}|\hat{H}|\Psi_{\mathrm{tot}}\rangle = \mathrm{Tr}(\mathbf{H}_{\mathrm{spin}}\rho). \tag{30}$$

From the general form of the density matrix [Eq. (25)] and relationship (30), it then follows that $\mathbf{H}_{\mathrm{spin}}$ must have the general representation,

$$\mathbf{H}_{\mathrm{spin}} = E_s(t)\mathbf{S} + \sum_{ij=1}^{3} E_{tij}(t)\mathbf{T}_{ij}, \tag{31}$$

where the functions $E_s(t)$ and $E_{tij}(t)$ satisfy the Hermiticity conditions: $E_s(t) = E_s^*(t)$ and $E_{tij}(t) = E_{tji}^*(t)$. When $H^{ts} \equiv 0$, one derives from Eq. (30)

$$E_s(t) = \langle a_s(t)|H^{ss}|a_s(t)\rangle / \langle a_s(t)|a_s(t)\rangle,$$

$$E_{tij}(t) = H_{ij}^{tt}. \tag{32}$$

Note that the Hamiltonian [Eq. (29)] fits the general representation form [Eq. (31)]. Also, it is clear that the Hamiltonian [Eq. (31)] is symmetric with respect to permutation of spin indices since the basis operators $\mathbf{S}$ and $\mathbf{T}_{ij}$ are symmetric with respect to spin permutations. In terms of single-spin operators $\vec{s}_1$ and $\vec{s}_2$, they take the form

$$\mathbf{S} = \tfrac{1}{4}I - \vec{s}_1 \cdot \vec{s}_2, \quad \mathbf{T}_{11} = \tfrac{1}{4}I + \tfrac{1}{2}S_z + s_{1z}s_{2z},$$

$$\mathbf{T}_{22} = \tfrac{1}{4}I + s_{1x}s_{2x} + s_{1y}s_{2y} - s_{1z}s_{2z},$$

$$\mathbf{T}_{33} = \tfrac{1}{4}I - \tfrac{1}{2}S_z + s_{1z}s_{2z},$$

$$\mathbf{T}_{12} = \tfrac{1}{\sqrt{2}}\left[\tfrac{1}{2}S_+ + J_s\right], \quad \mathbf{T}_{23} = \tfrac{1}{\sqrt{2}}\left[\tfrac{1}{2}S_+ - J_s\right],$$

$$\mathbf{T}_{13} = s_{1x}s_{2x} - s_{1y}s_{2y} + i(s_{1x}s_{2y} + s_{2x}s_{1y}),$$

$$\mathbf{T} = \tfrac{3}{4}I + \vec{s}_1 \cdot \vec{s}_2, \quad \mathbf{T}_{21} = \mathbf{T}_{12}^{\dagger},$$

$$\mathbf{T}_{31} = \mathbf{T}_{13}^{\dagger}, \quad \mathbf{T}_{32} = \mathbf{T}_{23}^{\dagger}, \tag{33}$$

where

$$J_s = s_{1z}s_{2x} + s_{1x}s_{2z} + i(s_{1z}s_{2y} + s_{1y}s_{2z}),$$

$$S_{\pm} = S_x \pm iS_y, \quad \vec{S} = \vec{s}_1 + \vec{s}_2,$$

and I is the 4×4 identity matrix. At the same time, the singlet-triplet basis operators $\mathbf{K}_i$ are asymmetric,

$$\mathbf{K}_1 = -\frac{i}{2\sqrt{2}}\{(\vec{J}_{as})_x - i(\vec{J}_{as})_y\}, \quad \mathbf{K}_2 = \frac{i}{2}(\vec{J}_{as})_z,$$

$$\mathbf{K}_3 = \frac{i}{2\sqrt{2}}\{(\vec{J}_{as})_x + i(\vec{J}_{as})_y\}, \tag{34}$$

where $\vec{J}_{as} = [\vec{s}_2 - \vec{s}_1 \times \vec{S}]$. This symmetry property of the Hamiltonian and spin density matrix is quite general since it is a consequence of the orthogonality of the coordinate wave functions in the singlet and triplet subspaces [Eq. (9)]. Moreover, it remains valid beyond the two-state approximation used here: with inclusion of excited states, spatial orbitals lying in singlet and triplet subspaces will still be orthogonal to each other. Indeed, let us assume we have a basis set of N one-electron orthonormalized orbitals: $\{\phi_i\}$, $i = 1, 2, \ldots, N$; $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. With inclusion of spin degrees of freedom, the one-electron basis set will contain $2N$ states. The correspond-

ing two-electron basis set, defined by Slater determinants, will contain $C_{2N}^2=N(2N-1)$ states. Now, let us take an arbitrary pair of orbitals ϕ_i and ϕ_j with $i\neq j$; then this pair will generate two-electron orbital states f_{sk}, $k=1,2,3$ and f_t in singlet and triplet subspaces, respectively. Here, f_{sk}, and f_t are defined by Eqs. (7) and (8) where the subindices A and B are replaced by i and j. It is easy to check that $\langle f_{sk}|f_{sk'}\rangle = \delta_{kk'}$ and $\langle f_{sk}|f_t\rangle=0$. This proves the claimed general symmetry property.

We emphasize that the recipe Eq. (30) implicitly assumes that the spin dynamics is unitary. Besides, observe that Eq. (30) is not invariant under the transformation $\mathbf{H}_{\text{spin}}\mapsto\mathbf{H}_{\text{spin}}+E_s(t)\mathbf{S}+E_t(t)\mathbf{T}$. Using Eq. (33), one can rewrite

$$E_s(t)\mathbf{S}+E_t(t)\mathbf{T}=\left(\frac{1}{4}E_s(t)+\frac{3}{4}E_t(t)\right)I+J_H(t)\vec{s}_1\cdot\vec{s}_2, \tag{35}$$

where

$$J_H(t)=E_t(t)-E_s(t) \tag{36}$$

and the last term, H_{ex}, is the familiar Heisenberg exchange interaction. Invariance of Eq. (26) under transformation (29) means that the spin density matrix will not change under a unitary transformation induced by this Hamiltonian transformation. In particular, it follows that the unitary transformation induced by the Heisenberg exchange interaction,

$$U_H(t)=\exp[-i\lambda_H(t)\vec{s}_1\cdot\vec{s}_2], \tag{37}$$

where $\lambda_H(t)=\int_0^t dt' J_H(t')$ does not affect the state,

$$\rho(0)\mapsto\rho(t)=U_H(t)\rho(0)U_H^\dagger(t)=\rho(0), \tag{38}$$

where $\rho(0)$ can be taken in the general form $\rho(0)=\rho_s\mathbf{S}+\Sigma_{ij}\rho_{tij}\mathbf{T}_{ij}$, with ρ_s and ρ_{tij} being arbitrary parameters specifying $\rho(0)$. It is easy to verify Eq. (38) directly using the commutativity identities $[S,T]=[S,T_{ij}]=[T,T_{ij}]=0$: (i) up to a phase factor $U_H(t)$ can be written as $\exp[-i\lambda_s(t)\mathbf{S}]\times\exp[-i\lambda_t(t)\mathbf{T}]$, where $\lambda_{s,t}(t)=\int_0^t dt' E_{s,t}(t')$; (ii) then, Eq. (38) in the general case follows from the obvious relations,

$$\exp[-i\lambda_s(t)\mathbf{S}]\mathbf{S}\exp[+i\lambda_s(t)\mathbf{S}]=\mathbf{S},$$

$$\exp[-i\lambda_s(t)\mathbf{S}]\mathbf{T}_{ij}\exp[+i\lambda_s(t)\mathbf{S}]=\mathbf{T}_{ij},$$

and

$$\exp[-i\lambda_t(t)\mathbf{T}]\mathbf{S}\exp[+i\lambda_t(t)\mathbf{T}]=\mathbf{S},$$

$$\exp[-i\lambda_t(t)\mathbf{T}]\mathbf{T}_{ij}\exp[+i\lambda_t(t)\mathbf{T}]=\mathbf{T}_{ij}.$$

The conclusion that the unitary transformation [Eq. (38)] does not affect pure-spin dynamics has important implications for schemes that rely on this transformation in order to enact universal quantum computation and/or decoherence control.[1–11,19–40] The pure-spin approach cannot be applied in these cases, i.e., one must be able to resolve spins in order for Heisenberg-based unitary quantum computation to work.

However, this conclusion does not mean that the Heisenberg interaction plays no role in pure-spin dynamics. In general, this dynamics is nonunitary and as we shall see below the constant J_H, characteristic of the magnitude of the Heisenberg interaction, appears in both the nonunitary term and in the unitary Lamb-shift energy, in the $\rho(t)$ dynamics described by Eq. (49).

In the general case, in order to obtain a correct effective spin Hamiltonian, one needs to analyze the exact Eq. (26). $\mathcal{L}_{ts}$ is seen to be a bilinear matrix function of the $a_s(t)$ and $a_t(t)$ amplitudes entering as a linear combination of their cross products, while $\rho(t)$ is a quadratic matrix function of the $a_s(t)$ and $a_t(t)$ amplitudes entering in separate combinations. Our goal is to express $\mathcal{L}_{ts}$ as a linear matrix function of ρ: $\mathcal{L}_{ts}=\mathcal{L}_{ts}[\rho(t)]$, so that the total initial state information recorded in the $a_s(t)$ and $a_t(t)$ amplitudes is compressed into ρ. To do so, we first consider the relationship between the amplitudes at the initial time $t=0$ and t using the time-evolution operator [Eq. (22)],

$$a_s(t)=U^{ss}(t)a_s(0)+U^{st}(t)a_t(0)$$

$$a_t(t)=U^{ts}(t)a_s(0)+U^{tt}(t)a_t(0). \tag{39}$$

Evidently, in general, it is not possible to establish a one-to-one correspondence between the $a_s(t)$ and $a_t(t)$ amplitudes. There should be some correlation between the amplitudes at $t=0$. Let us assume, for example, that initial conditions are set up such that we have a linear relation between the amplitudes, given by a correlation matrix $R_m(0)$,

$$a_s(0)=R_m(0)a_t(0). \tag{40}$$

Then, from Eqs. (39) and (40), we obtain

$$a_s(t)=R_m(t)a_t(t), \tag{41}$$

where

$$R_m(t)=[U^{ss}(t)R_m(0)+U^{st}(t)][U^{ts}(t)R_m(0)+U^{tt}(t)]^{-1}. \tag{42}$$

We will refer to this as the mixed case because the spin density matrix will have both singlet and triplet components if both $a_s(0)$ and $a_t(0)$ are nonzero.

Two other special cases where it is possible to establish a one-to-one correspondence between the $a_s(t)$ and $a_t(t)$ amplitudes are (i) singlet initial state, $a_t(0)=0$, and (ii) triplet initial state, $a_s(0)=0$. In the singlet (R_s) and triplet (R_t) cases, we have, respectively,

$$a_s(t)=R_{s,t}(t)a_t(t), \tag{43}$$

where

$$R_{s,t}(t)=\begin{cases}U^{ss}(t)[U^{ts}(t)]^{-1} & \text{singlet case}\\ U^{st}(t)[U^{tt}(t)]^{-1} & \text{triplet case.}\end{cases} \tag{44}$$

The triplet case is a particular case of the mixed one when $R_m(0)a_t(0)=0$. Assuming the existence of the inverse operators (below, we consider this issue in detail), the matrix F_α, $\alpha\in\{s,t,m\}$, in Eq. (28) can be rewritten as

$$F_\alpha = Q_\alpha(t)|a_t(t)\rangle\langle a_t(t)|. \tag{45}$$

where $Q_\alpha(t)=H^{ts}R_\alpha(t)$. In order to separate unitary from nonunitary evolution, we resolve Q_α into Hermitian and anti-Hermitian parts,

$$P_\alpha = Q_\alpha + Q_\alpha^\dagger,$$

$$D_\alpha = Q_\alpha - Q_\alpha^\dagger. \tag{46}$$

Then, using the identities

$$\mathbf{T}_{ij} = \mathbf{K}_i^\dagger \mathbf{K}_j, \quad \mathbf{K}_i\mathbf{K}_j^\dagger = \delta_{ij}\mathbf{S},$$

$$\mathbf{K}_i\rho\mathbf{K}_j^\dagger = (|a_t(t)\rangle\langle a_t(t)|)_{ij}\mathbf{S}, \tag{47}$$

we obtain

$$\mathcal{L}_{ts}^{(\alpha)} = -\frac{i}{2}[\mathbf{P}_\alpha,\rho] + \frac{1}{2}\sum_{ij}(iD_\alpha)_{ji}(2\mathbf{K}_i\rho\mathbf{K}_j^\dagger - \rho\mathbf{K}_j^\dagger\mathbf{K}_i - \mathbf{K}_j^\dagger\mathbf{K}_i\rho), \tag{48}$$

where $\mathbf{P}_\alpha=\Sigma_{ij}(P_\alpha)_{ij}\mathbf{T}_{ij}$. The first term in Eq. (48) describes the effect the singlet-triplet coupling has on the unitary part of the system (spin) dynamics and "renormalizes" the system Hamiltonian (an analog of the *Lamb shift*), while the second one—proportional to the matrix D_α—is responsible for nonunitary effects in the spin dynamics. Including this *Lamb shift* into the effective spin Hamiltonian $\tilde{\mathbf{H}}^{tt}=\Sigma_{ij}\tilde{H}_{ij}^{tt}\mathbf{T}_{ij}=\mathbf{H}^{tt}+\frac{1}{2}\mathbf{P}_\alpha$, we rewrite Eq. (26) as

$$\frac{\partial\rho(t)}{\partial t} = -i[\tilde{\mathbf{H}}^{tt},\rho(t)] + \frac{1}{2}\sum_{ij}\chi_{ij}([\mathbf{K}_i,\rho(t)\mathbf{K}_j^\dagger] + [\mathbf{K}_i\rho(t),\mathbf{K}_j^\dagger]), \tag{49}$$

where $\chi_{ij}=(iD_\alpha)_{ji}$.

Equation (49) is one of our central results. It is parametrized by the time-dependent functions $\tilde{H}_{ij}^{tt}(t)$ and $\chi_{ij}(t)$ which in turn can be expressed in terms of matrix elements of the Hamiltonian H [Eq. (22)]. Since these functions depend on which state (singlet/triplet/mixed) is specified as the initial state, $\rho(0)$, we further consider the first two cases separately.

We restrict ourselves to the case of a time-independent Hamiltonian. The general case can, in principle, be reduced to the time-independent one by dividing up the time interval into small subintervals and then approximating the Hamiltonian by average ones over each time subinterval.

First, we consider the eigenvalue problem,

$$\begin{pmatrix} H^{ss} & H^{st} \\ H^{ts} & H^{tt} \end{pmatrix}\begin{pmatrix} |e_{sk}\rangle \\ |e_{tk}\rangle \end{pmatrix} = \varepsilon_k\begin{pmatrix} |e_{sk}\rangle \\ |e_{tk}\rangle \end{pmatrix}, \quad k=1,\ldots,6. \tag{50}$$

Using the closure relation, one obtains

$$\chi_{s,t}^T = i(Q_{s,t} - Q_{s,t}^\dagger),$$

$$P_{s,t} = Q_{s,t} + Q_{s,t}^\dagger, \tag{51}$$

where

$$Q_t = \left\{\left(\sum_k \exp(-i\varepsilon_k t)H^{ts}|e_{sk}\rangle\langle e_{tk}|\right) \times\left(\sum_k \exp(-i\varepsilon_k t)|e_{tk}\rangle\langle e_{tk}|\right)^{-1}\right\}, \tag{52}$$

$$Q_s = \left\{\left(\sum_k \exp(-i\varepsilon_k t)H^{ts}|e_{sk}\rangle\langle e_{sk}|\right) \times\left(\sum_k \exp(-i\varepsilon_k t)|e_{tk}\rangle\langle e_{sk}|\right)^{-1}\right\} \tag{53}$$

are the exact expressions in terms of exact solutions of the eigenvalue (eigenvector) problem [Eq. (50)]. In general, Eq. (50) can be solved numerically using standard Hermitian symmetric eigenvalue problem routines (such as in the LAPACK library). Notice the oscillatory behavior predicted by Eqs. (52) and (53).

Let us consider an approximate solution to the eigenvalue problem assuming that H^{st} is a small perturbation. To zeroth order ($H^{st}\equiv 0$), the eigenvalue problem [Eq. (50)] is reduced to the separate singlet and triplet subspace eigenvalue problems,

$$(H^{ss} - \varepsilon_k^{(0)}I)|e_{sk}^{(0)}\rangle = 0, \quad k=1,2,3,$$

$$(H^{tt} - \varepsilon_k^{(0)}I)|e_{tk}^{(0)}\rangle = 0, \quad k=4,5,6, \tag{54}$$

and $|e_{sk}^{(0)}\rangle=|0\rangle$, $k=4,5,6$, and $|e_{tk}^{(0)}\rangle=|0\rangle$, $k=1,2,3$, where $|0\rangle$ is a zero vector. Up to first order in H^{st}, one obtains

$$\begin{aligned} |e_{sk}^{(1)}\rangle &= |e_{sk}^{(0)}\rangle, \\ |e_{tk}^{(1)}\rangle &= (\varepsilon_k^{(0)}I - H^{tt})^{-1}H^{ts}|e_{sk}^{(0)}\rangle, \end{aligned} \quad k=1,2,3,$$

$$\begin{aligned} |e_{tk}^{(1)}\rangle &= |e_{tk}^{(0)}\rangle, \\ |e_{sk}^{(1)}\rangle &= (\varepsilon_k^{(0)}I - H^{ss})^{-1}H^{st}|e_{tk}^{(0)}\rangle, \end{aligned} \quad k=4,5,6. \tag{55}$$

A. Triplet initial state

After substitution of the vectors [Eq. (55)] into Q_t Eq. (52), we have

$$Q_t = \left(\sum_{k=1}^{3}\sum_{l=4}^{6}\frac{\exp(-i\varepsilon_k^{(0)}t) - \exp(-i\varepsilon_l^{(0)}t)}{\varepsilon_k^{(0)} - \varepsilon_l^{(0)}}H^{ts}|e_{sk}^{(0)}\rangle\langle e_{sk}^{(0)}|H^{st}|e_{tl}^{(0)}\rangle \times\langle e_{tl}^{(0)}|\right) \tag{56}$$

$$\times\left(\sum_{l=4}^{6}\exp(-i\varepsilon_l^{(0)}t)|e_{tl}^{(0)}\rangle\langle e_{tl}^{(0)}| + \sum_{k=1}^{3}\sum_{l,m=4}^{6}\exp(-i\varepsilon_k^{(0)}t) \times\frac{|e_{tl}^{(0)}\rangle\langle e_{tl}^{(0)}|H^{ts}|e_{sk}^{(0)}\rangle}{(\varepsilon_k^{(0)} - \varepsilon_l^{(0)})(\varepsilon_k^{(0)} - \varepsilon_m^{(0)})}\langle e_{sk}^{(0)}|H^{st}|e_{tm}^{(0)}\rangle\langle e_{tm}^{(0)}|\right)^{-1}. \tag{57}$$

Neglecting the splitting of triplet energies, which is mainly due to the small magnetic Zeeman interaction, one can replace all $\varepsilon_k^{(0)}$, $k=4,5,6$ by an average value ε_t. Also, due to the strong interelectron repulsion in double occupancy

states, the difference of energies in doubly occupied and triplet states is much larger than the difference of energies in the singlet, singly occupied state, and the triplet ones (denote this energy difference, the Heisenberg exchange interaction constant, by $J_H=\varepsilon_t-\varepsilon_s$) so that we can safely neglect the contributions from the doubly occupied states. Within these approximations, Eq. (57) and (51) can be reduced to

$$Q_t = \frac{1-\exp(iJ_Ht)}{J_H} H^{ts}|e_{s1}^{(0)}\rangle\langle e_{s1}^{(0)}|H^{st},$$

$$\chi_t^T = 2\frac{\sin(J_Ht)}{J_H} H^{ts}|e_{s1}^{(0)}\rangle\langle e_{s1}^{(0)}|H^{st},$$

$$P_t = 2\frac{1-\cos(J_Ht)}{J_H} H^{ts}|e_{s1}^{(0)}\rangle\langle e_{s1}^{(0)}|H^{st}, \quad (58)$$

where $|e_{s1}^{(0)}\rangle$ is the singlet, singly occupied state ($|e_{s2,3}^{(0)}\rangle$ are correspondingly doubly occupied states).

Note that χ_t^T is not necessarily a positive definite matrix. Indeed, since

$$H^{ts}|e_{s1}^{(0)}\rangle\langle e_{s1}^{(0)}|H^{st}$$

is a positive Hermitian matrix, the sign of the oscillatory function $g(t)=2\sin(J_Ht)/J_H$ determines whether χ_t^T is positive [when $g(t)>0$] or negative ($g(t)<0$). Additionally, this conclusion is supported by the fact that one could, in principle, evolve the state in the backward time direction. In this case, $g(t)<0$ even at small t.

Alternatively, and for consistency, one can use the direct asymptotic expansions at small t in order to derive Eq. (58),

$$U^{st}(t) = U^{st}(0) + \dot{U}^{st}(0)t + \ddot{U}^{st}(0)\frac{t^2}{2} + \cdots,$$

$$U^{tt}(t) = U^{tt}(0) + \dot{U}^{tt}(0)t + \ddot{U}^{tt}(0)\frac{t^2}{2} + \cdots. \quad (59)$$

Obtaining from Eq. (22) explicit expressions for the time derivatives, Eq. (59) takes the form

$$U^{st}(t) = -iH^{st}t - (H^{ss}H^{st} + H^{st}H^{tt})\frac{t^2}{2} + \cdots,$$

$$U^{tt}(t) = I - iH^{tt}t - [H^{ts}H^{st} + (H^{tt})^2]\frac{t^2}{2} + \cdots. \quad (60)$$

Inserting these asymptotic expressions into Eq. (51), we obtain

$$\chi_t^T = 2H^{ts}H^{st}t,$$

$$P_t = (H^{ts}H^{st}H^{tt} - H^{ts}H^{ss}H^{st})t^2. \quad (61)$$

It can be easily verified that the asymptotic expansions [Eq. (61)] coincide with the corresponding expressions [Eq. (58)] at small t (lifting some approximations made above concerning singlet and triplet energies).

Also, using Eq. (60), one can calculate the triplet states population at small t,

$$\langle a_t(t)|a_t(t)\rangle = \langle a_t(0)|[U^{tt}(t)]^\dagger U^{tt}(t)|a_t(0)\rangle = 1-\alpha_t t^2,$$

$$\alpha_t = \langle a_t(0)|H^{ts}(H^{ts})^\dagger|a_t(0)\rangle. \quad (62)$$

Observe that the triplet state probability decreases with time, while the singlet state probability, $\langle a_s(t)|a_s(t)\rangle=1-\langle a_t(t)|a_t(t)\rangle$, increases due to the singlet-triplet coupling, with the constant α_t being quadratically dependent on the singlet-triplet interaction matrix H^{ts}. In other words, the total spin of the system is not conserved if there is a nonzero coupling between singlet and triplet states.

B. Purity for a triplet initial state

The time dependence of the purity $p(t)\equiv\mathrm{Tr}\,\rho^2(t)$ may serve as a measure of nonunitarity in dynamics [$p(t)=1$ if and only if the state is pure; $p(t)$ is constant if and only if the dynamics is unitary]. With Eq. (62), we have

$$p(t) = \mathrm{Tr}\,\rho^2(t) = 1 - 2\langle a_t(t)|a_t(t)\rangle + 2\langle a_t(t)|a_t(t)\rangle^2 = 1 - 2\alpha_t t^2 \quad (63)$$

at small t. Observe that nonunitary effects are proportional to the constant $2\alpha_t$ which can also be defined as the expectation value of the time derivative of the matrix χ_t^T in Eq. (61): $2\alpha_t=\mathrm{Tr}[\dot{\chi}_t^T(t)\rho(0)]$, where $\dot{\chi}_t^T=\Sigma_{ij}\dot{\chi}_{tij}^T(t)\mathbf{T}_{ij}$. In Part II,[41] we investigate numerically how the triplet states population, purity, and Lamb-shift depend on time and other relevant physical parameters.

C. Singlet initial state

This case differs qualitatively from the triplet one by the fact that the inverse operator in Q_s [Eq. (53)] is singular at $t=0$. From the asymptotic expansions,

$$U^{ts}(t) = -iH^{ts}t - (H^{ts}H^{ss} + H^{tt}H^{ts})\frac{t^2}{2} + \cdots,$$

$$U^{ss}(t) = I - iH^{ss}t - [H^{st}H^{ts} + (H^{ss})^2]\frac{t^2}{2} + \cdots, \quad (64)$$

at small t, one finds

$$Q_s = \frac{i}{t}H^{ts}\left\{I - iH^{ss}t - [H^{st}H^{ts} + (H^{ss})^2]\frac{t^2}{2}\right\} \times \left[H^{ts} - i(H^{ts}H^{ss} + H^{tt}H^{ts})\frac{t}{2}\right]^{-1}. \quad (65)$$

Assuming that the matrix H^{ts} is nonsingular, $Q_s=\frac{i}{t}I$ as $t\to 0$. However, since Q_s is defined on the vectors $|a_t(t)\rangle$, it operates on the outer product $|a_t(t)\rangle\langle a_t(t)|$ in F_s [Eq. (45)] and $|a_t(t)\rangle=-iH^{ts}t|a_s(0)\rangle$ at small t. Therefore, their product, $F_s=itH^{ts}|a_s(0)\rangle\langle a_s(0)|H^{st}$, goes to zero as $t\to 0$. If H^{ts} is a singular matrix and $|a_s(0)\rangle$ belongs to the kernel of H^{ts}, then $Q_s=O(t^{-2})$ but $|a_t(t)\rangle=-(H^{ts}H^{ss}+H^{tt}H^{ts})\frac{t^2}{2}|a_s(0)\rangle$ and $F_s=O(t^2)$ as $t\to 0$. When $|a_s(0)\rangle$ does not belong to the kernel of H^{ts}, the pseudoinverse of H^{ts} is defined in the Moor-Penrose sense (see, e.g., Ref. 49 and references therein).

Thus, in spite of the singular behavior of Q_s at zero, we have regular behavior of all the corresponding terms in Eq. (49) and the operator Q_s is well defined at $t \neq 0$ (it is not defined in the pathological case where $H^{ts} \equiv 0$, but in this case, there is no connection between singlet and triplet subspaces and $\mathcal{L}_{ts} \equiv 0$).

Keeping up to the second order terms, Eq. (65) can be rewritten as

$$Q_s = \frac{i}{t} I - \frac{1}{2}(H^{tt} - \tilde{H}^{ss}) + \frac{it}{2}(\tilde{H}^{ss} - H^{ts}H^{st}), \tag{66}$$

where $\tilde{H}^{ss} = H^{ts}H^{ss}(H^{ts})^{-1}$ is the similarity transformed matrix H^{ss} and one obtains

$$\chi_s^T = -\frac{2}{t} I + \frac{i}{2}(\tilde{H}^{ss} - \tilde{H}^{ss\dagger}) - \frac{t}{2}(\tilde{H}^{ss} + \tilde{H}^{ss\dagger} - 2H^{ts}H^{st}),$$

$$P_s = -H^{tt} + \frac{1}{2}(\tilde{H}^{ss} + \tilde{H}^{ss\dagger}) + \frac{it}{2}(\tilde{H}^{ss} - \tilde{H}^{ss\dagger}). \tag{67}$$

Comparing Eqs. (61) and (67), notice the qualitative difference between singlet and triplet cases. While in the triplet case, the corresponding matrices are basically of the second order in the H^{ts} interaction coupling, the singlet state matrices, χ_s^T and P_s, are of the order of $1/t$, H^{tt}, and H^{ss}, respectively, at small t. Observe that at small t, χ_s^T is positive when $t<0$ and negative when $t>0$.

Similar to the triplet case above, we compute the triplet states population,

$$\langle a_t(t)|a_t(t)\rangle = \langle a_s(0)|[U^{ts}(t)]^\dagger U^{ts}(t)|a_s(0)\rangle = \alpha_s t^2,$$

$$\alpha_s = \langle a_s(0)|H^{st}(H^{st})^\dagger|a_s(0)\rangle. \tag{68}$$

Here, the constant α_s is the average of the H^{st} $(H^{st})^\dagger$ interaction operator over the initial state $|a_s(0)\rangle$.

D. Purity for a singlet initial state

Now, we have for the purity

$$p(t) = \mathrm{Tr}\,\rho^2(t) = 1 - 2\alpha_s t^2. \tag{69}$$

Alternatively, the rate of nonunitarity, $2\alpha_s$, can be defined as the expectation value of the time derivative of the matrix χ_s^T, now in the triplet states $|a_t(t)\rangle$, since χ_s^T is defined on $|a_t(t)\rangle$ and $a_t(0)=0$,

$$2\alpha_s = \langle a_t(t)|\dot{\chi}_s^T|a_t(t)\rangle = \mathrm{Tr}[\dot{\chi}_s^T(t)\rho(t)], \tag{70}$$

where $|a_t(t)\rangle = -iH^{ts}t|a_s(0)\rangle$ and $\dot{\chi}_s^T = (2/t^2)I$, $\dot{\chi}_s^T(t) = \Sigma_{ij}\dot{\chi}_{sij}^T(t)\mathbf{T}_{ij}$ at small t.

IV. TIME-CONVOLUTIONLESS FORM OF THE MASTER EQUATION

In the previous section, we have examined the possibility of constructing a master equation based on the explicit structure of the spin density matrix in terms of the $a_{s,t}(t)$ amplitudes. We found that a meaningful *quasiclosed* form of the master equation can be derived if the initial state is assumed to be in a product form of orbital and spin functions, correspondingly in singlet and triplet states, or in a correlated mixed state. The quasiclosed character of the equations we obtained stems from the fact that the matrix operators in Eq. (49) are defined differently in the singlet and triplet cases, although they do not depend on the initial state amplitudes, $a_s(0)$ and $a_t(0)$ correspondingly. In the correlated mixed case, we have a correlation matrix $R_m(0)$ fixing the relation between $a_s(0)$ and $a_t(0)$ amplitudes, and this correlation information is present in the operators appearing in the dynamical equation [cf. Eqs. (40)–(49)].

In the present section, we approach the problem of constructing the dynamical equation using projection operator techniques, as applied in the derivation of the TCL master equation.[18]

A. Derivation of the time-convolutionless master equation

For the analysis of the general mixed case, we start with the exact equation for ρ_{tot},

$$\dot{\rho}_{\mathrm{tot}} = -i[H, \rho_{\mathrm{tot}}] = -iL\rho_{\mathrm{tot}}, \tag{71}$$

where $L = L^\dagger$ is the Liouvillean superoperator corresponding to H. The density matrix ρ_{tot} contains both relevant and irrelevant information about the coordinate dependence (bath), which will be averaged out after integration over the coordinates: $\rho = \mathrm{Tr}_{\bar{r}}\,\rho_{\mathrm{tot}}$. Let us assume that the irrelevant information can be eliminated by virtue of a time-independent projection operator P, and the relevant information is assumed to be given by the projected density matrix $P\rho_{\mathrm{tot}}$. Using the projection operator technique,[18,50,51] one obtains the well-known TCL master equation for $P\rho_{\mathrm{tot}}$,

$$P\dot{\rho}_{\mathrm{tot}}(t) = K(t)P\rho_{\mathrm{tot}}(t) + I(t)Q\rho_{\mathrm{tot}}(0),$$

$$K(t) = -iPL\theta(t),$$

$$I(t) = K(t)\exp(-iQLt),$$

$$\theta(t) = [P + \exp(-iQLt)Q\exp(iLt)]^{-1}, \tag{72}$$

where $Q = I - P$. For simplicity, we restricted ourselves to the case where the Liouvillian is time independent. This is an exact, inhomogeneous, first order linear differential equation. Both the TCL generator $K(t)$ of the linear part and the inhomogeneity $I(t)$ are explicitly time-dependent superoperators which do not depend on which initial state $\rho_{\mathrm{tot}}(0)$ is taken . Observe that the inhomogeneous term vanishes if the initial state satisfies the relation $Q\rho_{\mathrm{tot}}(0)=0$, i.e., if

$$P\rho_{\mathrm{tot}}(0) = \rho_{\mathrm{tot}}(0). \tag{73}$$

This coincides with having factorized initial conditions.[18] Below, we consider when this is possible in our setting.

The condition that $P\rho_{\mathrm{tot}}$ contains all the relevant information means that the following condition,

$$\rho = \mathrm{Tr}_{\bar{r}}\,\rho_{\mathrm{tot}} = \mathrm{Tr}_{\bar{r}}\,P\rho_{\mathrm{tot}}, \tag{74}$$

together with $P^2 = P$ should be imposed on P as a projection operator. Let us take any orthogonal decomposition of the

unit operator $I_{\vec{r}}$ on the coordinate state space span $\{f_{si}, f_t\}_{i=1,2,3}$,

$$I_{\vec{r}} = \sum_{i=1}^{3} |f_{si}\rangle\langle f_{si}| + |f_t\rangle\langle f_t|, \tag{75}$$

i.e., a collection of projection operators Π_a that satisfy

$$\Pi_a \Pi_b = \delta_{ab}\Pi_b, \quad \sum_a \Pi_a = I_{\vec{r}}. \tag{76}$$

Then, following Ref. 18, we can define a linear map by means of

$$P\rho_{\text{tot}} = \sum_a \text{Tr}_{\vec{r}}\{\Pi_a \rho_{\text{tot}}\} \otimes \frac{1}{N_a}\Pi_a, \tag{77}$$

where $N_a = \text{Tr}_{\vec{r}}\{\Pi_a\}$. It is easy to check that this superoperator fulfills the above conditions. As an example, let us consider the case where $\Pi_a = \Pi_s = \Sigma_{i=1}^3 |f_{si}\rangle\langle f_{si}|$ and $\Pi_b = \Pi_t = |f_t\rangle\langle f_t|$. Then, the 6×6 density matrix,

$$\rho_{\text{tot}} = \begin{pmatrix} \rho^{ss} & \rho^{st} \\ \rho^{ts} & \rho^{tt} \end{pmatrix}, \tag{78}$$

is transformed under the map Eq. (77) to

$$P\rho_{\text{tot}} = \begin{pmatrix} \rho_{\text{av}}^{ss} I & 0 \\ 0 & \rho^{tt} \end{pmatrix}, \tag{79}$$

where $\rho_{\text{av}}^{ss} = \frac{1}{3}\Sigma_{i=1}^3 \rho_{ii}^{ss}$. Notice, however, that the projection superoperator P must be realizable as a superoperator independent of ρ_{tot}, i.e., the matrix state [Eq. (79)] must be obtained by multiplying the matrix [Eq. (78)] from the left and right by some matrices independent of ρ_{tot}. It is clear that by taking $\Pi_a = \{\Pi_{si} = |f_{si}\rangle\langle f_{si}|, i = 1,2,3; \Pi_t\}$, the projection superoperator P can be written as

$$P\rho_{\text{tot}} = \begin{pmatrix} \text{diag}(\rho_{ii}^{ss}) & 0 \\ 0 & \rho^{tt} \end{pmatrix} = \sum_{i=1}^{3} E_{si}\rho_{\text{tot}}E_{si} + E_t\rho_{\text{tot}}E_t, \tag{80}$$

where $\text{diag}(\rho_{ii}^{ss})$ is a diagonal matrix with ρ_{ii}^{ss}, $i = 1,2,3$ entries on the diagonal; E_{si} and E_t are orthogonal projection matrices independent of ρ_{tot} and defined by

$$E_{si} = \begin{pmatrix} 1_i & 0 \\ 0 & 0 \end{pmatrix}, \quad E_t = \begin{pmatrix} 0 & 0 \\ 0 & I \end{pmatrix}. \tag{81}$$

Here, 1_i is a diagonal matrix with all zero entries except 1 in the ith entry. However, without changing matrix dimension, it is not possible to change the diagonal entries ρ_{ii}^{ss} in Eq. (80) to ρ_{av}^{ss} by multiplying the matrix Eq. (80) by some diagonal matrices independent of ρ_{tot}. Hence, in order to comply with the requirement of state independency, one should extend the definition of the projection superoperator to Eq. (80). Observe that the state Eq. (80) contains two extra pieces of information: besides the probability of single state occupation, ρ_{11}^{ss}, also, the probabilities of double state occupancy, ρ_{22}^{ss} and ρ_{33}^{ss}, which will be compressed after averaging $\text{Tr}_{\vec{r}} P\rho_{\text{tot}}$ to ρ_{av}^{ss}. Then, it follows from Eq. (80) that

$$Q\rho_{\text{tot}} = E_s\rho_{\text{tot}}E_t + E_t\rho_{\text{tot}}E_s + \sum_{i\neq j} E_{si}\rho_{\text{tot}}E_{sj}, \tag{82}$$

where $E_s = \Sigma_i E_{si}$.

In principle, one can "compress" $\text{diag}(\rho_{ii}^{ss})$ in Eq. (80) by applying a rectangular 6×4 matrix,

$$C = \begin{pmatrix} 1 & \\ 1 & 0_{3\times 3} \\ 1 & \\ 0_{3\times 1} & I_{3\times 3} \end{pmatrix}, \tag{83}$$

so that

$$P\rho_{\text{tot}} \mapsto \rho = C^T\left(\sum_{i=1}^{3} E_{si}\rho_{\text{tot}}E_{si} + E_t\rho_{\text{tot}}E_t\right)C = \begin{pmatrix} \sum_i \rho_{ii}^{ss} & 0_{1\times 3} \\ 0_{3\times 1} & \rho^{tt} \end{pmatrix}. \tag{84}$$

However, transformation (84) is not a projection operation: $C^T C \neq C$.

In numerical computations, it is often convenient to rewrite matrix operator equations in tensor product form (see, for example, Ref. 49 and references therein),

$$Y = CXB^T \Leftrightarrow |Y\rangle = (B\otimes C)|X\rangle, \tag{85}$$

where $Y, C, X, B \in \mathbb{C}^{n\times n}$, $B\otimes C \in \mathbb{C}^{n^2\times n^2}$ are matrices and we introduced the Liouville vector space $|X\rangle \in \mathbb{C}^{n^2}$ by applying the "vectorization" operation to a matrix,

$$X \mapsto |X\rangle = \begin{pmatrix} X_{\cdot 1} \\ \vdots \\ X_{\cdot n} \end{pmatrix}, \tag{86}$$

which amounts to a "stacking" of matrix columns. It is easy to check that $\langle X|Y\rangle = \text{Tr}(X^\dagger Y)$.

Using these rules, Eqs. (85) and (86), we can rewrite the superoperators in Eq. (72) in the tensor product form,

$$L = I\otimes H - H^T\otimes I, \quad P = \sum_{i=1}^{3} E_{si}\otimes E_{si} + E_t\otimes E_t,$$

$$Q = E_s\otimes E_t + E_t\otimes E_s + \sum_{i\neq j} E_{si}\otimes E_{sj}. \tag{87}$$

Then, with the use of identities $(A\otimes B)(C\otimes D) = AC\otimes BD$ and $(A+B)\otimes C = A\otimes C + B\otimes C$, one obtains

$$\begin{aligned} QLQ = \sum_{ij} &(E_t\otimes E_{si}HE_{sj} - E_{si}H^TE_{sj}\otimes E_t) + (E_s\otimes E_tHE_t \\ &- E_tH^TE_t\otimes E_s) + \sum_i \sum_{j\neq i,k\neq i} (E_{si}\otimes E_{sj}HE_{sk} \\ &- E_{sj}H^TE_{sk}\otimes E_{si}) + \sum_i \sum_{j\neq i} \{E_{si}\otimes (E_tHE_{sj} + E_{sj}HE_t) \\ &- (E_tH^TE_{sj} + E_{sj}H^TE_t)\otimes E_{si}\}, \end{aligned} \tag{88}$$

$$PLP = \sum_i (E_{si} \otimes E_{si} H E_{si} - E_{si} H^T E_{si} \otimes E_{si}) + E_t \otimes E_t H E_t - E_t H^T E_t \otimes E_t, \tag{89}$$

$$QLP = E_t \otimes E_s H E_t - E_s H^T E_t \otimes E_t + \sum_i (E_{si} \otimes E_t H E_{si} - E_t H^T E_{si} \otimes E_{si}) + \sum_{i \neq j} (E_{si} \otimes E_{sj} H E_{si} - E_{si} H^T E_{sj} \otimes E_{sj}),$$

$$PLQ = (QLP)^\dagger. \tag{90}$$

Having obtained the basic superoperators in tensor product form, in the next step, we can consider how to compute the superoperators $K(t)$ and $I(t)$ in Eq. (72) and then find the conditions under which Eq. (73) (factorized initial conditions) is fulfilled. Inspection of Eq. (72) shows that in order to calculate $K(t)$ and $I(t)$, one needs to calculate the exponentials $\exp(-iQLQt)$ and $\exp(iLt)$ and take an inverse of a matrix to obtain $\theta(t)$. Calculation of $\exp(iLt)$ does not introduce any difficulties and can be reduced to the eigenvalue problem Eq. (50), namely, the eigenvalue problem for the Liouvillean superoperator,

$$(I \otimes H - H^T \otimes I)|E_{nm}\rangle = \varepsilon_{nm}|E_{nm}\rangle, \quad n,m = 1,2,\ldots,6, \tag{91}$$

is solved in terms of eigenvalue solutions to Eq. (50): $\varepsilon_{nm} = \varepsilon_n - \varepsilon_m$ and $E_{nm} = |e_n\rangle\langle e_m|$, where

$$|e_n\rangle = \begin{pmatrix} |e_{sn}\rangle \\ |e_{tn}\rangle \end{pmatrix}$$

and $|E_{nm}\rangle$ is obtained according to the rule Eq. (86). Then,

$$\exp(iLt) = \sum_{nm} \exp(i\varepsilon_{nm} t)|E_{nm}\rangle\langle E_{nm}|. \tag{92}$$

A direct calculation of $\exp(-iQLQt)$ does not seem to have a similar simple solution due to the rather complicated tensor structure of QLQ [Eq. (88)]. However, one can overcome this problem by simplifying $\theta(t)$ to

$$\theta(t) = \{\exp(-iQLQt)[\exp(iQLQt)P + Q\exp(iLt)]\}^{-1} = [P + Q\exp(iLt)]^{-1}\exp(iQLQt), \tag{93}$$

where we have used the identity $\exp(iQLQt)P = P$ and unitarity of $\exp(-iQLQt)$. Since the $\theta(t)$ superoperator in $K(t)$ operates on the state $P|\rho_{\text{tot}}\rangle$ and the Q-projected exponential is canceled in the $I(t)$ superoperator, the TCL equation can be rewritten in the form

$$\frac{d}{dt}|P\rho_{\text{tot}}(t)\rangle = -iK(t)(|P\rho_{\text{tot}}(t)\rangle + |Q\rho_{\text{tot}}(0)\rangle), \tag{94}$$

$$K(t) = PL[P + Q\exp(iLt)]^{-1}, \tag{95}$$

free from $\exp(-iQLQt)$. In fact, as one can see $K(t)$ and $I(t)$ are the same superoperators.

Equation (94) along with Eq. (49) is our central results. Knowing how to calculate the exponential Eq. (92), it is then straightforward to compute $K(t)$ [Eq. (95)] by applying standard matrix multiplication and inversion routines.

B. Separation of unitary and nonunitary dynamics

Condition (73) for a factorized initial state can be rewritten as

$$Q\rho_{\text{tot}}(0) = \begin{pmatrix} \rho^{ss}(0) - \text{diag}[\rho^{ss}_{ii}(0)] & \rho^{st}(0) \\ \rho^{ts}(0) & 0 \end{pmatrix} = 0. \tag{96}$$

It can be fulfilled exactly in the following two cases: (i) the singlet case: $a_t(0) = 0$ and any of the singlet state amplitudes $a_{si}(0) \neq 0$ with all the others being zero, $a_{sj}(0) = 0$, $j \neq i$; (ii) the triplet case: $a_s(0) = 0$. In other cases, including the mixed one, Eq. (94) will not be in closed form and will contain a nonzero inhomogeneous term. Notice that unlike the Lindblad formulation [Eq. (49)], the superoperator $K(t)$ [Eq. (95)] does not depend on which initial state—singlet or triplet—is taken.

Henceforth, we neglect the inhomogeneity for simplicity. To separate unitary effects from nonunitary ones, we decompose the dynamics generator $K(t)$ into Hermitian and non-Hermitian parts,

$$K(t) = K_+(t) + K_-(t),$$

$$K_\pm(t) = \frac{1}{2}\{K(t) \pm K^\dagger(t)\}. \tag{97}$$

Transforming to the interaction representation (denoted by a superscript hat), we have for the unitarily transformed state,

$$|P\hat{\rho}_{\text{tot}}(t)\rangle = T_{\rightarrow} \exp\left(i\int_0^t K_+(\tau)d\tau\right)|P\rho_{\text{tot}}(t)\rangle, \tag{98}$$

the following equation of motion:

$$\frac{d}{dt}|P\hat{\rho}_{\text{tot}}(t)\rangle = -i\hat{K}_-(t)|P\hat{\rho}_{\text{tot}}(t)\rangle, \tag{99}$$

where

$$\hat{K}_-(t) = T_{\rightarrow} \exp\left(i\int_0^t K_+(\tau)d\tau\right) K_-(t) T_{\leftarrow} \exp\left(-i\int_0^t K_+(\tau)d\tau\right). \tag{100}$$

Here, $(T_{\rightarrow})T_{\leftarrow}$ denotes the (anti)chronological ordering operator. One can see that Eq. (99) describes nonunitary dynamics since the generator $\hat{K}_-^\dagger(t) = -\hat{K}_-(t)$ is an anti-Hermitian superoperator. If $K_-(t) \equiv 0$, then the evolution is unitary,

$$|P\rho_{\text{tot}}(t)\rangle = T_{\leftarrow} \exp\left(-i\int_0^t K_+(\tau)d\tau\right)|P\rho_{\text{tot}}(0)\rangle. \tag{101}$$

C. Short time expansion

Expanding $K(t)$ in powers of t, one obtains

$$K_+(t) = PLP + (\{(QLP)^\dagger(QLP), PLP\} - 2(QLP)^\dagger(QLQ) \times (QLP))\frac{t^2}{4} + \cdots,$$

$$K_-(t) = -i(QLP)^\dagger(QLP)t + [(QLP)^\dagger(QLP), PLP]\frac{t^2}{4} + \cdots \tag{102}$$

where $\{\cdot,\cdot\}$ denotes the anticommutator. In the zeroth order approximation $K(t) \equiv PLP$, Eq. (94) is reduced to a unitary matrix equation of the form

$$\dot{\rho}^{ss}_{ii} = 0, \quad i = 1,2,3,$$

$$\dot{\rho}^{tt} = -i[H^{tt}, \rho^{tt}], \tag{103}$$

which describes a unitary evolution of the triplet state density matrix ρ^{tt} under the Hamiltonian H^{tt} with the singlet state population probabilities $\rho^{ss}_{ii}(t) = \rho^{ss}_{ii}(0)$ being constant in time. Let us consider the nonunitary effects which are induced by the first term proportional to t in the expansion of $K_-(t)$ [Eq. (102)].

D. Purity

Observe that $\mathrm{Tr}\, P\rho_{\mathrm{tot}} = \mathrm{Tr}\, \rho$ but $\mathrm{Tr}(P\rho_{\mathrm{tot}})^2 \neq \mathrm{Tr}\, \rho^2$. In order to obtain ρ from $P\rho_{\mathrm{tot}}$, we first have to apply the "compression" transformation [Eq. (84)] so that the purity becomes

$$p(t) = \mathrm{Tr}\, \rho^2(t) = \langle P\rho_{\mathrm{tot}}(t)|CC^T P\rho_{\mathrm{tot}}(t)CC^T\rangle, \tag{104}$$

where

$$CC^T = \begin{pmatrix} J_{3\times 3} & 0 \\ 0 & I_{3\times 3} \end{pmatrix}, \quad J_{3\times 3} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}. \tag{105}$$

Then, using Eq. (94), we obtain an expression for the time derivative,

$$\frac{d}{dt}\mathrm{Tr}\, \rho^2(t) = i\langle P\rho_{\mathrm{tot}}(t)|(K^\dagger(t)CC^T - CC^T K(t))P\rho_{\mathrm{tot}}(t)CC^T\rangle. \tag{106}$$

It is easy to check that the first term, PLP, in the expansion of $K(t)$ does not contribute to Eq. (106) and the first nonzero contribution comes from the first term in the expansion of $K_-(t)$ [Eq. (102)], which can be written as

$$\frac{d}{dt}\mathrm{Tr}\, \rho^2(t) = -2t\langle QLP\rho_{\mathrm{tot}}(0)|QLPCC^T P\rho_{\mathrm{tot}}(0)CC^T\rangle. \tag{107}$$

Further, with the use of Eq. (90), one obtains

$$QLP\rho_{\mathrm{tot}}(0) = \begin{pmatrix} c_{11} & c_{12} \\ -c_{12}^\dagger & 0 \end{pmatrix},$$

$$c_{11} = \{H^{ss}, \mathrm{diag}[\rho^{ss}(0)]\},$$

$$c_{12} = H^{st}\rho^{tt}(0) - \mathrm{diag}[\rho^{ss}(0)]H^{st}, \tag{108}$$

and

$$QLPCC^T P\rho_{\mathrm{tot}}(0)CC^T = \begin{pmatrix} 0 & d_{12} \\ d_{21} & 0 \end{pmatrix},$$

$$d_{12} = H^{st}\rho^{tt}(0) - \rho^{ss}_a(0)H^{st},$$

$$d_{21} = H^{ts}\rho^{ss}_a(0) - \rho^{tt}(0)H^{ts}, \tag{109}$$

where $\rho^{ss}_a(0) = \Sigma_i \rho^{ss}_{ii}(0) J_{3\times 3}$ and Eq. (107) is reduced to

$$\frac{d}{dt}\mathrm{Tr}\, \rho^2(t) = -2t(\mathrm{Tr}[H^{ts}\rho^{ss}_a(0) - \rho^{tt}(0)H^{ts}]\{\mathrm{diag}[\rho^{ss}(0)]H^{st} - H^{st}\rho^{tt}(0)\} + \mathrm{Tr}[H^{st}\rho^{tt}(0) - \rho^{ss}_a(0)H^{st}]\{\rho^{tt}(0)H^{ts} - H^{ts}\mathrm{diag}[\rho^{ss}(0)]\}). \tag{110}$$

Finally, from Eq. (110), one obtains

$$\frac{d}{dt}\mathrm{Tr}\, \rho^2(t) = -4t\begin{cases} (H^{st}H^{ts})_{ii} & \\ \rho^{ss}_{ii}(0) \neq 0 & \text{singlet case,} \\ \langle a_t(0)|H^{ts}H^{st}|a_t(0)\rangle & \\ \rho^{tt}(0) \neq 0 & \text{triplet case,} \end{cases} \tag{111}$$

which is equivalent to the results we obtained in the Lindblad analysis for the purity, Eqs. (69) and (63), respectively. We provide a detailed discussion of the behavior of the purity and other physically relevant quantities in Part II.[41]

E. Time-convolutionless versus Lindblad-type dynamics

Note that the Lindblad-type and TCL [Eqs. (49) and (94)] are not mathematically equivalent formulations. In the Lindblad-type formulation, we allowed correlations between initial singlet and triplet states to be incorporated into the dynamics, whereas in the TCL formulation, we assumed that all operators appearing in the dynamical equations are totally state independent. The first approach gave us the flexibility needed to cover mixed states, whereas the TCL equations become nonclosed [inhomogeneous term in Eq. (94) is nonzero] in the mixed state case.

V. SUMMARY, DISCUSSION, AND CONCLUSIONS

In this work, we have shown that the time evolution of the spin density matrix $\rho(t)$ that describes a system of two electron spins is in general nonunitary when spatial degrees of freedom are accounted for, without coupling to a "true" bath. The nonunitary effects (e.g., the total spin is unconserved) in the pure-spin evolution are due to a nonzero coupling between singlet and triplet states. Our primary focus in this work was the derivation of dynamical equations for the spin density matrix, and a corresponding study of nonunitary effects. Invoking standard ideas from the theory of open quantum systems, one can define a "system+bath" by formally associating the spin variables with the "system" degrees of freedom, and the spatial variables with the "bath" degrees of freedom. With system and bath thus defined, one can apply the standard machinery of open quantum systems theory to

attack the above problem. We did this by first constructing an analog of the Kraus operator sum representation for $\rho(t)$ and then deriving master equations for $\rho(t)$ in the Lindblad and TCL forms.

The Kraus representation [Eq. (15)] has the shortcoming that its Kraus operators are dependent on the initial state $\rho(0)$. This is a consequence of the fact that an arbitrary initial state $\rho(0)$ cannot be represented as a product state with some reference state in coordinate space due to the Pauli antisymmetry principle, which is imposed on the total wave function. As a result of this dependence, the complete positivity property of the mapping [Eq. (15)] is not guaranteed.

The Lindblad-type master equation [Eq. (49)] describes the *exact* dynamics of $\rho(t)$ (it is not a Markovian approximation in our case). Again, the generators of this dynamics are not totally independent of initial conditions. This is to be expected; after all, the ρ dynamics is inherited from the total system unitary dynamics described by Eq. (11). In the total Hilbert space, the state is defined by 11 real parameters [six complex amplitudes $\{a_s(t), a_t(t)\}$ minus the normalization condition], while ρ is defined by five real parameters ("system degrees of freedom"): three amplitude moduli $|a_{ti}(t)|$, $i=1,2,3$, and two relative phase angles between the amplitudes $a_{t1}(t)$, $a_{t2}(t)$ and $a_{t1}(t)$, $a_{t3}(t)$ [$\rho_{tij}(t)=a_{ti}(t)a_{tj}^{*}(t)$, $\rho_s(t)=1-\Sigma_i\rho_{tii}(t)$]. Thus, we have six extra degrees of freedom [four real parameters defining two complex double-ocupancy amplitudes, $a_{s2}(t)$ and $a_{s3}(t)$, and two phases of the amplitudes, $a_{s1}(t)$ and $a_{t1}(t)$] in the reduction $\Psi_{\mathrm{tot}}\rightarrow\rho$, which should be present in the dynamics equation if it is exact. The three complex-valued equations [Eq. (40)], which establish relationships between amplitudes a_s and a_t at the initial moment, allow us to express six extra degrees of freedom as a function of system degrees of freedom. Fixing the correlation matrix $R_m(0)$ appearing there defines a domain in the space of 11 real parameters so that dynamical operators in Eq. (49) acquire a dependence on the domain on which a correlated mixed state is defined. Of course, during time evolution, $R_m(t)$ evolves according to Eq. (42) and the $\{a_s(t), a_t(t)\}$ point can move out of the domain, fixed by $R_m(0)$, on which the initial states were defined. In this case, $R_m(t)$ will define a new domain at time t, which can be considered as the initial state domain for later times.

It turns out that the Heisenberg interaction does not affect the pure-spin dynamics as long as the coupling between singlet and triplet states is neglected [see Eq. (38)]. If there is a nonzero coupling, the Heisenberg interaction modifies the corresponding nonunitary terms: the Heisenberg interaction constant J_H appears in Eq. (58). It also appears in the unitary Lamb shift term [the matrix P_t, which defines this shift, depends on J_H]. Note that the matrix functions in Eq. (58), responsible for the singlet-triplet coupling, depend quadratically on the magnitude of the interaction between singlet and triplet states, described by the H^{ts} matrix elements.

The TCL equation [Eq. (94)] is also exact and describes a nonunitary evolution; the dynamical generator $K(t)$ is non-Hermitian and does not depend on initial conditions. However, the TCL equation is not closed with respect to the $|P\rho_{\mathrm{tot}}(t)\rangle$ state since it contains an inhomogeneous term, which is nonzero in the mixed initial state case. In the nonmixed case defined by Eq. (96), when the TCL equation becomes closed, we found a short-time expansion [Eq. (111)] for the purity function $p(t)$, whose time dependence signifies nonunitary effects in time evolution. For consistency, we obtained the same short-time formulas within the Lindblad-type formulation [Eqs. (63) and (69)]. In Part II,[41] we provide a detailed numerical example demonstrating these nonunitary effects.

In conclusion, the spin density matrix completely describes the pure-spin dynamics of a two-electron system in the case where the electrons cannot be spatially resolved. The formalism we have developed can be generalized in several directions. First, one could take into consideration excited-state orbitals, which will increase the dimensionality of the total Hilbert space. Another interesting generalization is to consider several interacting QDs along the lines developed in Refs. 32–34 and to derive for this few-body case the corresponding spin-density matrix dynamics.

Note added. After completion of this work, we learned from Kaplan about his paper (Ref. 52), where in the Appendix, the author also makes a clear distinction between pure and pseudospins operators. The pseudospins are called site spin operators in Kaplan's work.

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