

Retrodictive derivation of the radical-ion-pair master equation and Monte Carlo simulation with single-molecule quantum trajectories

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Radical-ion-pair reactions, central in photosynthesis and the avian magnetic compass mechanism, have been recently shown to be a paradigm system for applying quantum information science in a biochemical setting. The fundamental quantum master equation describing radical-ion-pair reactions is still under debate. Here we use quantum retrodiction to formally refine the theory put forward in the paper by Kominiis [I. K. Kominiis, *Phys. Rev. E* **83**, 056118 (2011)]. We also provide a rigorous analysis of the measure of singlet-triplet coherence required for deriving the radical-pair master equation. A Monte Carlo simulation with single-molecule quantum trajectories supports the self-consistency of our approach.

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I. INTRODUCTION

Radical-ion pairs and their spin-dependent reactions [1,2] have been recently shown [3–19] to be a paradigm system for the emerging field of quantum biology [20], that is, the study of quantum coherence effects or, in general, the study of quantum information science in the context of biological systems. The biological significance of radical-ion-pair (RP) reactions is twofold: (i) they are understood to underlie the avian magnetic compass mechanism [21–26] and (ii) they participate in the electron-transfer cascade reactions taking place in photosynthetic reaction centers [27,28]. In any case, the experimentally founded science of spin chemistry [29] deals with such reactions in a wide range of chemical contexts. Hence the theoretical understanding of RP reactions at the fundamental level is of importance for current experimental work in spin chemistry, for further exploring quantum effects in biological systems, as well as for the design of novel and potentially quantum-limited biomimetic devices and sensors.

Theoretically, the fate of radical-ion-pair reactions and all relevant predictions are fully accounted for by the time evolution of ρ , the RP's spin density matrix. The time evolution of ρ was until recently understood to be driven by (i) unitary Hamiltonian evolution due to all magnetic interactions within the RP and (ii) RP population loss due to spin-dependent charge recombination. We have recently shown that the spin degrees of freedom of the RP form an open quantum system, i.e., there is a third source of time evolution: (iii) the spin decoherence inherent in the radical-pair mechanism [3,5]. Moreover, since the RP is, in general, in a coherent (or partially coherent) superposition of spin states (we refer in particular to singlet-triplet coherence), the description of the RP's reaction kinetics appears not to be as straightforward as originally thought. In [5], we demonstrated that singlet-triplet (S-T) coherence of the RP is a central concept in understanding the intimately related effects (i)–(iii) and put forward a master equation satisfied by the density matrix ρ . While S-T decoherence was described [3] by first-principles perturbation theory (similar to most applications of

the theory of Markovian open quantum systems leading to a Lindblad decoherence term), the reaction kinetics had been accounted for in a phenomenological manner open to criticism. Moreover, the introduction [5] of the coherence measure p_{coh} quantifying the “strength” of S-T coherence was also done intuitively.

In this work, we formalize our approach along both fronts previously mentioned. In particular, (i) we show that the measure of S-T coherence introduced in [5] is not well defined. We then introduce a measure of S-T coherence based on recently published rigorous considerations by Plenio and co-workers [30], (ii) we formally derive the reaction terms of the master equation using quantum retrodiction, a concept borrowed from the field of quantum communications; and (iii) we introduce the Monte Carlo (MC) simulation of single-RP quantum trajectories [31,32]. The MC simulation contains, by design, all relevant phenomena at the single-molecule level, and hence forms a unique tool to test the predictions of our master equation.

We show that our introduced measure of S-T coherence, properly scaling with the off-diagonal elements of the density matrix, is essential for the decomposition of ρ into a mixture of maximally coherent and maximally incoherent states. This decomposition underlies the retrodictive derivation of the reaction terms, which lead to (a) a significantly improved agreement of the master equation prediction with MC and (b) the derivation of precise and experimentally measurable decay rates for the S-T coherence.

In particular, in Sec. III, we introduce the Monte Carlo simulation of single-RP quantum trajectories including only S-T decoherence and compare it with the master equation for nonrecombining RPs where perfect agreement is expected by definition. In Sec. IV, we elaborate on the shortcomings of our previous measure of S-T coherence and then introduce a measure based on [30]. The decomposition of ρ into a mixture of maximally coherent and maximally incoherent states is presented in Sec. V. This decomposition is the basis of the rigorous theory of quantum retrodiction used to derive the reaction terms of the master equation, presented in Sec. VI. In Sec. VII, we perform a Monte Carlo simulation of RP quantum trajectories including recombination, comparing the trajectory average with the prediction of our master equation. Finally, in Sec. VIII, we discuss the decay of S-T coherence in a way

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that could be relevant to experimentally accessible observables and we compare our theory with the predictions of competing theoretical approaches. In the following section, we start with a few definitions and a brief review of previous work in order to make this work as comprehensive as possible for the general reader.

II. DEFINITIONS AND PREVIOUS WORK

The quantum degrees of freedom of RPs are formed by a multipin system embedded in a biomolecule. In particular, RPs are biomolecular ions created by a charge transfer from a photo-excited D^*A donor-acceptor biomolecular dyad DA, schematically described by the reaction $DA \rightarrow D^*A \rightarrow D^{\bullet+}A^{\bullet-}$, where the two dots represent the two unpaired electrons of the two radicals. The excited state D^*A is usually a spin zero state, hence the initial spin state of the two unpaired electrons is a singlet, denoted by $^S D^{\bullet+}A^{\bullet-}$.

Now, both D and A contain a number of magnetic nuclei which hyperfine couple to the donor's and acceptor's electron, respectively, effectively creating a different magnetic environment for the two unpaired electrons. This leads to S-T mixing, i.e., a coherent oscillation of the spin state of the electrons. Charge recombination terminates the reaction and leads to the formation of the neutral reaction products. Angular momentum conservation at this step empowers the molecule's spin degrees of freedom and their minuscule (relative to thermal) energy to determine the reaction's fate: singlet state RPs, $^S D^{\bullet+}A^{\bullet-}$, recombine to reform the neutral spin zero DA molecules, whereas triplet RPs, $^T D^{\bullet+}A^{\bullet-}$, recombine to a different (metastable) triplet neutral product $^T DA$. For completeness, we note that the reaction can, in principle, close through the so-called intersystem crossing $^T DA \rightarrow DA$. The above are schematically shown in Fig. 1.

The straightforward part of RP dynamics is the unitary dynamics embodied in the magnetic Hamiltonian \mathcal{H} , which mainly contains (i) hyperfine couplings of the donor's (acceptor's) electron with the donor's (acceptor's) nuclear spins,

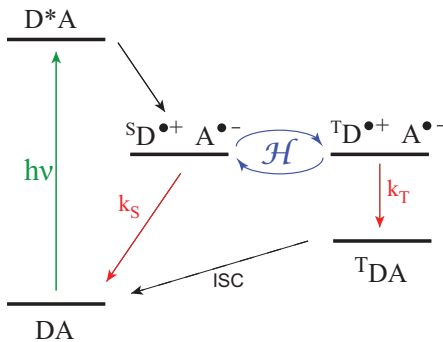


FIG. 1. (Color online) Simplified energy level diagram depicting radical-ion-pair reaction dynamics. A donor-acceptor dyad is photo excited and a subsequent charge transfer produces a singlet radical-ion pair. Magnetic interactions within the radical pair induce coherent singlet-triplet mixing, while spin-dependent charge recombination leads to singlet and triplet neutral products at the respective reaction rates k_S and k_T . The reaction can, in principle, close through intersystem crossing from the triplet to the singlet ground state.

(ii) Zeeman interaction of the donor's and acceptor's electrons with the externally applied magnetic field (nuclear Zeeman interaction is usually neglected), and (iii) spin-exchange and dipolar interactions between the donor's and the acceptor's electron [8,33].

Were this a closed system, its dynamics would be fully described by Liouville's equation $d\rho/dt = -i[\mathcal{H}, \rho]$. However, it is not, and hence there are more terms that make up the master equation, which will be elaborated in the following. These terms involve two central operators, the singlet and triplet projectors Q_S and Q_T , respectively. Before defining them, we note that the density matrix ρ describes the spin state of the RP's two electrons and M magnetic nuclei located in D and A. The dimension of ρ is $d = 4\prod_{j=1}^M (2I_j + 1)$, where I_j is the nuclear spin of the j th nucleus, with $j = 1, 2, \dots, M$. For our numerical work, we consider the simplest possible RP, namely an RP containing just one spin-1/2 nuclear spin hyperfine coupled to, e.g., the donor's electron. In this case, the density matrix has dimension $d = 8$. This simple model system exhibits the essential physics without the additional complication of more nuclear spins. We stress that the master equation we derive is general and equally applicable for any number of nuclear spins entering the magnetic Hamiltonian \mathcal{H} and any sort of interactions included in \mathcal{H} .

Angular momentum conservation at the recombination process splits the RP's Hilbert space into an electron singlet and an electron triplet subspace, defined by the respective projectors Q_S and Q_T . These are $d \times d$ matrices given by $Q_S = \frac{1}{4}\mathbb{1}_d - \mathbf{s}_D \cdot \mathbf{s}_A$ and $Q_T = \frac{3}{4}\mathbb{1}_d + \mathbf{s}_D \cdot \mathbf{s}_A$, where \mathbf{s}_D and \mathbf{s}_A are the spin operators of the donor and acceptor electrons written as d -dimensional operators, e.g., the j th component of \mathbf{s}_D is written as $s_{jD} = \hat{s}_j \otimes \mathbb{1}_2 \otimes \mathbb{1}_{2I_1+1} \otimes \mathbb{1}_{2I_2+1} \cdots \otimes \mathbb{1}_{2I_M+1}$, where the first operator in the previous Kronecker product refers to the donor's electron spin, the second to the acceptor's electron spin, and the rest to the nuclear spins. By \hat{s} , we have denoted the regular (two-dimensional) spin-1/2 operators and, by $\mathbb{1}_m$, we have denoted the m -dimensional unit matrix. We note that the RP's singlet subspace has dimension $\prod_{j=1}^M (2I_j + 1)$, while the triplet subspace has dimension $3\prod_{j=1}^M (2I_j + 1)$. The electron multiplicity 1 in the former corresponds to the singlet state $|S\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$, while the multiplicity of 3 in the latter stems from the three triplet states $|T_0\rangle = (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$, $|T_+\rangle = |\uparrow\uparrow\rangle$, and $|T_-\rangle = |\downarrow\downarrow\rangle$.

The projectors Q_S and Q_T are complete and orthogonal, i.e., $Q_S + Q_T = \mathbb{1}_d$ and $Q_S Q_T = Q_T Q_S = 0$. There are also two rates to consider, i.e., the singlet and triplet recombination rates, k_S and k_T , respectively. These are defined as follows: consider an RP ensemble with no magnetic interactions ($\mathcal{H} = 0$) to be in the singlet (triplet) state. Then its population would decay exponentially at the rate k_S (k_T). Finally, in any given time interval dt , the measured singlet and triplet neutral products will be $dn_S = k_S dt \text{Tr}\{\rho Q_S\}$ and $dn_T = k_T dt \text{Tr}\{\rho Q_T\}$. These relations are simple to understand, namely, in the time interval dt there would be $k_S dt$ singlet and $k_T dt$ triplet recombinations if all RPs were in the singlet or triplet state, respectively. If they are in the general state described by ρ , then $k_S dt$ and $k_T dt$ have to be multiplied by the respective probabilities to be in the singlet or triplet state.

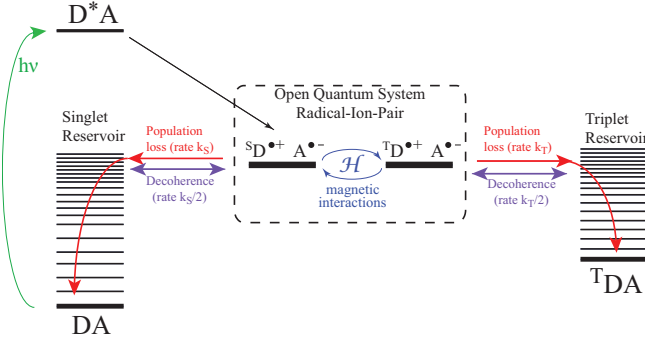


FIG. 2. (Color online) Detailed energy level structure of radical-ion pairs. The vibrational excitations of the singlet (DA) and the triplet (TDA) ground state form a reservoir that probes the electron spin state of the RP, leading to an intramolecule measurement of Q_S . Virtual transitions (rates $k_S/2$ and $k_T/2$) to the reservoir levels and back to the RP lead to S-T decoherence, while real transitions (rates k_S and k_T) to the reservoir states followed by their decay to the ground state lead to recombination.

The initial state most often considered when doing calculations with the density matrix is the singlet electron-unpolarized nuclear spin state written as $\rho = Q_S/\text{Tr}\{Q_S\}$.

A. Singlet-triplet decoherence

A more detailed look at the energy level structure of Fig. 1 reveals the picture depicted in Fig. 2, where we show the vibrational excited states of the singlet and triplet ground states, which form the singlet and triplet reservoir. Radical-pair recombination proceeds as a *real* transition of the RP to one of the quasiresonant and quasicontinuous reservoir states. As we have demonstrated in [6], there cannot be any coherence between the RP state and the neutral ground states, but only population transfer from the former to the latter, due to which the RP is an open system. What we have shown in [3] is that it is “doubly open” because the same reservoir states lead to S-T decoherence. Using second-order perturbation theory, we have shown that *virtual* transitions to these vibrational reservoir states *and back* interrupt the coherent S-T mixing in individual RPs and hence cause the decay of the ensemble S-T coherence. This is described with a Lindblad-type and trace-preserving master equation,

$$\frac{d\rho}{dt}|_{\text{decoh}} = -i[\mathcal{H}, \rho] - \frac{k_S + k_T}{2}(Q_S\rho + \rho Q_S - 2Q_S\rho Q_S). \quad (1)$$

In other words, this equation describes the null quantum measurement of the RP’s neutral reaction products: there is a certain probability that the RP will recombine during a time interval dt . If this does not happen, i.e., if no reaction product is detected, then there are three different possibilities that could be realized within dt : (i) a projection to the singlet state, (ii) a projection to the triplet state, and (iii) Hamiltonian evolution. In the following section, we present a Monte Carlo simulation of individual quantum trajectories and elaborate in detail on these issues.

III. MONTE CARLO SIMULATION OF S-T DECOHERENCE USING SINGLE-MOLECULE QUANTUM TRAJECTORIES

As is well known from quantum optics, the absence of a detection event, e.g., a photon detection, in a quantum measurement, called “null” measurement, also has an effect on the system’s quantum state. What we have shown in [3] is that the quantum state evolution of a nonrecombining RP (absence of detection of recombination events) is given by the Lindblad master equation (1). This trace-preserving master equation encompasses the following three possibilities that a nonrecombining RP faces during the time evolution of its quantum state: (i) a quantum jump to the singlet state $\rho_S = Q_S\rho Q_S/\text{Tr}\{\rho Q_S\}$, taking place with probability

$$dp_S = \frac{(k_S + k_T)dt}{2}\text{Tr}\{\rho Q_S\}, \quad (2)$$

(ii) a quantum jump to the triplet state $\rho_T = Q_T\rho Q_T/\text{Tr}\{\rho Q_T\}$, taking place with probability

$$dp_T = \frac{(k_S + k_T)dt}{2}\text{Tr}\{\rho Q_T\}, \quad (3)$$

(iii) unitary evolution driven by the Hamiltonian \mathcal{H} , taking place with probability $1 - dp_S - dp_T$.

In an ensemble of RPs, these single-molecule possibilities are unobservable, so we have to average over them. This averaging *exactly* reproduces the master equation (1). In other words, writing $\rho_{t+dt} = dp_S\rho_S + dp_T\rho_T + (1 - dp_S - dp_T)(\rho_t - idt[\mathcal{H}, \rho_t])$ leads to (1) for $d\rho/dt = (\rho_{t+dt} - \rho_t)/dt$.

The physical significance of the sum $k_S + k_T$ appearing in the probabilities dp_S and dp_T is the fact that both singlet and triplet reservoirs continuously “measure” the same observable, namely, Q_S . The result of this measurement is either 1 or 0, corresponding to the singlet and triplet projections, respectively. In particular, the singlet reservoir measures the observable Q_S at the rate $k_S/2$. The “yes” result of this measurement corresponds to $Q_S = 1$ and the singlet projection, while the “no” or null result corresponds to the triplet projection. Similarly, the triplet reservoir measures the observable $Q_T = \mathbb{1} - Q_S$ at the rate $k_T/2$. The yes result of this measurement corresponds to $Q_S = 0$ and a triplet projection, while the no or null result corresponds to the singlet projection. Equivalently, Q_S is measured at the total rate $(k_S + k_T)/2$. Again, these measurements are unobservable and lead to the aforementioned S-T dephasing. What is observable is the detection of a neutral recombination product. The corresponding null detection implies the possibilities (i)–(iii).

For testing our code and providing a “baseline” for the simulations of Sec. VII, we show in Fig. 3 an example of an MC simulation of just the singlet-triplet decoherence described by (1). To simulate the quantum trajectories of nonrecombining RPs, we start with 10^4 RPs all being in the singlet state at $t = 0$. We then evolve the state of each RP, using, in each time increment dt , a random number r uniformly distributed between 0 and 1. If $r < dp_S$, we project the RP trajectory to the singlet state; if $dp_S < r < dp_S + dp_T$, we project it to the triplet state; and if $1 > r > dp_S + dp_T$, we evolve the RP state with the Hamiltonian \mathcal{H} . Due to these random quantum jumps, the S-T oscillations of the RPs suffer dephasing,

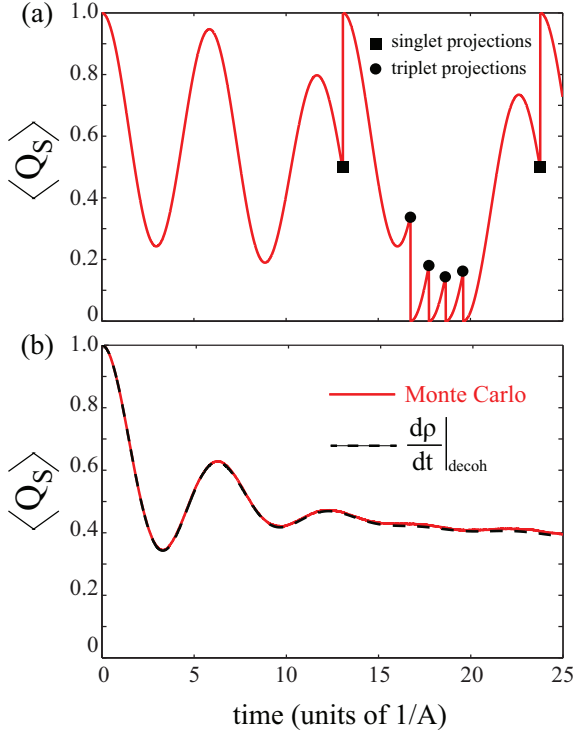


FIG. 3. (Color online) The time evolution of $\langle Q_S \rangle$ for a model RP with one nuclear spin, taking into account only S-T decoherence and S-T mixing driven by the Hamiltonian $\mathcal{H} = \omega(s_{1z} + s_{2z}) + A\mathbf{s}_1 \cdot \mathbf{I}$, where the Larmor frequency is taken $\omega = A/10$ and the recombination rates are $k_S = k_T = A/4$. These parameters represent a typical RP at earth's field with a hyperfine coupling on the order of 1 mT and recombination times on the order of 20 ns. (a) Single-RP quantum trajectory, depicting singlet and triplet projections at random instants in time. The initial RP state for this trajectory is $|S\rangle \otimes |\uparrow\rangle$. (b) Average of 20 000 such trajectories (red solid line), half of which have initial state $|S\rangle \otimes |\uparrow\rangle$ while the other half have initial state $|S\rangle \otimes |\downarrow\rangle$. The time axis was split into 10 000 steps dt , in every one of which one out of the three possibilities outlined in Sec. III was realized. The prediction of the trace-preserving master equation (1) is shown by the black dashed line. The initial state for the density matrix was the usually considered singlet state with unpolarized nuclear spin, $\rho = Q_S/\text{Tr}\{Q_S\}$.

and hence the trajectory-averaged expectation value of Q_S exhibits S-T oscillations of decaying amplitude. The perfect agreement between MC and the master equation (1) shown in Fig. 3(b) is expected *by definition*, i.e., the physics included in the MC simulation is those exactly reproducing the master equation. This agreement does not convey any information other than that our code is working properly and that the 10 000 trajectories are statistically adequate for the comparison undertaken in the following.

IV. SINGLET-TRIPLET COHERENCE

Since $Q_S + Q_T = \mathbb{1}$ (the unit matrix is henceforth understood to have the dimension of the particular RP under consideration), any density matrix ρ can be written as $\rho = (Q_S + Q_T)\rho(Q_S + Q_T)$, or

$$\rho = \rho_{SS} + \rho_{TT} + \rho_{ST} + \rho_{TS}, \quad (4)$$

where $\rho_{xy} = Q_x\rho Q_y$, with $x, y = S, T$. It is clear that $\rho_{SS} + \rho_{TT}$ forms the incoherent part of ρ , whereas the S-T coherence is represented by $\rho_{ST} + \rho_{TS}$. A naturally arising question is how coherent is a particular RP state described by some density matrix ρ . Consider, for simplicity, an imaginary four-dimensional RP. The state $|\psi\rangle = (|S\rangle + |T_0\rangle)/\sqrt{2}$ or, equivalently, $\rho = \frac{1}{2}|S\rangle\langle S| + \frac{1}{2}|T_0\rangle\langle T_0| + \frac{1}{2}|S\rangle\langle T_0| + \frac{1}{2}|T_0\rangle\langle S|$ clearly is maximally S-T coherent, whereas the state $\rho = \frac{1}{2}|S\rangle\langle S| + \frac{1}{2}|T_0\rangle\langle T_0|$ is maximally incoherent. There could also be an intermediate case of partial coherence, such as $\rho = \frac{1}{2}|S\rangle\langle S| + \frac{1}{2}|T_0\rangle\langle T_0| + a|S\rangle\langle T_0| + a|T_0\rangle\langle S|$, with $a < 1/2$. We thus need a measure of the “strength” of the “off-diagonal part” ρ_{ST} of the density matrix. In [5], we introduced the measure of coherence,

$$p_{\text{coh}}(\rho) = \frac{\text{Tr}\{\rho_{ST}\rho_{TS}\}}{\text{Tr}\{\rho_{SS}\}\text{Tr}\{\rho_{TT}\}}. \quad (5)$$

However, this definition of p_{coh} is flawed in the following sense. S-T coherence is reflected by the value of the off-diagonal elements of the density matrix in the S-T basis. It is intuitively expected that such a measure should scale linearly with the off-diagonal elements; however, p_{coh} scales as the square of the off-diagonal elements of ρ . Hence, if they decay at some rate Γ , p_{coh} will decay at 2Γ , and this will skew the description of the relevant dynamics.

A. Rigorous analysis of S-T coherence

Although essential, a rigorous quantification of coherence in quantum systems has received little attention, at least compared to the quantification of entanglement which has advanced through the definition of several measures [34,35]. Recently, Plenio and co-workers introduced a rigorous approach to quantifying quantum coherence [30]. We will follow this approach to introduce a well-behaved measure of S-T coherence.

The first step is to define the set of incoherent states \mathcal{I} . Since we are interested in S-T coherence, it is straightforward to define \mathcal{I} as the set containing all density matrices ρ for which $\rho = \rho_{SS} + \rho_{TT}$, i.e., the coherences ρ_{ST} and ρ_{TS} are absent. Plenio and co-workers then define a set of three criteria that any measure of coherence should satisfy. The first and most obvious (and the one that will be used in the following) is that $p_{\text{coh}}(\rho) = 0$ for $\rho \in \mathcal{I}$. In order not to overburden this discussion with technical details, this and the other two criteria are reproduced in Appendix A, where we also demonstrate in more detail the shortcomings of our previous definition (5).

In the definition of p_{coh} to be shortly introduced, p_{coh} scales linearly with the off-diagonal elements of ρ , as it conforms with the Hilbert-Schmidt norm $C_l(\rho)$ shown in [30] to be an acceptable measure of coherence. In this measure, Plenio and co-workers sum the absolute value of all off-diagonal elements of the density matrix. However, we are not interested in quantifying coherences within the triplet subspace, e.g., among $|T_+\rangle$ and $|T_-\rangle$. Neither are we interested in nuclear spin coherences. We are only concerned with the coherence between the electron singlet and triplet subspaces. So, in our definition, we will sum the absolute value of the amplitudes appearing in the coherences $|S\rangle\langle T_0|$, $|S\rangle\langle T_+\rangle$, and $|S\rangle\langle T_-\rangle$. To

do so, we define

$$\mathcal{C}(\rho) = \sum_{j=0,\pm} \sqrt{\text{Tr}\{\rho_{\text{ST}}|\text{T}_j\rangle\langle\text{T}_j|\rho_{\text{TS}}\}}. \quad (6)$$

This definition is visualized by a simple example in Appendix B. Before defining the measure p_{coh} , we note the following: (i) Since $\text{Tr}\{\rho\}$ is a decaying function of time due to recombination, we have to normalize $\mathcal{C}(\rho)$ by $\text{Tr}\{\rho\}$ in order to get the genuine measure of coherence for the surviving RPs. (ii) As mentioned in [30], the state of maximum coherence in a d -dimensional Hilbert space with basis $|j\rangle$ is $\sum_{j=1}^d \frac{1}{\sqrt{d}}|j\rangle$. In our case, the most general pure state of an RP can be written as $|\psi\rangle = \alpha_{\text{S}}|\text{S}\rangle \otimes |\chi_{\text{S}}\rangle + \sum_{j=0,\pm} \alpha_j|\text{T}_j\rangle|\chi_j\rangle$, where $|\chi_{\text{S}}\rangle$ and $|\chi_j\rangle$ are normalized nuclear spin states. Here S-T coherence is maximum when $|\alpha_{\text{S}}| = |\alpha_j| = 1/2$, and this maximum value is $\sum_{j=0,\pm} |\alpha_{\text{S}}\alpha_j| = 3/4$. However, if the Hamiltonian excites a subset of these coherences, e.g., only the S-T₀ coherence, the maximum value of the coherence would be smaller. Since in the following we use p_{coh} as a probability measure, we normalized $\mathcal{C}(\rho)$ with its maximum value obtained when ρ evolves unitarily under the action of \mathcal{H} . So now we define

$$p_{\text{coh}}(\rho) = \frac{1}{\text{Tr}\{\rho\}} \frac{\mathcal{C}(\rho)}{\max\{\mathcal{C}(\tilde{\rho})\}}, \quad (7)$$

where $d\tilde{\rho}/dt = -i[\mathcal{H}, \tilde{\rho}]$. We note that this definition of p_{coh} is numerically very similar to the square root of our earlier definition (5).

V. DEFINITION OF ρ_{coh} AND ρ_{incoh}

It is clear from (6) that if we scale ρ_{ST} and ρ_{TS} with a positive number λ , i.e., if $\rho_{\text{ST}} \rightarrow \lambda\rho_{\text{ST}}$ and $\rho_{\text{TS}} \rightarrow \lambda\rho_{\text{TS}}$, then $p_{\text{coh}} \rightarrow \lambda p_{\text{coh}}$. So going back to the general form (4) of the density matrix ρ , if we choose $\lambda = 1/p_{\text{coh}}$, that is, if we define the density matrix

$$\rho_{\text{coh}} = \rho_{\text{SS}} + \rho_{\text{TT}} + \frac{1}{p_{\text{coh}}}\rho_{\text{ST}} + \frac{1}{p_{\text{coh}}}\rho_{\text{TS}}, \quad (8)$$

then ρ_{coh} will describe a maximally coherent state, $p_{\text{coh}}(\rho_{\text{coh}}) = 1$. The density matrix ρ_{coh} can be thought of as the S-T coherence distillation of ρ . We can also define a maximally incoherent density matrix ρ_{incoh} :

$$\rho_{\text{incoh}} = \rho_{\text{SS}} + \rho_{\text{TT}}, \quad (9)$$

for which $p_{\text{coh}}(\rho_{\text{incoh}}) = 0$. Using Eqs. (4), (8), and (9), it is then trivial to show that *any* density matrix ρ can be written as

$$\rho = (1 - p_{\text{coh}})\rho_{\text{incoh}} + p_{\text{coh}}\rho_{\text{coh}}. \quad (10)$$

This will be the starting point for the retrodictive derivation presented in the following section. We note that this general decomposition of ρ into ρ_{incoh} and ρ_{coh} was possible due to the particular definition of ρ_{coh} and its property that $p_{\text{coh}}(\rho_{\text{coh}}) = 1$, which itself relies on the linear scaling of p_{coh} mentioned previously. In other words, the following formal derivation based on quantum retrodiction would not be possible without the proper definition of the S-T coherence measure.

VI. QUANTUM RETRODICTION AND RADICAL-ION-PAIR RECOMBINATION

A. Radical-ion-pair recombination from the single-molecule and from the ensemble perspective

The density matrix of an ensemble of N RPs is $\rho_t = \sum_{i=1}^N |\psi_i(t)\rangle\langle\psi_i(t)|$, where $|\psi_i\rangle$ is the spin state of the i th RP. Each $|\psi_i\rangle$ has suffered a number of S- or T-quantum jumps until the time t . Due to recombination, N is time dependent, since if the i th RP recombines at time t , its quantum state $|\psi_i\rangle\langle\psi_i|$ at time t must be subtracted from ρ_t in order to update ρ_t into ρ_{t+dt} . Although this is a simple physical picture from the perspective of quantum trajectories, it is not straightforward to translate it into a master equation. The root of the difficulty is S-T dephasing, which transforms a pure initial state into a mixture.

As is well known, there is no unique way to unravel a density matrix into its component pure states. Hence we have to instead utilize the following physical scenario. Given the density matrix ρ_t at some time t , and given the *measured* singlet and triplet neutral products during the infinitesimal interval dt , dn_{S} , and dn_{T} , respectively, how do we update ρ_t into ρ_{t+dt} ? In general, the change $d\rho = \rho_{t+dt} - \rho_t$ is caused by (i) the change of state of RPs that did not recombine during dt , call it $d\rho_{\text{decoh}}$, given by (1), and (ii) the RPs that did recombine during dt , call it $d\rho_{\text{recomb}}$, i.e., $d\rho = d\rho_{\text{decoh}} + d\rho_{\text{recomb}}$. Clearly, $\text{Tr}\{d\rho\} = \text{Tr}\{d\rho_{\text{recomb}}\} = -dn_{\text{S}} - dn_{\text{T}}$, but that alone cannot lead to the form of $d\rho_{\text{recomb}}$.

We will now derive $d\rho_{\text{recomb}}$ using the formal tools of quantum retrodiction. We then compare the predictions of the master equation to the Monte Carlo simulation. The latter turns out to be a very useful tool, since dealing with an ensemble of pure states allows us, by default, to subtract the particular component states $|\psi_i\rangle$ of the recombined RPs from the considered ensemble.

B. Radical-ion-pair recombination and quantum retrodiction

The predictive approach to quantum measurements, which we are most familiar with, addresses the following question: Given the density matrix describing a physical system, what are the probabilities of specific measurement outcomes? The so-called retrodictive approach [36,37], used less often, is about the reverse: Given a specific measurement outcome, what is the probability that the system's state prior to the measurement was this or that? Quantum retrodiction is relevant to quantum communication [38,39] since Bob, the receiver of quantum information, attempts to reconstruct the quantum state delivered to him by Alice, the sender, based on specific measurement outcomes.

The idea relating RP recombination to the concept of retrodiction and S-T coherence is the following. When an RP is in a particular state $|\psi\rangle$ just before it recombines, we must subtract $|\psi\rangle\langle\psi|$ from the density matrix to account for this recombination event. But since S-T dephasing produces a mixture of pure states, given the recombination product, which is either the singlet or the triplet ground state, one cannot unambiguously retrodict the prerecombination state $|\psi\rangle$. A singlet recombination could, for example, result from a singlet RP as much as from an S-T coherent RP. The theory of quantum

retrodiction allows us to retrodict $|\psi\rangle$ “on average.” The way this is done depends on how coherent the RP state is that is described by the density matrix ρ , and hence the necessity of defining p_{coh} .

This is seen by examining the two extreme cases of minimum and maximum S-T coherence, for which $d\rho_{\text{recomb}}$ is straightforward to derive. Based on the general decomposition (10), the theory of quantum retrodiction can then be seamlessly applied in the general case of a density matrix with partial S-T coherence.

C. Recombination of maximally coherent radical-ion pairs

Suppose that at time t , we have an ensemble of N RPs all in some maximally S-T coherent state $|\psi\rangle$. Suppose further that the only change during the interval dt is the recombination of just one RP, i.e., the detection of one neutral product. Clearly, scaling the normalization of ρ from 1 to N just for the sake of this discussion, it is $\rho_t = N|\psi\rangle\langle\psi|$ and $\rho_{t+dt} = (N-1)|\psi\rangle\langle\psi|$, since now we have one less RP in the state $|\psi\rangle$. This can be formalized as follows. For a maximally coherent ensemble of RPs all in the same state $|\psi\rangle$, the single-molecule density matrix will be $\rho/\text{Tr}\{\rho\}$. If we define $\delta\rho_{\text{coh}}^{\text{IS}}$ ($\delta\rho_{\text{coh}}^{\text{IT}}$) to be the change in ρ due to the measurement of *just one* singlet (triplet) neutral product, it will be

$$\delta\rho_{\text{coh}}^{\text{IS}} = \delta\rho_{\text{coh}}^{\text{IT}} = -\frac{\rho}{\text{Tr}\{\rho\}}. \quad (11)$$

D. Recombination of maximally incoherent radical-ion pairs

In the other extreme, suppose that ρ_t is a maximally incoherent mixture of singlet and triplet RPs, i.e., $\rho_t = \rho_{\text{SS}} + \rho_{\text{TT}}$. Then the detection of a singlet (triplet) recombination product leads us to conclude with certainty that it resulted from a singlet (triplet) RP and hence we can reduce the population of singlet (triplet) RPs by one. If we define $\delta\rho_{\text{incoh}}^{\text{IS}}$ ($\delta\rho_{\text{incoh}}^{\text{IT}}$) to be the change in ρ due to the recombination of *just one* singlet (triplet) RP, it will be

$$\delta\rho_{\text{incoh}}^{\text{IS}} = -\frac{Q_S\rho Q_S}{\text{Tr}\{Q_S\rho Q_S\}} = -\frac{Q_S\rho Q_S}{\text{Tr}\{\rho Q_S\}}, \quad (12)$$

$$\delta\rho_{\text{incoh}}^{\text{IT}} = -\frac{Q_T\rho Q_T}{\text{Tr}\{Q_T\rho Q_T\}} = -\frac{Q_T\rho Q_T}{\text{Tr}\{\rho Q_T\}}. \quad (13)$$

The last equality in the above equations follows from the cyclic property of the trace and the fact that Q_S and Q_T are projectors, and hence idempotent.

E. Recombination of radical-ion pairs having partial S-T coherence

We will now use the formalism of quantum retrodiction to derive the reaction operators for the general case of partial S-T coherence. The retrodiction formalism [38,39] uses the preparation operators Λ_i and the measurement operators Π_j . In particular, suppose that a system is prepared in a state ρ_i with probability $P(i)$. The preparation operator is then defined as $\Lambda_i = P(i)\rho_i$. If the particular preparation is unknown, then we have to average over all possible preparations and the system will be described by the density matrix $\rho = \sum_i \Lambda_i$. Suppose

further that a measurement defined by the positive operator-valued measure (POVM) set Π_i , where $\sum_i \Pi_i = \mathbb{1}$, returns the j th result. Defining $\rho_j^r = \Pi_j/\text{Tr}\{\Pi_j\}$, the main result of retrodiction theory is that the *conditional probability* that state ρ_i was prepared, given the measurement result j , is

$$P(i|j) = \frac{\text{Tr}\{\Lambda_i\rho_j^r\}}{\sum_i \text{Tr}\{\Lambda_i\rho_j^r\}}. \quad (14)$$

The POVM set of measurement operators of interest in our case consists of $\Pi_1 = Q_S$ and $\Pi_2 = Q_T$, already mentioned to satisfy the condition $Q_S + Q_T = \mathbb{1}$. As shown before, the general form of the RP density matrix at time t can be written as $\rho = \Lambda_1 + \Lambda_2 = (1-p_{\text{coh}})\rho_{\text{incoh}} + p_{\text{coh}}\rho_{\text{coh}}$, i.e., we identify $\Lambda_1 = (1-p_{\text{coh}})\rho_{\text{incoh}}$ and $\Lambda_2 = p_{\text{coh}}\rho_{\text{coh}}$, where ρ_{coh} and ρ_{incoh} have been defined by (8) and (9), respectively.

Suppose that during the interval dt we have detected one x neutral product, where $x = S, T$. To apply Eq. (14), we note that since $\rho_x^r = Q_x/\text{Tr}\{Q_x\}$, the denominator $\text{Tr}\{Q_x\}$ of ρ_x^r will drop out of Eq. (14). Further, since $\rho = \sum_i \Lambda_i$, the denominator in Eq. (14) is proportional to the expectation value of Q_x at time t , i.e., $\sum_i \text{Tr}\{\Lambda_i\rho_x^r\} \propto \text{Tr}\{\rho Q_x\}$; hence, given the detection of one x neutral product, the probabilities that it originated either from ρ_{incoh} or from ρ_{coh} are

$$P(\text{incoh}|x) = \frac{\text{Tr}\{\Lambda_1 Q_x\}}{\text{Tr}\{\rho Q_x\}} = (1-p_{\text{coh}}) \frac{\text{Tr}\{\rho_{\text{incoh}} Q_x\}}{\text{Tr}\{\rho Q_x\}},$$

$$P(\text{coh}|x) = \frac{\text{Tr}\{\Lambda_2 Q_x\}}{\text{Tr}\{\rho Q_x\}} = p_{\text{coh}} \frac{\text{Tr}\{\rho_{\text{coh}} Q_x\}}{\text{Tr}\{\rho Q_x\}}. \quad (15)$$

Since the expectation value of Q_x in ρ is the same as in ρ_{incoh} and ρ_{coh} , it readily follows that

$$P(\text{incoh}|S) = P(\text{incoh}|T) = 1 - p_{\text{coh}},$$

$$P(\text{coh}|S) = P(\text{coh}|T) = p_{\text{coh}}.$$

We have shown how the density matrix changes upon detecting just one product in the extreme cases of maximum and minimum coherence. In the general case when the RP ensemble is described by ρ , detecting *just one* singlet (triplet) neutral product leads to a change in ρ given by $\delta\rho^{\text{IS}}$ ($\delta\rho^{\text{IT}}$), where

$$\delta\rho^{\text{IS}} = P(\text{incoh}|S)\delta\rho_{\text{incoh}}^{\text{IS}} + P(\text{coh}|S)\delta\rho_{\text{coh}}^{\text{IS}},$$

$$\delta\rho^{\text{IT}} = P(\text{incoh}|T)\delta\rho_{\text{incoh}}^{\text{IT}} + P(\text{coh}|T)\delta\rho_{\text{coh}}^{\text{IT}}.$$

The generalization to the case of detecting $dn_S = k_S dt \text{Tr}\{\rho Q_S\}$ singlet and $dn_T = k_T dt \text{Tr}\{\rho Q_T\}$ triplet neutral products is now straightforward:

$$d\rho_{\text{recomb}} = dn_S \delta\rho^{\text{IS}} + dn_T \delta\rho^{\text{IT}}. \quad (16)$$

Since $\text{Tr}\{\delta\rho_{\text{coh}}^{\text{IS}}\} = \text{Tr}\{\delta\rho_{\text{coh}}^{\text{IT}}\} = \text{Tr}\{\delta\rho_{\text{incoh}}^{\text{IS}}\} = \text{Tr}\{\delta\rho_{\text{incoh}}^{\text{IT}}\} = -1$, it is $\text{Tr}\{d\rho_{\text{recomb}}\} = -dn_S - dn_T$, as it should be.

Using (1) and (16), we arrive at the master equation describing RP quantum dynamics:

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] \quad (17)$$

$$- \frac{k_S + k_T}{2} (\rho Q_S + Q_S \rho - 2Q_S \rho Q_S) \quad (18)$$

$$- (1 - p_{\text{coh}}) (k_S Q_S \rho Q_S + k_T Q_T \rho Q_T) \quad (19)$$

$$- p_{\text{coh}} \frac{dn_S + dn_T}{dt} \frac{\rho_{\text{coh}}}{\text{Tr}\{\rho\}}. \quad (20)$$

The term in (17) is the unitary Hamiltonian evolution which generates S-T coherence, the dissipation of which is given by term (18), while (19) and (20) are the spin-dependent reaction terms. This master equation has a form identical to the one derived in [5], the crucial difference being the different definition of p_{coh} and the last term (20) where we now have the appearance of ρ_{coh} instead of ρ that was used phenomenologically in [5].

Finally, we rewrite the master equation (17)–(20) in a more “user-friendly” form involving only the matrices $\rho_{xy} = Q_x \rho Q_y$, where $x, y = S, T$:

$$\begin{aligned} \frac{d\rho}{dt} = & -i[\mathcal{H}, \rho] - \frac{k_S + k_T}{2}(\rho_{ST} + \rho_{TS}) \\ & - (1 - p_{\text{coh}})(k_S \rho_{SS} + k_T \rho_{TT}) \\ & - \frac{1}{\text{Tr}\{\rho\}}(k_S \text{Tr}\{\rho_{SS}\} + k_T \text{Tr}\{\rho_{TT}\}) \\ & \times (p_{\text{coh}} \rho_{SS} + p_{\text{coh}} \rho_{TT} + \rho_{ST} + \rho_{TS}). \end{aligned}$$

VII. MONTE CARLO SIMULATION OF S-T DECOHERENCE AND RECOMBINATION USING SINGLE-MOLECULE QUANTUM TRAJECTORIES

To the simulation presented in Sec. III, we now add two additional possibilities in each time step dt : singlet and triplet recombination with probability $dr_S = k_S dt \langle Q_S \rangle$ and $dr_T = k_T dt \langle Q_T \rangle$, respectively. In the event that the j th RP recombines within dt at time t , its state $|\psi_j\rangle\langle\psi_j|$ is subtracted at time t from the sum $\rho = \sum_i |\psi_i\rangle\langle\psi_i|$.

For a more comprehensive understanding of the considerations to follow, we first show in Fig. 4 just the Hamiltonian evolution (no decoherence, no reaction) of $\langle Q_S \rangle = \text{Tr}\{\tilde{\rho} Q_S\}$ and $\mathcal{C}(\tilde{\rho})$ for the model RP considered in our numerical examples. Clearly, when $\langle Q_S \rangle = 1$, it is $\mathcal{C}(\tilde{\rho}) = 0$, as expected since we have no coherence between the singlet and triplet subspace. This coherence is maximum at intermediate times in-between the extrema of $\langle Q_S \rangle$.

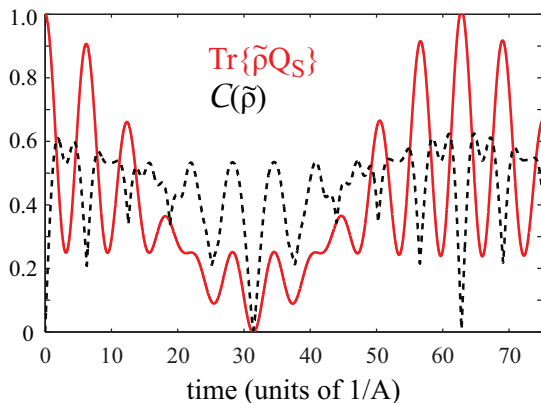


FIG. 4. (Color online) Time evolution of $\text{Tr}\{\tilde{\rho} Q_S\}$ (red solid line) and S-T coherence $\mathcal{C}(\tilde{\rho})$ (black dashed line) for the same RP considered in Fig. 3, taking into account only S-T mixing driven by the Hamiltonian \mathcal{H} , i.e., $d\tilde{\rho}/dt = -i[\mathcal{H}, \tilde{\rho}]$. The singlet state obviously corresponds to zero S-T coherence, while the state in-between the extrema of $\text{Tr}\{\tilde{\rho} Q_S\}$ corresponds to an S-T superposition and hence maximum S-T coherence.

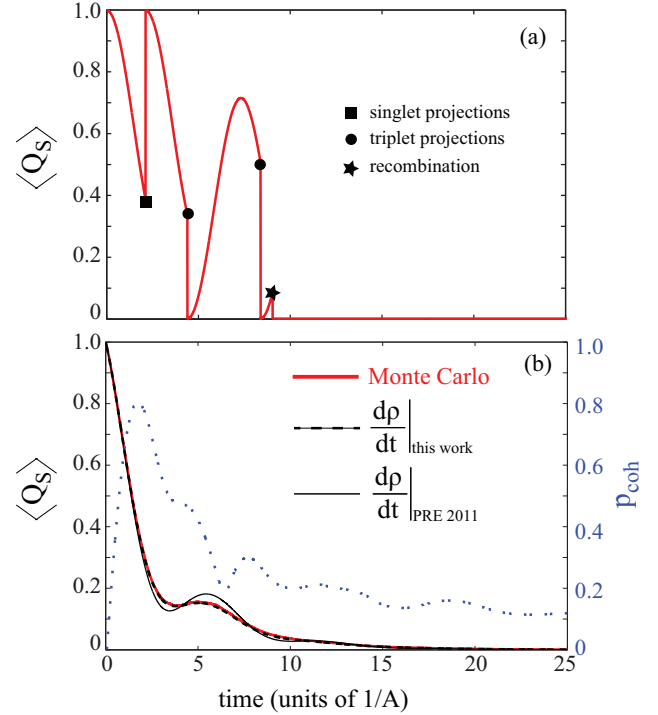


FIG. 5. (Color online) Time evolution of $\langle Q_S \rangle$ including S-T mixing, S-T decoherence, and recombination for the same RP Hamiltonian used in Figs. 3 and 4, with $k_S = k_T = A/4$. (a) Example of a single-RP quantum trajectory with initial state $|S\rangle \otimes |\uparrow\rangle$. (b) Monte Carlo simulation (red solid line) using 10 000 trajectories (two initial states $|S\rangle \otimes |\uparrow\rangle$ and $|S\rangle \otimes |\downarrow\rangle$, with 5000 trajectories for each), prediction of the master equation of this work (dashed line), and the earlier theory (solid line) introduced in [5]. The corresponding measure of S-T coherence p_{coh} is shown with the blue dotted line. The Monte Carlo and the theoretical prediction of this work coincide.

In Fig. 5(a), we depict a single-RP quantum trajectory, similar to the one shown in Fig. 3(a), but now also including recombination. The recombination rates are taken equal, $k_S = k_T$. In Fig. 5(b), we show that using the master equation (17)–(20) derived here, we obtain a perfect agreement with the MC simulation that was lacking with the earlier theory. The MC simulation is the average of 10^4 trajectories, such as the one shown in Fig. 5(a). In Fig. 5(b), we also include the time evolution of p_{coh} .

We next move to the asymmetric regime where $k_T \neq 0$ and $k_S = 0$. This is of interest as it is found in the RPs appearing in a large number of photosynthetic reaction centers [28]. In Figs. 6(a) and 6(b), we again plot $\langle Q_S \rangle$ for $k_S = 0$, $k_T = A/4$, and $k_T = A/2$, respectively. While for the former we get a very good agreement between the Monte Carlo simulation and the master equation, the agreement is not perfect for the latter, but still much better than our earlier theory. We comment on this in Sec. IX.

VIII. DECAY RATE OF SINGLET-TRIPLET COHERENCE

For the sake of completeness, we present a comparison between our theory, the traditional (or Haberkorn) approach

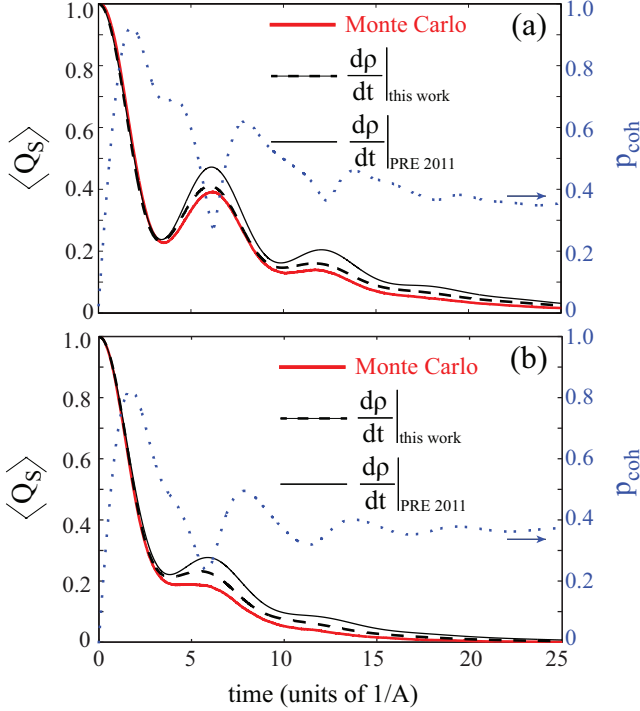


FIG. 6. (Color online) Similar plots as Fig. 5, but with asymmetric recombination rates. (a) $k_S = 0, k_T = A/4$. (b) $k_S = 0, k_T = A/2$.

[40], and the theory put forward by Jones and Hore [11]. First we reiterate [5] that the traditional theory results from our theory by forcing $p_{\text{coh}} = 0$. We also note that our master equation (17)–(20) is identical with the Jones-Hore equation in the case $k_S = k_T$. In this special case, p_{coh} drops out of our master equation (17)–(20). In Fig. 7(a), we plot the time evolution of $\langle Q_S \rangle$ for all three theories, which qualitatively look quite similar. Their most obvious difference is how fast the S-T coherence is lost. By inspection, it readily appears that the amplitude of the S-T oscillations in Fig. 7(a) decays faster in the Jones-Hore theory, slower in our theory, and even slower in the traditional approach. We will now rigorously quantify this observation by following a general approach equally applicable to all three theories. This is based on the general decomposition (4), in particular we will consider the coherent part of ρ which is $\rho_c = \rho_{S_T} + \rho_{T_S}$. In our master equation, ρ_c appears both in term (18) and in term (20). The latter is obvious, while the former can be seen by simple operator manipulations leading to $Q_S \rho + \rho Q_S - 2Q_S \rho Q_S = \rho_c$. Thus, if we right (left) multiply the master equation (17)–(20) with Q_S (Q_T), then vice versa, and take the sum, we find that ρ_c obeys the equation

$$\frac{d\rho_c}{dt} = -i[\mathcal{H}, \rho]_c - \Gamma_c \rho_c, \quad (21)$$

where $[\mathcal{H}, \rho]_c = Q_S[\mathcal{H}, \rho]Q_T + Q_T[\mathcal{H}, \rho]Q_S$. The decay of ρ_c is governed by the rate

$$\Gamma_c = k_S \left(\frac{1}{2} + \langle \tilde{Q}_S \rangle \right) + k_T \left(\frac{1}{2} + \langle \tilde{Q}_T \rangle \right), \quad (22)$$

where we defined $\langle \tilde{Q}_x \rangle = \text{Tr}\{\rho Q_x\} / \text{Tr}\{\rho\}$ with $x = S, T$. Moreover, since it will be needed in the following, by taking

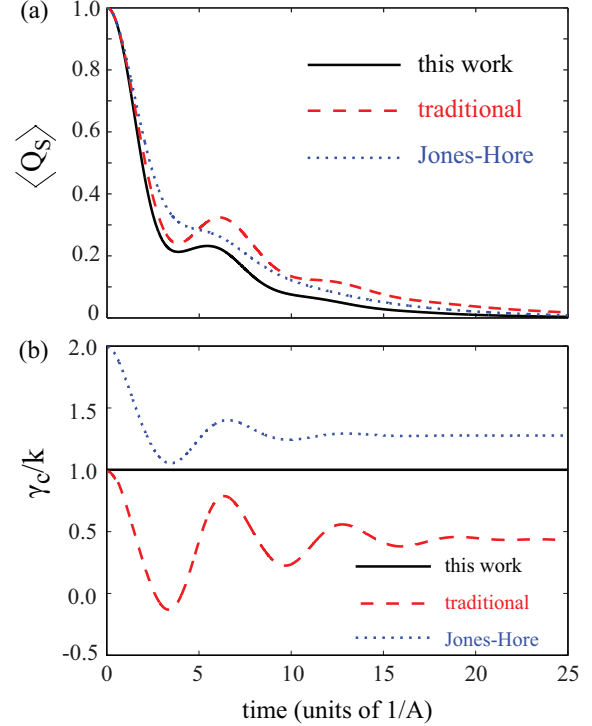


FIG. 7. (Color online) Comparison of the three theories for the case presented in Fig. 6(b), i.e., $k_S = 0$ and $k_T = A/2$. (a) The S-T coherence, embodied by the amplitude of the oscillation of $\langle Q_S \rangle$, decays faster in the Jones-Hore theory, slower in our theory, and even slower in the traditional theory. (b) The corresponding decay rate γ_c/k , where $k_T = 2k$.

the trace of both sides in (17)–(20), we find that $\text{Tr}\{\rho\}$, the normalization of ρ , obeys the equation

$$\frac{d\text{Tr}\{\rho\}}{dt} = -\kappa \text{Tr}\{\rho\}, \quad (23)$$

where

$$\kappa = k_S \langle \tilde{Q}_S \rangle + k_T \langle \tilde{Q}_T \rangle. \quad (24)$$

We finally define the “genuine” S-T decoherence rate as $\gamma_c = \Gamma_c - \kappa$. This describes the decay of S-T coherence due to all effects other than the changing normalization of ρ . This definition follows if we normalize ρ_c by $\text{Tr}\{\rho\}$ and then use (21) and (23). Then we indeed find that the decay rate of $\rho_c / \text{Tr}\{\rho\}$ is γ_c .

We now consider two cases: (a) $k_S = k_T = k$, and (b) $k_S = 0$ and $k_T = 2k$, so that $k_S + k_T$ is the same in both cases. In case (a), we find that $\Gamma_c = 2k$ since $\langle \tilde{Q}_S \rangle + \langle \tilde{Q}_T \rangle = 1$. Moreover, $\kappa = k$, hence, $\gamma_c = k$. In case (b), it is $\Gamma_c = k(1 + 2\langle \tilde{Q}_T \rangle)$, while $\kappa = 2k\langle \tilde{Q}_T \rangle$, hence, $\gamma_c = k$.

We will now perform the same calculation for the traditional and the Jones-Hore theory. We first note that Eqs. (23) and (24) are common for all three theories. The traditional master equation is $d\rho/dt = -i[\mathcal{H}, \rho] - k_S(Q_S \rho + \rho Q_S)/2 - k_T(Q_T \rho + \rho Q_T)/2$. Again, multiplying from left and right with the projection operators as before, we find that the decay rate of ρ_c is $\Gamma_c = (k_S + k_T)/2$. In case (a), it is found that $\gamma_c = 0$, while in case (b), we get $\gamma_c = k(1 - 2\langle \tilde{Q}_T \rangle)$. The Jones-Hore master

TABLE I. Decay rate of S-T coherence γ_c .

γ_c	This work	Trad. theory	J.-H. theory
$k_S = k_T = k$	k	0	k
$k_S = 0, k_T = 2k$	k	$k(1 - 2\langle\tilde{Q}_T\rangle)$	$2k(1 - \langle\tilde{Q}_T\rangle)$

equation is $d\rho/dt = -i[\mathcal{H}, \rho] - k_S(Q_S\rho + \rho Q_S - Q_S\rho Q_S) - k_T(Q_T\rho + \rho Q_T - Q_T\rho Q_T)$. We similarly find that $\Gamma_c = k_S + k_T$. Then, in case (a), it follows that $\gamma_c = k$ and, in case (b), $\gamma_c = 2k(1 - \langle\tilde{Q}_T\rangle)$. For clarity, we summarize the results in Table I.

The asymmetric case $k_T \gg k_S$ together with the singlet initial state is the regime of the quantum Zeno effect [3,41–44] (most pronounced if $k_T \gg \Omega$, where Ω is the S-T mixing frequency). In this regime, when the RP's spin state is about to evolve from the initial singlet state, it is strongly back projected to it due to the high k_T . Thus, $\langle\tilde{Q}_S\rangle$ decreases slowly from its initial value of 1, and hence $\langle\tilde{Q}_T\rangle$ can be quite small, in particular, quite smaller than 1/2. This observation is common to all three theories. It thus follows that $2k(1 - \langle\tilde{Q}_T\rangle) > k > k(1 - 2\langle\tilde{Q}_T\rangle)$. Indeed, as shown in Fig. 7(b), the Jones-Hore theory predicts the largest decay rate for the S-T coherence, ours is intermediate, and, for the traditional theory, it is the smallest.

IX. DISCUSSION

We will finally comment on the success of the master equation (17)–(20) in matching the MC simulation, which has built in the fundamental physical processes of RP reactions at the single-molecule level. While for the case $k_S = k_T$ there is a perfect agreement between theory and MC, independent of the particular definition of p_{coh} , for the asymmetric case $k_T \gg k_S$, we have the more noticeable theory-MC deviation the higher k_T is. For most practical purposes, such a small deviation should be of little concern; however, it is worthwhile to discuss.

To our understanding, the problem is an underestimation of S-T coherence that in principle can be hardly overcome. The reason is the impossibility to unravel a density matrix into its component pure states. S-T decoherence will produce a mixture of S-T coherent, yet dephased, states, which when described by a density matrix will look equivalent to a mixture of S-T incoherent and S-T coherent states, as we have shown with the decomposition into Λ_1 and Λ_2 . To exacerbate the problem for the sake of this discussion, consider, for example, a mixture of the coherent states $|\psi_1\rangle = (|S\rangle + |T_0\rangle)/\sqrt{2}$ and $|\psi_2\rangle = (|S\rangle - |T_0\rangle)/\sqrt{2}$ with equal weights. Then, $\rho = \frac{1}{2}|\psi_1\rangle\langle\psi_1| + \frac{1}{2}|\psi_2\rangle\langle\psi_2| = \frac{1}{2}(|S\rangle\langle S| + |T_0\rangle\langle T_0|)$. This state appears as maximally incoherent, yet it is formed by maximally coherent states. Having access to the information embodied by ρ , it is impossible to unravel or retrodict the constituents $|\psi_1\rangle$ or $|\psi_2\rangle$.

From (19), it is seen that in the asymmetric case where $k_S = 0$, if p_{coh} is underestimated, then we remove a correspondingly larger triplet character from ρ , and hence ρ appears to be more singlet than it really is, as is evident from Fig. 6, i.e., the master equation overshoots the MC. Moreover, this deviation

is noticeable at the minima of p_{coh} , while it is indiscernible at the maxima of p_{coh} . Again, this is due to the reaction term (19) of the master equation, which is more pronounced for low values of p_{coh} .

We finally reiterate that what we have treated is the fundamental quantum dynamics of RP reactions governed by the physical processes inherent in the radical-pair mechanism, i.e., S-T dephasing and charge recombination, stemming from virtual and real transitions to the products' vibrational reservoirs, respectively. Clearly, other sources of decoherence could be present, which are either fundamental or technical, and the manifestation of which could depend on the physical realization of the RP dynamics, e.g., whether the molecules are in solution or in the solid state as in photosynthetic reaction centers. Dephasing due to a bath of surrounding nuclear spins that have not been included in the magnetic Hamiltonian has analogues in the study of quantum dots [45–47] and has been considered by several authors [12,48,49]. To our understanding, a consensus on the physical significance and the quantitative details of this hyperfine relaxation is still lacking in the literature. Whether the S-T dephasing we consider is a dominant process or not will at the end depend on the comparison between the particular recombination rates k_S and k_T of the RP under consideration and the hyperfine relaxation rate, or, in general, the rates of other relaxation processes in the particular RP environment.

A detailed understanding of the interplay of all possible decoherence mechanisms, whether fundamental or technical, is outside the scope of this work. It is, however, a basic requirement for connecting the microscopic dynamics of RP reactions with behavioral observations of the avian compass mechanism, which is a nontrivial exercise recently undertaken in [13,50–52].

X. CONCLUSIONS

To summarize, we have used formal considerations for quantifying the strength of singlet-triplet coherence in radical-ion pairs, which is central for understanding their quantum state evolution. We have also applied the formalism of quantum retrodiction to provide a theoretically solid basis for deriving the master equation for radical-ion-pair quantum dynamics. This represents a refinement of our previous work, which is substantiated by Monte Carlo simulations. These have their own interest as they can realistically and precisely simulate the dynamics of RP reactions including all relevant physical processes. For most practical purposes, however, the master equation we derive should be adequate.

This work is about the self-consistency of our approach and not about making the case of which among the competing theories is the correct one. In other words, if the model presented in Fig. 2 is a physically adequate model for describing RPs, as we believe it is, our master equation introduced here represents a first-principles result that alleviates problems with our previous phenomenological treatment. Nevertheless, we have compared the predictions of our approach with the other two competing theories and discussed in detail how all three theories describe the decay of S-T coherence, which is a central observable in RP reactions.

ACKNOWLEDGMENTS

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APPENDIX A

According to [30], any measure of coherence, $p_{\text{coh}}(\rho)$, should satisfy the following requirements: (1) $p_{\text{coh}}(\rho) = 0$ for $\rho \in \mathcal{I}$. (2) $p_{\text{coh}}(\rho)$ should be monotonous under all incoherent positive and trace-preserving maps, i.e., $p_{\text{coh}}(\rho) \geq p_{\text{coh}}[\Phi_{\text{ICPTP}}(\rho)]$, where the map $\Phi_{\text{ICPTP}}(\rho) = \sum_n K_n \rho K_n^\dagger$ is defined by a set of Kraus operators K_n . These satisfy $\sum_n K_n^\dagger K_n = 1$ and $K_n \mathcal{I} K_n^\dagger \subset \mathcal{I}$. (3) There is a stronger requirement, namely that $p_{\text{coh}}(\rho)$ is monotonous under selective measurements *on average*, i.e., $p_{\text{coh}}(\rho) \geq \sum_n p_n p_{\text{coh}}(\rho_n)$, where $\rho_n = K_n \rho K_n^\dagger / p_n$, again with $\sum_n K_n^\dagger K_n = 1$ and $K_n \mathcal{I} K_n^\dagger \subset \mathcal{I}$. The probability to select ρ_n in the measurement defined by K_n is $p_n = \text{Tr}\{K_n \rho K_n^\dagger\}$.

We can now demonstrate that the previously defined measure (5) is not a good measure of S-T coherence. An S-T decoherence process can be described by

the following Kraus operators: $K_1 = \sqrt{1-\lambda}Q_S$, $K_2 = \sqrt{1-\lambda}Q_T$, and $K_3 = \sqrt{\lambda}1$. This set of operators has the effect of scaling ρ_{ST} and ρ_{TS} by the factor $0 \leq \lambda \leq 1$. We would expect that the measure of coherence also scales by λ ; however, defining $\rho' = \sum_{n=1}^3 K_n \rho K_n^\dagger$, we easily find that $p_{\text{coh}}(\rho') = \lambda^2 p_{\text{coh}}(\rho)$ when using definition (5) for p_{coh} . Put differently, the measure (5) is similar to the squared Hilbert-Schmidt norm $C_{L_2}(\rho)$, which does not satisfy [30] the strong monotonicity criterion (3) above.

APPENDIX B

To visualize the definition of $\mathcal{C}(\rho)$ in (6), we consider a simple example of an S-T coherent state of a single-nucleus RP, e.g., $|\psi\rangle = \alpha|S\rangle \otimes |\downarrow\rangle + \beta|T_-\rangle \otimes |\uparrow\rangle$. The corresponding density matrix is

$$\rho = |\alpha|^2 |S\rangle\langle S| \otimes |\downarrow\rangle\langle\downarrow| + |\beta|^2 |T_-\rangle\langle T_-\rangle \otimes |\uparrow\rangle\langle\uparrow| + \alpha\beta^* |S\rangle\langle T_-\rangle \otimes |\downarrow\rangle\langle\uparrow| + \alpha^*\beta |T_-\rangle\langle S| \otimes |\uparrow\rangle\langle\downarrow|. \quad (\text{B1})$$

We wish to pick the amplitude $\alpha\beta^*$ of the S-T off-diagonal term in Eq. (B1), i.e., the third term. This can be done as follows. In this simple example, $\rho_{ST} = \alpha\beta^* |S\rangle\langle T_-\rangle \otimes |\downarrow\rangle\langle\uparrow|$. If we right-multiply ρ_{ST} with $|T_-\rangle\langle S| \otimes \mathbb{1}_2$, we are left with $r = \alpha\beta^* |S\rangle\langle S| \otimes |\downarrow\rangle\langle\uparrow|$. If we then right-multiply r with r^\dagger and take the trace of the resulting expression, it readily follows that $|\alpha\beta| = \sqrt{\text{Tr}\{rr^\dagger\}}$. In the general case, we will have $|S\rangle\langle T_0|$, $|S\rangle\langle T_+|$, and $|S\rangle\langle T_-|$ coherences, and hence the definition (6).

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