



Reply to comment

## Reply to the comment on “Quantum trajectory tests of radical-pair quantum dynamics in CIDNP measurements of photosynthetic reaction centers” by G. Jeschke



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## ABSTRACT

We recently unraveled a major inconsistency in the traditional description of radical-pair quantum dynamics by studying single-molecule quantum trajectories and comparing their prediction with Haberkorn's master equation. A comment by Jeschke claimed that the inconsistency arises because we did not properly include quantum state projections in the traditional approach. We here show that Jeschke stipulates quantum trajectories involving unphysical quantum states with negative populations. Moreover, the author's Monte Carlo simulation and its agreement with Haberkorn's master equation is a demonstration of an algebraic tautology, establishing the consistency of an unphysical master equation with circularly defined unphysical trajectories.

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## 1. Introduction

Quantum trajectories are a physically intuitive way of looking at the time evolution of an open quantum system from the perspective of pure state evolution of a single system [1]. Averaging such single-system trajectories should ideally reproduce the master equation satisfied by the system's density matrix. It is the latter used in calculations when the relevant experiments do not probe single quantum systems, i.e. when experimental observables are indeed described by particular moments of the density matrix  $\rho$ .

Which is the fundamental master equation satisfied by  $\rho$  has been at the heart of an ongoing debate in spin chemistry, which deals with spin-selective chemical reactions involving radical-ion pairs. Using a number of theoretical arguments [2–7] recently reviewed comprehensively [8], we have shown that the conventional (Haberkorn) master equation used in most spin chemical calculations can not stand as a fundamental theory, and we have derived a new master equation based on several concepts of quantum information science. By *fundamental* we mean the inherent quantum dynamics of the radical-pair mechanism, that is, apart from any additional spin relaxation effects that might or might not be relevant in a given experiment.

In simple quantum systems quantum trajectories identically reproduce the master equation. For example, considering the decay

of a two-level atom due to spontaneous emission [9], a Monte Carlo simulation using single-atom trajectories involving jumps identically reproduces the atomic master equation, which is equivalent to the optical Bloch equations.

In more complex systems such an ideal circumstance, i.e. an exactly known master equation identically reproduced by quantum trajectories, might not be the case, since the master equation is most often some sort of approximation of the underlying dynamics. We recently [7] explored the internal consistency of both our theory, and for the first time, also Haberkorn's theory, looking at radical-pair spin dynamics from the perspective of single-molecule quantum trajectories. In our approach we can produce *well-defined and physically acceptable single-radical-pair trajectories*, but casting the physical picture these trajectories seamlessly describe into a master equation has been a non-trivial exercise still under development. In parallel [7], we discovered a major inconsistency in Haberkorn's approach, showing that the trajectories one is led to from Haberkorn's perspective lead to predictions far off Haberkorn's master equation.

In his comment [10], Jeschke claims that we underestimated the capabilities of Haberkorn's theory by not including quantum state projections, purportedly part of the traditional theory, taking place in unsuccessful recombination events of the radical-pair. The author went on to define what sort of quantum trajectories are supported by the traditional theory and show that they identically reproduce the traditional master equation.

Unfortunately, the author introduces unphysical trajectories involving non-existent quantum states, in particular 'density

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matrices' with negative eigenvalues, while the author's Monte Carlo simulation is a computing-time-intensive demonstration of an algebraic tautology, concerning unphysical trajectories circularly defined by the very same terms appearing in Haberkorn's master equation.

## 2. Jeschke's trajectories

Haberkorn's master equation reads  $d\rho/dt = -i[\mathcal{H}, \rho] - k_S(Q_S\rho + \rho Q_S)/2 - k_T(Q_T\rho + \rho Q_T)/2$ , where the Hamiltonian  $\mathcal{H}$  drives unitary dynamics, and the other two terms form Haberkorn's singlet and triplet reaction operators, with  $k_S$  and  $k_T$  being the singlet and triplet recombination rates, and  $Q_S$  and  $Q_T$  the singlet and triplet projection operators, respectively. The projectors have three properties: ( $\Pi_1$ ) orthogonality,  $Q_S Q_T = Q_T Q_S = 0$ , ( $\Pi_2$ ) completeness,  $Q_S + Q_T = \mathbb{1}$ , and ( $\Pi_3$ ) idempotence,  $Q_S^2 = Q_S$ ,  $Q_T^2 = Q_T$ . The unit operator is  $\mathbb{1}$ .

Using  $\Pi_2$ , Jeschke rewrites Haberkorn's master equation as

$$d\rho/dt = -i[\mathcal{H}, \rho] - k_S\rho + k_S \frac{Q_T\rho + \rho Q_T}{2} - k_T\rho + k_T \frac{Q_S\rho + \rho Q_S}{2} \quad (1)$$

Based on (1), Jeschke postulates trajectories with five events (E1–E5) potentially realized, with their respective probabilities, within the time interval  $dt$ . Specifically, the author considers two 'reaction attempts', one in the singlet channel with probability  $k_S dt$ , and one in the triplet channel with probability  $k_T dt$ . If the singlet attempt is realized, then (E1) with probability  $p_1 = k_S dt \text{Tr}\{\rho Q_S\}$  the attempt is successful due to singlet recombination, while (E2) with probability  $p_2 = k_S dt \text{Tr}\{\rho Q_T\}$  the attempt is unsuccessful and the radical-pair is 'projected' to

$$\rho_S^U = \frac{Q_T\rho + \rho Q_T}{2\text{Tr}\{\rho Q_T\}} \quad (2)$$

If the triplet attempt is realized, then (E3) with probability  $p_3 = k_T dt \text{Tr}\{\rho Q_T\}$  the attempt is successful due to triplet recombination, while (E4) with probability  $p_4 = k_T dt \text{Tr}\{\rho Q_S\}$  the attempt is unsuccessful and the radical-pair is 'projected' to

$$\rho_T^U = \frac{Q_S\rho + \rho Q_S}{2\text{Tr}\{\rho Q_S\}} \quad (3)$$

Finally, (E5) if neither the singlet nor the triplet attempt is realized, with probability  $p_5 = 1 - k_S dt - k_T dt$ , the radical-pair evolves unitarily with the Hamiltonian  $\mathcal{H}$ .

## 3. Fallacy: $\rho_S^U$ and $\rho_T^U$ are not physical states

Let us consider the radical-pairs undergoing an 'unsuccessful' singlet reaction, so that they are 'projected', as Jeschke claims, to  $\rho_S^U$ . We have used quotes in the word 'projected', because  $\rho_S^U$  does not represent a projection. If a pure state  $|\psi\rangle$  is projected to another state by some projector  $P$ , then  $|\psi\rangle \rightarrow P|\psi\rangle$ , and the density matrix  $\rho \rightarrow P\rho P^\dagger$ . The state  $\rho_S^U$  is not of such a form.

Importantly,  $\rho_S^U$  (and similarly  $\rho_T^U$ ) is not a physical density matrix. In other words, Jeschke asserts that in each time step  $dt$ , a fraction  $p_2$  and  $p_4$  of the radical-pairs are 'projected' to non-existent states. We will now formally prove this, and in a following section we will demonstrate numerically that Jeschke's unphysical trajectories involve 'density matrices' having negative eigenvalues.

**Theorem.** For any physical radical-pair state described by the density matrix  $\rho$ , the transformation  $\rho_S^U$  (and similarly  $\rho_T^U$ ) is not a physical state, because it can **neither** be written as a pure state  $\rho_S^U = |\psi\rangle\langle\psi|$  for some  $|\psi\rangle$ , **nor** as a mixture of pure states,  $\rho_S^U = \sum_\psi p_\psi |\psi\rangle\langle\psi|$ , weighted by some non-negative probabilities  $p_\psi$  summing up to unity.

**Proof.** Any radical-pair state described by the physical density matrix  $\rho$  can in general be written as

$$\begin{aligned} \rho &= \mathbb{1}\rho\mathbb{1} = (Q_S + Q_T)\rho(Q_S + Q_T) \\ &= Q_S\rho Q_S + Q_T\rho Q_T + Q_S\rho Q_T + Q_T\rho Q_S \end{aligned} \quad (4)$$

Using the projector properties  $\Pi_1$  and  $\Pi_3$ , it is

$$\rho_S^U = \frac{Q_T\rho + \rho Q_T}{2\text{Tr}\{\rho Q_T\}} = \frac{2Q_T\rho Q_T + Q_T\rho Q_S + Q_S\rho Q_T}{2\text{Tr}\{\rho Q_T\}} \quad (5)$$

If there is non-zero singlet–triplet coherence in the state  $\rho$ , as is the case in general, the terms  $Q_T\rho Q_S + Q_S\rho Q_T$  will be non-zero, hence the pseudo-state  $\rho_S^U$  contains singlet–triplet coherence *without* singlet population, since by property  $\Pi_1$  it is  $Q_S\rho_S^U Q_S = 0$ . It is impossible for any physical state, pure or mixed, to contain singlet–triplet coherence without singlet population. In general, (see pp. 39 in the textbook [11]) the off-diagonal matrix elements of a physical density matrix satisfy the inequality  $|\rho_{mn}|^2 \leq \rho_{nn}\rho_{mm}$ . Thus  $\rho_{mn}$  is zero if  $\rho_{nn}$  or  $\rho_{mm}$  is zero.  $\square$

Thus, Jeschke's 'trajectories' involve non-existent states, hence his approach is not a quantum trajectory analysis, since it cannot provide a **physical** single-molecule state evolution, i.e. it cannot provide a succession of physical radical-pair states  $|\psi\rangle$  describing single-molecule dynamics. That is, taking as example the particular model considered in [7,10], i.e. a radical-pair with one nuclear spin, if one starts the simulation from an initial state like  $|\psi\rangle = |S\rangle \otimes |\uparrow\rangle$  (singlet for the two electrons and up for the nuclear spin), Jeschke's approach cannot provide the states  $|\psi\rangle$  that the single radical-pair might assume after  $t=0$ , since in a particular trajectory one of the two 'unsuccessful reaction attempts' is realized, the state would be 'transformed' to  $\rho_S^U$  or  $\rho_T^U$ , which is not a physical state. Although quantum trajectories are about pure state evolution, similar results follow if one were to start the evolution with a mixed state, i.e. at some point in time some trajectories will become physically non-existent.

We will show next that Jeschke's Monte Carlo simulation and its 'perfect' agreement with the master equation represents a circular argument merely demonstrating an algebraic tautology. We will then use this tautological approach to show that any kind of master equation, no matter how absurd, can be recast into equally absurd 'quantum trajectories'.

## 4. Updating the density matrix

To this end, we first note that Jeschke states that events E1–E5 identically reproduce Haberkorn's master equation. For the trajectories to identically reproduce the master equation, a relation of the following form must hold

$$\rho_{t+dt} = p_1\rho_1 + p_2\rho_2 + p_3\rho_3 + p_4\rho_4 + p_5\rho_5 \quad (6)$$

That is, event  $j$  leads to a system's density matrix  $\rho_j$ , which is some transformation of  $\rho_t$ , the system's density matrix at time  $t$ . Hence,  $\rho_{t+dt}$  is the weighted sum of the system's density matrix  $\rho_j$  resulting from the realization of event  $j$  during  $dt$ , the weights being the probabilities  $p_j$ . Then the master equation follows from  $d\rho/dt = (\rho_{t+dt} - \rho_t)/dt$ . Plugging in (6) Jeschke's events E1–E5 we get

$$\begin{aligned} \rho_{t+dt} &= p_1 \times \rho_1 + p_2 \times \rho_S^U + p_3 \times \rho_3 + p_4 \times \rho_T^U \\ &\quad + p_5 \times (\rho_t - idt[\mathcal{H}, \rho_t]) \end{aligned} \quad (7)$$

By setting  $\rho_1 = \rho_3 = 0$  we identically retrieve Haberkorn's master equation. Thus, Jeschke considers that if the radical-pair recombines (events E1 and E3) it contributes zero to the systems' state at time  $t+dt$ . We will revisit this assertion later on.

As evident from (7) and the definitions (2) and (3), Jeschke's physically non-existent 'trajectories' are just an algebraic

reformulation of the master equation, so there is no need to wait for 500 000 trajectories to run at the computer, since by their circular definition through the terms appearing in the master equation, they will be on top of the master equation prediction, as in Jeschke's simulation.

## 5. 'Proving' a tautology

With this approach, one can 'prove' the consistency of any master equation, even the most absurd, with equally absurd and circularly defined trajectories, thus defeating the purpose of using quantum trajectories to understand the time evolution of an open quantum system at the single-molecule level.

Indeed, take as master equation  $d\rho/dt = -i[\mathcal{H}, \rho] + k_S R_S(\rho) + k_T R_T(\rho)$ , where  $R_S(\rho)$  and  $R_T(\rho)$  are some arbitrary reaction operators having no correspondence to physical reality. Their traces,  $\text{Tr}\{R_S(\rho)\}$  and  $\text{Tr}\{R_T(\rho)\}$ , should equal  $-\text{Tr}\{\rho Q_S\}$  and  $-\text{Tr}\{\rho Q_T\}$ , respectively, so that we indeed describe the spin-selective decay of radical-pair population, i.e. so that it is  $d\text{Tr}\{\rho\}/dt = -k_S \text{Tr}\{\rho Q_S\} - k_T \text{Tr}\{\rho Q_T\}$ , where we also used the fact [12] that  $\text{Tr}\{[\mathcal{H}, \rho]\} = 0$ . There are infinite absurd reaction operators satisfying this constraint and also keeping  $\rho$  a positive-definite, hence physical density matrix. For example, take  $R_S(\rho) = -\frac{1}{2}(Q_S \rho + \rho Q_S) - \frac{1}{69} Q_T \rho Q_S - \frac{1}{69} Q_S \rho Q_T$  and  $R_T(\rho) = -\frac{1}{2}(\rho Q_T + Q_T \rho) - \frac{1}{131}(\rho - \text{Tr}\{\rho\})$ .

Now, following Jeschke's argument, write  $d\rho/dt = -i[\mathcal{H}, \rho] - k_S \rho - k_T \rho + k_S R'_S(\rho) + k_T R'_T(\rho)$ , where  $R'_S(\rho) = R_S(\rho) + \rho$  and  $R'_T(\rho) = R_T(\rho) + \rho$ . Here are Jeschke's 'trajectories': (E1) with probability  $p_1 = k_S dt \text{Tr}\{\rho Q_S\}$  we have a singlet recombination (successful singlet reaction attempt), (E2) with probability  $p_2 = k_S dt \text{Tr}\{\rho Q_T\}$  we have a 'projection' to the 'state'  $\frac{R'_S(\rho)}{\text{Tr}\{\rho Q_T\}}$  (unsuccessful singlet reaction attempt), (E3) with probability  $p_3 = k_T dt \text{Tr}\{\rho Q_T\}$  we have a triplet recombination (successful triplet reaction attempt), (E4) with probability  $p_4 = k_T dt \text{Tr}\{\rho Q_S\}$  we have a 'projection' to the 'state'  $\frac{R'_T(\rho)}{\text{Tr}\{\rho Q_S\}}$ , and with probability  $p_5 = 1 - k_S dt - k_T dt$  we have Hamiltonian evolution.

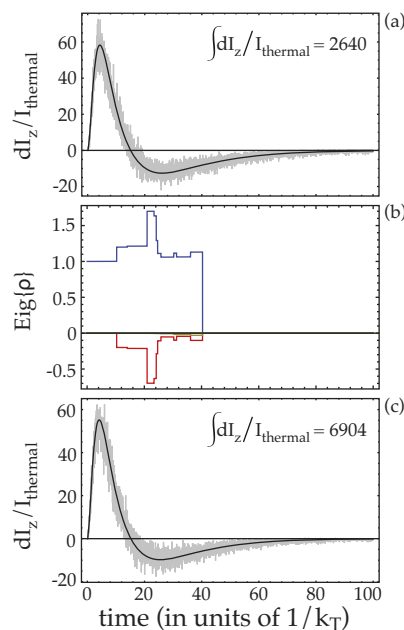
Of course, normalization alone does not render any matrix a physically acceptable density matrix. Indeed, the 'states'  $R'_S(\rho)/\text{Tr}\{\rho Q_T\}$  and  $R'_T(\rho)/\text{Tr}\{\rho Q_S\}$  are physically as non-existent as  $\rho_S^U$  and  $\rho_T^U$ , yet properly normalized [13]. By using Jeschke's update rule for  $\rho_{t+dt}$ , it is

$$\rho_{t+dt} = p_1 \times 0 + p_2 \times \frac{R'_S(\rho_t)}{\text{Tr}\{\rho Q_T\}} + p_3 \times 0 + p_4 \times \frac{R'_T(\rho_t)}{\text{Tr}\{\rho Q_S\}} + p_5 \times (\rho_t - idt[\mathcal{H}, \rho_t]) \quad (8)$$

exactly retrieving the master equation  $d\rho/dt = -i[\mathcal{H}, \rho] + k_S R_S(\rho) + k_T R_T(\rho)$ !

Even though the Monte Carlo simulation is expected, by its circular design, to be on top of the master equation prediction, it is instructive to look at the simulation results, presented in Figure 1. For the same Hamiltonian used by Jeschke we calculate  $dI_z$ , the nuclear spin deposited to the neutral reaction products during the time interval  $dt$ , using Haberkorn's master equation and Jeschke's trajectories. The result is shown in Figure 1a, where we also show the integral  $\int dI_z/I_{\text{thermal}}$ , the total nuclear spin of the reaction products at the end of the reaction, normalized by the thermal equilibrium value. The perfect agreement between master equation and Monte Carlo is illusionary, stemming from the circularly defined trajectories postulated by Jeschke.

That these trajectories describe physically non-existent states is revealed by considering a single trajectory. Indeed, running Jeschke's simulation for one trajectory at a time can lead to trajectories shown in Figure 1b, where we plot the eigenvalues of  $\rho$ , the single-molecule state evolving according to Jeschke's rules. It is



**Figure 1.** (a) Master equation and Monte Carlo simulation comparison for the same Hamiltonian used in [10], using 250 000 trajectories as defined by Jeschke. The agreement is deluding, since Jeschke's trajectories describe physically non-existent states. This is shown in (b) depicting the eigenvalues of  $\rho$  resulting from evolving a single trajectory. The system is 8-dimensional, there are 6 eigenvalues approximately equal to zero, one eigenvalue larger than 1 and one negative eigenvalue, ensuring the normalization of  $\rho$ . (c) A similarly deluding agreement between some master equation having arbitrary reaction operators  $R_S$  and  $R_T$ , with circularly defined and physically non-existent trajectories.

seen that the eigenvalues of  $\rho$  exceed 1, and there are also negative eigenvalues securing the normalization  $\text{Tr}\{\rho\} = 1$ . Thus the single-molecule states entering Jeschke's trajectories do not have any physical correspondence. Finally, in Figure 1c we 'demonstrate the perfect agreement' between another master equation involving the randomly chosen reaction operators  $R_S$  and  $R_T$  previously introduced, with the equally unphysical trajectories tautologically postulated by generalizing Jeschke's approach.

Although Figure 1a and c do not convey any useful information, they are instructive. This is because the traces  $dI_z$  are qualitatively very similar, yet the integrated nuclear spin, shown in the insets of Figure 1a and c, is 260% different. This difference is brought about by a minute change in the reaction operators, demonstrating the sensitivity of CIDNP to the detailed form of the reaction operators and elucidating the point made in [7]. That is, correcting Haberkorn's phenomenological and inconsistent reaction operators will lead to significant corrections in the properties of photosynthetic reaction centers extracted from CIDNP data.

## 6. Properly updating the density matrix

Having formally proved that Jeschke's analysis cannot stand physically, we will now elaborate on some more subtle problems with Jeschke's trajectories. In particular, we will explain why obtaining a master equation for a radical-pair ensemble is a non-trivial task, even though the dynamics at the single-molecule level following from our approach are straightforward.

Jeschke, albeit incorrectly, does accommodate the concept we introduced [2], namely that unsuccessful reaction events have a physical effect on the surviving radical-pairs' state. When trying to obtain the master equation for the ensemble of radical-pairs, that is, when trying to describe an actual experiment involving a macroscopic number of radical-pairs, we don't have access to the

pure states  $|\psi\rangle$  describing individual radical-pairs. The reason why this is so are the random projections to the singlet and triplet states (events K1 and K2 of [7]). If it were not for these projections, the radical-pairs would evolve unitarily and their state would be a well known pure state  $|\psi\rangle$  evolving by the Hamiltonian. In that case the density matrix would be needed only to compactly account for an initially mixed state, e.g. random nuclear spin orientations. But in the presence of these random projections, the density matrix becomes necessary even when the initial radical-pair state is a perfectly well known pure state.

Thus, in the ensemble picture at any given moment we have a collection of pure radical-pair states described by  $\rho$ . Jeschke's update rule is not applicable in this realistic case. Jeschke correctly considers that when dealing with a *single-molecule trajectory* starting from some pure initial state  $|\psi\rangle$ , in the event that the radical-pair recombines (event E1 and E3), this particular molecule will contribute a zero to all observables from the instant of recombination and on. This is how we take into account the recombination event in our Monte Carlo analysis [7], and this is also how Jeschke does it.

But to use the same reasoning in updating the density matrix, which describes a collection of pure states having various phases (due to the S and T projections) is again circular and incorrect. This is because in the event of recombination, the new radical-pair density matrix describing a collection of pure states,  $\rho_{t+dt}$ , will equal  $\rho_t$  minus the pre-recombination state of the recombined molecules. That is,  $\rho_1$  and  $\rho_3$  in (6) should be  $\rho - \rho_S$  and  $\rho - \rho_T$ , where  $\rho_S$  and  $\rho_T$  are the pre-recombination states of the radical-pairs that recombined in the singlet and triplet channel during  $dt$ , respectively. Obtaining  $\rho_S$  and  $\rho_T$  has been at the core of our work, and is a non-trivial task that we have addressed using the theory of quantum retrodiction [6]. It is this non-trivial task prohibiting us to translate the simple physics described by our quantum trajectories into an exact master equation. Moreover, it is this difficulty that requires the genuine test of our master equation with our physical quantum trajectories performed in [7].

## 7. Constraint for $k_S = k_T$

To our understanding, casting Haberkorn's theory in terms of quantum trajectories in the general case  $k_S \neq k_T$  is impossible, just because Haberkorn's master equation is a phenomenological theory unable to capture the fundamental quantum dynamics of radical-pairs. Nevertheless, in [7] we formally proved a constraint that has to be met by the contenders of Haberkorn's approach, a constraint that has gone unnoticed by Jeschke. In the special case  $k_S = k_T \equiv k$ , Haberkorn's master equation becomes  $d\rho/dt = -i[\mathcal{H}, \rho] - k\rho$ , and can be solved exactly. The solution is  $\rho_t = e^{-kt}R$ , where  $dR/dt = -i[\mathcal{H}, R]$ . This describes the evolution of radical-pairs **just** undergoing unitary evolution until they recombine. In order to prevent ill-fated future attempts to introduce single-molecule trajectories from the perspective of Haberkorn's theory in the general case  $k_S \neq k_T$ , we reiterate that any such attempt must meet the above constraint, i.e. leave the radical-pair state undisturbed when  $k_S = k_T$ .

## 8. Conclusions

As mentioned in the introductory remarks, the purpose of using quantum trajectories is not to stipulate unphysical states in order to artificially 'match' some master equation, but to simulate realistic evolution of single quantum systems, that in principle is experimentally observable if single quantum systems are addressable, as e.g. in atom-cavity [15] or trapped-ion [14] experiments. We stress

that in our approach we provide a clear and physically meaningful analysis of single-radical-pair quantum trajectories, whereas it is our master equation that needs to be further refined in order to be perfectly consistent with the trajectory analysis.

In contrast, Jeschke's approach defeats the purpose of using quantum trajectories to understand single-radical-pair quantum dynamics. On the other hand, Jeschke's considerations fruitfully serve to further illustrate the inadequacy of Haberkorn's conventional theory from a fundamental perspective, highlighting subtle details one has to consider when addressing the fundamental quantum dynamics of spin-selective radical-pair reactions.

Regarding any future attempts analogous to Jeschke's, we ought to clarify that the proponents of Haberkorn's approach have to surmount the following impasse: if they concede that the physically acceptable projections we introduced, namely to the singlet and triplet state (events K1 and K2 outlined in [7]) are indeed part of the picture, then Haberkorn's master equation fails when  $k_S = k_T$ . If they claim that there is no effect whatsoever on surviving radical-pairs besides Hamiltonian evolution, then Haberkorn's master equation fails when  $k_S \neq k_T$ . At this point, the proponents of Haberkorn's approach might claim that radical-pair spin dynamics are not amenable to any quantum trajectory analysis whatsoever, or that one needs two fundamental theories (yet to be formulated), one for those radical-pairs for which  $k_S = k_T$  and another one for those radical-pairs for which  $k_S \neq k_T$ . For obvious reasons, both of these potential claims are scientifically unacceptable.

The conclusions of [7] are still valid. We have established the inadequacy of spin chemistry's foundations without the need of any experiment. Moreover, the theoretical interpretation of a large number of CIDNP experiments must be carefully revisited, since Haberkorn's theory forces the physical information of interest, hiding in the Hamiltonian, to attain incorrect values due to the unphysical reaction terms describing radical-pair kinetics in photosynthetic reaction centers. As alluded to in Figure 1a and c, and as we will show in detail in forthcoming works, CIDNP measurements are exquisitely sensitive to fine details of the reaction operator, hence the corrections brought about in the physical information extracted from data after introducing consistent reaction kinetics can be quite severe.

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