

# Nature's Biochemical Double Slit: How Many Molecules React?

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Radical-ion-pair reactions were recently shown to represent a rich biophysical laboratory for the application of quantum measurement theory methods and concepts. We here show that radical-ion-pair reactions essentially are a biochemical double slit. Quantum coherence effects are visible when "which path" information is limited, and the incoherent limit is approached when measurement-induced decoherence sets in.

The double slit experiment is the archetypal system manifesting the core concepts of quantum physics. We here show that Nature has already designed biologically significant chemical reactions that act as a double slit interferometer. Spin-selective radical-ion-pair reactions are perhaps the only example in chemistry where spin degrees of freedom and their relatively small interaction energy can have a disproportionately large effect on the outcome of chemical reactions. Their study is at the core of spin chemistry [1], by now a mature research field directly related to photochemistry [2] and photosynthesis [3].

Radical-ion pairs are biomolecular ions created by a charge transfer from a photo-excited  $D^*A$  donor-acceptor molecular dyad  $DA$ , schematically described by the reaction  $DA \rightarrow D^*A \rightarrow D^+A^-$ , where the two dots represent the two unpaired electrons. The magnetic nuclei of the donor and acceptor molecules couple to the two electrons via the hyperfine interaction, leading to singlet-triplet mixing, i.e. a coherent oscillation of the spin state of the electrons. The reaction is terminated by the reverse charge transfer, resulting to the charge recombination of the radical-ion-pair and the formation of the neutral reaction products. It is angular momentum conservation at this step that empowers the molecule's spin degrees of freedom to determine the reactions fate: only singlet state radical-ion pairs can recombine to reform the neutral  $DA$  molecules, whereas triplet radical-ion pairs recombine to a different metastable triplet neutral product.

Theoretically, the fate of radical-ion-pair reactions is accounted for by the time evolution of  $\rho$ , the density matrix describing the spin state of the molecule's two electrons and magnetic nuclei. It was recently shown [4] that the master equation used until now to pursue all theoretical work in spin chemistry masked the existence of non-trivial quantum effects in this biologically significant chemical reaction. A new master equation was derived [4] based on quantum measurement theory, as the radical-ion-pair recombination process was interpreted to be a continuous quantum measurement of the pair's spin state. This master equation accounts for the spin decoherence of not-yet reacted radical-ion pairs. The kinetics of the recombination process, i.e. the loss of radical-ion pairs due to the formation of neutral products, must also be taken into account. The treatment of this problem in [4] applies only to the case when we have maxi-

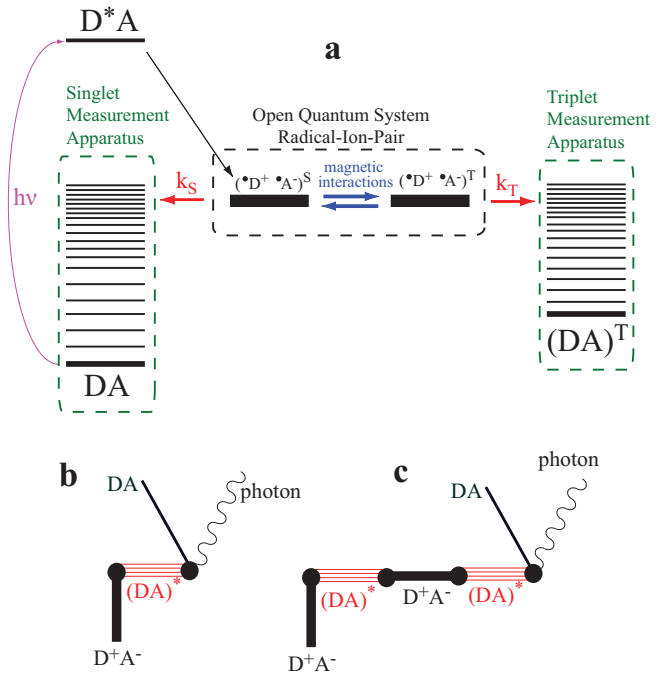


FIG. 1: (a) Energy level structure of radical-ion-pair reaction dynamics. A photon excites the singlet neutral precursor molecule  $DA$  into  $D^*A$ , and a charge transfer creates the radical-ion pair. The excited vibrational levels  $(DA)^*$  of the neutral  $DA$  molecule form the measurement reservoir, which has two functions: it acts as a measurement device for the spin state of the radical-ion pair, and it acts as a sink of radical-ion pairs, i.e. if a radical-ion pair recombines into the singlet channel, the electron tunnels into a reservoir state, and a fast spontaneous decay results in the ground state  $DA$  (which is the singlet product) and a photon emission. Similar for the triplet reservoir. (b) Radical-ion-pair recombination as a Feynman diagram. (c) Virtual process contributing to spin decoherence of non-reacting radical pairs, as described by Eq. 1.

mal singlet-triplet coherence. Describing the continuous range of partial coherence down to the other extreme of maximal incoherence is what we need in order to account for physical reality. In this Letter we develop exactly this complete description radical-ion-pair reactions, shown to be a perfect analog of Young's double slit experiment with partial "which-path" information. A more detailed account of this work will appear elsewhere.

*Radical-ion pairs as an open quantum system* We will first describe in detail the physical system under consideration. The reaction dynamics and energy levels of radical-ion pairs are depicted in Fig.1. We completely neglect effects like diffusion in solutions, collisions with other molecules, spin relaxation and any other complication not related to the fundamental quantum dynamics inherent in the recombination process. Now, in all experimental studies we have a macroscopic number of radical-ion pairs. Each one of them is a single open quantum system regarding the spin degrees of freedom, because the recombination process inherent in each molecule disturbs a what would be a unitary spin evolution. Moreover, due to recombination, radical-ion pairs disappear and form neutral chemical products. That is, what we deal with is an ensemble of open quantum systems with varying number of particles. This non-trivial aspect of radical-ion-pair reactions has been the source of much confusion lately [5–7].

By properly identifying the quantum system and the environment "watching" the system's evolution, we recently derived [4] a *trace-preserving* master equation describing the evolution of the radical-ion-pair's spin state until it reacts:

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

Here  $\mathcal{H}$  is the Hamiltonian that embodies the magnetic interactions within the molecule,  $Q_S$  is the singlet projection operator (the triplet projection operator is denoted by  $Q_T$ ), and  $k_S$  and  $k_T$  are the singlet and triplet recombination rates, respectively. Equation (1) embodies the *decoherence* of the radical-pair's spin state brought about by the *internal* to the molecule recombination dynamics, (a process contributing to the spin decoherence is shown in Fig.1c). The kinetics of the reaction were modelled [4] by another equation evolving the number of radical-ion pairs,  $dN = -Ndt(k_S\langle Q_S \rangle + k_T\langle Q_T \rangle)$ . As will be explained in the following, this description is part of the picture, and applies at a single instant of time when the radical-ion pair is in a maximally coherent singlet-triplet state. However, the effect of the recombination-induced quantum measurement on the molecule's spin state is to turn coherent superpositions into incoherent mixtures and the above update rule for  $N(t)$  is insufficient for describing the evolution of such mixtures. The question we will address is the following: suppose that at time  $t$  an *ensemble* of radical-ion pairs is described by the density matrix  $\rho$ . For sure, in the time interval between  $t$  and  $t + dt$  we will observe  $dn_S = k_S dt \text{Tr}\{\rho Q_S\}$  singlet products and  $dn_T = k_T dt \text{Tr}\{\rho Q_T\}$ . Knowing  $\rho_t$ ,  $dn_S$  and  $dn_T$ , how can one consistently evolve  $\rho_t$  into  $\rho_{t+dt} = \rho_t + d\rho$  in order to have the maximum predictive power? We emphasize that the measurement of these product molecules represents classical information, the acquisition of which or not cannot have any back-action on the ensemble's state, as much as the detection of photons on the observation screen beyond Young's double

slit does not back-react on the quantum state of the rest of the photons flying through the double slit. However, such an unphysical statement is at the core of the traditional theory as will be analysed in the following. For this discussion we neglect nuclear spins and consider just two levels [8], the singlet  $|S\rangle$  and the triplet  $|T\rangle$ .

#### *Maximum incoherence extreme*

If we knew that at time  $t$  we had an incoherent singlet-triplet mixture, i.e. if  $\rho_t = \alpha Q_S + \beta Q_T$ , where  $Q_S = |S\rangle\langle S|$  and  $Q_T = |T\rangle\langle T|$ , then we would know *for sure* that e.g. the detected  $dn_S$  singlet products must have originated from singlet state radical-ion pairs. Thus we would write  $d\rho_{\text{incoh}} = -k_S dt Q_S \rho Q_S - k_T dt Q_T \rho Q_T$ , i.e. we project out the singlet and independently the triplet part of  $\rho$  by the reacted number of singlet ( $k_S dt$ ) and triplet ( $k_T dt$ ) radical-ion pairs.

#### *Maximum coherence extreme*

Suppose, on the other hand, that at time  $t$  all radical-ion pairs are in the state  $\rho_t = |\psi\rangle\langle\psi|$  with  $|\psi\rangle = (|S\rangle + |T\rangle)/\sqrt{2}$ . Since  $\text{Tr}\{\rho Q_S\} = \text{Tr}\{\rho Q_T\} = 1/2$ , we expect  $dn_S = k_S dt/2$  singlet and  $dn_T = k_T dt/2$  triplet products. What information does  $\rho_t$  convey about the possible precursors of the  $dn_S$  singlet and  $dn_T$  triplet products? None. As the reacted radical-ion pairs cease to exist, so does the information about their particular quantum state just prior to recombination. So now, in order to update  $\rho_t$  we have to remove the complete single-molecule density matrix  $\rho_t/\text{Tr}\{\rho_t\}$  as many times as many products we measured, i.e.  $d\rho_{\text{coh}} = -(dn_S + dn_T)\rho_t/\text{Tr}\{\rho_t\}$ . This is a crucial point. The spin state of e.g. the singlet neutral product will indeed be  $Q_S \rho Q_S$ , but that does not imply that the state of the precursor radical-ion pair was the same. Hence due to the reaction, we cannot just remove "singlet character", we have to remove the complete information (or lack thereof) in order to update  $\rho_t$ .

#### *General case: partial coherence*

Suppose that at time  $t$  the ensemble density matrix is  $\rho_t$ , which can be an arbitrary mixture. What we need is a measure of singlet-triplet coherence of the state  $\rho_t$ , that will continuously span the intermediate region between the above two extremes. This measure is easily derived as follows. By multiplying  $\rho_t$  from left and right by the unit operator, and replacing the latter by  $Q_S + Q_T = 1$ , we can write  $\rho = \rho_{SS} + \rho_{TT} + \rho_{ST} + \rho_{TS}$ , where  $\rho_{SS} = Q_S \rho Q_S$ ,  $\rho_{TT} = Q_T \rho Q_T$ ,  $\rho_{ST} = Q_S \rho Q_T$  and  $\rho_{TS} = Q_T \rho Q_S$ . The coherence of  $\rho$  is obviously  $\rho_{ST} + \rho_{TS}$ . We define

$$p_{\text{coh}} = \frac{\text{Tr}\{\rho_{ST}\rho_{TS}\}}{\text{Tr}\{\rho_{SS}\}\text{Tr}\{\rho_{TT}\}} \quad (2)$$

For the maximal coherence extreme it is  $p_{\text{coh}} = 1$ , while for the completely incoherent mixture we have  $p_{\text{coh}} = 0$ , with all other values covering the intermediate partial coherence regime. Of course we have no way of knowing how  $\rho_t$  was prepared. We only have at our disposal the matrix elements of  $\rho_t$ , from which we can calculate  $p_{\text{coh}}$ . The only statement we can make about  $\rho_{t+dt}$  consistent with the information at hand is that  $d\rho = (1 - p_{\text{coh}})d\rho_{\text{incoh}} + p_{\text{coh}}d\rho_{\text{coh}}$ . Finally, we have to

add the change of the density matrix of the non-reacted radical-ion pairs, leading to

$$\frac{d\rho}{dt} = \frac{d\rho_{nr}}{dt} - (1 - p_{\text{coh}})(k_S Q_S \rho Q_S + k_T Q_T \rho Q_T) - p_{\text{coh}}(k_S \text{Tr}\{Q_S \rho\} + k_T \text{Tr}\{Q_T \rho\}) \frac{\rho}{\text{Tr}\{\rho\}} \quad (3)$$

This equation describes the fundamental quantum dynamics of spin-selective recombination reactions of radical-ion pairs. It embodies (a) the single-molecule effect of spin decoherence induced by the internal to the molecule recombination dynamics (first term) and (ii) the update of the ensemble density matrix due to the loss of reacted radical-ion pairs (second and third terms). Since  $d\text{Tr}\{\rho_{nr}\} = 0$ , it is seen that the trace of  $\rho$  decays as it should, i.e. according to the number of recombined radical-ion pairs,  $d\text{Tr}\{\rho\} = -dn_S - dn_T$ . The singlet and triplet yields are then  $Y_S = \int_0^\infty dn_S$  and  $Y_T = \int_0^\infty dn_T$ , respectively.

We will now illustrate the most striking difference between this description of radical-ion-pair quantum dynamics and the traditional theory [9] (a more recent variant by Jones & Hore [5] conjectured to follow from quantum measurement theory largely reproduces the traditional theory and hence only the latter will be addressed here). Specifically, we consider the most simple case of no hyperfine interactions and a single recombination channel, i.e. we completely eliminate singlet-triplet mixing and we take  $k_S = 0$ . We take as initial state the coherent singlet-triplet superposition  $(|S\rangle + |T\rangle)/\sqrt{2}$ . We plot the expectation values of the projectors  $Q_S$  and  $Q_T$  in Fig.2. It is evident that the traditional master equation of spin chemistry predicts that half of the radical-ion pairs stay locked in the non-reacting singlet state, whereas the other half produce triplet recombination products. It is as if at  $t = 0$  we make a von-Neumann measurement of the entire population of radical-pairs and the molecules have to decide in which state they are, i.e. they are projected into either the non-reacting singlet and stay there forever, or into the reacting triplet, of course with probability of 0.5 for both cases. We will explain shortly how this behavior comes about. In contrast, the full quantum dynamic analysis presented here predicts that 75% of the molecules will react (Fig.2). This is because what actually exists in radical-ion pairs is a continuous weak measurement operating within individual radical-ion pair, resulting to spin decoherence. Before the latter sets in, radical-ion pairs react through the triplet channel and "take with them" their previous singlet character. As time progresses, the initial coherent state is transformed into an incoherent mixture, and the remaining molecules that "realize" they are singlet get locked in this state.

Radical-ion pair recombination is a single molecule process, similar to the interference pattern observable in the double slit experiment which is a *single photon effect*. In that case, the detection of a photon on the observation screen after the two slits does in no way affect the quantum state of the rest of the pho-

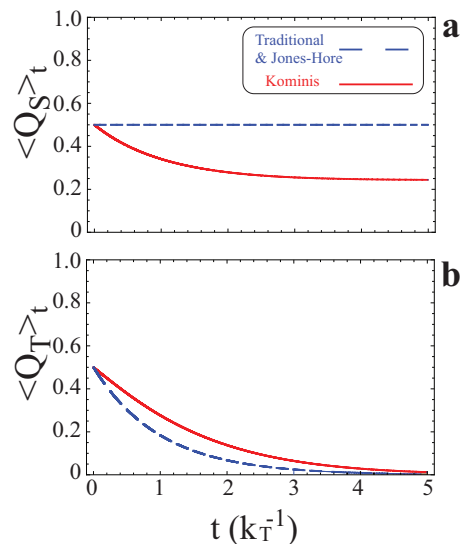


FIG. 2: Radical-ion-pair recombination dynamics in the absence of singlet-triplet mixing. (a) Time evolution of  $\text{Tr}\{Q_S \rho\}$  and (b) of  $\text{Tr}\{Q_T \rho\}$  as predicted by Eq.3 (red solid line) and the traditional as well as the Jones-Hore theory (blue dashed line).

tons. However, such a statement is embedded in the traditional theory. Here it is why. Suppose that at time  $t$  we have  $N$  radical-ion pairs all prepared in the coherent state  $\alpha|S\rangle + \beta|T\rangle$ . Hence  $\rho = N\rho_1$ , where  $\rho_1 = |\alpha|^2|S\rangle\langle S| + |\beta|^2|T\rangle\langle T| + \alpha\beta^*|S\rangle\langle T| + \alpha^*\beta|T\rangle\langle S|$  is the single-molecule density matrix. We can obviously write  $d\rho = \rho_1 dN + N d\rho_1$ . The first term represents the change in the density matrix due to reaction and the second the change in the density matrix of the non-yet-reacted radical pairs. Since  $\langle Q_T \rangle_t = |\beta|^2$ , we expect  $dn_T = Nk_T|\beta|^2 dt$  triplet products. Using Eq.1 to calculate  $d\rho_1$  we find

$$d\rho = -dn_T \rho_1 - \frac{k_T dt}{2} \rho_{\text{coh}} \quad (4)$$

where  $\rho_{\text{coh}} = N(\alpha\beta^*|S\rangle\langle T| + \alpha^*\beta|T\rangle\langle S|)$  is the coherence of  $\rho_t$ . Of course we can arrive at Eq.4 starting from the general master equation (3) since at this instant we have  $p_{\text{coh}} = 1$ . The interpretation of Eq.4 is that we lose  $dn_T$  radical-ion pairs and the rest (unreacted) lose some coherence. On the contrary, from the traditional master equation we find

$$d\rho = -dn_T \rho_1 + \left(\frac{dn_T}{N} - \frac{k_T dt}{2}\right) \rho - \frac{dn_T}{2} |T\rangle\langle T| + \frac{Nk_T dt}{2} |\alpha|^2 |S\rangle\langle S| \quad (5)$$

Here the terms after the first are highly problematic. In the analogy with the double slit, these terms suggests that a particular observation of clicks on the detector results in a concomitant change in the quantum state of the other photons flying through the screen. This is impossible.

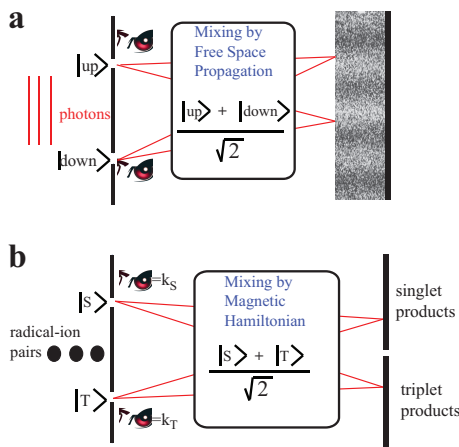


FIG. 3: Analogy between (a) the photon double slit experiment and (b) spin-selective radical-ion-pair reactions.

We can put this differently, returning to the specific example of the initial state  $(|S\rangle + |T\rangle)/\sqrt{2}$ . Here  $\langle Q_S \rangle_t = \langle Q_T \rangle_t = 1/2$ . If the molecule recombines in the time interval between  $t$  and  $t + dt$  we will be left with no radical-ion pairs, hence  $\langle Q_S \rangle_{t+dt} = \langle Q_T \rangle_{t+dt} = 0$ . That is,  $\langle Q_S \rangle_{t+dt} < \langle Q_S \rangle_t$ , contrary to the prediction of the traditional theory (Fig.2a). To keep the average of  $\langle Q_S \rangle$  constant at  $1/2$  in the traditional theory, one has to consider a different realization, in which a non-reacting radical-ion-pair changes its state from  $(|S\rangle + |T\rangle)/\sqrt{2}$  to  $|S\rangle$ , so that the average of these two realizations satisfies  $\langle Q_S \rangle_t = 1/2$ . However, the traditional theory *by design cannot* predict the change of state of non-reacting radical-ion pairs. Such concept did not exist in spin chemistry until the work in [4]. To take that into account, one is led unambiguously to Eq. 1 and the rest of the arguments presented here.

We will now dwell further upon the analogy with the double slit (Fig.3a). As is well known, if there is a photon detector (eye) in the upper and/or lower slit providing definite "which-path" information, the interference pattern will be destroyed. Weak "which path" information will reduce the fringe visibility. Whether a photon detector is placed at the upper or lower slit (or both) is indifferent, since even with just one detector, say at

the upper path, the absence of detection will imply that the photon passed through the lower slit, hence the interference pattern will be suppressed. Now in the case of radical-ion pairs (Fig.3b), we can imagine two screens, the clicks on which measure the singlet and triplet products respectively. If we block one path, e.g. the triplet, that is, if we know for sure that the radical-pair is in the singlet state, only the singlet products will be populated. The magnetic Hamiltonian generates singlet-triplet coherence, hence in general, a click on e.g. the singlet detector does not provide any clue as to which state the precursor radical-ion-pair was in. In the example treated previously, we started with a coherent initial state without specifying how it was created so that we do not complicate things by including magnetic interactions. The measurement rates  $k_S$  and  $k_T$  potentially provide "which path" information. For the decoherence brought about by this measurement, it does not matter whether  $k_S$  is small and  $k_T$  large or vice versa, i.e. it does not matter in which slit we place the "eye", because if the radical-ion-pair is not in the triplet state it will be in the singlet ( $Q_S + Q_T = 1$ ). What matters is the total measurement rate  $k_S + k_T$  of the observable  $Q_S$ , and this is what enters in Eq. (1) predicting the recombination-dynamics induced spin decoherence of the not-yet-reacted molecules. What is the fringe analog in this case? In this case the interference pattern is in time, and since the reaction proceeds in one-go we have an aperiodic interference pattern, which is the time evolution of  $\langle Q_S \rangle_t$  depicted in Fig.2a. In fact, setting  $p_{\text{coh}} = 0$  for all times we exactly retrieve the traditional theory, which in the studied example shows no interference. The traditional theory "by hand" kills the interference pattern by updating the state of the incoming photons based on the detected "clicks" on the screen. In contrast, in our description we allow the spin coherence to form this interference pattern which is gradually and partly suppressed due to decoherence setting in.

Concluding, we have elucidated the role spin coherence plays determining the fate of radical-ion-pair reactions, a role that was hidden by the projective approach of the traditional theory. We expect significant deviations from the previous theoretical understanding when  $p_{\text{coh}}$  is close to 1.

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 [8] We consider only the zero projection  $|T_0\rangle$  state of the triplet manifold, which for notational simplicity is denoted by  $|T\rangle$ .  
 [9] The traditional master equation reads  $d\rho/dt = -i[\mathcal{H}, \rho] - \frac{k_S}{2}(Q_S\rho + \rho Q_S) - \frac{k_T}{2}(Q_T\rho + \rho Q_T)$ .