Spin-selective radical-ion-pair reactions are at the core of spin chemistry [1]. It was recently shown [2] that radical-ion-pair reactions manifest non-trivial quantum effects that were masked by the traditional treatment of these reactions used since the advent of spin chemistry. Using the specific Hamiltonian interactions pertaining in radical-ion pairs, specifically taking into account electron tunnelling during charge recombination, the density matrix equation describing non-reacting radical-ion pairs was derived [2] based on basic quantum measurement theory considerations. Most recently, yet another density matrix equation supposed to describe radical-ion-pair reactions was suggested by Jones & Hore [3], advocated to also follow from quantum measurement theory. Moreover, two papers appeared [4, 5] purporting to have derived from first principles the traditional master equation. A different approach was introduced by Jones & Hore [3], based on the master equation

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

We will here examine the repercussions of this theory regarding the purity of the spin state of radical-ion pairs. For simplicity, we will here consider an idealized radical-ion pair with no nuclear spins and at zero magnetic field. That is, we completely neglect singlet-triplet mixing induced by magnetic interactions. Furthermore, we consider just one recombination channel, e.g. the singlet, and thus set $k_T = 0$. Finally, we take as initial state the coherent superposition $|\psi\rangle = (|S\rangle + |T\rangle)/\sqrt{2}$. So in this example the Jones-Hore master equation reads

$$\frac{d\rho}{dt} = -k_S \rho + k_S Q_T \rho Q_T$$ (3)

The philosophy of postulating such a master equation is the following [3]: if the density matrix of a single radical-ion pair at time $t$ is $\rho_t$, then there are three different scenarios for what can happen in the following time interval $dt$: (i) with probability $1 - k_S dt$ nothing happens, keeping $\rho_{t+dt} = \rho_t$, (ii) with probability $k_S dt \text{Tr}(Q_S \rho_t)$ a singlet recombination takes place leading to $\rho_{t+dt} = 0$, and (iii) with probability $k_S dt \text{Tr}(Q_T \rho_t)$ the molecule’s state is projected to the triplet state, making $\rho_{t+dt} = Q_T \rho_t Q_T / \text{Tr}(Q_T \rho_t)$. Averaging all three possibilities leads to (3). However, equation (3) was not derived from the usual procedure of considering (i) the quantum system under study and (ii) the measurement-reservoir degrees of freedom, evolving the combined state under the specific system-reservoir coupling and then tracing out the reservoir degrees of freedom. It was postulated to follow from general considerations in analogy with the well known textbook example [4] of a single two-level atom observed by a photodetector. If the atom is initially in a coherent state $(|e\rangle + |g\rangle)/\sqrt{2}$, and if the photodetector does not register a photon until time $t$, the state of the atom becomes $(e^{-\Gamma t/2} |e\rangle + |g\rangle) / \mathcal{N}$, where $\mathcal{N}$ is the normalization constant and $\Gamma$ the spontaneous decay rate. The interpretation is that not observing a photon, our knowledge of the atom’s state acquires more
ground-state "character". The Jones-Hore theory makes the seemingly innocent analogy that in the case of a radical-ion pair that reacts through the singlet channel, the state of a non-reacting radical-ion pair acquires more triplet-state "character". However, this analogy breaks down if examined more carefully. Before explaining why this is the case, we will present the solution of (3) for the specific example we are considering.

In Fig.1 we plot as a function of time (a) the expectation value $\langle Q_S \rangle = \text{Tr}\{Q_S \rho \}$, (b) the expectation value $\langle Q_T \rangle = \text{Tr}\{Q_T \rho \}$, (c) the normalization of the density matrix $\text{Tr}\{\rho\}$, which represents the number of surviving radical-ion pairs, and (d) the purity of the state $\text{Tr}\{\rho^2 \}$.

The interpretation of these results is that (a) half of the radical-ion pairs react through the singlet channel, (b) the other half remain locked in the non-reacting triplet state, (c) the number of radical ion pairs is, as expected, reduced by half as $t \to \infty$, and (d) we start with a pure state and end up with a pure (triplet) state. The latter conclusion can be better visualized by considering non-reacting radical-ion pairs. To that end, we normalize $\langle Q_S \rangle$ and $\langle Q_T \rangle$ with $\text{Tr}\{\rho\}$ whereas we normalize the state purity $\text{Tr}\{\rho^2 \}$ with $\text{Tr}\{\rho\}^2$. The results are shown in Fig.2. The interpretation is that as long as a radical-ion pair does not react, its state approaches the pure triplet. From the construction of the Jones-Hore master equation (3), in the example at hand there are the following two possibilities for a non-reacting evolution between $t$ and $t + dt$: (i) $\rho_{t+dt} = \rho_t$, or (ii) $\rho_{t+dt} = |T\rangle \langle T|$. The average of all possible trajectories embodying these two possibilities is what is plotted in Fig.2. So we start from a pure state, this becomes mixed, and then it returns to be pure again. At first glance this result is intuitive and acceptable. It seems to be analogous to a situation where a decaying atom is initially in the pure excited state, it becomes entangled with the radiation field, hence the atomic state is mixed, and then it decays to the ground state, becoming pure again. Or, if we have an ensemble of spins initially in the coherent state $|\uparrow\rangle + |\downarrow\rangle / \sqrt{2}$, and they undergo a $T_2$ process, the state becomes mixed, $|\uparrow\rangle \langle\uparrow|/2 + |\downarrow\rangle \langle\downarrow|/2$. If a $T_1$ process follows, we would end up with a pure spin state again. However, here there is a problem. Among the $N$ molecules, $N/2$ non-reacting ones will evolve in trajectories that average to Fig.2. So for the ensemble of non-reacting radical-ion pairs we have the entropy initially increasing $\langle\text{Tr}\{\rho^2\}\rangle$ falls), and then decreasing $\langle\text{Tr}\{\rho^2\}\rangle$ rises back to 1). What makes up for this entropy decrease? The molecules are freely evolving, i.e. there is no energy exchange nor any entropy exchange with the environment. These molecules do not react, so there is nothing to take up the entropy loss, as in the case of decaying atoms or spins. For example, when atoms spontaneously decay to the ground state, the entropy decrease mentioned above is counterbalanced
by the entropy increase of the radiation field. Similarly, when the spins undergo a $T_1$ process and end up in a pure state after having been mixed by a $T_2$ process, the entropy is taken up by the reservoir responsible for the $T_1$ process. How is the loss of entropy of non-reacting radical-ion pairs balanced?

To illustrate these considerations in more detail, we consider single quantum trajectories of reacting and non-reacting radical-ion pairs according to the Jones-Hore theory. As mentioned previously, the density matrix $\rho_t$ of a radical-ion pair at time $t$ can evolve in either of the three ways (i) $\rho_{t+dt} = \rho_t$; (ii) $\rho_{t+dt} = |T\rangle\langle T|$ and (iii) $\rho_{t+dt} = 0$. Let us first look at the evolution of a radical-ion pair that does react at some point, i.e. at some random time possibility (iii) is realized. Of course, until then $\rho_t = \rho_0$, i.e. possibility (i) is realized. An example of such a trajectory is shown in Fig.3. At time $t_1$ the radical pair’s state jumps to the singlet state and recombines at the same instant. An example of a non-reacting trajectory is shown in Fig.3. At some random time $t_2$, $\langle Q_S \rangle$ jumps to $\langle Q_S \rangle = 0$ ($\langle QT \rangle = 1$) and the state is locked there forever. So the average of non-reacting trajectories up to time $t$ includes trajectories that have remained at the initial state $\rho_0$ up to time $t$ and trajectories that have been projected to the triplet state at some earlier time. That’s where the decreasing purity of the non-reacting trajectories stems from. According to the Jones-Hore theory, the weight of the former decays as $e^{-k_ST}$, whereas the weight of the latter approaches $1/2$ as $(1-e^{-k_ST})/2$. That’s why as $t \to \infty$ the purity of the state of non-reacting trajectories approaches 1. But what after all compensates for the unphysical spontaneous entropy loss of the non-reacting radical-ion pairs? Is it the information gained from the reacting molecules? Not really. In Fig.4 we plot (i) the von-Neumann entropy of $\rho_{nr}$, the density matrix of the non-reacting radical-ion pairs, which is $S_t = -\text{Tr}\{\rho_{nr} \ln \rho_{nr}\}$, and (ii) the information gained up to time $t$ from the reacting molecules. This is easily calculated as follows: Let $p_S = \text{Tr}\{Q_S \rho_{nr}\}$ be the singlet probability at time $t$ of a radical-ion pair just before it reacts. The information content of this molecule’s state is $s_t = -p_S \ln p_S - (1-p_S) \ln(1-p_S)$. When the radical-ion pair reacts we have $p_S = 1$, hence the information gain is $s_I$ itself. There are $k_ST \text{Tr}\{Q_S \rho\}$ molecules reacting in the time interval between $t$ and $t + dt$, so the total information gain up to time $t$ is $I_t = \int_0^t dt k_S \text{Tr}\{Q_S \rho\}$. From Fig.4 it is seen that from $t \approx 1/k_S$ and on, the von-Neumann entropy of $\rho_{nr}$ drops from 0.4 to zero, but the information gain is just about 0.1, i.e. it cannot accommodate for this entropy loss.

We will now analyze the root of this shortcoming of the Jones-Hore theory. We will show where the analogy with the single atom mentioned above fails. In Fig.5 we pictorially depict the atom’s two energy levels and the radiation reservoir coupled to the excited state. An atom initially in a coherent superposition of the ground and excited states has the possibility of decaying. A photon will thus occupy one of the states of the radiation reservoir coupled to $|e\rangle$. If no photon is observed up to time $t$, one can claim that the atom’s state has more $|g\rangle$ character. There is no other possibility. In other words, if a single occupation leaves the atomic system (spanned by $|g\rangle$ and $|e\rangle$) and goes to the radiation reservoir, then this event is definitely observable in the outside world as a photon. From the non-observation of a photon an unambiguous inference about the atom’s state can be made. However, the situation is not the same with radical-ion pairs. In Fig.5 we show the energy levels of a radical-ion pair and in Fig.6 we simplify this picture for use in the following. Evidently, we here have two reservoirs. One is the reservoir of the excited vibrational states of the neutral molecule. There is a second one. Each of those excited states is coupled to a radiation reservoir.
FIG. 5: (a) Two-level atom initially in a coherent state \( |(e) + |g\rangle)/\sqrt{2} \). The radiation field reservoir is coupled to the excited state \( |e\rangle \). (b) If the atom decays, a photon occupies one of the radiation reservoir states. This is definitely observable. If the atom does not decay, then the probability that it is in the ground state increases.

(or another phonon reservoir, it does not matter).

How is the event of the charge recombination transmitted to the outside world? It is by the emission of the photon by the excited vibrational level and the creation of the singlet neutral product \( \text{DA} \). If the radical-ion pair is at time \( t \) in the coherent superposition \( (|S\rangle + |T\rangle)/\sqrt{2} \) or in any state for that matter, and no photon is detected, i.e. no reaction takes place within the following time interval \( dt \), the only inference to be made is that the singlet reservoir state was not occupied in this time interval. No inference can be made about the radical-ion pair spin state. It is exactly this point where the analogy with the atom’s case fails. In other words, the basis of the Jones-Hore theory is the erroneous association of the quantum measurement going on internally in radical-ion pairs due to the internal spin-state-measurement dynamics with the recombination event itself. To clarify this statement, in Fig. 7 we depict a radical-ion pair initially in the coherent state \( (|S\rangle + |T\rangle)/\sqrt{2} \), i.e. the occupation resides in the quantum system spanned by \( |S\rangle \) and \( |T\rangle \). If the occupation leaves the system and goes to the singlet reservoir, this is not observable (Fig. 7b). What is observable is the next possible step (Fig. 7c), i.e. the decay of the reservoir state and the creation of a photon and the ground state DA. But this is just one possibility. There is a second possibility (Fig. 7b). The occupation tunnels back to \( |S\rangle \) and the spin state evolution continues on from there. This possibility is described by the second-order perturbation theory from which follows the master equation \( \text{DA} \) derived in [2]. It is these virtual processes that lead to singlet-triplet decoherence introduced in [2]. In other words, during a possible trajectory of a single radical-ion pair, one can have many instances where the continuous measurement induced by the singlet reservoir (and the triplet reservoir when it exists) results in \( Q_S = 1 \) or \( Q_S = 0 \). The Jones-Hore theory wrongly associates the former possibility with a concomitant singlet recombination. If the triplet recombination channel was also open, then the Jones-Hore theory would wrongly associate both

FIG. 6: (a) Radical-ion pair quantum dynamics. A photon excites the singlet neutral precursor molecule \( \text{DA} \) into \( \text{D}^* \text{A} \), and a charge transfer creates the radical-ion pair. The excited vibrational levels \( (\text{DA})^* \) of the neutral DA molecule form the measurement reservoir, which (i) acts as a measurement device for the radical pair’s spin state, and (ii) acts as a sink of radical-ion pairs, i.e. in the event of recombination, 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) A simplified version of (a) in the case of just a singlet recombination channel. The (orange) reservoir on the left of the singlet reservoir depicts the radiation reservoir (or some other phonon reservoir) to which the excited vibrational states of the singlet reservoir are coupled.

FIG. 7: Radical-ion pair (a) initially in the coherent singlet-triplet state. (b) The electron might tunnel to a singlet reservoir state, from which will follow (c) either a photon emission and the production of a singlet neutral product i.e. the molecule DA (possibility 1), or it might tunnel back (possibility 2) to the singlet radical-ion pair state (virtual process) commencing again the spin-state evolution.
The average of all such pure non-reacting trajectories produces the decaying state purity resulting from (1) for the example under study.

The singlet \((Q_S = 1)\) and the triplet \((Q_S = 0)\) measurement outcomes with the singlet and triplet recombination event. The actual charge recombination event is, however, completely independent and can take place at any time. This is shown schematically for a more general example than the one considered here in Fig 8. The kinks produced in a smooth state evolution by the jumps to \(Q_S = 1\) or \(Q_T = 1\) are responsible for singlet-triplet decoherence. That is, the average of all trajectories like the one in Fig 8 without a recombination event reproduces the master equation (1) derived in [2]. If we calculate the state purity according to this master equation, we find that it is a decreasing function of time. In the particular example we are considering here, a possible quantum trajectory for a reacting radical-ion pair is shown in Fig 9a. The radical-pair’s spin state jumps to the singlet at time \(t_1\) (measurement outcome \(Q_S = 1\)), from which it recombines at time \(t_2\). There is nothing against \(t_2 > t_1\), and this fact is what the Jones-Hore theory fails to account for. An example of a non-reacting trajectory is shown in Fig 9b. At some random instant \(t_3\), the measurement outcome is \(Q_S = 0\), and the state jumps to the pure triplet, where it remains forever. We stress that up to time \(t_2\) both trajectories are non-reacting trajectories. The average of all such pure non-reacting trajectories reproduces the singlet-triplet decoherence embodied in (1), which results in a monotonically decreasing state purity, as shown in Fig 9c. In other words, in this particular example the infinite-time state of non-reacting trajectories is \(\rho_\infty = \frac{1}{2} |S\rangle\langle S| + \frac{1}{2} |T\rangle\langle T|\) as opposed to \(\rho_\infty = |T\rangle\langle T|\) of the Jones-Hore theory. In our approach, it is easy to see that the von-Neumann entropy of non-reacting trajectories monotonically increases. Hence the problem facing the Jones-Hore theory does not exist.

We can recapitulate the following consistent picture of what really happens. Up to some time \(t\), non-reacting trajectories involve pure-state trajectories of molecules that have been projected to the triplet state, and pure-state trajectories of molecules that have been projected to the singlet state at some time earlier than \(t\) and have not yet recombined. Until the latter do recombine, we have a mixed state of increased entropy. After they do, we end up with a pure triplet state. This entropy loss is counter-balanced by the entropy increase in the final photon/phonon reservoir. It is through the reacting molecules that entropy is transferred from the radical-ion-pair system to the environment. In contrast, the Jones-Hore theory ignores the presence of the singlet vibrational-reservoir states of the radical-ion pair. This reservoir is in between the quantum system (radical-ion pair) and the outside world (photon reservoir). What goes on in this singlet reservoir is unobservable. Hence any information or the lack thereof in the outside world cannot be associated with the quantum system’s state. However, the Jones-Hore theory does exactly that. Hence in this description, the non-reacting trajectories involve pure state-trajectories still in their initial state, and pure...
state trajectories that have been projected to the triplet state based on the non-observation of a reaction. The latter is, as explained before, an ambiguous inference on the radical-pair’s spins state, and that’s why it results in an unphysical entropy loss of non-reacting trajectories. The difference between our consistent physical picture and the Jones-Hore theory is not just a philosophical curiosity. It has measurable consequences on the reaction time. If we define the latter to be the time at which the radical-ion pair population has decayed to a specified fraction of its original value, then the two approaches will predict different reaction times, exactly because the Jones-Hore theory makes the association “measurement outcome=recombination”. We will further analyze reaction times in another manuscript.

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