Should recombinations of radical pairs be considered as
accompanied by measurements?

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Abstract. The so-called “phenomenological” kinetic equation for one-pair density operator for spin-selective reactions is defended. We derive this equation from the kinetic equation for density operator of \textit{all} pairs which are treated as singlet and triplet bosons. There presented some reasons for inconsistency of measurement-like approach to the problem.

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1. Introduction

We address the problem of correct treating and interpretation of recombination events in the ensemble of radical pairs. Particularly we deal with the relation between the spin-selective recombinations of pairs and measurements of their spin. Our main statement concerns the radical distinction between a measurement-like process and proper act of recombination. In numerical works by Kominis (see \cite{1} and references therein) any recombination event is considered as that of measurement-like. On the basis of this viewpoint his critics of the well-known ’phenomenological’ kinetic equation \cite{2,3}

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

(1)

is based ($\hbar = 1$). Here $\rho$ is the density matrix of a pair; $\mathcal{H}$ – its Hamiltonian; $2k_S$ and $2k_T$ are the rate constants of singlet and triplet recombinations respectively. For simplicity we take into account only spin variables of the pairs. In this case $\rho$ is an operator in a 4-dimensional Hilbert space with the basis \{\ket{S}, \ket{T_-, T_0, T_+}\}

\[
Q_S = \ket{S}\bra{S}, \quad Q_T = \sum_{\sigma=0,\pm1} \ket{T_\sigma}\bra{T_\sigma}
\]  

(2)

are the projectors onto the corresponding spin subspaces. In literature one can find a misleading interpretation of the last two anticommutator terms in rhs of (1) as remnants of a full Lindblad-type structure \cite{4} upon elimination of the so-called ’sandwich’ gain term:

\[
2Q\rho Q - Q\rho - \rho Q \rightarrow -(Q\rho + \rho Q)
\]  

(3)
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(here $Q$ stands for $Q_S$ as well as for $Q_T$). In accordance with this interpretation the transformation (3) is considered as the elimination of the gain term because of recombination. Note that the Lindblad-type structure in lhs of (3) provides strait associations with the spin-measurement-like process. The central point of the Kominis’ approach is the restoration of the full Lindblad structures in (1) in the framework of the measurement paradigm.

We are going to show that there is a firm background behind the equation (1), which has practically nothing common with any measurement-like process.

2. Spin-selective recombinations

Our starting point is the kinetic equation for the multi-pair quantum state $\hat{\rho}$. In contrast with $\rho$ this operates in the infinite-dimensional Hilbert space with the Fock basis \{\ket{n_S, n_{T^+}, n_{T^0}, n_{T^-}}\}, where $n$ are the numbers of pairs in the corresponding states. We should write the kinetic equation in terms of annihilation, $\hat{a}_S$, $\hat{a}_{T^+}$, and creation, $\hat{a}_S^\dagger$, $\hat{a}_{T^+}^\dagger$, operators for singlet and triplet pair respectively. So we treat any pair as an individual ‘particle’. These ‘particles’ are bosons, i.e. one has the following commutator relations:

$$[\hat{a}_S, \hat{a}_S^\dagger] = 1; \quad [\hat{a}_{T^+}, \hat{a}_{T^+}^\dagger] = \delta_{\sigma_1, \sigma_2}; \quad [\hat{a}_S, \hat{a}_{T^+}^\dagger] = 0. \quad (4)$$

The mathematical description of the process of spontaneous acts of death of the ‘particles’ (the acts of recombinations) is known. For the both types of recombinations (singlet and triplet ones) we have the corresponding three-term Lindblad structure in rhs of the kinetic equation:

$$\frac{d}{dt}\hat{\rho}(t) + i[\hat{H}, \hat{\rho}(t)] = k_S(2\hat{a}_S\hat{\rho}(t)\hat{a}_S^\dagger - \hat{a}_S^\dagger\hat{a}_S\hat{\rho}(t) - \hat{\rho}(t)\hat{a}_S\hat{a}_S^\dagger) + k_T\sum_\sigma (2\hat{a}_{T^+}\hat{\rho}(t)\hat{a}_{T^+}^\dagger - \hat{a}_{T^+}^\dagger\hat{a}_{T^+}\hat{\rho}(t) - \hat{\rho}(t)\hat{a}_{T^+}\hat{a}_{T^+}^\dagger) \quad (5)$$

The Hamiltonian $\hat{H}$ in (5) should not be confused with $\mathcal{H}$ from (1). The evaluation of this equation is made in Appendix.

The one-pair density matrix $\rho$ from (1) is obtained by the following standard way:

$$\rho = |S\rangle\langle\hat{a}_S^\dagger\hat{a}_S| + \sum_\sigma \left(|T_\sigma\rangle\langle\hat{a}_{T^+}\hat{a}_{T^+}^\dagger|S\rangle + |S\rangle\langle\hat{a}_{T^+}^\dagger\hat{a}_S|T_\sigma\rangle + \sum_{\sigma_1, \sigma_2} |T_{\sigma_1}\rangle\langle\hat{a}_{T_{\sigma_2}}\hat{a}_{T_{\sigma_1}}|T_{\sigma_2}\rangle\right) \quad (6)$$

where $\langle\ldots\rangle = Tr(\hat{\rho}(t)\ldots)$. The mean value of any multi-pair operator $\hat{O}$ evolves according to the equation

$$\frac{d}{dt}\langle\hat{O}\rangle + i\langle[\hat{O}, \hat{H}]\rangle = k_S\left(\langle\hat{a}_S^\dagger[\hat{O}, \hat{a}_S]\rangle + \langle[\hat{a}_S^\dagger, \hat{O}]\hat{a}_S\rangle\right) + k_T\sum_\sigma \left(\langle\hat{a}_{T^+}^\dagger[\hat{O}, \hat{a}_{T^+}]\rangle + \langle[\hat{a}_{T^+}^\dagger, \hat{O}]\hat{a}_{T^+}\rangle\right) \quad (7)$$

Substituting the operator $\hat{O}$ with proper bilinear products of $\hat{a}^\dagger$ and $\hat{a}$, one gets the kinetic equation for all elements of $\rho$:

$$\frac{d}{dt}\langle\hat{a}_S^\dagger\hat{a}_S\rangle + i\langle[\hat{a}_S^\dagger\hat{a}_S, \hat{H}]\rangle = -2k_S\langle\hat{a}_S^\dagger\hat{a}_S\rangle \quad (8)$$
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\[
\frac{d}{dt} \langle \hat{a}_s^\dagger \hat{a}_{T_s} \rangle + \imath \langle [\hat{a}_s^\dagger \hat{a}_{T_s}, \hat{H}] \rangle = -(k_S + k_T) \langle \hat{a}_s^\dagger \hat{a}_{T_s} \rangle
\]  

(9)

\[
\frac{d}{dt} \langle \hat{a}_{T_s}^\dagger \hat{a}_s \rangle + \imath \langle [\hat{a}_{T_s}^\dagger \hat{a}_s, \hat{H}] \rangle = -(k_S + k_T) \langle \hat{a}_{T_s}^\dagger \hat{a}_s \rangle
\]  

(10)

\[
\frac{d}{dt} \langle \hat{a}_{T_{s_2}}^\dagger \hat{a}_{T_{s_1}} \rangle + \imath \langle [\hat{a}_{T_{s_2}}^\dagger \hat{a}_{T_{s_1}}, \hat{H}] \rangle = -2k_T \langle \hat{a}_{T_{s_2}}^\dagger \hat{a}_{T_{s_1}} \rangle
\]  

(11)

Combining these equations with the use of (6) and (2) we arrive at an equation for \( \rho \) with rhs identical to that of (1).

It's worth to stress that the equation (5) describes the process of spontaneous spin-selective 'annihilation' of pairs, not measurement of their spins. 'If it were the case' picture of a measurement-like process will be discussed later.

3. Hypothetical measurement-like recombinations

Let us consider an imaginary process in which recombination and pair’s spin measurement are really inseparable. It will be shown that the evolution equation for the one-pair density matrix \( \rho \) resembles neither (1) nor the equation by Kominis [1].

Note that any measurement of a pair’s spin create information about the spin value. This information is written down in the environment. Hence the pair appears to be entangled with the environment. Let us first consider the following phenomenological equation for \( \rho \) where the pairs are subjected to spin measurements but no recombinations take place:

\[
\frac{d}{dt} \rho + \imath [\hat{H}, \rho] = k(Q_S \rho Q_S + Q_T \rho Q_T - \rho).
\]  

(12)

Here \( k \) is the number of measurement events per second. The first two terms in the brackets in rhs of (12) stand for the two possible outcome of a measurement (singlet or triplet states). Any singlet-triplet coherence vanish in accordance with rhs of (1). This is due to the mentioned entangling process. At the same time the total number of pairs conserves: \( Tr \rho = const \) (no recombinations).

Now assume that upon a spin measurement with the singlet outcome the pair recombines (in the singlet channel) with the probability \( p_S \), and the same for the triplet outcome. One may account the loss of pairs due to these recombinations eliminating parts of the gain terms in rhs of (12):

\[
\frac{d}{dt} \rho + \imath [\hat{H}, \rho] = k \left( (1 - p_S) Q_S \rho Q_S + (1 - p_T) Q_T \rho Q_T - \rho \right).
\]  

(13)

If we introduce the notations \( \tilde{k}_S = p_S k, \tilde{k}_T = p_T k \) and take into account that \( Q_T = 1 - Q_S \), we arrive at

\[
\frac{d}{dt} \rho + \imath [\hat{H}, \rho] = (2k - \tilde{k}_S - \tilde{k}_T) Q_S \rho Q_S - (k - \tilde{k}_T)(Q_S \rho + \rho Q_S) - \tilde{k}_T \rho.
\]  

(14)

The 'sandwich' as well as anticommutator terms are present. Note that if \( \tilde{k}_T = 0 \) and \( \tilde{k}_S = k \) the equation (13) lies just in between the same cases of (1) and equation (5) from [1].

In the work [5] the equation (14) for the special case \( k = \tilde{k}_S + \tilde{k}_T \) was developed. The comparative numerical analysis of the derived equation and that one from (1) revealed a slight difference.
4. Conclusions

Resuming we state that the kinetic equation for one-pair density matrix $\rho$ in the case of spin-selective recombinations has been shown to have the following form:

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

Our approach is only valid for geminate pairs. In the opposite case (for possibility of cross-recombinations) one may not consider the radical pairs as bosons.

We show that the kinetic equation for the measurement-like recombination process differs radically both from the conventional equation and from Kominis’ results. We also do not share the opinion from [5] “...that the quantum measurement approach should normally be used in future simulations of spin-selective radical pair reactions”. From our viewpoint the spin-selective recombination is not a measurement. In the hypothetic opposite case when any recombination is preceded by spin measurement there emerges an information concerning the spin of survived pairs. This option corresponds to the terms from (13) proportional to $1 - p_S$ and $1 - p_T$. There is no any basis to suppose such a phenomenon takes place in recombination process.

Appendix

There is a regular derivation of equations like (5) from the first principles [6, 7]. As an example, we will give a sketch of such a derivation for singlet Lindblad structure in rhs of (5). For example it can be obtained in the second order of perturbation with respect to the following dynamics:

$$\hat{V} = \lambda \hat{a}_s \otimes (\hat{b}^\dagger \cdot \hat{E}^\dagger) + H.c. \tag{15}$$

responsible for transformation of a singlet pair into a product $b$. This process is accompanied by photon emission. Electromagnetic field is the vector operator $\hat{E}^\dagger$ (this part is responsible for photon creation). So the product should be vector as well, to make $\hat{V}$ invariant under rotations, i.e. it should have total unit angular momentum. Let $\hat{R}(t)$ be the total statistical operators of pairs, products and photons. $\hat{R}(t)$ evolves with respect to the following equation

$$\frac{d}{dt} \hat{R}(t) = -i[\hat{H}_a + \hat{H}_b + \hat{H}_{ph} + \hat{V}, \hat{R}(t)], \tag{16}$$

where $\hat{H}_a, \hat{H}_b$ and $\hat{H}_{ph}$ are free Hamiltonians of pairs, products and photons, respectively. In the interaction representation

$$\hat{R}_I(t) = \exp[i(\hat{H}_a + \hat{H}_b + \hat{H}_{ph})t] \hat{R}(t) \exp[-i(\hat{H}_a + \hat{H}_b + \hat{H}_{ph})t], \tag{17}$$

$$\hat{V}_I(t) = \exp[i(\hat{H}_a + \hat{H}_b + \hat{H}_{ph})t] \hat{V} \exp[-i(\hat{H}_a + \hat{H}_b + \hat{H}_{ph})t] \tag{18}$$

(16) turns into

$$\frac{d}{dt} \hat{R}_I(t) = -i[\hat{V}_I(t), \hat{R}_I(t)]. \tag{19}$$
In the second order with respect to $\hat{V}_I(t)$ one has
\[
\hat{R}_I(t + \Delta t) = \hat{R}_I(t) - i \int_t^{t + \Delta t} dt' [\hat{V}_I(t'), \hat{R}_I(t)] - \int_t^{t + \Delta t} dt' \int_t^{t + \Delta t} dt'' [\hat{V}_I(t'), [\hat{V}_I(t''), \hat{R}_I(t)]]
\]
(20)

In the last term in rhs we replaced $\hat{R}_I(t)$ with $\hat{R}_I(t)$ due to the assumption $\Delta t \ll \tau_{rel}$, where $\tau_{rel}$ is a typical relaxation time. There is another time scale, $\tau_{corr}$ – the correlation time which will appear later. If $\Delta t \gg \tau_{corr}$ one can neglect all correlations between pairs and their environment (products and photons):
\[
\hat{R}_I(t) = \hat{\varrho}_I(t) \otimes \hat{\varrho}_{b,ph}
\]
(21)
The statistical operator $\hat{\varrho}_{b,ph}$ is assumed stationary. We also suppose that
\[
\hat{E}\hat{\varrho}_{b,ph} = \hat{\varrho}_{b,ph}\hat{E}^\dagger = 0,
\]
(22)
i.e. all emitted photons are rapidly absorbed so that $\hat{\varrho}_{b,ph}$ is the vacuum with respect to electromagnetic field.

From (20) we get the ’coarse-grained’ equation
\[
\frac{\Delta \hat{\varrho}_I(t)}{\Delta t} = -\frac{|\lambda|^2}{\Delta t} \int_0^{\infty} d\tau \int_t^{t + \Delta t} dt' \left[ g(\tau) \left( \hat{a}_S^\dagger(t')\hat{a}_S(t' - \tau) - \hat{a}_S(t' - \tau)\hat{a}_S^\dagger(t') \right) + g(-\tau) \left( \hat{\varrho}_I(t)\hat{a}_S^\dagger(t' - \tau)\hat{a}_S(t') - \hat{a}_S(t')\hat{\varrho}_I(t)\hat{a}_S^\dagger(t' - \tau) \right) \right].
\]
(23)

Omitting details we arrive at
\[
\frac{\Delta \hat{\varrho}_I(t)}{\Delta t} = -\frac{|\lambda|^2}{\Delta t} \int_0^{\infty} d\tau \int_t^{t + \Delta t} dt' \left[ g(\tau) \left( \hat{a}_S^\dagger(t')\hat{a}_S(t' - \tau) - \hat{a}_S(t' - \tau)\hat{a}_S^\dagger(t') \right) + g(-\tau) \left( \hat{\varrho}_I(t)\hat{a}_S^\dagger(t' - \tau)\hat{a}_S(t') - \hat{a}_S(t')\hat{\varrho}_I(t)\hat{a}_S^\dagger(t' - \tau) \right) \right].
\]
(24)

Here
\[
g(\tau) = g(-\tau)^* \equiv Tr_{b,ph}(\hat{b}_I(\tau) \cdot \hat{E}_I(\tau))(\hat{b}_I^\dagger(0) \cdot \hat{E}_I^\dagger(0))\hat{\varrho}_{b,ph}
\]
(25)
is the correlation function; $\tau_{corr}$ is its typical scale. For simplicity we assume $\langle \hat{H}_a \rangle \tau_{corr} \ll 1$.

Coming back to the Schrodinger representation we get
\[
\frac{d}{dt} \hat{\varrho}(t) + i[\hat{H}_a, \hat{\varrho}(t)] =
\]
(26)
\[
(k_S + \imath \kappa_S)(\hat{a}_S\hat{\varrho}(t)\hat{a}_S^\dagger - \hat{a}_S^\dagger\hat{a}_S\hat{\varrho}(t)) + (k_S - \imath \kappa_S)(\hat{a}_S\hat{\varrho}(t)\hat{a}_S^\dagger - \hat{a}_S^\dagger\hat{a}_S\hat{\varrho}(t)) = \imath \kappa_S \hat{a}_S^\dagger \hat{a}_S - \hat{\varrho}(t) \hat{a}_S^\dagger \hat{a}_S\hat{\varrho}(t),
\]
where
\[
k_S = |\lambda|^2 Re \int_0^{\infty} g(\tau)d\tau
\]
(27)
is the rate constant of singlet recombinations and
\[
\kappa_S = |\lambda|^2 Im \int_0^{\infty} g(\tau)d\tau
\]
(28)
is a parameter of a slight Hamiltonian renormalization:
\[
\hat{H}_a \rightarrow \hat{H}_a + \kappa_S \hat{a}_S^\dagger \hat{a}_S = \hat{H}.
\]
(29)

We get the first line of (5).
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