Reaction operators for radical pairs

Purtov Peter A.[1*]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia*

Novosibirsk State University, Novosibirsk, Russia

* *E-mail:* purtov@kinetics.nsc.ru

Spin chemistry concerned with electron and nuclear spins behavior as well as with the manifestation of magneto-spin interactions in chemical reactions is developed quite well both experimentally and theoretically. Most frequently spin chemistry deals with radical pair reactions in liquid solutions. Commonly recombination of radical pairs occurs at the immediate contact of radicals, when the overlap of radical pairs orbitals is considerable, and singlet-triplet transitions take place in the intervals between re-contacts, when the exchange interaction is insignificant. However, in some reactions, for example, in electron transfer, the reaction and spin evolution proceed simultaneously. To describe such processes, a phenomenological exponential model was developed about 50 years ago. According to this model, the evolution of the spin density matrix of a radical pair (RP) obeys the equation

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H},\rho] - \frac{K_S}{2}(Q_S\rho + \rho Q_S) - \frac{K_T}{2}(Q_T\rho + \rho Q_T)$$
$$Q_S = |S\rangle\langle S| \;, \qquad Q_T = |T_0\rangle\langle T_0| + |T_-\rangle\langle T_-| + |T_+\rangle\langle T_+| \qquad (1)$$

In the spin chemistry, eq. (1) are widely used to describe various effects. Although these equations are phenomenological, it well describes the effects observed. In [1] the exactly solvable model is used to verify eq. (1). However, in the spin chemistry, the cases are possible where the processes are reversible (e.g., electron transfer). Thus, eq. (1) needs to be generalized. In the present work, we have derived the exactly solvable model which contains both the reversible and irreversible processes. Expression for the reaction operator of this model is more complex due to the expanded basis of spin states. The reaction operator of eq. (1) is a particular case. These operators coincide only in the limiting case of the fully irreversible recombination process. This work continues the study begun in [2,3]. It is considered more common exactly solvable model. Expression for the reaction operator of this model is more complex due to the expanded basis of spin states. The reaction operator of eq. (1) is a particular case. These operators coincide only in the limiting case of the fully irreversible process of recombination.

The simultaneous consideration of recombination from the singlet and triplet states is much more complicated. Here we also built an exact model. However, in this more general case, equation (1) is not always justified even for an irreversible process. The applicability limits of the approximation are indicated. A more general case of reversible recombination is studied [4].

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