Reaction operators for radical pair

Peter A. Purtov

Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia

Novosibirsk State University, Novosibirsk, Russia

Main equation of spin chemistry

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}, \rho\right] - \frac{K_S}{2}\left(Q_S \rho + \rho Q_S\right) - \frac{K_T}{2}\left(Q_T \rho + \rho Q_T\right)$$

$$\frac{\partial \rho(t)}{\partial t} = \hat{L}(\mathrm{q})\rho - \frac{i}{\hbar}\left[\hat{H}, \rho\right] - \frac{K_S}{2}\left(Q_S \rho + \rho Q_S\right) - \frac{K_T}{2}\left(Q_T \rho + \rho Q_T\right)$$

The evolution of the spin density matrix of a radical pair (RP) obeys the phenomenological equation

$$Q_S = |S\rangle\langle S| \quad Q_T = |T\rangle\langle T|$$

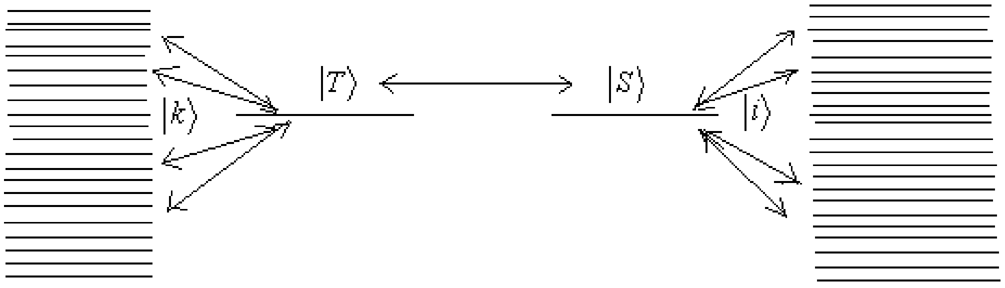
Modification

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}, \rho\right] - \frac{K_S}{2}\left(Q_S\rho + \rho Q_S - 2Q_S\rho Q_S\right)$$

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}, \rho\right] - K_S\left(2Q_S\rho + 2\rho Q_S - 2Q_S\rho Q_S\right)$$

1. I.K. Kominis, Phys. Rev. E 80 (2009) 056115
2. J.A. Jones, P.J. Hore, Chem. Phys. Letters, 488 (2010) 90

The exactly solvable model



The exactly solvable model

$$i\frac{\partial\psi(t)}{\partial t}=\hat{H}\psi(t)$$

$$-i\psi(0)+ik\varphi(k)=\hat{H}\varphi(k)$$

$$\varphi(k)=\int_0^\infty\psi(t)\exp(-kt)dt$$

$$\phi(k)=i\left(ik-\hat{H}\right)^{-1}\psi(0)=\mathrm{i}\hat{G}(ik)\psi(0)$$

$$\langle S|\phi(k)\rangle=i\langle S|\hat{G}(ik)|S\rangle$$

$$\langle T|\phi(k)\rangle=i\langle T|\hat{G}(ik)|S\rangle$$

$$\langle S|\phi(k)\rangle=i\langle S|\hat{G}(ik)|T\rangle$$

$$\langle T|\phi(k)\rangle=i\langle T|\hat{G}(ik)|T\rangle$$

The exactly solvable model

$$\hat{G}(z) = \hat{G}_0(z) + \hat{G}_0(z)\hat{V}\hat{G}(z)$$

$$\hat{G}(z) = \sum_n \frac{|n\rangle\langle n|}{z - E_n}$$

$$\hat{G}_0(z) = \frac{|S\rangle\langle S|}{z - E_S} + \frac{|T\rangle\langle T|}{z - E_T} + \sum_k \frac{|k\rangle\langle k|}{z - E_k} + \sum_i \frac{|i\rangle\langle i|}{z - E_i}$$

$$G_{SS}(z) = \frac{\left(z - E_T - \sum_i \frac{\langle T|\hat{V}|k\rangle\langle k|\hat{V}|T\rangle}{z - E_k}\right)}{\left(z - E_S - \sum_i \frac{\langle S|\hat{V}|i\rangle\langle i|\hat{V}|S\rangle}{z - E_i}\right)\left(z - E_T - \sum_i \frac{\langle T|\hat{V}|k\rangle\langle k|\hat{V}|T\rangle}{z - E_k}\right) - \langle S|\hat{V}|T\rangle\langle T|\hat{V}|S\rangle}$$

$$G_{ST}(z) = \frac{\langle S|\hat{V}|T\rangle}{\left(z - E_S - \sum_i \frac{\langle S|\hat{V}|i\rangle\langle i|\hat{V}|S\rangle}{z - E_i}\right)\left(z - E_T - \sum_i \frac{\langle T|\hat{V}|k\rangle\langle k|\hat{V}|T\rangle}{z - E_k}\right) - \langle S|\hat{V}|T\rangle\langle T|\hat{V}|S\rangle}$$

The exactly solvable model

$$\sum_i \frac{\langle S|\hat{V}|i\rangle\langle i|\hat{V}|S\rangle}{z-E_i} \to \int \rho_S(E)\frac{|V_S(E)|^2}{z-E}dE \equiv \chi_S(z)$$

$$\sum_i \frac{\langle T|\hat{V}|k\rangle\langle k|\hat{V}|T\rangle}{z-E_k} \to \int \rho_T(E)\frac{|V_T(E)|^2}{z-E}dE \equiv \chi_T(z)$$

$$G_{SS}(z) = \frac{\left(z-E_T-\chi_T(z)\right)}{\left(z-E_S-\chi_S(z)\right)\left(z-E_T-\chi_T(z)\right)-|V_{ST}|^2}$$

$$G_{ST}(z) = \frac{V_{ST}}{\left(z-E_S-\chi_S(z)\right)\left(z-E_T-\chi_T(z)\right)-|V_{ST}|^2}$$

$$G_{TT}(z) = \frac{\left(z-E_S-\chi_S(z)\right)}{\left(z-E_S-\chi_S(z)\right)\left(z-E_T-\chi_T(z)\right)-|V_{ST}|^2}$$

$$G_{TS}(z) = \frac{V_{TS}}{\left(z-E_S-\chi_S(z)\right)\left(z-E_T-\chi_T(z)\right)-|V_{ST}|^2}$$

RESULTS

$$\chi_S(z) = -i\pi\rho_S \left|V_S\right|^2 \equiv -iK_S / 2,$$

$$\chi_T(z) = -i\pi\rho_T \left|V_T\right|^2 \equiv -iK_T / 2$$

RESULTS

$$\rho_S(E) = \frac{\rho_0 \beta^2}{(E - E_0)^2 + \beta^2}.$$

$$\chi_S(z) = \frac{\beta K_S / 2}{z - E_0 + i\beta}$$

$$\rho_S(E) = \frac{\rho_{0S} \beta_{1S}^2}{(E - E_{1S})^2 + \beta_{1S}^2}, \qquad \rho_T(E) = \frac{\rho_{0T} \beta_{1T}^2}{(E - E_{1T})^2 + \beta_{1T}^2}.$$

$$\chi_S(z) = -i\pi\rho_{0S} \left|V_{0S}\right|^2 \beta_{1S}\beta_{2S} \left(\frac{a_{1S}}{z - E_{1S} + i\beta_{1S}} + \frac{a_{2S}}{z - E_{2S} + i\beta_{2S}} \right),$$

$$a_{1S} = \frac{1}{E_{1S} - E_{2S} - i(\beta_{1S} + \beta_{2S})} - \frac{1}{E_{1S} - E_{2S} - i(\beta_{1S} - \beta_{2S})},$$

$$a_{2S} = -\frac{1}{E_{1S} - E_{2S} + i(\beta_{1S} + \beta_{2S})} + \frac{1}{E_{1S} - E_{2S} - i(\beta_{1S} - \beta_{2S})}.$$

Results

$$\partial\rho / \partial t = -\hat{\hat{K}}_0 \rho.$$

$$\hat{\hat{K}}_0 = \begin{pmatrix} 0 & -\omega_S & -\omega_S & 0 \\ \omega_S & -i(E_{2S} - E_S) + \beta_{2S} & 0 & -\omega_S \\ \omega_S & 0 & i(E_{2S} - E_S) + \beta_{2S} & -\omega_S \\ 0 & \omega_S & \omega & 2\beta_{2S} \end{pmatrix}.$$

$$\omega_S^2 = \beta_{2S} K_S / 2$$

Result

- In the spin chemistry, eq. (1) and (2) are widely used to describe various effects. Although this equations are phenomenological, it well describes the effects observed. In (30) the exactly solvable model is used to verify eq. (1) or (2). However, in the spin chemistry, the cases are possible where the processes are reversible (e.g., electron transfer). Thus, eq. (1) or (2) 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 (34). 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) and (2) are a particular case. These operators coincide only in the limiting case of the fully irreversible process of recombination.