The influence of spin relaxation and locally strong spin exchange on magneto-spin effects in radical pairs in high magnetic fields

Alexander B. Doktorov

V. V. Voevodsky Institute of Chemical Kinetics and Combustion, SB RAS, Institutskaya 3, 630090, Novosibirsk, Russia

E-mail: doktorov@kinetics.nsc.ru

Content

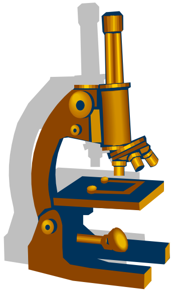
1. Introduction
2. Interactions in radical pairs (RPs)
3. Stochastic Liouville equation (LSE)
4. Magneto-spin effects
5. Effective radii and efficiencies
6. Locally weak and strong exchange
7. General results
8. Examples in the absent of spin relaxation

Introduction

- Magneto-spin effects in high magnetic fields have a significant effect on the formation of spin chemistry phenomena. They are recombination yield and chemically induced dynamic electron polarization (CIDEP) of geminate radical pairs (RPs). Polarization of electrons is manifested in abnormal intensities (as compared to equilibrium ones) of ESR spectral lines which can be either emission or enhanced absorption. There are various mechanisms of the formation of this phenomenon. We consider the radical pair mechanism.

Introduction

Theoretical consideration of recombination and stationary electron polarization has a long history and was based both on numerical methods and on analytical calculations. However, consistent analytical consideration of magneto-spin effects was conducted under condition of locally weak exchange interaction and neglecting the longitudinal relaxation. Based on the generalization of gyroscopic model we consider the most general case for spherically symmetric system and contact recombination. It has been shown that longitudinal spin relaxation essentially influences effective radius of dephasing induced by non-local exchange interaction of radicals.



Interaction of radical spins with high external magnetic field and nuclear spins

Spin operators $\hat{S}_{zA}$ and $\hat{S}_{zB}$. Hamiltonian

$$\hat{H}_0 = \omega_0 \left(\hat{S}_{zA} + \hat{S}_{zB} \right) + \delta \left(\hat{S}_{zA} - \hat{S}_{zB} \right),$$

$$\omega_0 = \frac{1}{2}\left(\omega_A + \omega_B\right), \quad \delta = \frac{1}{2}\left(\omega_A - \omega_B\right)$$

$$\omega_A = g_A \beta B + \sum_i a_i^A m_i^A, \quad \omega_B = g_B \beta B + \sum_k a_k^B m_k^B$$

Spin relaxation

- Relaxation Liouvillian $\hat{\hat{R}}$ has elements

Transverse (phase) relaxation

$$K_{2A} = \frac{1}{T_{2A}}, \quad K_{2B} = \frac{1}{T_{2B}}, \quad K_2 = K_{2A} + K_{2B}$$

Longitudinal relaxation

$$K_{1A} = \frac{1}{T_{1A}}, \quad K_{1B} = \frac{1}{T_{1B}}, \quad K_1 = K_{1A} + K_{1B}$$

Singlet and triplet recombination

- Recombination Liouvillian

$$\hat{\hat{K}}(r) = \frac{1}{2}\left\{\hat{K}(r), \ldots\right\} + \hat{\hat{K}}'_d(r)$$

Here braces denote anti-commutator.

$$\hat{K}(r) = K_S(r)\hat{P} + K_T(r)\hat{Q} =$$

$$= \left(K_S\hat{P} + K_T\hat{Q}\right)\frac{\delta(r-d)}{4\pi r d}$$

$$d - \text{closest approach distance}$$

$$\hat{P} \text{ and } \hat{Q} - \text{projection operators}$$

Dephasing interactions

$$K_d \geq \frac{1}{2}\left(K_S + K_T\right),$$

$$K_i = 4\pi d^2 \Delta \cdot K_i(d) \equiv \upsilon K_i(d) \quad (i = S, T, d),$$

Δ – decay scale, $\quad \upsilon$ – reaction volume

$$\hat{J}(r) = -J(r)\left(\frac{1}{2} + 2\hat{\mathbf{S}}_A \hat{\mathbf{S}}_B\right), \; J(r) = J(d)\exp\left(-\frac{(r-d)}{\Delta_{ex}}\right)$$

$\hat{\mathbf{S}}_M = \left\{\hat{S}_{xM}, \hat{S}_{yM}, \hat{S}_{zM}\right\}$ $(M = A, B)$ – spin operators

Basic equation

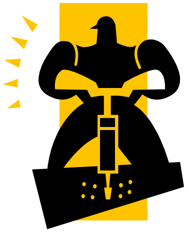
- Stochastic Liouville Equation for density matrix

$$\frac{\partial}{\partial t}\rho(q;t) = -i\left[\hat{H}_0 + \hat{J}(q), \rho(q;t)\right] +$$

$$+\left(\hat{\hat{R}} + \hat{\hat{K}}(q)\right)\rho(q;t) + \hat{\mathcal{L}}_q \rho(q;t)$$

$$\hat{\mathcal{L}}_r = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 D(r) \exp(-u(r)) \frac{\partial}{\partial r} \exp(u(r))$$

$$u(r) = \frac{U(r)}{\mathrm{kT}} - \text{force interaction}$$



Magneto-spin effects

- Singlet recombination yield

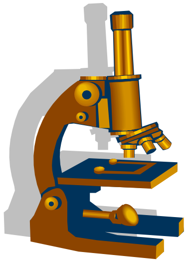
$$\mathrm{R}_S = 4\pi \int_0^{\infty} dt \int K_S(r)\, \rho_{SS}(r,t)\, r^2 dr$$

- Electron spin stationary polarization

$$P_A = -8\pi \lim_{t\to\infty} Tr\, \hat{S}_{zA} \int \rho(r,t)\, r^2\, dr$$

- Initial space distribution in RP

$$f_S(r) = f_T(r) = \frac{\delta(r-d)}{4\pi r d}$$



Free Green function (Resolvent)

Equation and connected "relaxation" parameters

$$\left(s-\hat{\mathcal{L}}_r\right)G_0\left(r,\,x;s\right)=\frac{\delta\left(r-x\right)}{4\pi r x}$$

$$c_0=4\pi D\,d\cdot G_0\left(d,d;0\right),\; c_T=4\pi D\,d\cdot G_0\left(d,d;K_1\right),$$

$$c_A=4\pi D\,d\cdot G_0\left(d,d;K_{1A}\right),\; c_B=4\pi D\,d\cdot G_0\left(d,d;K_{1B}\right),$$

$$c_{AB}=4\pi D\,d\cdot G_0\left(d,d;\frac{1}{2}\left(K_{1A}+K_{1B}\right)\right),\;\left(D=D\left(d\right)\right)$$

Other connected parameters

- “Frequency” *parameters*

$$a_0 = 4\pi Dd \cdot \operatorname{Re} G_0\left(d, d; K_2 - 2i\delta\right)$$

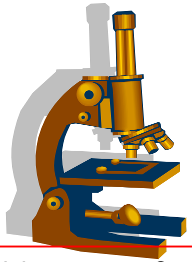
$$b_0 = 4\pi Dd \cdot \operatorname{Im} G_0\left(d, d; K_2 - 2i\delta\right)$$

- Reduced (dimensionless) reaction constants

$$k_i = \frac{K_i}{4\pi Dd} = K_i\left(d\right)\frac{d \cdot \Delta}{D} \equiv K_i\left(d\right)\tau_e \quad \left(i = S, T, d\right)$$

- Reaction efficiencies of recombination

$$p_S = \frac{R_S}{d} = \frac{k_S c_0}{1 + k_S c_0}, \qquad p_T = \frac{R_T}{d} = \frac{k_T c_0}{1 + k_T c_0}$$



Combined parameters

"Triplet recombination" parameters

$$\bar{g}_T = \frac{1}{2}\frac{c_A + c_B + 2k_T c_A c_B}{1 + \frac{1}{2}k_T\left(c_A + c_B\right)} \qquad \begin{pmatrix} \bar{g}_T = c_A = c_B \\ \text{if } K_{1A} = K_{1B} \end{pmatrix}$$

$$\bar{g}_0 = \frac{1}{2}\frac{c_A - c_B}{1 + \frac{1}{2}k_T\left(c_A + c_B\right)} \qquad \begin{pmatrix} \bar{g}_0 = 0 \\ \text{if } K_{1A} = K_{1B} \end{pmatrix}$$

"Logitudinal relaxation" parameter

$$\eta = \frac{1}{2}\frac{c_0 - c_T}{c_0\left(1 + k_T c_T\right)} \equiv \frac{1}{2}\frac{\left(c_0 - c_T\right)\left(1 - p_T\right)}{c_0 - \left(c_0 - c_T\right)p_T}$$

Effective values

Effective population difference

$$n_0^{eff} = \sigma_0 \left\{ 1 - \frac{1}{2} p_S (1+\eta) - \frac{1}{2} p_T (1-\eta) \right\}^{-1}$$

$$\sigma_0 = (1 - p_S)\sigma_S - (1 - p_T)\sigma_{T_0} +$$

$$+ (p_S - p_T)\eta \left(\sigma_{T_0} - \frac{1}{2}(\sigma_{T_+} + \sigma_{T_-}) \right)$$

Effective recombination constant

$$k_e = \frac{k_S + k_T + 2k_S k_T c_0 - k_T (k_S - k_T) c_0 \eta}{2 + (k_S + k_T) c_0 - (k_S - k_T) c_0 \eta}$$

Exchange (dephasing) resolvent

$$\left(s + K_d \frac{\delta(r-d)}{4\pi r d} - 2i\,J(r) - \hat{\mathcal{L}}_r \right) \bar{G}(r, x; s) = \frac{\delta(r-x)}{4\pi r x}$$

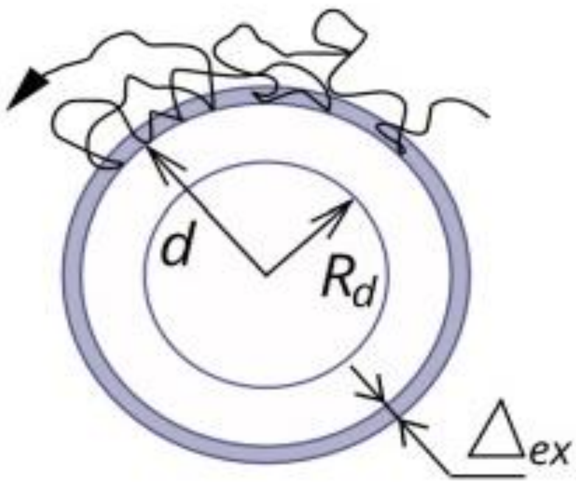
$$t\left(r, x; \frac{1}{2} K_1 \right) = V(r) \frac{\delta(r-x)}{4\pi r x} + V(r) \bar{G}\left(r, x; \frac{1}{2} K_1 \right) V(x)$$

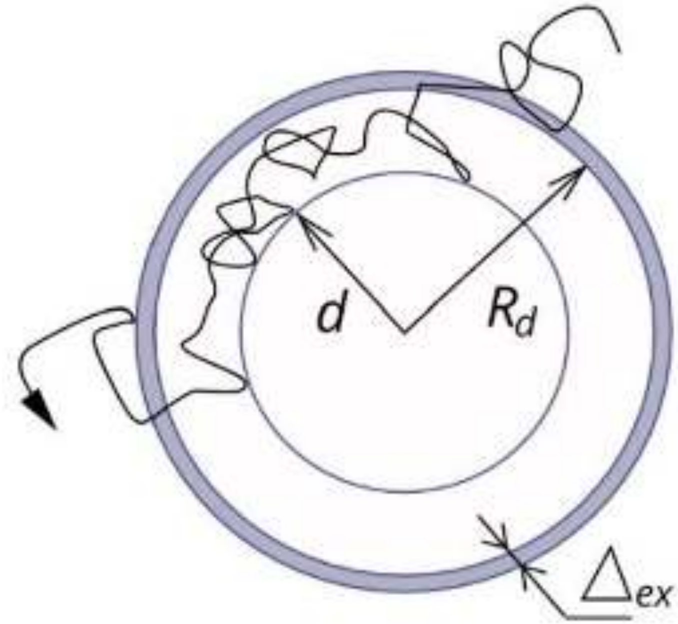
$$V(r) = -K_d \frac{\delta(r-d)}{4\pi r d} + 2i\,J(r), \qquad p_d = \frac{R_d}{D} =$$

$$= -\frac{16\pi^2 c_{AB}}{4\pi D d} e^{u(d)} \int_d^\infty r^2 \int_d^\infty x^2\, t\left(r, x; \frac{1}{2} K_1 \right) e^{(-u(d))}\, dr\, dx$$

Weak and strong exchange

- **Week exchange** | **Strong exchange**





$$R_d \le d, \quad j_c << 1$$

$$R_d > d, \quad j_c \ge 1$$

$$j_c = 2J(d)\frac{\Delta_{ex}^2}{D} = 2J(d)\tau_c$$

Stationary Electron Polarization

General condition

$$\boxed{\sqrt{\left|K_2 - 2i\delta\right|\tau_c} << 1}$$

T_{1A} relaxation of A spin must be ignored

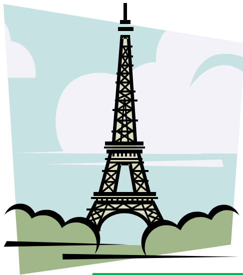
$$K_{1A} = 0, \qquad\qquad c_A = c_0, \quad c_T = c_B$$

$$P_A = \frac{1}{c_0}\frac{\left(\bar{g}_T + \bar{g}_0\right)b_0 \operatorname{Im}\Delta_d n_0^{eff}}{1 + a_0 \operatorname{Re}\Delta_d + k_e\left(a_0 + \left(a_0^2 + b_0^2\right)\operatorname{Re}\Delta_d\right)}$$

Singlet Recombination Yield

$$\mathrm{R}_S = \frac{p_S}{2-p_S\left(1+\eta\right)-p_T\left(1-\eta\right)} \times \left\{\left(1-p_T\right)\left[\left(\sigma_S+\sigma_{T_0}\right)\left(1-\eta\right)+\left(\sigma_{T_+}+\sigma_{T_-}\right)\eta\right]+\frac{S}{c_0}\right\}$$

$$S = \frac{\left\{a_0+\left(a_0^2+b_0^{\ 2}\right)\mathrm{Re}\,\Delta_d\right\} n_0^{eff} - \bar{g}_0 b_0\,\mathrm{Im}\,\Delta_d\left(\sigma_{T_+}-\sigma_{T_-}\right)}{1+a_0\,\mathrm{Re}\,\Delta_d + k_e\left(a_0+\left(a_0^2+b_0^{\ 2}\right)\mathrm{Re}\,\Delta_d\right)}$$



Dephasing characteristic

$$\Delta_d = \frac{1}{c_{AB}} \frac{p_d + g\left|p_d\right|^2}{1 - \operatorname{Re} p_d + g\left(\operatorname{Re} p_d - \left|p_d\right|^2\right)},$$

$$g = \frac{\overline{g}_T}{c_{AB}} - 1$$

$$K_{1A} = K_{1B},\ \ \overline{g}_T = c_{AB} = c_A = c_B,\ g = 0$$

$$\Delta_d = \frac{1}{c_{AB}} \frac{p_d}{1 - \operatorname{Re} p_d}$$

Dephasing at weak exchange

Contact exchange

$$j_e = 2J(d)\frac{\Delta_{ex} d}{D} = 2J(d)\tau_e$$

$$\bar{G}\left(d, d; \frac{1}{2}K_1\right) = \frac{c_{AB}}{4\pi Dd\left(1+\left(k_d - i\cdot j_e\right)c_{AB}\right)}$$

$$p_d = \frac{R_d}{d} = \frac{\left(k_d - i\, j_e\right)c_{AB}}{1+\left(k_d - i\, j_e\right)c_{AB}} \qquad \left(\mathrm{Re}\, p_d < 1\right)$$

$$\Delta_d = k_d + j_e^2 \frac{\bar{g}_T}{1+k_d\bar{g}_T} - i\cdot j_e \frac{1}{1+k_d\bar{g}_T}$$

Neglect of spin relaxation

$$P_A = \frac{b_0 \,\mathrm{Im}\, p_d \left(1 + c_0 k_e\right)\sigma_0}{c_0\left(1 + k_e a_0\right)\left(1 - \mathrm{Re}\, p_d\right) + \left(a_0 + k_e\left(a_0^2 + b_0^2\right)\right)P}$$

$$P = \left(\mathrm{Re}\, p_d + \frac{2c_0 q\left(a_0^2 + b_0^2\right)}{b_0}\left(p_e - 1\right)\right),$$

$$p_e = \begin{cases} 1 & \text{at } j_c \le 1 \\ \mathrm{Re}\, p_d & \text{at } j_c >> 1 \end{cases},$$

$$\frac{1}{1 + c_0 k_e} = 1 - \bar{p}, \quad \bar{p} = \frac{p_S + p_T}{2}$$

Neglect of spin relaxation

$$\mathrm{R}_S = \frac{p_S}{2(1-\bar{p})}\left\{(1-p_T)\left[\left(\sigma_S+\sigma_{T_0}\right)\right]+S\sigma_0\right\}$$

$$S = \frac{\left\{a_0\left(1-\operatorname{Re} p_d\right)+\dfrac{\left(a_0^2+b_0^2\right)}{c_0}\operatorname{Re} p_d\right\}\left(1+c_0k_e\right)}{\left\{c_0\left(1+k_e a_0\right)\left(1-\operatorname{Re} p_d\right)+\left(a_0+k_e\left(a_0^2+b_0^2\right)\right)\operatorname{Re} p_d\right\}}$$

$$\sigma_0 = -\frac{1-p_T}{3}, \qquad \mathrm{R}_S = \frac{1}{6}\frac{p_S\left(1-p_T\right)}{1-\bar{p}}\left(1-S\right)$$

Parameters for freely diffusive RP

$$4\pi D d G_0\left(d,d;-2i\delta\right)=\frac{1}{1+\left(1-i\right)\sqrt{q}},\quad q=\delta\frac{d^2}{D}$$

$$a_0=\frac{1+\sqrt{q}}{1+2\sqrt{q}+2q},\qquad b_0=\frac{\sqrt{q}}{1+2\sqrt{q}+2q},\quad c_0=1$$

$$p_d=\begin{cases}\dfrac{k_d-i\,j_e}{1+k_d-i\,j_e}=\dfrac{k_d\left(1+k_d\right)+j_e^2-i\,j_e}{\left(1+k_d\right)^2+j_e^2} & j_c\le 1\\[2ex] 1+2\dfrac{\Delta_{ex}}{d}\ln\left(\gamma\sqrt{j_c}\right)-i\dfrac{\Delta_{ex}}{d}\dfrac{\pi}{2} & j_c>1\end{cases}$$

Magneto-spin effects

$$P_A = \frac{\sqrt{q}\,\mathrm{Im}\,p_d}{1+\Delta_1+\Delta_2+2\Delta_1\Delta_2}\,\sigma_0$$

$$\Delta_1 = \sqrt{q}\left(p_e - \bar{p}\right),\quad \Delta_2 = \sqrt{q}\left(p_e - \mathrm{Re}\,p_d\right)$$

$$\mathrm{R}_S = \frac{1}{6}\sqrt{q}\,p_S\left(1-p_T\right)\frac{1+2\bar{\Delta}_2}{1+\bar{\Delta}_1+\bar{\Delta}_2+2\bar{\Delta}_1\bar{\Delta}_2}$$

$$\bar{\Delta}_1 = \sqrt{q}\left(1-\bar{p}\right),\qquad \bar{\Delta}_2 = \sqrt{q}\left(1-\mathrm{Re}\,p_d\right)$$

Parameters in micelle

$$g_0\left(d,d;-2i\delta\right)=\frac{1}{1+\left(1-i\right)\sqrt{q}\left(1+\dfrac{2\gamma\left(q\right)}{1-\gamma\left(q\right)}\right)},\quad \alpha=\frac{D_m}{D},\ l=\frac{L}{d}$$

$$\gamma=\frac{c_0-1+\left(1-i\right)\sqrt{q}\left(l\left(c_0-1\right)+1-\sqrt{\alpha}\right)}{c_0-1-\left(1-i\right)\sqrt{q}\left(l\left(c_0-1\right)+1+\sqrt{\alpha}\right)}\exp\left(-2\left(1-i\right)\left(l-1\right)\sqrt{q}\right)$$

$$A\left(q\right)=\mathrm{Re}\left(1-i\right)\frac{2\gamma\left(q\right)}{1-\gamma\left(q\right)},\qquad B\left(q\right)=-\mathrm{Im}\left(1-i\right)\frac{2\gamma\left(q\right)}{1-\gamma\left(q\right)}$$

$$a_0=\frac{1+\sqrt{q}\left(1+A\left(q\right)\right)}{Q},\ b_0=\frac{\sqrt{q}\left(1+B\left(q\right)\right)}{Q},\ c_0=\left(1+\frac{1}{l}\left(\alpha\exp u_0-1\right)\right)$$

$$Q=1+2\sqrt{q}\left(1+A\left(q\right)\right)+q\left(\left(1+A\left(q\right)\right)^2+\left(1+B\left(q\right)\right)^2\right)$$

Recombination yield in micelle

$$\sigma_0 = -\frac{1-p_T}{3}, \qquad \mathrm{R}_S = \frac{1}{6}\frac{p_S\left(1-p_T\right)}{1-\bar{p}}\left(1-S\right)$$

$$S = \frac{\Delta_{20} + \Delta_2\left(q\right)}{\Delta_{10}\Delta_{20} + \Delta_{20}\Delta_1\left(q\right) + \Delta_{10}\Delta_2\left(q\right) + \left(1 + \left(\frac{1+B\left(q\right)}{1+A\left(q\right)}\right)^2\right)\Delta_1\left(q\right)\Delta_2\left(q\right)}$$

$$\Delta_{10} = c_0 - \left(c_0 - 1\right)\mathrm{Re}\,\bar{p}, \quad \Delta_1\left(q\right) = \sqrt{q}\left(1 + A\left(q\right)\right)c_0\left(1 - \mathrm{Re}\,\bar{p}\right)$$

$$\Delta_{20} = c_0 - \left(c_0 - 1\right)\mathrm{Re}\,p_d, \quad \Delta_2\left(q\right) = \sqrt{q}\left(1 + A\left(q\right)\right)c_0\left(1 - \mathrm{Re}\,p_d\right)$$

Polarization in micelle

$$p_d=\begin{cases}\dfrac{\left(k_d-i\,j_e\right)c_0}{1+\left(k_d-i\,j_e\right)c_0}=\dfrac{k_d\,c_0\left(1+k_d\,c_0\right)+j_e^2\,c_0^2-i\,j_e\,c_0}{\left(1+k_d\,c_0\right)^2+j_e^2\,c_0^2} & \text{at } j_c\le 1\\[2ex] 1+2\dfrac{\Delta_{ex}}{c_0\,d}\ln\left(\gamma\sqrt{j_c}\right)-i\,\dfrac{\Delta_{ex}}{c_0\,d}\,\dfrac{\pi}{2},\quad \gamma=\exp\mathbf{C} & \text{at } j_c>1\end{cases}$$

$$P_A=\frac{\sqrt{q}\left(1+B(q)\right)c_0\,\mathrm{Im}\,p_d}{\Delta_{10}\Delta_{20}+\Delta_{20}\Delta_1(q)+\Delta_{10}\Delta_2(q)+\left(1+\left(\dfrac{1+B(q)}{1+A(q)}\right)^2\right)\Delta_1(q)\Delta_2(q)+P}$$

$$P=2\left(\Delta_{10}(q)+\Delta_1(q)\right)\Delta_3(q),\quad \Delta_3=\frac{c_0\sqrt{q}}{1+B(q)}\left(p_e-1\right))$$

Thank you

Gyroscopic model

$$S_x = \rho_{ST_0}(r,t) + \rho_{T_0 S}(r,t),\; S_y = i\left(\rho_{ST_0}(r,t) - \rho_{T_0 S}(r,t)\right)$$

$$S_z = \rho_{SS}(r,t) - \rho_{T_0 T_0}(r,t),\;\; T_z = \rho_{T_+ T_+}(r,t) - \rho_{T_- T_-}(r,t)$$

$$S_+ = \rho_{SS}(r,t) + \rho_{T_0 T_0}(r,t),\quad T_+ = \rho_{T_+ T_+}(r,t) + \rho_{T_- T_-}(r,t)$$

$$\mathbf{S} = \left\{S_x^L(r),\, S_y^L(r),\, S_z^L(r),\, T_z^L(r)\right\}^\dagger$$

$$\left(\mathbf{\Omega} + \mathbf{R} + \mathbf{J}(r) + \mathbf{K}\frac{\delta(r-d)}{4\pi r d} + \hat{\mathcal{L}}_r\right)\mathbf{S}(r) = -\mathbf{S}_0\frac{\delta(r-d)}{4\pi r d}$$

$$S_{0x} = S_{0y} = 0,\quad S_{0z} = n_0^{eff},\quad T_{0z} = \sigma_{T_+} - \sigma_{T_-},$$

Liouvillians

$$\mathbf{\Omega}+\mathbf{R}+\mathbf{J}(r)=\begin{pmatrix} -\frac{1}{2}K_1 & -2J(r) & 0 & -\frac{1}{2}\Delta K_1 \\ 2J(r) & -K_2 & -2\delta & 0 \\ 0 & 2\delta & -K_2 & 0 \\ -\frac{1}{2}\Delta K_1 & 0 & 0 & -\frac{1}{2}K_1 \end{pmatrix}$$

$$\mathbf{K}=\begin{pmatrix} -K_d & 0 & 0 & 0 \\ 0 & -K_d & 0 & 0 \\ 0 & 0 & -K_e & 0 \\ 0 & 0 & 0 & -K_T \end{pmatrix}$$

$$\Delta K_1 = K_{1A} - K_{1B}$$