EPR permeability model

The time evolution of nuclear (electron) magnetization is phenomenologically described by the Bloch equations

$$\frac{\mathrm{d}\mathbf{M}}{\mathrm{d}t} = \mathbf{M} \times \gamma\mathbf{B} - \mathbf{R}\left(\mathbf{M}(t) - \mathbf{M}_0\right),$$

where γ is the gyromagnetic ratio, $\mathbf{M}$ denotes the magnetization vector, and $\mathbf{B}$ is the magnetic field. The relaxation term $\mathbf{R}\left(\mathbf{M}(t) - \mathbf{M}_0\right)$ ensures that after switching off the perturbing time-dependent field $\mathbf{B}_1$, the magnetization tends to some equilibrium value $\mathbf{M}_0$ given by the static external magnetic field $\mathbf{B}_0$. For simplicity, our static magnetic field is oriented along the z-axis, while the vector of perturbing field lies in the xy-plane, i.e. the static and the perturbing field are perpendicular to each other. Moreover, we will assume that the perturbing field oscillates with frequency ω and is circularly polarized with handedness determined by the sign in the expression for B_y

$$\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1(t),$$

$$\begin{aligned} B_x &= B_1 \cos\omega t, \\ B_y &= \pm B_1 \sin\omega t, \\ B_z &= B_0. \end{aligned}$$

With such definition of magnetic fields, the Bloch equations read

$$\begin{aligned} \frac{\mathrm{d}M_x}{\mathrm{d}t} &= \gamma\left(M_y B_z - M_z B_y\right) - \frac{M_x}{T_2}, \\ \frac{\mathrm{d}M_y}{\mathrm{d}t} &= \gamma\left(M_z B_x - M_x B_z\right) - \frac{M_y}{T_2}, \\ \frac{\mathrm{d}M_z}{\mathrm{d}t} &= \gamma\left(M_x B_y - M_y B_x\right) - \frac{M_z(t) - M_0}{T_1}, \end{aligned}$$

where we introduced two relaxation times T_1 and T_2, which reflects the fact that the transverse components of the magnetization vector (with respect to the static field) usually relax to the equilibrium at a different rate.

In the stationary state, the longitudinal magnetization will be constant so that only the tranverse components will vary with time

$$\begin{aligned} M_x &= \alpha_1^x \cos\omega t + \alpha_2^x \sin\omega t, \\ M_y &= \alpha_1^y \cos\omega t + \alpha_2^y \sin\omega t, \\ M_z &= \mathrm{const.} \end{aligned}$$

where the coefficients $\alpha_i^{x,y}$ are yet to be determined. After inserting all these expressions into Bloch equations, capitalizing on the time invariance of M_z and comparing separately terms containing $\cos\omega t$ and $\sin\omega t$, we arrive at

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = 0 \qquad \Rightarrow \qquad \alpha_1^y = \mp\alpha_2^x, \qquad \alpha_2^y = \pm\alpha_1^x,$$

$$
\begin{aligned}
{}^{\pm}\alpha_1^x &= \pm M_0 \frac{\gamma B_1 \Omega_{\pm} T_2^2}{1+\Omega_{\pm}^2+\gamma^2 B_1^2 T_1 T2}, \\
{}^{\pm}\alpha_2^x &= \mp M_0 \frac{\gamma B_1 T_2}{1+\Omega_{\pm}^2+\gamma^2 B_1^2 T_1 T2}, \\
{}^{\pm}\alpha_1^y &= M_0 \frac{\gamma B_1 T_2}{1+\Omega_{\pm}^2+\gamma^2 B_1^2 T_1 T2}, \\
{}^{\pm}\alpha_2^x &= M_0 \frac{\gamma B_1 \Omega_{\pm} T_2^2}{1+\Omega_{\pm}^2+\gamma^2 B_1^2 T_1 T2}, \\
M_z &= M_0 \frac{1+\Omega_{\pm}^2}{1+\Omega_{\pm}^2+\gamma^2 B_1^2 T_1 T2}, \\
\Omega_{\pm} &= \omega \pm \omega_0 = \omega \pm \gamma B_0.
\end{aligned}
$$

As we are looking for some complex anisotropic tensor $\overleftrightarrow{\xi}$, which would allow us to link the magnetization and the perturbing magnetic field by a simple linear constitutive relation $\mathbf{M} = \overleftrightarrow{\xi}\mathbf{B}$, it will be more convenient to switch to complex notation and work with expressions that describe the system's response to linearly polarized perturbing fields instead of the circularly polarized ones. We shall start with a perturbing magnetic field polarized along the x-axis. The corresponding components of the response tensor $\overleftrightarrow{\xi}$ can constructed from the coefficients $\alpha_i^{x,y}$ by taking their appropriate linear combination and then comparing the terms in front of $\cos\omega t$ and $\sin\omega t$.

$$
\frac{\circlearrowleft + \circlearrowright}{2} = x\text{−polarized} \qquad \Rightarrow \qquad \mathbf{B}_1 = B_1 \mathrm{Re}\left\{e^{-\mathrm{i}\omega t}\right\}\hat{\mathbf{x}},
$$

$$
\begin{aligned}
M_x &= \mathrm{Re}\left\{\xi_{xx} B_1 e^{-\mathrm{i}\omega t}\right\} = B_1\left(\mathrm{Re}\left\{\xi_{xx}\right\}\cos\omega t + \mathrm{Im}\left\{\xi_{xx}\right\}\sin\omega t\right), \\
M_y &= \mathrm{Re}\left\{\xi_{xy} B_1 e^{-\mathrm{i}\omega t}\right\} = B_1\left(\mathrm{Re}\left\{\xi_{xy}\right\}\cos\omega t + \mathrm{Im}\left\{\xi_{xy}\right\}\sin\omega t\right),
\end{aligned}
$$

$$
M_{x(y)} = \frac{{}^{+}\alpha_1^{x(y)} + {}^{-}\alpha_2^{x(y)}}{2}\cos\omega t + \frac{{}^{+}\alpha_2^{x(y)} + {}^{-}\alpha_2^{x(y)}}{2}\sin\omega t,
$$

$$
\Downarrow
$$

$$
\xi_{xx} = \frac{M_0\gamma\omega_0}{\omega_0^2 - \omega'^2}, \qquad \xi_{xy} = -\mathrm{i}\frac{M_0\gamma\omega'}{\omega_0^2-\omega'^2}, \qquad \omega' = \omega + \frac{\mathrm{i}}{T_2}.
$$

Please note that in the above expression, we have entirely omitted the term $\gamma^2 B_1^2 T_1 T2$, which is justifiable for sufficiently low microwave source powers. In a similar manner, we obtain the expressions for the magnetic field linearly polarized along the y-axis.

$$
\frac{\circlearrowleft - \circlearrowright}{2} = y\text{−polarized} \qquad \Rightarrow \qquad \mathbf{B}_1 = B_1 \mathrm{Re}\left\{\mathrm{i}e^{-\mathrm{i}\omega t}\right\}\hat{\mathbf{y}},
$$

$$
\begin{aligned}
M_x &= \mathrm{Re}\left\{\mathrm{i}\xi_{yx} B_1 e^{-\mathrm{i}\omega t}\right\} = B_1\left(-\mathrm{Im}\left\{\xi_{yx}\right\}\cos\omega t + \mathrm{Re}\left\{\xi_{xx}\right\}\sin\omega t\right), \\
M_y &= \mathrm{Re}\left\{\mathrm{i}\xi_{yy} B_1 e^{-\mathrm{i}\omega t}\right\} = B_1\left(-\mathrm{Im}\left\{\xi_{yy}\right\}\cos\omega t + \mathrm{Re}\left\{\xi_{xy}\right\}\sin\omega t\right),
\end{aligned}
$$

$$M_{x(y)} = \frac{{}^{+}\alpha_1^{x(y)} - {}^{-}\alpha_2^{x(y)}}{2}\cos\omega t - \frac{{}^{+}\alpha_2^{x(y)} + {}^{-}\alpha_2^{x(y)}}{2}\sin\omega t,$$

$$\Downarrow$$

$$\xi_{yx} = \mathrm{i}\frac{M_0\gamma\omega'}{\omega_0^2 - \omega'^2}, \qquad \xi_{yy} = \frac{M_0\gamma\omega_0}{\omega_0^2 - \omega'^2}, \qquad \omega' = \omega + \frac{\mathrm{i}}{T_2}.$$

The complex tensor can be now written in the following compact form

$$\overleftrightarrow{\xi} = \frac{M_0\gamma}{\omega_0^2 - \omega'^2}\begin{pmatrix} \omega_0 & \mathrm{i}\omega' \\ -\mathrm{i}\omega' & \omega_0 \end{pmatrix}.$$

Although the above expression already links the magnetization vector to the magnetic field, standard material relations are defined for the auxiliary magnetic field $\mathbf{H}$. The permeability tensor $\overleftrightarrow{\mu}$ is related to $\overleftrightarrow{\xi}$ via the following expressions

$$\mathbf{M} = \overleftrightarrow{\xi}\mathbf{B} = \overleftrightarrow{\chi}\mathbf{H} = \left(\overleftrightarrow{\mu} - \overleftrightarrow{\mathbb{I}}\right)\mathbf{H}, \qquad \mathbf{B} = \mu_0\overleftrightarrow{\mu}\,\mathbf{H} \qquad \Rightarrow \qquad \overleftrightarrow{\mu} = \left(\overleftrightarrow{\mathbb{I}} - \mu_0\overleftrightarrow{\xi}\right)^{-1},$$

$$\overleftrightarrow{\mu} = \begin{pmatrix} 1 + \dfrac{\kappa(\omega_0 - \kappa)}{(\omega_0 - \kappa)^2 - \omega'^2} & \mathrm{i}\dfrac{\kappa\omega'}{(\omega_0 - \kappa)^2 - \omega'^2} & 0 \\ -\mathrm{i}\dfrac{\kappa\omega'}{(\omega_0 - \kappa)^2 - \omega'^2} & 1 + \dfrac{\kappa(\omega_0 - \kappa)}{(\omega_0 - \kappa)^2 - \omega'^2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

where $\kappa = M_0\gamma\mu_0$. Importantly, the material properties in the direction of the static magnetic field are unaffected by the electron transtitions.

Also note that when choose to follow the $e^{\mathrm{i}\omega t}$ convention (used e.g. in Comsol), appropriate changes in signs have to be made:

$$\frac{\circlearrowleft + \circlearrowright}{2} = x\text{−polarized} \qquad \Rightarrow \qquad \mathbf{B}_1 = B_1\mathrm{Re}\left\{e^{\mathrm{i}\omega t}\right\}\hat{\mathbf{x}},$$

$$M_x = \mathrm{Re}\left\{\xi_{xx}B_1e^{\mathrm{i}\omega t}\right\} = B_1\left(\mathrm{Re}\left\{\xi_{xx}\right\}\cos\omega t - \mathrm{Im}\left\{\xi_{xx}\right\}\sin\omega t\right),$$
$$M_y = \mathrm{Re}\left\{\xi_{xy}B_1e^{\mathrm{i}\omega t}\right\} = B_1\left(\mathrm{Re}\left\{\xi_{xy}\right\}\cos\omega t - \mathrm{Im}\left\{\xi_{xy}\right\}\sin\omega t\right),$$

$$\frac{\circlearrowleft - \circlearrowright}{2} = y\text{−polarized} \qquad \Rightarrow \qquad \mathbf{B}_1 = B_1\mathrm{Re}\left\{-\mathrm{i}e^{\mathrm{i}\omega t}\right\}\hat{\mathbf{y}},$$

$$M_x = \mathrm{Re}\left\{-\mathrm{i}\xi_{yx}B_1e^{\mathrm{i}\omega t}\right\} = B_1\left(\mathrm{Im}\left\{\xi_{yx}\right\}\cos\omega t + \mathrm{Re}\left\{\xi_{xx}\right\}\sin\omega t\right),$$
$$M_y = \mathrm{Re}\left\{-\mathrm{i}\xi_{yy}B_1e^{\mathrm{i}\omega t}\right\} = B_1\left(\mathrm{Im}\left\{\xi_{yy}\right\}\cos\omega t + \mathrm{Re}\left\{\xi_{xy}\right\}\sin\omega t\right).$$

The complex permeability tensor now reads

$$\overleftrightarrow{\mu} = \begin{pmatrix} 1 + \dfrac{\kappa(\omega_0 - \kappa)}{(\omega_0 - \kappa)^2 - \omega'^2} & -\mathrm{i}\dfrac{\kappa\omega'}{(\omega_0 - \kappa)^2 - \omega'^2} & 0 \\ \mathrm{i}\dfrac{\kappa\omega'}{(\omega_0 - \kappa)^2 - \omega'^2} & 1 + \dfrac{\kappa(\omega_0 - \kappa)}{(\omega_0 - \kappa)^2 - \omega'^2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

where $\omega' = \omega - \dfrac{\mathrm{i}}{T_2}$.