1.3: Third Order Response

Since $R^{(2)}$ orientationally averages to zero for isotropic systems, the third-order nonlinear response described the most widely used class of nonlinear spectroscopies.

$$R^{(3)}\left(\tau_{1}, \tau_{2}, \tau_{3}\right)=\left(\frac{i}{\hbar}\right)^{3} \theta\left(\tau_{3}\right) \theta\left(\tau_{2}\right) \theta\left(\tau_{1}\right) \operatorname{Tr}\left\{\left[\mu_{I}\left(\tau_{1}+\tau_{2}+\tau_{3}\right),\mu_{I}\left(\tau_{1}+\tau_{2}\right)\right], \mu_{I}\left(\tau_{1}\right)\right], \mu_{I}(0)\right] \rho_{eq}\} \tag{1.3.1}$$

$$R^{(3)}\left(\tau_{1}, \tau_{2}, \tau_{3}\right)=\left(\frac{i}{\hbar}\right)^{3} \theta\left(\tau_{3}\right) \theta\left(\tau_{2}\right) \theta\left(\tau_{1}\right) \sum_{\alpha=1}^{4}\left[R_{\alpha}\left(\tau_{1}+\tau_{2}+\tau_{3}\right)-R_{\alpha}^{*}\left(\tau_{1}+\tau_{2}+\tau_{3}\right)\right] \tag{1.3.2}$$

Here the convention for the time-ordered interactions with the density matrix is R_1 = *ket* / *ket* / *ket* ; R_2 = *bra* / *ket* / *bra* ; R_3 = *bra* / *bra* / *ket* ; and $R_4 \Rightarrow$ *ket* / *bra* / *bra* . In the eigenstate representation, the individual correlation functions can be explicitly written in terms of a sum over all possible intermediate states (a,b,c,d)

$$\begin{array}{l}
R_{1}=\sum_{a, b, c, d} p_{a}\left\langle\mu_{ad}\left(\tau_{1}+\tau_{2}+\tau_{3}\right) \mu_{dc}\left(\tau_{1}+\tau_{2}\right) \mu_{cb}\left(\tau_{1}\right) \mu_{ba}(0)\right\rangle \\
R_{2}=\sum_{a, b, c, d} p_{a}\left\langle\mu_{ad}(0) \mu_{dc}\left(\tau_{1}+\tau_{2}\right) \mu_{cb}\left(\tau_{1}+\tau_{2}+\tau_{3}\right) \mu_{ba}\left(\tau_{1}\right)\right\rangle \\
R_{3}=\sum_{a, b, c, d} p_{a}\left\langle\mu_{ad}(0) \mu_{dc}\left(\tau_{1}\right) \mu_{cb}\left(\tau_{1}+\tau_{2}+\tau_{3}\right) \mu_{ba}\left(\tau_{1}+\tau_{2}\right)\right\rangle \\
R_{4}=\sum_{a, b, c, d} p_{a}\left\langle\mu_{ad}\left(\tau_{1}\right) \mu_{dc}\left(\tau_{1}+\tau_{2}\right) \mu_{cb}\left(\tau_{1}+\tau_{2}+\tau_{3}\right) \mu_{ba}(0)\right\rangle
\end{array} \tag{1.3.3}$$