

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.

$$R^{(3)}(\tau_1, \tau_2, \tau_3) = \left(\frac{i}{\hbar}\right)^3 \theta(\tau_3) \theta(\tau_2) \theta(\tau_1) \text{Tr}\{\mu_I(\tau_1 + \tau_2 + \tau_3), \mu_I(\tau_1 + \tau_2), \mu_I(\tau_1), \mu_I(0)] \rho_{eq}\} \quad (1.3.1)$$

$$R^{(3)}(\tau_1, \tau_2, \tau_3) = \left(\frac{i}{\hbar}\right)^3 \theta(\tau_3) \theta(\tau_2) \theta(\tau_1) \sum_{\alpha=1}^4 [R_{\alpha}(\tau_1 + \tau_2 + \tau_3) - R_{\alpha}^*(\tau_1 + \tau_2 + \tau_3)] \quad (1.3.2)$$

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)

$$\begin{aligned} R_1 &= \sum_{a,b,c,d} p_a \langle \mu_{ad}(\tau_1 + \tau_2 + \tau_3) \mu_{dc}(\tau_1 + \tau_2) \mu_{cb}(\tau_1) \mu_{ba}(0) \rangle \\ R_2 &= \sum_{a,b,c,d} p_a \langle \mu_{ad}(0) \mu_{dc}(\tau_1 + \tau_2) \mu_{cb}(\tau_1 + \tau_2 + \tau_3) \mu_{ba}(\tau_1) \rangle \\ R_3 &= \sum_{a,b,c,d} p_a \langle \mu_{ad}(0) \mu_{dc}(\tau_1) \mu_{cb}(\tau_1 + \tau_2 + \tau_3) \mu_{ba}(\tau_1 + \tau_2) \rangle \\ R_4 &= \sum_{a,b,c,d} p_a \langle \mu_{ad}(\tau_1) \mu_{dc}(\tau_1 + \tau_2) \mu_{cb}(\tau_1 + \tau_2 + \tau_3) \mu_{ba}(0) \rangle \end{aligned} \quad (1.3.3)$$

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