4.3: Nonlinear Response with the Energy Gap Hamiltonian

In a manner that parallels our description of the linear response from a system coupled to a bath, the nonlinear response can also be partitioned into a system, bath and energy gap Hamiltonian, leading to similar averages over the fluctuations of the energy gap. In the general case, the four correlations functions contributing to the third order response that emerge from eq. (2.3.3) are

$$\begin{aligned} R_1 &= \sum_{abcd} p_a \left\langle \mu_{ab}\left(\tau_3+\tau_2+\tau_1\right)\mu_{bc}\left(\tau_2+\tau_1\right)\mu_{cd}\left(\tau_1\right)\mu_{da}(0) F_{abcd}^{(1)}\right\rangle \\ R_2 &= \sum_{abcd} p_a \left\langle \mu_{ab}\left(\tau_1\right)\mu_{bc}\left(\tau_2+\tau_1\right)\mu_{cd}\left(\tau_3+\tau_2+\tau_1\right)\mu_{da}(0) F_{abcd}^{(2)}\right\rangle \\ R_3 &= \sum_{abcd} p_a \left\langle \mu_{da}(0)\mu_{ab}\left(\tau_2+\tau_1\right)\mu_{bc}\left(\tau_3+\tau_2+\tau_1\right)\mu_{cd}\left(\tau_1\right) F_{abcd}^{(3)}\right\rangle \\ R_4 &= \sum_{abcd} p_a \left\langle \mu_{da}\left(\tau_1\right)\mu_{ab}\left(t_1\right)\mu_{bc}\left(\tau_3+\tau_2+\tau_1\right)\mu_{cd}\left(\tau_2+\tau_1\right) F_{abcd}^{(4)}\right\rangle \end{aligned} \tag{4.3.1}$$

Here *a*,*b*,*c*, and *d* are indices for system eigenstates, and the dephasing functions are

$$\begin{aligned} F_{abcd}^{(1)} &= \exp\left[-i\int_{\tau_2+\tau_1}^{\tau_3+\tau_2+\tau_1}\omega_{ba}(\tau)d\tau - i\int_{\tau_1}^{\tau_2+\tau_1}\omega_{ca}(\tau)d\tau - i\int_0^{\tau_1}\omega_{da}(\tau)d\tau\right] \\ F_{abcd}^{(2)} &= \exp\left[-i\int_{\tau_2+\tau_1}^{\tau_3+\tau_2+\tau_1}\omega_{dc}(\tau)d\tau - i\int_{\tau_1}^{\tau_2+\tau_1}\omega_{db}(\tau)d\tau - i\int_0^{\tau_1}\omega_{da}(\tau)d\tau\right] \\ F_{abcd}^{(3)} &= \exp\left[-i\int_{\tau_2+\tau_1}^{\tau_3+\tau_2+\tau_1}\omega_{bc}(\tau)d\tau + i\int_{\tau_1}^{\tau_2+\tau_1}\omega_{ca}(\tau)d\tau + i\int_0^{\tau_1}\omega_{da}(\tau)d\tau\right] \\ F_{abcd}^{(4)} &= \exp\left[-i\int_{\tau_2+\tau_1}^{\tau_3+\tau_2+\tau_1}\omega_{bc}(\tau)d\tau + i\int_{\tau_1}^{\tau_2+\tau_1}\omega_{db}(\tau)d\tau + i\int_0^{\tau_1}\omega_{da}(\tau)d\tau\right] \end{aligned} \tag{4.3.2}$$

As before $\omega_{ab} = H_{ab}/\hbar$. These expressions describe the correlated dynamics of the dipole operator acting between multiple resonant transitions, in which the amplitude, frequency, and orientation of the dipole operator may vary with time.

As a further simplification, let's consider the specific form of the nonlinear response for a fluctuating two-level system. If we allow only for two states *e* and *g*, and apply the Condon approximation, eq. (5.3.2) gives

$$R_1(\tau_1,\tau_2,\tau_3) = p_g|\mu_{eg}|^4 e^{i\omega_{eg}(\tau_1+\tau_3)}\left\langle exp\left(-i\int_0^{\tau_1} d\tau\omega_{eg}(\tau) - i\int_{\tau_1+\tau_2}^{\tau_1+\tau_2+\tau_3} d\tau\omega_{eg}(\tau)\right)\right\rangle \tag{4.3.3}$$

$$R_2(\tau_1,\tau_2,\tau_3) = p_g|\mu_{eg}|^4 e^{-i\omega_{eg}(\tau_1-\tau_3)}\left\langle exp\left(i\int_0^{\tau_1} d\tau\omega_{eg}(\tau) - i\int_{\tau_1+\tau_2}^{\tau_1+\tau_2+\tau_3} d\tau\omega_{eg}(\tau)\right)\right\rangle \tag{4.3.4}$$

These are the rephasing (R_2) and non-rephasing (R_1) functions, written for a two-level system. These expressions only account for the correlation of fluctuating frequencies while the system evolves during the coherence periods τ_1 and τ_3. Since they neglect any difference in relaxation on the ground or excited state during the population period τ_2, R_2=R_3 and R_1= R_4. They also ignore reorientational relaxation of the dipole.

In the case that the fluctuations of those two states follow Gaussian statistics, we can also apply the cumulant expansion to the third order response function. In this case, for a two-level system, the four correlation functions are expressed in terms of the lineshape function as:

$$R_1 = e^{-i\omega_{eg}\tau_1 - i\omega_{eg}\tau_3}\left(\frac{i}{\hbar}\right)^3 p_g|\mu_{eg}|^4 \times exp\left[-g^*(\tau_3) - g(\tau_1) - g^*(\tau_2) + g^*(\tau_2+\tau_3) + g(\tau_1+\tau_2) - g(\tau_1+\tau_2+\tau_3)\right] \tag{4.3.5}$$

R_2=\left(\frac{i}{\hbar}\right)^3p_g|\mu_{eg}|^4e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\times exp\left[-g^*(\tau_3)-g^*(\tau_1)+g(\tau_2)-g(\tau_2+\tau_3)-g^*(\tau_1+\tau_2)+g^*(\tau_1+\tau_2+\tau_3)\right] \la

R_3=\left(\frac{i}{\hbar}\right)^3p_g|\mu_{eg}|^4e^{i\omega_{eg}\tau_1-i\omega_{eg}\tau_3}\times exp\left[-g(\tau_3)-g^*(\tau_1)+g^*(\tau_2)-g^*(\tau_2+\tau_3)-g^*(\tau_1+\tau_2)+g^*(\tau_1+\tau_2+\tau_3)\right]

$$R_4 = \left(\frac{i}{\hbar}\right)^3 p_g|\mu_{eg}|^4 e^{-i\omega_{eg}\tau_1 - i\omega_{eg}\tau_3} \times exp\left[-g(\tau_3) - g(\tau_1) - g(\tau_2) + g(\tau_2+\tau_3) + g(\tau_1+\tau_2) - g(\tau_1+\tau_2+\tau_3)\right] \tag{4.3.6}$$

These expressions provide the most direct way of accounting for fluctuations or periodic modulation of the spectroscopic energy gap in nonlinear spectroscopies.

Example 4.3.1: Two-Pulse Photon Echo

For the two-pulse photon echo experiment on a system with inhomogeneous broadening:

- Set $g(t) = \Gamma_{eg}t + \frac{1}{2}\Delta^2 t^2$ For this simple model $g(t)$ is real.
- Set $\tau_2 = 0$, giving

$$R_2 = R_3 = \left(\frac{i}{\hbar}\right)^3 p_g|\mu_{eg}|^4 e^{i\omega_{eg}\tau_1 - i\omega_{eg}\tau_3} exp\left[-2g(\tau_3) - 2g(\tau_1) + g(\tau_1+\tau_3)\right]$$

- Substituting $g(t)$ into this expression gives the same result as before.

$$R^{(3)} \propto e^{-i\omega_{eg}(\tau_1-\tau_3)} e^{-\Gamma_{eg}(\tau_1+\tau_3)} e^{-(\tau_1-\tau_3)^2\Delta^2/2} \tag{4.3.7}$$

Similar expressions can also be derived for an arbitrary number of eigenstates of the system Hamiltonian.[1] In that case, eqs. (5.3.1) become

$$\begin{aligned} R_1 &= \sum_{abcd} p_a \mu_{ab}\mu_{bc}\mu_{cd}\mu_{da}\exp\left[-i\langle\omega_{ba}\rangle\tau_3 - i\langle\omega_{ca}\rangle\tau_2 - i\langle\omega_{da}\rangle\tau_1\right]F_{abcd}^{(1)}(\tau_3,\tau_2,\tau_1) \\ R_2 &= \sum_{abcd} p_a \mu_{ab}\mu_{bc}\mu_{cd}\mu_{da}\exp\left[-i\langle\omega_{dc}\rangle\tau_3 - i\langle\omega_{db}\rangle\tau_2 - i\langle\omega_{da}\rangle\tau_1\right]F_{abcd}^{(2)}(\tau_3,\tau_2,\tau_1) \\ R_3 &= \sum_{abcd} p_a \mu_{ab}\mu_{bc}\mu_{cd}\mu_{da}\exp\left[-i\langle\omega_{bc}\rangle\tau_3 + i\langle\omega_{ca}\rangle\tau_2 + i\langle\omega_{da}\rangle\tau_1\right]F_{abcd}^{(3)}(\tau_3,\tau_2,\tau_1) \\ R_4 &= \sum_{abcd} p_a \mu_{ab}\mu_{bc}\mu_{cd}\mu_{da}\exp\left[-i\langle\omega_{bc}\rangle\tau_3 + i\langle\omega_{db}\rangle\tau_2 + i\langle\omega_{da}\rangle\tau_1\right]F_{abcd}^{(4)}(\tau_3,\tau_2,\tau_1) \end{aligned} \tag{4.3.8}$$

The dephasing functions are written in terms of lineshape functions with a somewhat different form:

$$\begin{aligned} -\ln\left[F_{abcd}^{(1)}(\tau_3,\tau_2,\tau_1)\right] &= h_{bb}(\tau_3) + h_{cc}(\tau_2) + h_{dd}(\tau_1) + h_{bc}^{+}(\tau_3,\tau_2) \\ &\quad + h_{cd}^{+}(\tau_3,\tau_2) + f_{bd}^{+}(\tau_3,\tau_1;\tau_2) \\ -\ln\left[F_{abcd}^{(2)}(\tau_3,\tau_2,\tau_1)\right] &= \left[h_{cc}(\tau_3)\right]^* + \left[h_{bb}(\tau_2)\right]^* + h_{dd}(\tau_1+\tau_2+\tau_3) + \left[h_{bc}^{+}(\tau_3,\tau_2)\right]^* \\ &\quad + h_{cd}^{-}(\tau_1+\tau_2+\tau_3,\tau_3) + \left[f_{bd}^{-}(\tau_2,\tau_1+\tau_2+\tau_3;\tau_3)\right]^* \\ -\ln\left[F_{abcd}^{(3)}(\tau_3,\tau_2,\tau_1)\right]^* &= \left[h_{bb}(\tau_3)\right]^* + h_{cc}(\tau_2+\tau_3) + h_{dd}(\tau_1) + h_{cd}^{+}(\tau_2+\tau_3,\tau_1) \\ &\quad - f_{bc}^{-}(\tau_3,\tau_2+\tau_3;\tau_2) - f_{bd}^{+}(\tau_3,\tau_1;\tau_2) \\ -\ln\left[F_{abcd}^{(4)}(\tau_3,\tau_2,\tau_1)\right]^* &= h_{cc}(\tau_3) + h_{dd}(\tau_1+\tau_2) + \left[h_{bb}(\tau_2+\tau_3)\right]^* - h_{bc}^{-}(\tau_3,\tau_2+\tau_3) \\ &\quad + h_{cd}^{+}(\tau_1+\tau_2,\tau_3) - f_{bd}^{-}(\tau_1+\tau_2,\tau_2+\tau_3;\tau_3) \end{aligned}$$

where:

$$\begin{aligned} h_{nm}(\tau) &= \int_0^{\tau} d\tau_2' \int_0^{\tau_2} d\tau_1' C_{nm}(\tau_2' - \tau_1') \\ h_{nm}^{\pm}(\tau_2, \tau_1) &= \int_0^{\tau_2} d\tau_2' \int_0^{\tau_1} d\tau_1' C_{nm}(\tau_2' \pm \tau_1') \\ f_{nm}^{\pm}(\tau_2, \tau_1; \tau_3) &= \int_0^{\tau_2} d\tau_2' \int_0^{\tau_1} d\tau_1' C_{nm}(\tau_2' \pm \tau_1' + \tau_3) \end{aligned}$$

References

1. J. Sung and R. J. Silbey, "Four-wave mixing spectroscopy for a multi-level system," J. Chem. Phys. 115, 9266 (2001).