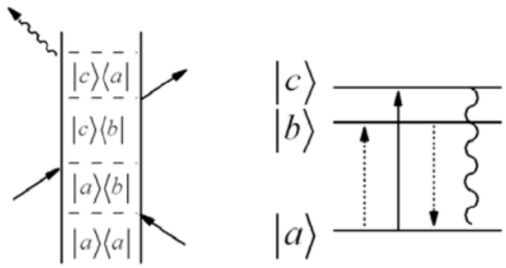
5.2: 2D Spectroscopy from Third Order Response

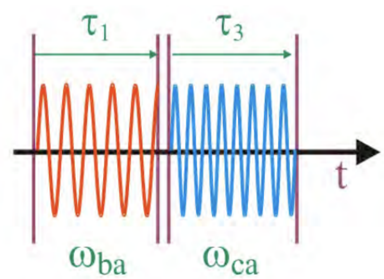
These examples indicate that narrow band pump-probe experiments can be used to construct 2D spectra, so in fact the third-order nonlinear response should describe 2D spectra. To describe these spectra, we can think of the excitation as a third-order process arising from a sequence of interactions with the system eigenstates. For instance, taking our initial example with three levels, one of the contributing factors is of the form R_2:



Setting $\tau_2 = 0$ and neglecting damping, the response function is

$$R_2(\tau_1, \tau_3) = p_a |\mu_{ab}|^2 |\mu_{ac}|^2 e^{-i\omega_{ba}\tau_1 - i\omega_{ca}\tau_3} \tag{5.2.1}$$

The time domain behavior describes the evolution from one coherent state to another—driven by the light fields:



A more intuitive description is in the frequency domain, which we obtained by Fourier transforming eq. (7.1):

$$\begin{aligned}
\tilde{R}_2(\omega_1, \omega_3) &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i\omega_1\tau_1 + i\omega_3\tau_3} R_2(\tau_1, \tau_3) d\tau_1 d\tau_3 \\
&= p_a |\mu_{ab}|^2 |\mu_{ac}|^2 \langle \delta(\omega_3 - \omega_{ca}) \delta(\omega_1 - \omega_{ba}) \rangle \\
&\equiv p_a |\mu_{ab}|^2 |\mu_{ac}|^2 P(\omega_3, \tau_2; \omega_1)
\end{aligned}$$

The function P looks just like the covariance $\langle xy \rangle$ that describes the correlation of two variables x and y. In fact P is a joint probability function that describes the probability of exciting the system at ω_{ba} and observing the system at ω_{ca} (after waiting a time τ_2). In particular, this diagram describes the cross peak in the upper left of the initial example we discussed.