

## 4.1: Eigenstate vs. system/bath perspectives

From our earlier work on electronic spectroscopy, we found that there are two equivalent ways of describing spectroscopic problems, which can be classified as the eigenstate and system/bath perspectives. Let's summarize these before turning back to nonlinear spectroscopy, using electronic spectroscopy as the example:

1) Eigenstate: The interaction of light and matter is treated with the interaction picture Hamiltonian  $H = H_0 + V(t)$ .  $H_0$  is the full material Hamiltonian, expressed as a function of nuclear and electronic coordinates, and is characterized by eigenstates which are the solution to  $H_0|n\rangle = E_n|n\rangle$ . In the electronic case  $|n\rangle = |e, n_1, n_2 \dots\rangle$  represent labels for a particular vibronic state. The dipole operator in  $V(t)$  couples these states. Given that we have such detailed knowledge of the matter, we can obtain an absorption spectrum in two ways. In the time domain, we know

$$C_{\mu\mu}(t) = \sum_n p_n \langle n | \mu(t) \mu(0) | n \rangle = \sum_{n,m} p_n |\mu_{nm}|^2 e^{-i\omega_{nm}t} \quad (4.1.1)$$

The absorption lineshape is then related to the Fourier transform of  $C(t)$ ,

$$\sigma(\omega) = \sum_{n,m} p_n |\mu_{nm}|^2 \frac{1}{\omega - \omega_{nm} - i\Gamma_{nm}} \quad (4.1.2)$$

where the phenomenological damping constant  $\Gamma_{nm}$  was first added into eq. (5.1.1). This approach works well if you have an intimate knowledge of the Hamiltonian if your spectrum is highly structured and if irreversible relaxation processes are of minor importance.

2) System/Bath: In condensed phases, irreversible dynamics and featureless lineshapes suggest a different approach. In the system/bath or energy gap representation, we separate our Hamiltonian into two parts: the system  $H_S$  contains a few degrees of freedom  $Q$  which we treat in detail, and the remaining degrees of freedom ( $q$ ) are in the bath  $H_B$ . Ideally, the interaction between the two sets  $H_{SB}(qQ)$  is weak.

$$H_0 = H_S + H_B + H_{SB} \quad (4.1.3)$$

Spectroscopically we usually think of the dipole operator as acting on the system state, i.e. the dipole operator is a function of  $Q$ . If we then know the eigenstates of  $H_S$ ,  $H_S|n\rangle = E_n|n\rangle$  where  $|n\rangle = |g\rangle$  or  $|e\rangle$  for the electronic case, the dipole correlation function is

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\langle\omega_{eg}\rangle t} \left\langle \exp \left[ -i \int_0^t H_{SB}(t') dt' \right] \right\rangle \quad (4.1.4)$$

The influence of the dark states in  $H_B$  is to modulate or change the spectroscopic energy gap  $\omega_{eg}$  in a form dictated by the time-dependent system-bath interaction. The systembath approach is a natural way of treating condensed phase problems where you can't treat all of the nuclear motions (liquid/lattice) explicitly. Also, you can imagine hybrid approaches if there are several system states that you wish to investigate spectroscopically.

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