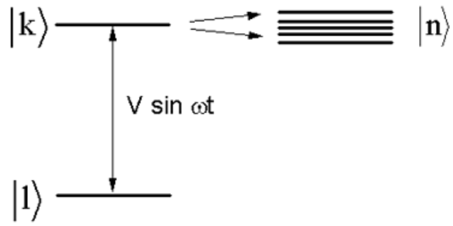
7.4: Relaxation and Line-Broadening

Let's describe absorption to a state that is coupled to a continuum. What happens to the probability of absorption if the excited state decays exponentially?



We can start with the first-order expression

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{kl} t} V_{k\ell}(t) \tag{7.4.1}$$

where we make the approximation $b_\ell(t) \approx 1$. We can add irreversible relaxation to the description of b_k using our earlier expression for the relaxation of

$$b_k(t) = \exp[-\overline{w}_{nk} t/2 - i\Delta E_k t/\hbar]. \tag{7.4.2}$$

In this case, we will neglect the correction to the energy $\Delta E_k = 0$, so

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{\mu l} t} V_{k\ell}(t) - \frac{\overline{w}_{nk}}{2} b_k \tag{7.4.3}$$

Or using $V(t) = -iE_0 \overline{\mu}_{kl} \sin \omega t$

$$\frac{\partial}{\partial t} b_k = \frac{-i}{\hbar} e^{i\omega_{kl} t} \sin \omega t V_{k\ell} - \frac{\overline{w}_{nk}}{2} b_k(t) \tag{7.4.4}$$

$$= \frac{E_0 \omega_{k\ell}}{2i\hbar\omega} \left[e^{i(\omega_{kl}+\omega)} - e^{i(\omega_{kl}-\omega)t} \right] \overline{\mu}_{k\ell} - \frac{\overline{w}_{nk}}{2} b_k(t) \tag{7.4.5}$$

The solution to the differential equation

$$\dot{y} + ay = be^{i\alpha t} \tag{7.4.6}$$

is

$$y(t) = Ae^{-at} + \frac{be^{i\alpha t}}{a + i\alpha} \tag{7.4.7}$$

with

$$b_k(t) = Ae^{-\overline{w}_{nk} t/2} + \frac{E_0 \overline{\mu}_{k\ell}}{2i\hbar} \left[\frac{e^{i(\omega_{kl}+\omega)t}}{\overline{w}_{nk}/2 + i(\omega_{k\ell} + \omega)} - \frac{e^{i(\omega_{kl}-\omega)t}}{\overline{w}_{nk}/2 + i(\omega_{k\ell} - \omega)} \right] \tag{7.4.8}$$

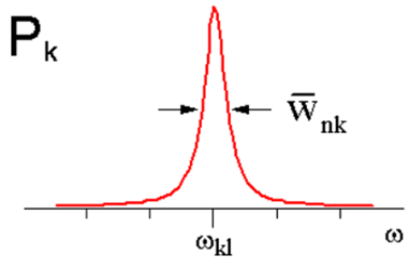
Let's look at absorption only, in the long time limit:

$$b_k(t) = \frac{E_0 \overline{\mu}_{k\ell}}{2\hbar} \left[\frac{e^{i(\omega_{kl}-\omega)t}}{\omega_{k\ell} - \omega - i\overline{w}_{nk}/2} \right] \tag{7.4.9}$$

For which the probability of transition to k is

$$P_k = |b_k|^2 = \frac{E_0^2 |\mu_{k\ell}|^2}{4\hbar^2} \frac{1}{(\omega_{k\ell} - \omega)^2 + \overline{w}_{nk}^2/4} \tag{7.4.10}$$

The frequency dependence of the transition probability has a Lorentzian form:



The FWHM line width gives the relaxation rate from k into the continuum n. Also the line width is related to the system rather than the manner in which we introduced the perturbation. The line width or line shape is an additional feature that we interpret in our spectra, and commonly originates from irreversible relaxation or other processes that destroy the coherence first set up by the light field.