Appendix E

Time-Dependent Yields in the Schrödinger or Mixed Methods

Since, for the exponential time-dependence, eqs. (3.13), (3.14), and (3.16) give

$$\mathcal{L}(\omega) = \int_0^\infty e^{i\omega t} f(t)dt = \frac{1}{\tau}\int_0^\infty e^{i\omega t} e^{-\frac{t}{\tau}} dt, \tag{E.1}$$

one can use $\omega' = \omega + ik_E = \omega + i/\tau$ (where ω is real) and $k_E = k_S = k_T = 1/\tau$ to get

$$\mathcal{L}(\omega) = k_T \int_0^\infty e^{i\omega' t} dt. \tag{E.2}$$

In fact, since ω' is complex, many of the expressions in this section should work in both the Schrödinger (Chapter 3) and mixed (Chapter 5) perturbation methods, the only differences being that Chapter 5 allows $k_E \neq k_S \neq k_T \neq 1/\tau$ and $\mathcal{L}(\omega)$ in (E.2) only holds for triplet yields (singlet yields use k_S instead of k_T as the leading factor). Note, however, that Chapter 3's Noyes time-dependence does not behave as simply as the exponential time-dependence treated here.

Generalizing (E.1)-(E.2) gives $\mathcal{L}(\omega, t)$ (the lineshape function at a certain time t):

$$\mathcal{L}(\omega, t) = \int_0^t e^{i\omega t'} f(t')dt' = k_T \int_0^t e^{i\omega' t'} dt' = \frac{k_T}{i\omega'}(e^{i\omega' t} - 1), \tag{E.3}$$

almost as in eq. (3.11) but with $\omega' \neq 0$ always true. Replacing $\mathcal{L}(\omega)$ by $\mathcal{L}(\omega, t)$ in eq. (3.24) or the analogous expressions in Chapter 5 allows calculation of the time-dependence of the yield, or $\Phi_{ST}(t)$, and this can be useful when simulating transient photolysis experimental data like that in [27, 108]. Fig. E.1 below gives an example of such a calculation. Note that time-dependent yields are a potentially rich source of information on the spin dynamics since they can give many inflection points with respect to time (compare the information content of Fig. E.1 to the $B_o = 0$ and 0.5G points in Fig. 2.1b) and since it may be possible to get (for different field configurations) different yields versus time even when the $t \to \infty$ yields are identical.

Next, the extrema of higher order terms (which go as $\frac{d^n \mathcal{L}(\omega)}{d\omega^n}$ for $t \to \infty$) have time-dependences that can be obtained from (E.3) as follows:

$$\frac{d^n \mathcal{L}(\omega, t)}{d\omega^n} = i^n k_T \int_0^t (t')^n e^{i\omega' t'} dt'$$

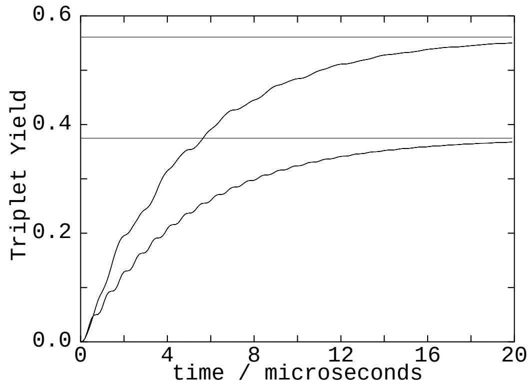

Figure E.1: Time-dependent singlet-to-triplet yields for simple system as in Fig. 2.1b with τ=5 μs, no oscillating field, and B_o=0 (lower curves) or 0.5 G (upper curves). Horizontal lines indicate steady-state yields (for $t \to \infty$). Plots show yields calculated every 100 ns using Schrödinger and Liouville Runge-Kutta methods and analytical expressions from the Schrödinger formalism (all methods give indistinguishable curves). Runge-Kutta methods use time steps δt of 10 ns. Many similar-looking plots appear in [114].

$$\begin{aligned} &= i^n k_T \left[e^{i\omega' t} \sum_{r=0}^{n} \frac{(-1)^r n! t^{n-r}}{(n-r)!(i\omega')^{r+1}} - \frac{(-1)^n n!}{(i\omega')^{n+1}} \right] \\ &= \frac{ik_T(-1)^n n!}{(\omega')^{n+1}} \left[1 - e^{i\omega' t} \sum_{r=0}^{n} \frac{(-i\omega' t)^r}{r!} \right], \end{aligned} \tag{E.4}$$

almost as in eq. (3.12) but with $\omega' \neq 0$ always true. Thus, one would expect to be able to fit time-dependent yields to a series of terms like those given in (E.4). Both direct differentiation of (E.3) and the series expansion (E.4) give the same results out to 2nd order:

$$\mathcal{L}(\omega, t) = \frac{ik_T}{\omega'}[1 - e^{i\omega' t}] \tag{E.5}$$

$$\frac{d\mathcal{L}(\omega, t)}{d\omega} = -\frac{ik_T}{\omega'^2}[1 - e^{i\omega' t}(1 - i\omega' t)] \tag{E.6}$$

$$\frac{d^2\mathcal{L}(\omega, t)}{d\omega^2} = \frac{2ik_T}{\omega'^3}\left[1 - e^{i\omega' t}(1 - i\omega' t - \frac{1}{2}\omega'^2 t^2)\right]. \tag{E.7}$$

Furthermore, since the yields all start out as zero and are monotonic functions with respect to time (i.e. they never decrease), it seems reasonable to expect that if the steady state yields $\Phi_{ST}(\infty)$ are accurate and well-behaved (convergent over several orders of perturbation theory), then the time-dependent yields will also be accurate and well-behaved.

Note that while the yield remains monotonic and is made up of terms like (E.4), its time-derivative is composed of terms like

$$\frac{d}{dt}\left[\frac{d^n\mathcal{L}(\omega, t)}{d\omega^n}\right] = \frac{ik_T(-1)^n n!}{(\omega')^{n+1}} \left[-i\omega' e^{i\omega' t} \sum_{r=0}^{n} \frac{(-i\omega' t)^r}{r!} + i\omega' e^{i\omega' t} \sum_{r=1}^{n} \frac{(-i\omega' t)^{r-1}}{(r-1)!} \right]$$

$$
\begin{aligned}
&= \frac{ik_T(-1)^n n!}{(\omega')^{n+1}}[-i\omega' e^{i\omega' t}]\left[\sum_{r=0}^{n}\frac{(-i\omega' t)^r}{r!} - \sum_{r=0}^{n-1}\frac{(-i\omega' t)^r}{r!}\right] \qquad \text{(E.8)}\\
&= \frac{k_T(-1)^n n!}{(\omega')^n} e^{i\omega' t}\frac{(-i\omega' t)^n}{n!}\\
&= k_T(it)^n e^{i\omega' t} = \frac{d}{dt}\left[i^n k\int_0^t (t')^n e^{i\omega' t'}dt'\right]
\end{aligned}
$$

which has real and imaginary parts that are not in general ≥ 0 or ≤ 0. Thus, terms like (E.4) are not in general monotonic. Thus, having a monotonic overall yield implies that there is a consistent relationship among the terms contributing to the yield.

Finally, since

$$\mathcal{L}(\omega, t) = k_T \int_0^t e^{i\omega' t'}dt' = \frac{k_T}{i\omega'}(e^{i\omega' t} - 1), \qquad \text{(E.9)}$$

when $\omega = 0$, one gets $\omega' = ik_E$ and

$$\mathcal{L}(0, t) = \frac{k_T}{k_E}(1 - e^{-k_E t}). \qquad \text{(E.10)}$$

Thus, to convert steady-state yield calculations to time-dependent yield calculations, one can substitute $\frac{k_T}{k_E}(1 - e^{-k_E t})$ for the very common $\mathcal{L}(0) = k_T/k_E$ terms (which equal 1 when $k_S = k_T$). Thus it seems reasonable that when $k_S = k_T = 1/\tau$, one gets $\Phi_{XS}(t) + \Phi_{XT}(t) = 1 - e^{-t/\tau}$ (this can also be proven using (2.23) and the facts that $Q_S + Q_T = 1$ and $\psi^*(t)\psi(t) = 1$ for all t). When $k_S \neq k_T$, however, the many different $\mathcal{L}(0, t)$ terms can decay at different rates k_E, giving for $\Phi_{XS}(t) + \Phi_{XT}(t)$ a sum of exponential decays with different rates.