Appendix A

Relationships among Yields

There are a number of relationships between the different yields $\Phi_{ST}(t)$, $\Phi_{TT}(t)$, $\Phi_{SS}(t)$, and $\Phi_{TS}(t)$ that can be derived.

A.1 Steady-State Yields

First, in the Schrödinger formalism, using $X = S$ or T to indicate initial singlet or triplet states, since

$$\Phi_{XS}(\infty) = \int_0^\infty \psi^*(t) Q_S \psi(t) f(t) dt \quad \text{and} \quad \Phi_{XT}(\infty) = \int_0^\infty \psi^*(t) Q_T \psi(t) f(t) dt, \tag{A.1}$$

one gets that

$$\Phi_{XS}(\infty) + \Phi_{XT}(\infty) = \int_0^\infty \psi^*(t)\psi(t) f(t) dt = \int_0^\infty f(t) dt = \mathcal{L}(0) = \mathcal{N}(0) = 1 \tag{A.2}$$

because the time-dependences $f(t)$ are always normalized ($\mathcal{L}(0)$ and $\mathcal{N}(0)$ are defined in Section 3.1.2). The above is done assuming $\psi(t)$ is normalized so that the total probability is always equal to one. The $\psi(t)$ in eqs. (2.24) and (2.26) do not behave this way.

Similarly, in the Liouville formalism, one has (using $\rho_X(t)$ in place of $\rho(t)$ to denote the initial state)

$$\Phi_{XS}(\infty) + \Phi_{XT}(\infty) = k_S tr \int_0^\infty Q_S \rho_X(t) dt + k_T tr \int_0^\infty Q_T \rho_X(t) dt. \tag{A.3}$$

Then, since

$$\frac{d\rho_X(t)}{dt} = -\frac{i}{\hbar}[H(t), \rho_X(t)]_- - \frac{k_S}{2}[Q_S, \rho_X(t)]_+ - \frac{k_T}{2}[Q_T, \rho_X(t)]_+ \tag{A.4}$$

one gets

$$\begin{aligned} & \int_0^\infty tr\left[\frac{d\rho_X(t)}{dt}\right] dt \qquad\qquad (A.5) \\ = \;& -\frac{i}{\hbar}\int_0^\infty tr[H(t), \rho_X(t)]_- dt - \frac{k_S}{2}\int_0^\infty tr[Q_S, \rho_X(t)]_+ dt - \frac{k_T}{2}\int_0^\infty tr[Q_T, \rho_X(t)]_+ dt \end{aligned}$$

which gives

$$tr\rho_X(\infty) - tr\rho_X(0) = -k_S tr\int_0^\infty Q_S\rho_X(t)dt - k_T tr\int_0^\infty Q_T\rho_X(t)dt \tag{A.6}$$

or

$$-tr\rho_X(0) = -\Phi_{XS}(\infty) - \Phi_{XT}(\infty) \tag{A.7}$$

and since $\rho_X(0) = Q_X/trQ_X$, this gives

$$1 = \Phi_{XS}(\infty) + \Phi_{XT}(\infty). \tag{A.8}$$

The above two proofs hold for any time-dependent Hamiltonian $H(t)$, for any set of k_S, k_T, and for any cage dynamics time-dependence $f(t)$ that satisfies $\int_0^\infty f(t)dt = 1$. The result of the above two proofs is reasonable since there are only two decay channels, and all the initial probability must eventually decay via one channel or the other.

A.2 Time-Dependent Yields

The next few proofs attempt to verify the relationship

$$k_S\Phi_{ST}(t) = 3k_T\Phi_{TS}(t) \tag{A.9}$$

which empirically seems to hold at all times for any steady Hamiltonian (even for very anisotropic Hamiltonians that do not commute with Q_S or Q_T), any set of k_S, k_T, and for some oscillating field configurations. All of the following proofs use the Liouville formalism.

A.2.1 $\rho(t)$ is Hermitian

The first thing to note is that when $A(t) = -\frac{i}{\hbar}H(t) - \frac{1}{2}(k_SQ_S + k_TQ_T)$

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar}[H(t),\rho(t)]_- - \frac{k_S}{2}[Q_S,\rho(t)]_+ - \frac{k_T}{2}[Q_T,\rho(t)]_+ = A(t)\rho(t) + \rho(t)A^+(t). \tag{A.10}$$

Here $A^+(t)$ is the adjoint (complex conjugate transpose) of $A(t)$.

$$A^+(t) = \frac{i}{\hbar}H^+(t) - \frac{1}{2}(k_SQ_S^+ + k_TQ_T^+) = \frac{i}{\hbar}H(t) - \frac{1}{2}(k_SQ_S + k_TQ_T) \tag{A.11}$$

holds because $H = H^+$ (since H is Hermitian) and $Q_S = Q_S^+$ and $Q_T = Q_T^+$ (since Q_S and Q_T are real and symmetric).

Thus, since the $\rho(0)$ used here are always Hermitian, $\rho(0) = \rho^+(0)$ holds, and initially one has

$$\begin{aligned}\frac{d\rho^+(t)}{dt} &= [A(t)\rho(t) + \rho(t)A^+(t)]^+ \qquad \text{(A.12)}\\ &= \rho^+(t)A^+(t) + A(t)\rho^+(t)\\ &= \rho(t)A^+(t) + A(t)\rho(t)\\ &= A(t)\rho(t) + \rho(t)A^+(t)\\ &= \frac{d\rho(t)}{dt}.\end{aligned}$$

Thus, since $\rho(0)$ begins as Hermitian, $\rho(t)$ remains Hermitian for all time t (as in eq. (2.41)). This result holds for any set of k_S, k_T and any time-dependent Hamiltonian $H(t)$.

A.2.2 $\Phi_{ST}(t) = 3\Phi_{TS}(t)$ when $k = k_S = k_T$

Next, if $k_S = k_T$, the term $\frac{1}{2}(k_S Q_S + k_T Q_T)$ becomes $\frac{k}{2}$ giving $A(t) = -\frac{i}{\hbar}H(t) - \frac{k}{2}$ and $A^+(t) = \frac{i}{\hbar}H(t) - \frac{k}{2}$. These allow $\rho_X(t)$ ($\rho(t)$ for the initial state X) to be written

$$\begin{aligned}\rho_X(t) &= e^{\int_0^t -\frac{i}{\hbar}H(t')dt'}\rho_X(0)e^{\int_0^t \frac{i}{\hbar}H(t')dt'}e^{-kt} \\ &= R(t)\rho_X(0)R^{-1}(t)e^{-kt}.\end{aligned} \tag{A.13}$$

Thus one gets, using $\rho_X(0) = Q_X/trQ_X$,

$$\begin{aligned}\Phi_{ST}(t) &= k\int_0^t tr[Q_T\rho_S(t')]dt' \\ &= k\int_0^t tr[Q_T R(t')\frac{Q_S}{trQ_S}R^{-1}(t')e^{-kt'}]dt' \\ &= k\int_0^t tr[Q_T R(t')Q_S R^{-1}(t')]\frac{1}{trQ_S}e^{-kt'}dt' \\ &= k\int_0^t [tr(R(t')Q_S R^{-1}(t')) - tr(Q_S R(t')Q_S R^{-1}(t'))]\frac{1}{trQ_S}e^{-kt'}dt' \\ &= k\int_0^t [trQ_S - tr(Q_S R(t')Q_S R^{-1}(t'))]\frac{1}{trQ_S}e^{-kt'}dt'\end{aligned} \tag{A.14}$$

and

$$\begin{aligned}3\Phi_{TS}(t) &= 3k\int_0^t tr[Q_S\rho_T(t')]dt' \\ &= 3k\int_0^t tr[Q_S R(t')\frac{Q_T}{trQ_T}R^{-1}(t')e^{-kt'}]dt' \\ &= 3k\int_0^t tr[Q_S R(t')Q_T R^{-1}(t')]\frac{1}{3trQ_S}e^{-kt'}dt' \\ &= k\int_0^t tr[Q_S R(t')Q_T R^{-1}(t')]\frac{1}{trQ_S}e^{-kt'}dt' \\ &= k\int_0^t [tr(Q_S R(t')R^{-1}(t')) - tr(Q_S R(t')Q_S R^{-1}(t'))]\frac{1}{trQ_S}e^{-kt'}dt' \\ &= k\int_0^t [trQ_S - tr(Q_S R(t')Q_S R^{-1}(t'))]\frac{1}{trQ_S}e^{-kt'}dt'\end{aligned} \tag{A.15}$$

so that for any time-dependent Hamiltonian $H(t)$ when $k = k_S = k_T$, the two quantities $\Phi_{ST}(t)$ and $3\Phi_{TS}(t)$ are equivalent (and so (A.9) holds).

Note that with the relations (A.8) and (A.9) proved so far, one gets

$$\Phi_{TT}(\infty) = 1 - \frac{1}{3}\Phi_{ST}(\infty) \quad \text{or} \quad 3\Phi_{TT}(\infty) = 3 - \Phi_{ST}(\infty) \tag{A.16}$$

which seem to hold in Fig. 2.1 for example.

A.2.3 $k_S\Phi_{ST}(t) = 3k_T\Phi_{TS}(t)$ when $k_S \neq k_T$

Finally, if $H(t)$ and $A(t)$ in eq. (A.10) are constants (no restrictions on k_S, k_T this time), one can expand the Hermitian matrix $\rho(t)$ in terms of t

$$\rho(t) = \sum_{n=0}^{\infty} \alpha_n t^n \tag{A.17}$$

where α_n are time-independent Hermitian matrices. Eq. (A.17) can be evaluated using

$$\rho(t) = \alpha_0 + (\alpha_1 + (...(\alpha_{n-2} + (\alpha_{n-1} + \alpha_n t)t)...)t)t. \tag{A.18}$$

Plugging eq. (A.17) into eq. (A.10) gives

$$\sum_{n=1}^{\infty} n\alpha_n t^{n-1} = \sum_{n=0}^{\infty} (A\alpha_n + \alpha_n A^+)t^n \tag{A.19}$$

$$\sum_{n=0}^{\infty} (n+1)\alpha_{n+1} t^n = \sum_{n=0}^{\infty} (A\alpha_n + \alpha_n A^+)t^n \tag{A.20}$$

or, equating powers of t,

$$\alpha_0 = \rho(0) \quad \text{and} \quad \alpha_{n+1} = \frac{1}{n+1}(A\alpha_n + \alpha_n A^+) \quad \text{for} \quad n \geq 0. \tag{A.21}$$

The above way can be useful for calculating yields versus time, but probably is comparable in speed to a Runge-Kutta method.

Using the above, or its equivalent

$$\begin{aligned} \alpha_0 &= \rho(0) \\ \alpha_n &= \frac{1}{n}(A\alpha_{n-1} + \alpha_{n-1}A^+) \quad \text{for} \quad n \geq 1 \end{aligned} \tag{A.22}$$

one gets that

$$\alpha_n = \frac{1}{n!} \sum_{r=0}^{n} \frac{n!}{r!(n-r)!} A^r \rho(0)(A^+)^{n-r} \tag{A.23}$$

so that

$$\begin{aligned} \alpha_1 &= A\rho(0) + \rho(0)A^+ \\ \alpha_2 &= \frac{1}{2}[A^2\rho(0) + 2A\rho(0)A^+ + \rho(0)(A^+)^2] \\ \alpha_3 &= \frac{1}{6}[A^3\rho(0) + 3A^2\rho(0)A^+ + 3A\rho(0)(A^+)^2 + \rho(0)(A^+)^3] \\ \alpha_4 &= \frac{1}{24}[A^4\rho(0) + 4A^3\rho(0)A^+ + 6A^2\rho(0)(A^+)^2 + 4A\rho(0)(A^+)^3 + \rho(0)(A^+)^4]. \end{aligned} \tag{A.24}$$

Also, using eq. (A.23) and the facts that α_0 is Hermitian and $(ABC)^+ = C^+B^+A^+$ (and swapping r for $n-r$) one gets

$$\alpha_n^+ = \frac{1}{n!} \sum_{r=0}^{n} \frac{n!}{r!(n-r)!} A^{n-r} \alpha_0^+ (A^+)^r = \frac{1}{n!} \sum_{r=0}^{n} \frac{n!}{r!(n-r)!} A^r \alpha_0 (A^+)^{n-r} = \alpha_n. \tag{A.25}$$

Thus one has that all α_n (and so $\rho(t)$) are Hermitian.

Next, to show that the relation

$$\frac{1}{k_T}\Phi_{ST}(t) = \frac{3}{k_S}\Phi_{TS}(t) \tag{A.26}$$

is true, it is useful to assume (A.26) is true and to convert it to an equivalent expression (like (A.38)) that can be proven true. Thus one has, using

$$\rho_S(0) = \alpha_0 = \frac{Q_S}{trQ_S} \quad \text{and} \quad \rho_T(0) = \beta_0 = \frac{Q_T}{trQ_T} \tag{A.27}$$

where α_n uses eq. (A.23) with $\rho(0) = \rho_S(0)$ and β_n is α_n in eq. (A.23) when $\rho(0) = \rho_T(0)$, that

$$tr\left(Q_T\int_0^t \rho_S(t')dt'\right) = 3tr\left(Q_S\int_0^t \rho_T(t')dt'\right) \tag{A.28}$$

$$tr\left(Q_T\int_0^t \sum_{n=0}^{\infty}\alpha_n(t')^n dt'\right) = 3tr\left(Q_S\int_0^t \sum_{n=0}^{\infty}\beta_n(t')^n dt'\right) \tag{A.29}$$

$$tr\left(Q_T\sum_{n=0}^{\infty}\frac{\alpha_n t^{n+1}}{n+1}\right) = 3tr\left(Q_S\sum_{n=0}^{\infty}\frac{\beta_n t^{n+1}}{n+1}\right) \tag{A.30}$$

$$\sum_{n=0}^{\infty}\frac{1}{n+1}tr(Q_T\alpha_n)t^{n+1} = 3\sum_{n=0}^{\infty}\frac{1}{n+1}tr(Q_S\beta_n)t^{n+1} \tag{A.31}$$

which holds for all t and so must give

$$tr(Q_T\alpha_n) = 3tr(Q_S\beta_n) \tag{A.32}$$

$$\sum_{r=0}^{n}\frac{1}{r!(n-r)!}\frac{tr(Q_TA^rQ_S(A^+)^{n-r})}{trQ_S} = \sum_{r=0}^{n}\frac{1}{r!(n-r)!}\frac{3tr(Q_SA^rQ_T(A^+)^{n-r})}{trQ_T} \tag{A.33}$$

$$\sum_{r=0}^{n}\frac{1}{r!(n-r)!}\frac{tr(Q_TA^rQ_S(A^+)^{n-r})}{trQ_S} = \sum_{r=0}^{n}\frac{1}{r!(n-r)!}\frac{tr(Q_SA^rQ_T(A^+)^{n-r})}{trQ_S} \tag{A.34}$$

$$\sum_{r=0}^{n}\frac{1}{r!(n-r)!}tr(Q_TA^rQ_S(A^+)^{n-r}) = \sum_{r=0}^{n}\frac{1}{r!(n-r)!}tr(Q_SA^rQ_T(A^+)^{n-r}) \tag{A.35}$$

$$\sum_{r=0}^{n}\frac{\left[\begin{array}{c} tr(A^rQ_S(A^+)^{n-r}) \\ -\ tr(Q_SA^rQ_S(A^+)^{n-r})\end{array}\right]}{r!(n-r)!} = \sum_{r=0}^{n}\frac{\left[\begin{array}{c} tr(Q_SA^r(A^+)^{n-r}) \\ -\ tr(Q_SA^rQ_S(A^+)^{n-r})\end{array}\right]}{r!(n-r)!} \tag{A.36}$$

which gives when the lower terms (which are equal) are dropped and the upper left trace is rearranged the result

$$\sum_{r=0}^{n}\frac{1}{r!(n-r)!}tr(Q_S(A^+)^{n-r}A^r) = \sum_{r=0}^{n}\frac{1}{r!(n-r)!}tr(Q_SA^r(A^+)^{n-r}). \tag{A.37}$$

Then using $tr(M) = tr(M^T)$ and $(ABC)^T = C^TB^TA^T$ (A^T is the transpose of A), (A.37) reduces to

$$\sum_{r=0}^{n}\frac{1}{r!(n-r)!}tr(Q_S(A^+)^{n-r}A^r) = \sum_{r=0}^{n}\frac{1}{r!(n-r)!}tr(Q_S(A^*)^{n-r}(A^T)^r). \tag{A.38}$$

Note that if the Hamiltonian H is all real, one gets from eq. (A.10) that $A^+ = A^*$ and $A = A^T$. This lets eq. (A.38) convert to:

$$\sum_{r=0}^{n} \frac{1}{r!(n-r)!} tr(Q_S(A^+)^{n-r}A^r) = \sum_{r=0}^{n} \frac{1}{r!(n-r)!} tr(Q_S(A^+)^{n-r}A^r) \qquad \text{(A.39)}$$

which lets the relation $k_S\Phi_{ST}(t) = 3k_T\Phi_{TS}(t)$ hold, as desired.

The proof for more general steady Hamiltonians (for which the relation still seems to hold) is less obvious. One case where the Hamiltonian is complex is when a magnetic field has a component along the y axis. If this y component is in the xy or yz plane, it can be treated via a coordinate transform as if the field were completely in the xz plane, thus giving a real Hamiltonian and letting the above proof hold. Nevertheless, the relation seems to hold for cases where the field has nonzero components along the x, y, and z axes simultaneously, cases in which the steady Hamiltonian will always contain some imaginary part.

Also, since one can use the rotating frame treatment to convert a time-dependent Hamiltonian into a time-independent one, the above proof should hold for rotating fields as well.

Note that if one could replace i by $-i$ in eq. (A.10) (in effect this swaps A for A^+) and get the same overall results (sort of like time-reversal symmetry), proof of (A.37) would be as easy as swapping r for $n - r$.

That both $A^n(A^+)^n$ and $(A^+)^nA^n$ are Hermitian can easily be proven using $(AB)^+ = B^+A^+$:

$$[A^n(A^+)^n]^+ = A^n(A^+)^n \quad \text{and} \quad [(A^+)^nA^n]^+ = (A^+)^nA^n \qquad \text{(A.40)}$$

Also, doing spot checks via Mathematica it seems that for a 4×4 Q_S and general A, n, m where $A = -iH + R$ (H is Hermitian, R is real symmetric), one gets

$$Q_SA^n(A^+)^mQ_S = Q_S(A^+)^mA^nQ_S = \alpha Q_S \qquad \text{(A.41)}$$

with a complex conjugate of

$$Q_SA^m(A^+)^nQ_S = Q_S(A^+)^nA^mQ_S = \alpha^* Q_S \qquad \text{(A.42)}$$

where α is a complex scalar. Also, when $n = m$, one gets eqs. (A.41) and (A.42) with the real scalar α=α^*. Eqs. (A.41) and (A.42) are important when examining eq. (A.37) since because $Q_S^2 = Q_S$,

$$tr(Q_SA^n(A^+)^mQ_S) = tr(Q_SA^n(A^+)^m). \qquad \text{(A.43)}$$