Appendix F

Phase/Orientation Averaging in the Schrödinger Method

The next few sections discuss what results from averaging eq. (3.24) over oscillating field phases or orientations. Phase averaging is needed when the oscillating field is produced coherently but the radical pair is formed at random times during the period of oscillation or, from the radical pair's perspective, when the oscillating field is produced incoherently (such phase averaging might be unnecessary if one uses flash photolysis to create the radical pairs at particular times during the oscillating field's period). Orientation averaging is needed in a number of different cases: for example, in powder averaging over an ensemble of randomly oriented anisotropic molecules. Nevertheless, here the focus is on two simple cases (a) and (b) of orientation averaging for a molecular system with axes x, y, z fixed with respect to the oscillating field source (which is assumed to produce random orientations of linearly polarized radiation), the steady field, and the laboratory frame. In case (a) the oscillating field is plane polarized (each linear oscillation is polarized $\perp$ to the z axis) so that an average over ϕ (the angle between the x axis and the projection of a particular $\vec{B}_{1j}$ onto the xy plane) is appropriate. Meanwhile, in case (b) the oscillating field is unpolarized so that an average over both θ (the angle between the z axis and a particular $\vec{B}_{1j}$) and ϕ is appropriate. Most of the above cases of phase or orientation averaging let certain terms in eq. (3.24) go to zero and thus simplify the calculations of overall yields. While the orientation averaging results for cases (a) and (b) should hold in nonzero steady fields because only the orientation of the oscillating field is varied, and case (b) in zero steady field is equivalent to powder averaging (over molecular orientations) the effects of an oscillation linearly polarized in the laboratory frame, powder averaging in combinations of steady and oscillating fields can be considerably more complicated because (unlike the very weak oscillating fields treated as time-dependent perturbations here) the relative orientation of the steady field with respect to the molecular axes can alter the eigenvalues and eigenvectors used in eq. (3.24).

F.1 Phase Averaging

The perturbation expansion, eq. (3.24), holds for time-dependent fields and Hamiltonians like the following:

$$\vec{B}(t) = \vec{B}_o + \sum_{j=1}^{N_p} \vec{B}_{1j} \cos(\alpha_j t + \phi_j) \tag{F.1}$$

$$H(t) = H_o + \sum_{j=1}^{N_p} V_j \cos(\alpha_j t + \phi_j). \tag{F.2}$$

Here one assumes that all the terms at one frequency $\alpha_j = \alpha$ are at a constant phase with respect to each other so that each $\phi_j = \phi_\alpha + \Delta\phi_j$ (for example, if a rotating magnetic field with $\vec{B}_{11} \perp \vec{B}_{12}$, $|\vec{B}_{11}| = |\vec{B}_{12}|$, and $\alpha_1 = \alpha_2 = \alpha$ is used, one always needs $\phi_1 - \phi_2 = \Delta\phi_1 - \Delta\phi_2 = \pm\pi/2$). Then one averages eq. (3.24) over each phase ϕ_α from 0 to 2π to account for the randomness of ϕ_α in an incoherent source. While averaging eq. (F.1) or (F.2) over each phase ϕ_α from 0 to 2π would give $\vec{B}(t) = \vec{B}_o$ or $H(t) = H_o$, the results of phase averaging eq. (3.24) are not just steady field results, as shown below. In a way, this is like describing the intensity of an incoherent oscillating field source: while the average field strength is 0, the average field intensity is not.

If eq. (3.24) is averaged over all ϕ_α from 0 to 2π, one gets the following:

Each 0th order term of $\Phi^{(0)}_{ST}$, which is independent of the phase, is unaffected.

Each 1st order term of $\Phi^{(1)}_{ST}$ depends on only one phase ϕ_j and so one phase ϕ_α. Each term goes as $e^{\pm i\phi_\alpha} = \cos\phi_\alpha \pm i \sin\phi_\alpha$, which goes to 0 when averaged over all of the different ϕ_α from 0 to 2π.

The 2nd order terms of $\Phi^{(2)}_{ST}$ are more complicated, and, instead of having terms go as $e^{\pm i\phi_\alpha}$ (as in the 1st order case), the terms go as $e^{\pm 2i\phi_\alpha}$, e^0, or $e^{\pm i\phi_{\alpha_1}} e^{\pm i\phi_{\alpha_2}}$ (here ϕ_{α_1} and ϕ_{α_2} designate phases ϕ_α for 2 different frequencies α_1 and α_2). The first and last kinds of terms both go to 0 when averaged over all the different ϕ_α, ϕ_{α_1}, and ϕ_{α_2}, but the e^0 terms will remain unchanged. The only terms that can yield e^0 are ones of the form $e^{\pm i(\phi_j - \phi_k)}$ that have $\alpha_j = \alpha_k = \alpha$. Only 4 of the 7 term types in eq. (3.24) are this way (2 $\mathcal{C}$ and 2 $\mathcal{D}$ type terms), and so only 4 of the 7 2nd order term types survive such phase averaging. It is interesting to note that the 4 term types remaining will not allow double quantum resonance effects; that is, their $\mathcal{L}(\omega + \Delta + \delta)$ and $\Delta + \delta$ terms will be independent of α rather than dependent on how close 2α is to an eigenfrequency, as would happen in the 3 term types that phase average to zero. Meanwhile, single quantum resonances, with peaks when α is near an eigenfrequency, can still occur via the $\mathcal{L}(\omega + \Delta)$, $\mathcal{L}(\omega + \delta)$, Δ, and δ terms that remain.

F.2 Orientation Averaging

To treat orientation averaging of a linear oscillation, it is useful to break up each perturbation matrix V_j (which are all linear in a field vector $\vec{B}_{1j}$) into a sum of the matrices x_j, y_j, and z_j:

$$V_j = x_j \cos\phi \sin\theta + y_j \sin\phi \sin\theta + z_j \cos\theta. \tag{F.3}$$

Such a sum will work for any combination of frequencies and phases if all the oscillating field vectors $\vec{B}_{1j}$ point in the same direction that is specified by the angles θ and ϕ. To do the orientation averaging of a function $f(\theta, \phi)$ one uses

$$\int_0^{2\pi} d\phi f(\theta,\phi) \Big/ \int_0^{2\pi} d\phi \qquad \text{or} \qquad \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin(\theta) f(\theta,\phi) \Big/ \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin(\theta). \tag{F.4}$$

While averaging eq. (F.1) or (F.2) over all θ from 0 to π and all ϕ from 0 to 2π would give $\vec{B}(t) = \vec{B}_o$ and $H(t) = H_o$, the results of orientation averaging eq. (3.24) are not just steady field results, as shown below. In a way, this is like describing the intensity of a plane polarized oscillating field: while the average field strength is 0, the average field intensity is not.

Orientation averaging eq. (3.24) over θ and/or ϕ gives the following:

Since each 0th order term of $\Phi^{(0)}_{ST}$ is independent of V_j, it is independent of θ and ϕ, and so is unchanged by orientation averaging.

Each 1st order term of $\Phi^{(1)}_{ST}$ is proportional to V_j. If one averages over ϕ only (as for radiation randomly polarized ⊥ to the z axis; that is, polarized in the xy plane), one gets that V_j becomes $z_j \cos\theta$, leaving nonzero only the component along the z axis. If one goes on and averages over θ (as for non-polarized radiation), one gets that V_j becomes 0, and each 1st order term drops out.

The 2nd order terms of $\Phi^{(2)}_{ST}$ all depend on $V_j V_k$ and so have the form

$$\begin{aligned} & A_{220}\cos^2\phi\sin^2\theta + A_{202}\sin^2\phi\sin^2\theta + A_{200}\cos^2\theta \\ + \quad & A_{211}\sin\phi\cos\phi\sin^2\theta + A_{210}\cos\phi\sin\theta\cos\theta + A_{201}\sin\phi\sin\theta\cos\theta \end{aligned} \tag{F.5}$$

where A_{nrs} is defined in eq. (F.7) below and represents the product of r x_j, s y_j, and $n-r-s$ z_j terms.

On ϕ averaging, (F.5) becomes $\frac{1}{2}(A_{220} + A_{202})\sin^2\theta + A_{200}\cos^2\theta$, and with additional θ averaging, using

$$\int_0^{\pi} d\theta \sin\theta = 2, \qquad \int_0^{\pi} d\theta \sin^3\theta = 4/3, \qquad \text{and} \qquad \int_0^{\pi} d\theta \cos^2\theta \sin\theta = 2/3, \tag{F.6}$$

it becomes $\frac{1}{3}(A_{220} + A_{202} + A_{200})$. Also, using x^2 for $x_j x_k$ and B^2_{1x} for $B_{1jx}B_{1kx}$, since $A_{220}, A_{202}, A_{200} = x^2, y^2, z^2$, the terms $A_{220}, A_{202}, A_{200}$ scale as B^2_{1x}, B^2_{1y}, B^2_{1z}, respectively. It is interesting that these 2nd order terms persist even for non-polarized radiation.

Higher order terms should follow a similar pattern; that is, at a higher order of perturbation theory n, one gets a series of terms

$$V^n = V_j V_k ... V_l V_m = \sum_{r=0}^{n} \sum_{s=0}^{n-r} A_{nrs} (\cos\phi)^r (\sin\phi)^s (\sin\theta)^{r+s} (\cos\theta)^{n-r-s} \tag{F.7}$$

which gives the following integrals for the term A_{nrs}

$$\begin{aligned} \int_0^{2\pi} d\phi (\cos\phi)^r (\sin\phi)^s &= 0 \quad \text{unless } r \text{ and } s \text{ are even} \qquad (\text{F.8}) \\ \int_0^{\pi} d\theta (\cos\theta)^{n-r-s} (\sin\theta)^{r+s+1} &= 0 \quad \text{unless } n-r-s \text{ is even.} \qquad (\text{F.9}) \end{aligned}$$

Thus, one can see that if there is only one V_j (so that $V^n = V_j^n$), one gets that (i)

$$A_{nrs} = x_j^r y_j^s z_j^{n-r-s} n!/r!s!(n-r-s)!, \tag{F.10}$$

(ii) the only A_{nrs} terms surviving the ϕ averaging will contain even powers r and/or s of B_{1jx} and/or B_{1jy} (and most any power $n-r-s$ of B_{1jz}), and (iii) the only A_{nrs} terms surviving both θ and ϕ averaging (for non-polarized radiation) will have even n and contain even powers of B_{1jx}, B_{1jy}, and/or B_{1jz}. The resultant even powers are reasonable considering symmetry arguments; that is, the orientation-averaged result should not depend on the sign (direction) of the oscillating field.