9. Transitions between Magnetic Levels Spin Transitions Between Spin States. Conservation of Spin Angular Momentum

From the magnetic energy diagram derived in the previous sections (Figures 14, 15 and 16), the **possible** magnet transitions are deduced by inspection. They are simply the transitions between any two levels which obey the law of conservation of energy. From this point of view, radiative transitions are possible only for states which differ in energy, since an energy gap is needed to balance the energy absrobed or emitted by a photon. Radiationless transitions are possible only between states which are degenerate or for which there is some source of themal energy to obey the energy conservation law in detail.

However, we now ask which of the possible transitions are plausible, even if energy is conserved. We can deduce the **plausible** transitions between spin states by considering the rules of conservation of angular momentum. The conservation of spin angular momentum defines the plausible transitions as those for which spin angular momentum is preserved during the transition. In general, the total angular momentum and the angular momentum on the z axis must be preserved in any transition between spin states. In addition, of course, energy must be concerved.

Vector Model for Transitions between Magnetic States. Visualization of the Transitions.

The dominant selection rule for plausibility of transitions is that under ordinary circumstances, the spin remains unchanged or will change by one unit of angular momentum, with this change being exactly compensated by an equal and opposite change of angular momentum (not necessarily spin!) as the result of spin coupling. For example, a photon possesses an angular momentum of 1 \, so it can couple to an electron spin and induce any of the plausible transitions for which the spin changes by one unit. This process for conservation of angular momentumis the basis of the rule that for raditive transitions the change in spin must be exactly 1 \. As another example, a proton or a ^{13}C nucleus possesses an angular momentum of 1/2 \, so hyperfine coupling with these nuclei can induce any of the plausible transitions if the change in the nuclear spin angular momentum is exactly the same as the change in the electron spin angular momentum. Similarly, spin-orbit coupling or spin-lattice coupling or couping with an electron spin can induce the plausible transitions.

We now consider the vector description of the magnetic transitions that are important for photochemistry. If the transitions occur radiatively, we are dealing with the field of **magnetic resonance spectroscopy**; if they occur radiationlessly, we are dealing with the field of **magnetic relaxation**. The vector description does not concern itself with the type of magnetic interaction or coupling which causes the transition, so that we can use a general description referring to a transition of a magnetic system involving a single spin (D $\times$ D) or two spins (S $\times$ T and T $\times$ T).

Coupling of a Single Spin to Another Source of Angular Momentum

Let us first consider the simplest case for the coupling of a single electron spin, $\mathbf{S_1}$ with some other, unspecified source of angular momentum, $\mathbf{H_i}$. The latter is a vector quantity and therefore can be viewed as coupling effectively with $\mathbf{S}_1$ under the proper conditions. What are the proper conditions? The proper conditions are identical for all effective magnetic couplings: (1) the magnetic moment of $\mathbf{S_1}$ must interact with the magnetic moment of $\mathbf{H}_i$ through either the dipolar interaction or the contact interaction and the two vectors must be possess identical Larmor frequencies and phases; (2) the strength of the magnetic coupling between $\mathbf{S_1}$ and $\mathbf{H_i}$ must be greater than the coupling of $\mathbf{S_1}$ to other magentic moments.

Figure 20 shows the process of the coupling of $\mathbf{S_1}$ to $\mathbf{H_i}$ schematically. In the example, the spin function of $\mathbf{S_1}$ (shown as a solid vector) is taken to be α and the orientation of the angular momentum $\mathbf{H_i}$ (shown as an open vector) is taken to be opposite to that of $\mathbf{S_1}$. Since the source of $\mathbf{H_i}$ is not specified, it need not be an electron or nuclear spin and therefore strictly speaking, we should not use the terms α or β (which is reserved for spin functions) to describe $\mathbf{H_i}$ for the general case. However, for clarity we shall use these terms, since the concrete example of coupled spins follows exactly the same principles as any other magnetic couplings. Returning to Figure 20 (left, top), we start by imagining that $\mathbf{S_1}$ and $\mathbf{H_i}$ are positioned in cones or orientation, but are uncoupled. We then couple the two vectors to generate a resultant. If $\mathbf{H_i}$ were a spin 1/2 particle, coupling could produce a final angular momentum state of 0 (singlet, S) or 1 (triplet, T). The triplet coupling is shown in the example. We now imagine that the coupling between $\mathbf{S_1}$ and $\mathbf{H_i}$ is stronger than that of any other source of angular momentum available to $\mathbf{S_1}$. The result of this strong coupling is the the precession of the $\mathbf{S_1}$ and $\mathbf{H_i}$ about their resultant (Figure 20, top right). This precessional motion causes $\mathbf{S_1}$ to "flip" cyclically between the α and β orientations (Figure 20, middle) which we term $\mathbf{S_1}^{\alpha}$ and $\mathbf{S_1}^{\beta}$. This spin flip corresponds to the application of a magnetic field along the x or y axis. Increasing the strength of the coupling along the z axis (Figure 20, bottom) increases the frequency of oscillation (Larmor frequency) but produces no tendancy for reorientation of the spin.

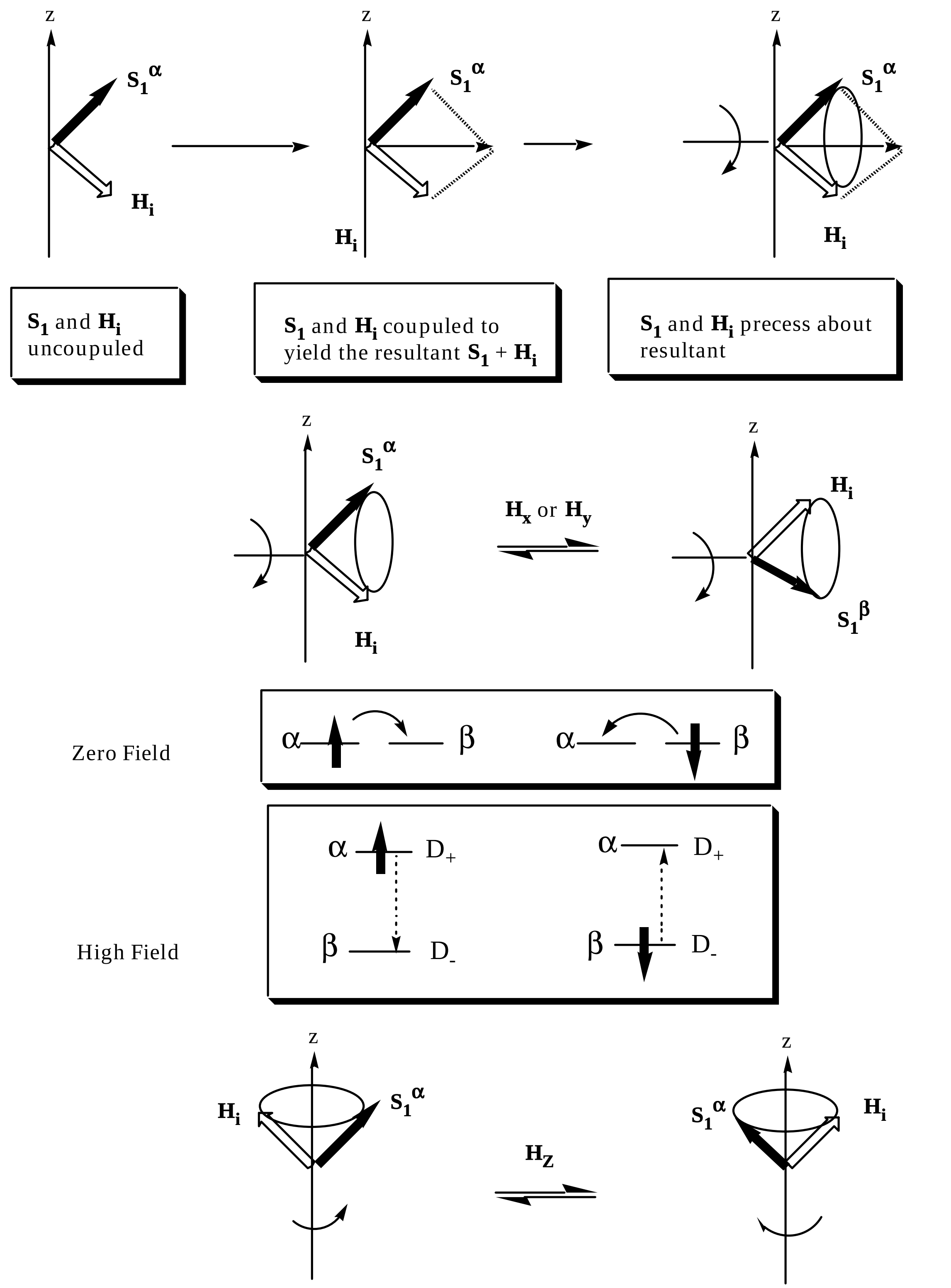

Figure 21. Vectro representation of transitions of a single coupled electron spin, $\mathbf{S_1}$. See text for discussion.

At zero field the conversion of $\mathbf{S_1}^{\alpha}$ to $\mathbf{S_1}^{\beta}$ occurs at approximately the Larmor frequency, ω, which is directly related to the strength of the coupling of $\mathbf{S_1}$ to $\mathbf{H_i}$ (Eq. 15). At high applied field the two states $\mathbf{S_1}^{\alpha}$ and $\mathbf{S_1}^{\beta}$ have different energies because of the Zeeman splitting. As a result, the interconversion of $\mathbf{S_1}^{\alpha}$ to $\mathbf{S_1}^{\beta}$ is "quenched" unless energy is conserved. In a radiative process, energy is conserved by coupling the oscillating magnetic moment of the electromagnetic field which possesses the correct frequency and phase for the transition. In the case of radiative transitions, energy is conserved precisely by the energy of the absorbed or emitted photon, i.e., $\Delta E = h\nu$, where ν is the frequency required to achieve resonance.

In the case of radicationless transitions if the states undergoing transition are not exactly degenerate, then the magnetic energy gap must be made up by coupling with a "third" body. The larger the energy gap the more difficult becomes effective coupling and the transition becomes implaulsible. The energy conserving process for the radiationless transition is accomplished by coupling the transition to the oscillating magnetic field produced by the environment such as the molecules of a solvent. This process is viewed as a magnetic energy transfer between the spin system undergoing transition and some magnetic moments that are oscillating at the correct frequency in the solvent (the oscillating magnetic species are termed the "lattice"). To maiontain energy conservation, the lattice may provide energy or absorb energy and can therefore assist in both absorptive or emissive transitions. With this description fo the lattice we can imagine that the oscillating magnetic moments behave just like the oscillating magnetic field of electromagnetic radiation. Instead of photons, the lattice provides "phonons" to the spin system. The lattice thus behaves analogously to a lamp that emits magnetic phonons or an absorber of magnetic phonons. The overall process is termed **spin-lattice magnetic relaxation** and is simply magnetic energy transfer between spin states. The most important interaction which couples the electron spin to the lattice is usually dipolar. This interaction has exactly the same mathematical form as Förster electronic energy transfer discussed in Chapter XX.

Coupling Involving Two Correlated Spins. T_+ ∅ S and T_- ∅ S Transitions.

The visualization of a single spin coupled to a second spin (or any other generalized magnetic moment) is readily extended infigure 21 to the visualization of two correlated spins coupled to a third spin (or any other generalized magnetic moment). In Figure 21 (upper left) two electron spins, $\mathbf{S_1}$ and $\mathbf{S_2}$ are shown as correlated in the T_+ state (the correlation is indicated by showing the resultant vector produced by coupling and precession about the resultant). Now we suppose that a third spin, either an electron spin or a nuclear spin (represented as $\mathbf{H_i}$ in the Figure) is capable of coupling specifically to the spin $\mathbf{S_2}$ (shown in the middle top of Figure 21 in terms of a new resultant and precession about the resultant). As for the single coupled spin in Figure 20, the coupling of $\mathbf{S_2}$ to $\mathbf{H_i}$ causes $\mathbf{S_2}$ to precess about the x or y axis and the α and β orientations. From the vector diagram it is readily seen that this oscillation produced by coupling of $\mathbf{S_2}$ and $\mathbf{H_i}$ causes triplet (T_+) to singlet (S) intersystem crossing.

At zero field the three T sublevels are usually strongly mixed by dipolar interactions between electron spins. Thus, radiationless T_+ ∅ S ISC is plausible and will depend on the strength of the coupling between $\mathbf{S_2}$ and $\mathbf{H_i}$ and the strength of the exchange interaction. For simplicity, in Figure 21 (bottom) we assume that J = 0. There is no radiative transitions between T and S possible at zero field because there is no energy gap between the states.

At high field the T_+ ∅ S ISC transition is not plausible by aradiationless pathways. The radiationless pathway is inefficient because it requires some source of magnetic energy conservation by coupling with the lattice. The plausibility of a radiative T_+ ∅ S transition depends on the relative coupling of the electron spins to one another (value of J) and to the radiative field. If the value of J is very small, the individual spins behave more or less independently so that radiative transitions of each spin ("doublet" transitions) become plausible. The vector diagram for the T_- ∅ S transition is readily constructed from the symmetry relationships of the T_- vector representation to that of the T_+ vector representation.

Coupling Involving Two Correlated Spins. T_0 ∅ S Transitions.

As for a single spin, it is also posssible for $\mathbf{H_i}$ to operate on correlated electron spins along the z axis. This situation is shown in Figure 22 for an initial T_0 state. Again under the assumption that J = 0, rephasing along the z axis occurs is if $\mathbf{H_i}$ is coupled selectively to one of the electron spins (say, $\mathbf{S_1}$). This rephasing causes T_0 ∅ S ISC at low field or at high field if J = 0.

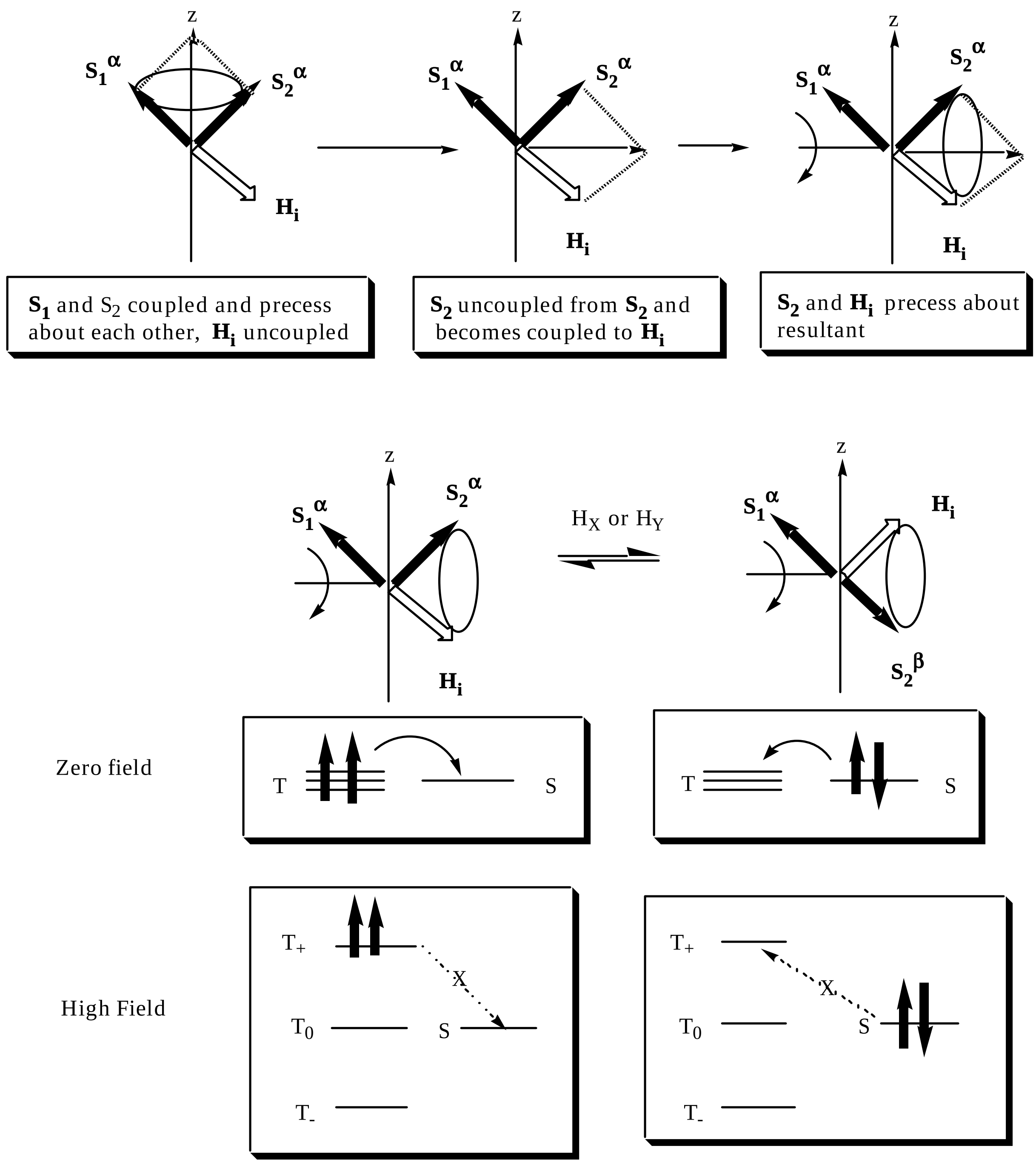

Figure 21. Vector representaion of coupling of two correlated spins with a third spin along the x or y axis. See text for discussion.

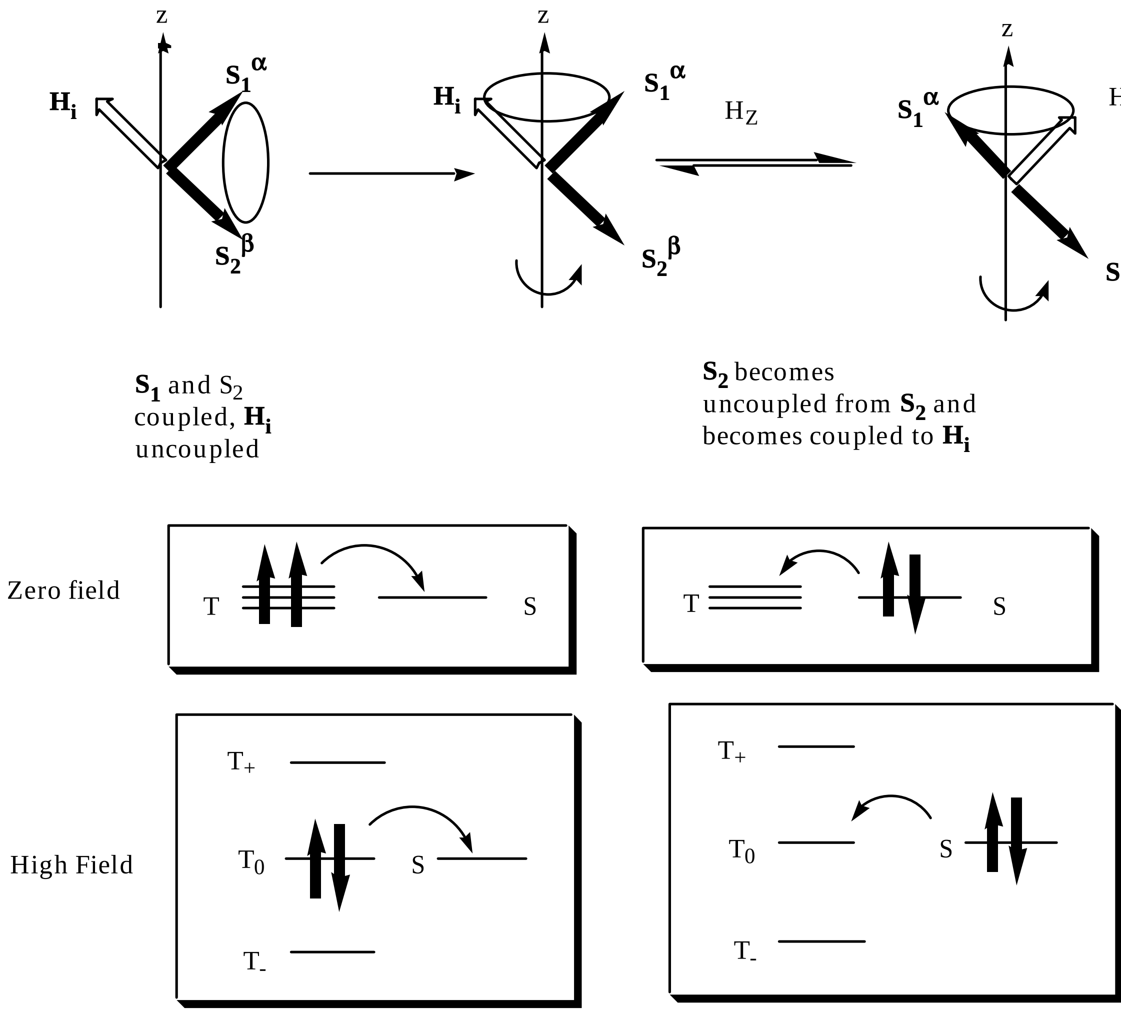

Figure 22. Vector representation of two correlated spins in a T_0 state coupled to a third spin along the z axis. See text for discussion.