7. Examples of Magnetic Energy Diagrams.

There are serveral very important cases of electron spin magnetic energy diagrams to examine in detail, because they appear repeatedly in many photochemical systems. The fundamental magnetic energy diagrams are those for a single electron spin at zero and high field and two correlated electron spins at zero and high field. The word correlated will be defined more precisely later, but for now we use it in the sense that the electron spins are correlated by electron exchange interactions and are thereby required to maintain a strict phase relationship. Under these circumstances, the terms singlet and triplet are meaningful in discussing magnetic resonance and chemical reactivity. From these fundamental cases the magnetic energy diagram for coupling of a single electron spin with a nuclear spin (we shall consider only couplings with nuclei with spin 1/2) at zero and high field and the coupling of two correlated electron spins with a nuclear spin are readily derived and extended to the more complicated (and more realistic) cases of couplings of electron spins to more than one nucleus or to magnetic moments generated from other sources (spin orbit coupling, spin lattice coupling, spin photon coupling, etc.).

Magentic Energy Diagram for A Single Electron Spin and Two Coupled Electron Spins. Zero Field.

Figure 14 displays the magnetic energy level diagram for the two fundamental cases of : (1) a single electron spin, a doublet or D state and (2) two correlated electron spins, which may be a triplet, T, or singlet, S state. In zero field (ignorning the electron exchange interaction and only considering the magnetic interactions) all of the magnetic energy levels are degenerate because there is no prefered orientation of the angular momentum and therefore no prefered orientation of the magnetic moment due to spin. We can therefore use the zero field situation as a point of calibration of magnetic coupling energy in devising the magnetic energy diagram. The concept is the same as using the energy of a non-bonding p orbital as a zero of energy and then to consider bonding orbitals as lower in energy than a p orbital and anti-bonding orbitals as higher in energy than a p orbital. Ignoring the exchange interaction is not realistic for many important cases. However, the exchange interaction is Coulombic and not magnetic, so we shall "turn it on" after considering the magnetic interactions.

At zero field the D state may be considered as either an α state or a β state, but we cannot distinguish these magnetic states in an experiment without applying a field. Both states have a well defined angular momentum of precisely 1/2 \ but have no defined value of M_S. Similarly, the T state may be considered as either a αα, ββ or αβ + βα spin function. All three states have a well defined angular momentum of precisely 1 \, but have no defined value of M_S. The S state is characterized as a αβ - βα state at zero field and possesses a well defind value of zero spin angular momentum. Thus, the T state and S states, although degenerate at zero field, are clearly distinguishable through the total angular momentum label.

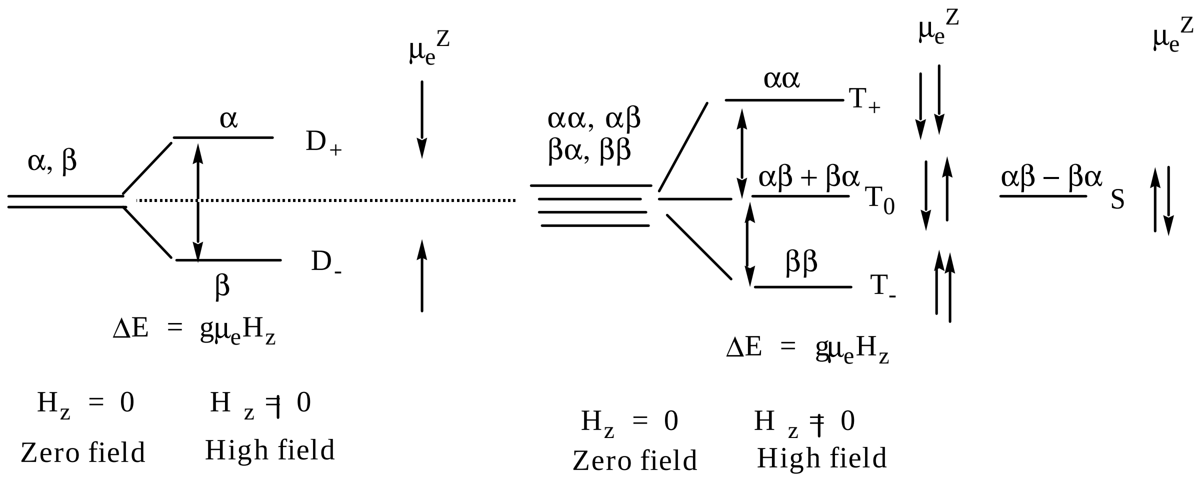

Figure 14. Magnetic energy diagram for a single electron spin and two correlated electron spins.

Thus, at zero field, the magnetic energy diagram for a D, T and S state is quite simple: all the states have the same magnetic energy and that energy corresponds to the zero of magnetic energy. In Figure 14 the degenerate levels are show as being close together and at the energy of zero field. We shall see that even at zero field interactions between spins (electron-electron, electron-nuclear or nuclear-nuclear) can lead to splitting of levels even at zero field.

Magentic Energy Diagram for A Single Electron Spin and Two Coupled Electron Spins. High Field.

Applying an external magnetic field, H_Z, removes some of the degeneracies of the D, T and S states through the Zeeman interaction. We now can refer exclusively to the z axis as a reference point, since angular momentum and magnetic moment will be strictly quantized on the z axis. Employing the formula for the quantum magnetic energy of a quantum magnet in a magnetic field of strength H_Z (eq. 11), we can readily rank the energies of the levels from knowledge of the value of M_S from eq. 11

$$E_S = g\mu_e H_z M_S \qquad (11)$$

which relates the magnetic energy to the g factor, the inherent magnetic moment of the electron, the field strength and the quantum number for orientation along the z axis. From the formula we have already shown (Table 1) that the β spin state (M_S = -1/2, termed D_-) is lower in energy than the α spin state (M_S = +1/2, termed D_+), remembering that negative values of the magnetic energy are defined as more stable than positive values of the magnetic energy (the magnitudes of g, μ_e and H_z are positive quantities.

The same conclusion concerning the energies of D_- and D_+ is reached by consideration of the physical picture of the spin's magnetic moment in a magnetic field. In Figure 14 the magnetic moments along the z axis(μ_e^Z), which determine the observable magnetic enegy diagram, are shown for individual electrons. Since magnetic moments are more stable when they are parallel to a coupling field (Eq. 10), we expect the β spin [D_-( )H_z( )] to be lower in energy than the α spin [D_+(¬)H_z( )], since the β spin's magnetic moment is parallel to the direction of H_Z, i.e., it is antiparallel to the direction of its spin angular momentum which is opposed to the magnetic field. The vector representations of the magnetic moments are shown to the right of the energy levels in Figure 14. Thus, from the coupling of magnetic moments shown in Figure 14 we conclude that the D_- state is lower in energy than the D_+ state in a magnetic field, although these two states are degenerate in the absence of a magnetic field.

Similarly, the relative energies of the three levels of the triplet state can be deduced from consideration of the values of M_S or from consideration of the alignment of magnetic moments (Figure 14). We note that the triplet sublevel with M_S = -1 (termed T_-) is lowest in energy, the triplet sublevel with M_S = 0 (termed T_0) possesses 0 magnetic energy on the z axis (the same energy as in the absence of an applied field) and the triplet sublevel with M_S = +1 (termed T_+) is highest in energy. Finally, for two spins the singlet state also possesses M_S = 0 (termed S), possesses 0 magnetic energy on the z axis or on any axis. It is important to note that although the T_0 state possesses a magnetic moment and 1 \ of angular momentum, it possesses zero magnetic moment or angular momentum on the z axis (because M_S = 0). Thus, as far as measurments on the z axis is concerned the S and T states are indistinguishable. This interesting feature will be seen important when we consider intersystem crossing mechanism for S and T interconversions. The same conclusions concerning the relative energies are obtained by consider magnetic moment alignments: T_-(¬¬)H_z( ) < T_0(¬)H_z( ) < T_+( )H_z( ).

Magnetic Energy Diagrams for Coupling of Electron Spins to Nuclear Spins. Zero Field.

We now consider the magnetic energy diagram for the coupling of a single electron spin (D state) to a magnetic nucleus of spin 1/2. The most important nuclei of organic chemistry either possess spin of zero (^{12}C and ^{16}O) or spin 1/2 (^{1}H and ^{13}C). Either of the latter may be considered as the coupling nucleus in the energy diagrams to be described.

The angular momentum rules for spin coupling are independent of the type of spins (electrons or nuclei) which couple. Thus, when two 1/2 spins couple the possible correlated spin states will be a singlet, S, and a triplet, T, i.e., a single state of spin angular momentum of zero and three states of angular momentum of one, respectively. For both electron electron and electron-nuclear coupling (and even nuclear-nuclear), four spin states are generated, but due to dipolar magnetic interactions, the T state and the S state are not quite degenerate at zero field. In the case of two correlated electrons, the exchange interaction must also be considered.

Consider the states that result from the hyperfine coupling of an electron to a nucleus. Let the labels e and n refer to electron and nuclear spins, respectively. The two correlated states resulting from the coupling be termed T_{en} (electron-nuclear) state and S_{en} (electron-nuclear) state. The magnetic energy splitting of the T_{en} and S_{en} is equal in energy to the hyperfine coupling, a (Figure 15). The hyperfine spitting (a) due to electron-nuclear spin coupling is analogous to the exchange splitting (J) due to electron-electron exchange. However, J is distant dependent whereas hyperfine couplings are usually distant independent and dependent only on molecular structure.

Magnetic Energy Diagrams for Coupling of Electron Spins to Nuclear Spins. Strong Field.

Let α_n be the spin function for the nuclear spin state with angular moment vector pointing in the positive direction of the z axis and let β_n be the spin function for the nuclear spin state with the angular momentum vector pointing in the negative direction of the z axis (this the case for the proton and the ^{13}C nucleus, for which the angular momentum and magnetic moment vectors point in the same direction). Let the subscript e will refer to the analogous electron spin function, α_e and β_e, respectively. In a strong field the S_{en} state ($\alpha_e\beta_n$ - $\beta_e\alpha_n$) and the three T_{en} states ($\alpha_e\alpha_n$, $\alpha_e\beta_n$ + $\beta_e\alpha_n$, and $\beta_e\beta_n$) split into four magnetic levels as shown in Figure 15. The relative energy rankings are readily understood in terms of the magnetic energy of the coupled electron and nuclear magnetic moments in the strong external field. Since μ_e is roughly 1000 times that of μ_n (recall than $\gamma_e >>> \gamma_n$), and since the strong field is defined as one that is much stronger than the internal (hyperfine interaction) the two levels corresponding to μ_e being parallel to the field (D_-, $M_S = -1/2$, α_e) are much lower in energy than the two levels corresponding to μ_e being antiparallel to the field (D_+, $M_S = +1/2$, β_e). Because the system is in a strong field it is now convenient to classify the states in terms of the individual spins on the z axis. According to the coorelation diagram (Figure 15), the three low field T_{en} states correlate to $\alpha_e\alpha_n$ ($D_+\alpha_n$), $\alpha_e\beta_n$ ($D_+\beta_n$) and $\beta_e\alpha_n$ ($D_-\alpha_n$) states at high field and the low field S_{en} state correlates with the $\beta_e\beta_n$ ($D_-\alpha_n$) state at high field.

The relative energies of the four states at high field are also readily deduced from consideration of the energies of interaction of the electron and nuclear magnetic moments of each state. Within the pair of α_ε levels, one possesses a magnetic moment orientation that is parallel to that of the electron and a magnetic moment orientation that is antiparallel to that of the electron. The lower energy state corresponds to the situation for which the magnetic moments are parallel, i.e., $\beta_e(\ )\alpha_n(\ )$ is lower in energy than $\beta_e(\ )\beta_n(\neg)$. Similarly, for the higher energy pair of levels with α_e, the level $\alpha_e(\neg)\beta_n(\neg)$ is lower in energy than the level $\alpha_e(\neg)\alpha_n(\ )$. Thus, the final energy ranking is $\beta_e(\ )\alpha_n(\ ) < \beta_e(\ )\beta_n(\neg) << \alpha_e(\neg)\beta_n(\neg) < \alpha_e(\neg)\alpha_n(\ )$.

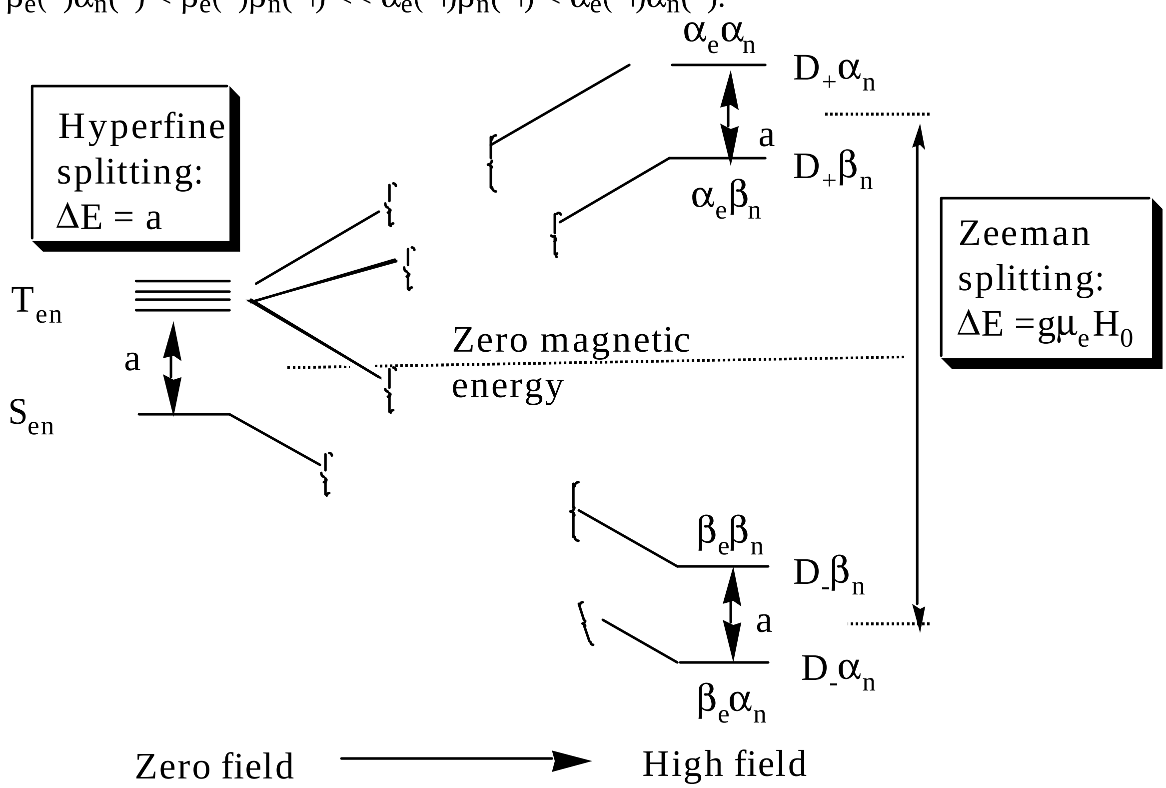

Figure 15. Energy Diagram for the coupling of an electron spin to a nuclear spin 1/2 (e.g., a proton or a ^{13}C nucleus).

Magnetic Energy Diagrams for Two Corrlated Electron Spins and a Third (Nuclear or Electron) Spin. Zero Field.

We now consider two important cases of the coupling of two correlated electron spins (S and T) with a third spin, either that of a third electron or a nucleus of spin 1/2. In zero field the coupling of a S state with a spin 1/2 particle can only lead to one final angular momentum state with a net spin of 1/2 \, i.e, a doublet state, D. The coupling of a T state with a spin 1/2 particle can lead to two possible states: a quartet state, Q, of spin 3/2 \ and and a doublet state, D, 1/2 \. Thus, there are four possible states involved when two correlated electron spins couple with a third spin: S, T, D and Q. As a specific example we consider coupling with a nuclear spin because we wish to emphasize the couplings which cause the important triplet singlet intersystem crossings. Furthermore, the vector model of a nuclear spin coupling is readily extended to other magnetic couplings (spin orbit, spin lattice, etc.) which induce intersystem crossing.

Magnetic Energy Diagrams for Two Corrlated Electron Spins and a Third (Nuclear or Electron) Spin. High Field.

The magnetic energy diagram for two correlated electron spins (Figure 14, right) in a strong field (and absence of electron exchange) consists of two levels at the zero of magentic energy (T and S), one level at lower energy (T_-) and one at higher energy (T_+). Coupling with a nuclear spin of 1/2 will cause a doubling of each level (Figure 16). In the case of T_- and T_+ the levels are split in energy by the hyperfine interaction, a. Since we want to focus on the correlated electron pair, we shall employ the T, S terminology for the electron pair and employ the spin function symbols, $\alpha_n$and β_n to denote the nuclear spin functions. Using the same magnetic energy arguments as above for the T_- pair, the T_-( )α_n( ) level will be lower in energy than T_-( )β_n(¬); for the T_+ pair, the T_+(¬¬)β_n(¬) level will be lower in energy than T_+(¬¬)α_n( ) level. An interesting situation applies to the T_0 and S levels when they are coupled to a nuclear spin: **they are not split in energy**. The reason is that the electron magnetic moment of these levels lies perpendicular to the applied magnetic field direction where as the nuclear magnetic moment lies parallel to the applied magnetic field direction. Thus, the electron and nuclear magnetic moments are perpendicular to each other. Recall that when magentic moments are perpendicular to each other (eq. 10), the magnetic interaction between the moments is zero! Another path to the same conclusion is to note that the magnetic energy in an applied field depends directly on M_S (eq. 11). Since $M_S = 0$ for both S and T_0, the net magnetic energy of couplings of these states in a magnetic field must be equal to zero.

From these considerations the magnetic energy diagram for the coupling of a correlated pair of electrons and a nuclear spin of 1/2 is constructed and shown in Figure 16.

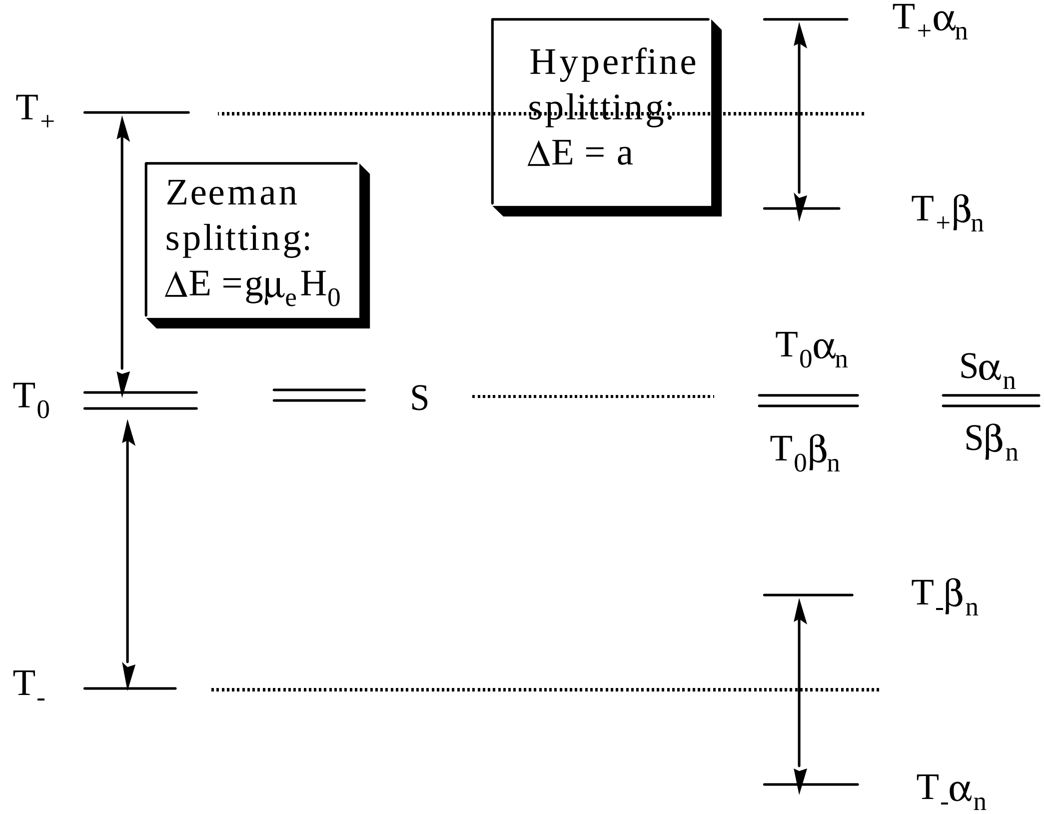

Figure 16. Energy diagram for the interaction of a triplet state and a nuclear spin in a strong magnetic field: left, no hyperfine interaction, right hyperfine interaction turned on.

Magnetic Energy Diagrams Including the Electron Exchange Interaction.

The exchange interaction, J, between two electrons, results in a Coulombic (non-magentic) splitting of the energy of the singlet state from the triplet states. As a result, the energy diagrams shown in Figures 14 and 16 must be modified in the presence of electron exchange. There are four important conditions which are commonly encountered in photochemical systems, two corresponding to zero of low field and two corresponding to high field. The first is the condition for which J = 0 in the presence of a zero (or low) magentic field. Condition I is typical of solvent separated spin correlated geminate pairs and extended biradicals. The second condition is in the presence of zero (or low) magnet field with a finite value of J. Condition II is typical of molecular triplets, spin correlated pairs in a solvent cage and small biradicals. Condition III occurs at high field for values of J which 0 or are comparable to the Zeeman splitting (i.e., $J = 0$ or $J \sim g\mu_e H$) and condition IV occurs for values of J which are much larger than the Zeeman splitting (i.e., $J >> g\mu_e H$). these situations will be analyzed in detail in the following sections with a "case history" example.

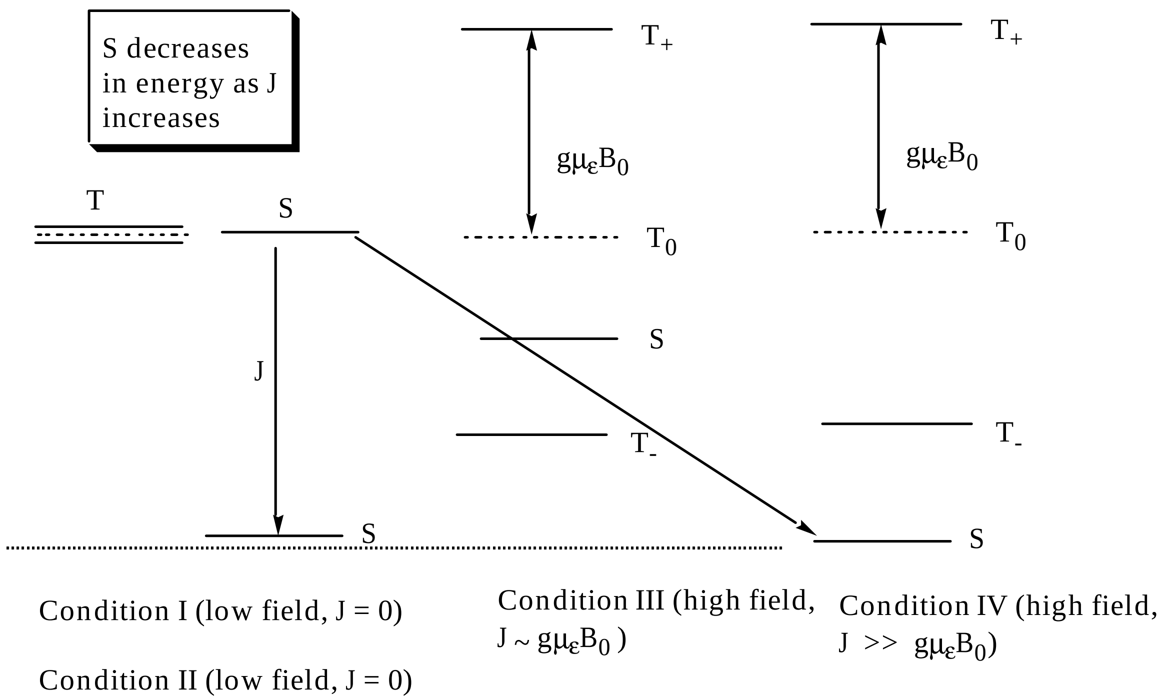

Figure 17. Three important situations of Zeeman splitting and exchange splitting. See text for discusion.

Summary

The magnetic energy diagrams discussed in this section are typical of those encounted in a wide range of photochemical system involving electron spin magnetic resonance (ESR), nuclear magentic resonance (NMR) and intersystem crosssing (ISC). These simple situations capture the critical features required to understand even very complicated situations encountered in practise. We now consider the interactions and couplings which are responsible for ESR, NMR and ISC and presence a concrete example which exemplifies the principles of this chapter.