8. Magnetic Interactions and Magnetic Couplings.

Transitions between the magnetic energy levels discussed in the previous section can be visualized as occuring through the result of magnetic torques exerted on the magnetic moment vectors of an electron spin, or equivalently, as the result of coupling of spin angular momentum to another angular momentum. We shall discuss the magnetic torques as arising from two fundamental magnetic **interactions**: a **dipolar** interaction between magnetic moments and a **contact** interaction between magnetic moments. These arise from some specific source of magnetic moments resulting from the motion of charged particles or spins. The coupling may occur through either a dipolar or contact interaction. In the literature the terms interaction and coupling are used more or less interchangeably. However, we use the term **coupling** to describe the source of the magnetic moment that causes the spin transition.

The vector model allows the dipolar and contact interactions to be visualized in an analogous manner, irrespective of the source of the coupling. In addition, the vector model allows the transitions resulting from the coupling of an electron spin to any magnetic moment to be visualized in an analogous form. These features of the vector model provide a powerful and simplifying tool for discussing magnetic resonance spectroscopy and intersystem crossing through a common conceptual framework.

Couplings of a magnetic field along the z axis.

For example, let us consider the specific example of the intersystem crossing of a T_0 state to a degernate S state or vice-versa (Figure 18, top). On the left and right of the figure the two spins are represented as "tightly" coupled to each other by electron exchange by showing their precessional cones in contactat a common point. For intersystem crossing to occur, the electron exchange coupling must decrease to a value comparable to that of magnetic torques capable of acting on one of the spin vectors, say S_2. This is indicated by showing the spin vectors separated by a line to indicate a "weakening" of the exchange interaction (for example due to separation of the doublet centers in a radical pair or biradical). To cause ISC a coupling is required with a magnetic moment from some source that is capable of interacting with S_2 via a dipolar or contact interaction. As shown the interaction occurs along the z axis and does not cause a reorientation of S_2, i.e., does not "flip" the vector S_2, but rephases S_1 relative to the vector S_1. We may therefore consider the torques as a magnetic field along the z axis which couples spectifically with S_2.

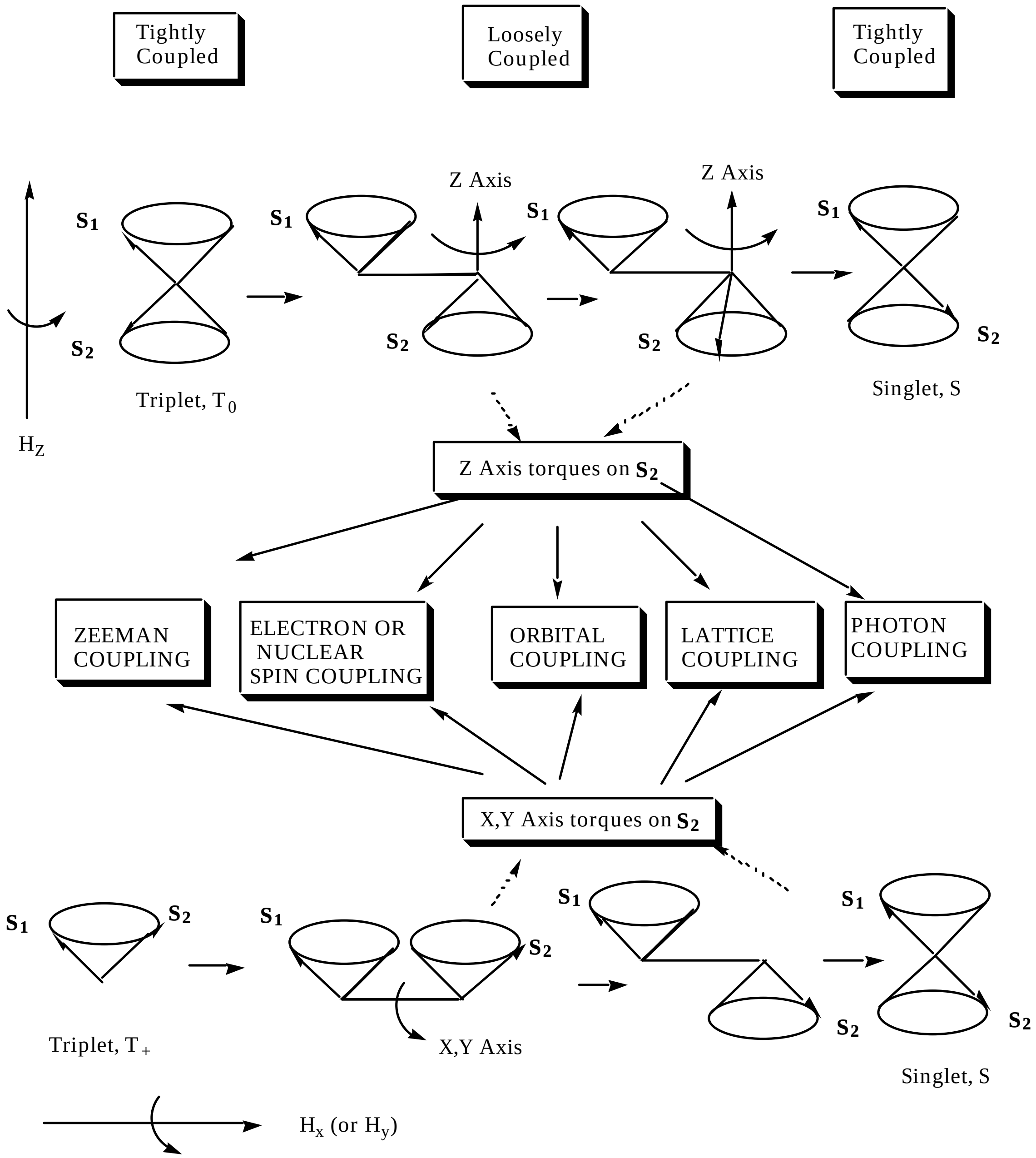

Figure 18. Example of magnetic couplings causing a triplet to singlet (or singlet to triplet transition. The torque on spin S_2 may result from the coupling of the magnetic moment of S_2 with magnetic moments due to any one of a numbers of sources as indicated in the figure.

The situation may be generalized as follows. An electron spin will tend to precess about another electron spin through the exchange interaction or about the magnetic moment produced by some external or internal source. The precessional motion due to exchange must be diminished to a value comparable with or smaller than the magnetic coupling if a transition is to occur. The coupled magnet moment may operate along the z axis or along the x or y axis.

The former coupling produces rephasing of the electron spin and the latter produces spin reorientation.

Couplings of a magnetic field along the x (or y) axis.

The influence of a magnetic field along the x axis is equivalent, by symmetry, to that along the y axis. Thus, the precessional motion of a spin vectror along the x axis is equivalent to precessional motion along the y axis. Therefore, we shall discuss only the x axis, recognizing that the discussion applies also to the y axis. Coupling of a magnetic field along the x or y axis leads to precessional motion about that axis in the same way that coupling to the z axis results in precessional motion about the z axis axis. However, coupling to the z axis does not cause a change in the orientation of the spin, only a change in the precessional frequency. In the case of coupling to the x or y axis, the coupling results in a change in the orientation of the electron spin from α to β (or β to α). As the coupling increases in strength, the precessional frequency increases, leading to a faster frequency of reorientation back and forth between the α and β orientations.

Figure 18 (bottom) shows an examplet of a triplet (T_+) to singlet ISC which results from coupling of the S_2 spin to a magnetic field along the x axis, after it has been decoupled from S_1. The magnetic coupling of S_2 to the x axis causes the spin vector to precess about the x axis. This precessional motion continuously reorients the S_2 spin from the α position to the β position.

In the next section we will develop a vector model for concrete visualization of the coupling responsible for the transitions shown in Figure 18 and spin transitions in general. But first we shall consider briefly (1) the two important magnetic interactions that couple spins to other magnetic moments and (2) the important sources of magnetic moments that can couple to the electron spins and induce transitions.

Dipolar and Contact Magnetic Interactions

A magnetic moment is a magentic dipole, i.e., the magnetic moment gives rise to a magnetic field in its vicinity. Whatever the source of the magnetic moment, the interaction of the field with an electron spin generated may be treated one of two mathematical forms: as a dipole-dipole interaction between the magnetic moment of the spin and the second magnetic moment or as a contact interaction between electron spins. We are interested in the energies associated with each of these interactions. We shall investigate the mathematical forms of the two interactions in order to obtain some intuition concerning the magnitude of the interactions as a function of molecular structure.

Dipole-dipole Interaction

Insight to the nature of the magnetic dipole-dipole interaction is available from consideration of the mathematical formulation of the interaction and its interpretation in terms of the vector model. The beauty of the formulation is that its representation provides an identical basis to consider all forms of dipole-dipole interactions. These may be due to electric dipoles interacting (two electric dipoles, an electric dipole and a nuclear dipole or two nuclear dipoles) or to magnetic dipoles interacting (two electron spins, an electron spin and a nuclear spin, two nuclear spins, a spin and a magnetic field, a spin and an orbital magnetic dipole, etc.).

Classically, the dipole-dipole interaction energy depends on the relative orientation of the magnetic moments (consider two bar magnets). To obtain some concrete insight to the dipolar interaction consider the case for which the two magnetic dipoles, μ_1 and μ_2, are held parallel to one another (this is the case for two interacting magnetic dipoles in a strong magnetic field (Figure 19). We can obtain an intuitive feeling for the nature of the dipole-dipole interaction by considering the terms of the dipole-dipole interaction in eq 19. In general, the strength of the interaction is proportional to several factors: (1) the magnitudes of the individual interacting dipoles; (2) the distance separating the interacting dipoles; (3) the orientation of the dipoles relative to one another; and (4) the "spectral overlap" of resonances that satisfy the conservation of angular momentum and energy. In fact, eq. 19 strictly speaking refers to the interaction of two "point" dipoles (if r is large relative to the dipole length, the dipole may be considered a "point" dipole).

$$\text{Dipole-dipole interaction } \alpha \ [(\mu_1\mu_2)/r^3](3\cos^2\theta - 1)(\text{overlap integral}) \qquad (19)$$

The rate of processes involving dipole-dipole interactions is typically proportional to the **square** of the strength of the dipole-dipole interaction. Thus, the field strength falls off as $1/r^3$ but the rate of a process driven by dipolar interactions falls off as $1/r^6$.

The term involving the $3\cos^2\theta - 1$ (Figure 19) is particularly important because of two of its features: (1) for a fixed value of r and interating magnetic moments, this term causes the interaction energy to be highly dependent on the angle θ that the vector r makes with the z axis and (2) the value of this term averages to zero if all angles are represented, i.e., the average value of $\cos^2\theta$ over all space is $1/3$. A plot of $y = 3\cos^2\theta - 1$ is shown at the bottom of Figure 19. It is seen that the values of y are symmetrical about $\alpha = 90^{o}$. It is interesting to note that for values of $\alpha = 54^{o}$ and 144^{o}, the value of y = 0, i.e., for these particular angles, the dipolar interaction disappears even when the

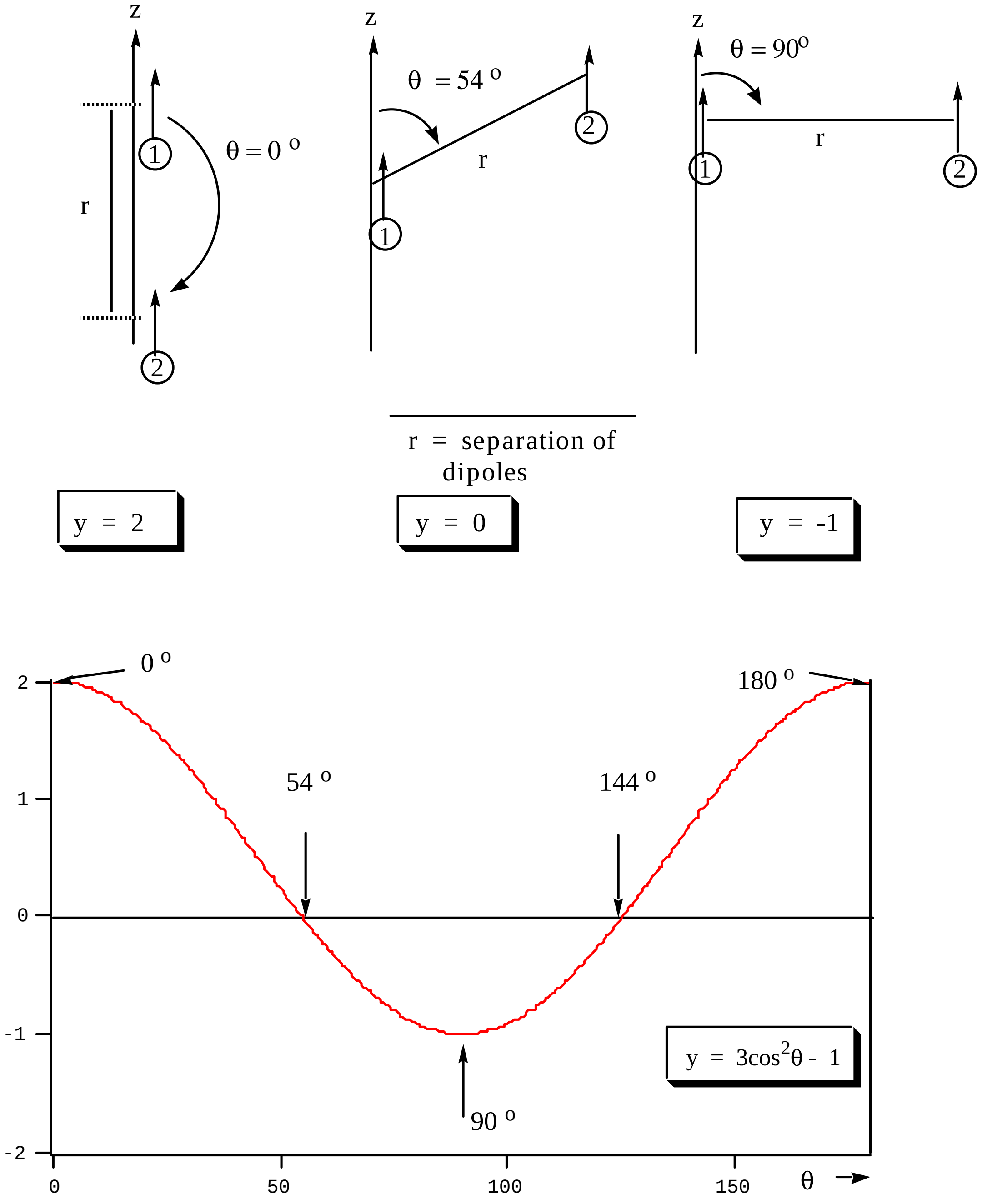

Figure 19. Dipole-dipole interactions of parallel magnetic moments. Top: vector representation of dipoles interacting at a fixed separation, r, and various orientations relative to a z axis. Bottom: plot of the value of $3\cos^2\theta - 1$ as a function of θ.

spins are close in space! This is the familar "magic angle" employed to spin samples in the magnetic field of an NMR spectrometer for removing chemical shifts due to dipolar interactions. It is important to note that certain values of y are positive (magnetic energy raising) and certain values of y are negative (magnetic energy decreasing).

Contact Interaction.

The contact interaction arises when the wave functions for two object overlap in space. The most important cases are (1) the overlap of the electronic wave functions of a spin with the electronic wave function of another spin and (2) the overlap of the electronic wave function of a spin with the electronic wave function of a nucleus. For two electrons in the triplet state the two unpaired electrons are forbidden from "making contact" by the Pauli principle (overlap leads to a triplet singlet splitting, however). However, for an electron and a nucleus, a form of contact is possible and leads to a **hyperfine interaction** between the electron spin and the nuclear spin.

Magnetic interactions can often be well approximated by the dipolar interaction of eq. 19. However, this approximation breaks down when the interacting spins approach and the point dipole approximation is no longer valid. In particular, an electron in an orbital possessing s character has a finite probability of approaching and entering a magnetic nucleus (of, say, a proton). As the electron approaches the nucleus, it brings with it a magnetic moment and discovers that the magnetic field very close to the nucleus is no longer purely dipolar. The interaction of the magnetic moment of the nucleus and the electron spin within the "contact" zone of the nucleus is quite different from the dipolar interaction of the magnetic nucleus and the electron spin when the electron is outside the nucleus. The non-dipolar interaction of an electron spin and the nucleus is termed the **Fermi contact interaction.** For the 1s orbital of a proton, the contact interaction, a, corresponds to an average magnetic field of ca 510 G (ca 1400 x 10^6 Hz) acting on the electron spin. From this simple analysis, we expect that the greater the amount of s character, the larger the value of a, so that there should be a correlation between the value of a and molecular structure. The magnitude of the contact interaction depends on the magnitude of the magnetic moment of the electron, μ_e, and the magnetic moment of the nucleus, μ_p, and the probability of finding the electron at the nucleus, $|\Psi(0)|^2$ (eq. 20).

$$\text{contact interaction } \alpha\, \mu_e \mu_p\, |\Psi(0)|^2 \qquad (20)$$

Figure 19b shows schematically the dipolar interaction between the electron and the nucleus (left) and the contact interaction between the electron and the nucleus (right).

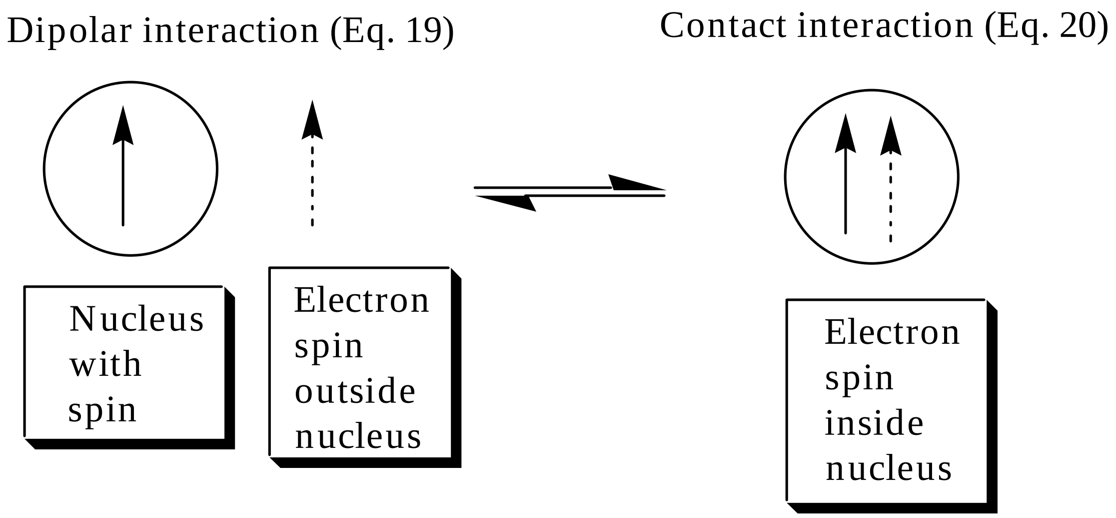

Figure 19b. Schematic representation of the dipolar and contact interactions between electron and nuclear spins responsible for hyperfine coupling.

Because s orbitals are sperically symmetric, the contact interaction does not average to zero as the result of molecular motion, as is the case for the dipolar interaction and that this effect is absent for all other orbitals, because p, d, etc. orbitals possess nodes at the nucleus, so the electron cannot penetrate them. It is also interesting to note that the ideas behind the electron nuclear hyperfine interations are employed to explain the basis of nuclear spin-nuclear spin coupling in NMR.

Couplings of an electron spin with external and internal magnetic fields

The term **external** magnetic coupling refers to applied **laboratory static** or **oscillating** magnetic fields whose strengths and directions can be controlled by the experimenter. The external static fields are those produced by ordinary laboratory magnets. The strengths of the static fields of available laboratory magnets may be varied from 0 gauss (0 Tesla) to over 100,000 gauss (10 Tesla). The external oscillating fields are those produced by electromagnetic radiation. The oscillating fields, in contrast to the static fields, are only effective in interacting with electron spins when the frequency of oscillation is close to, or identical to, the frequency corresponding to the energy gap between two magnetic levels for which a transition is allowed ($\backslash\omega = \Delta E$). The strengths, i.e., the intensities (photons/s), of the external oscillating fields may be varied over many orders of magnitude and the frequency of the external oscillating fields may be varied continuously. However, coupling with the magentic moments only occurs when the energy matching condition is met.

The term **internal** magnetic couplings refers to **microscopic static or oscillating** fields whose strengths and directions are due to the electronic and nuclear structures in the vicinity of the electron spin. Whether these couplings are considered static or oscillating depends on the motion and direction magnetic moments in the vicinity of the electron spin. The strengths and frequencies of oscillations of these microscopic fields may vary over many orders of magnitude and are related to the molecular structure and motion of the molecule containing the electron spin and to the molecular structure and motion of the solvent surrounding the electron spin. The most important microscopic magnetic couplings may be classified in terms of the molecular structure in the vicinity of the electron spin as (1) **electron spin-electron orbit** or **spin-orbit** couplings, by which the electron spin experiences magnetic coupling with its own orbital motion (in general the magnetic couplings due to the orbital motion of other electrons is negligible); (2) **electron spin-nuclear spin** or **hyperfine** couplings, by which the electron spin experiences magnetic coupling resulting from nuclear spins; (3) **electron spin-lattice** couplings, by which the electron spin experiences magnetic coupling resulting from the surrounding molecules in the solvent (termed the "lattice" because the origin of the theory of spin-lattice couplings referred to crystal lattices); (4) **electron spin-electron spin** or **electron exchange** couplings, by which an electron spin experiences magnetic coupling resulting from another electron spin.

Coupling mechanisms

In quantum mechanics, a convenient means of classifying the coupling mechanism of an electron spin with other magnetic moments involves the so-called **spin Hamiltonian**. This Hamiltonian contains all of the important magnetic couplings that will influence the energy and therefore the precessional frequency of the electron spin. These couplings of an electron spin vector, $\mathbf{S_1}$, with other magnetic moments are typically of a certain mathematical form given in the followin discussion. These forms have been simplified for the purposes of clarity and are only of qualitative significance. Each may, however, be readily interpreted in terms of the vector model.

(1) A magnetic coupling of the electron spin to the magnetic moment of an applied laboratory field. As we have noted, this **external** coupling is called the **Zeeman** coupling and its contribution to the spin Hamiltonian is $H_Z = g\mu_e\mathbf{H_z}\cdot\mathbf{S_1}$, , where g is the g factor (dimensionless units) for the electron, μ_e is the magnetic moment of the electron in a molecule, H_0 is the strength of the applied laboratory magnetic field and S_z is the value of the angular momentum in the direction of the applied field.. This coupling has the same form if the source is an internal field applied along the z axis, except that the source of the value of the coupling strenght is that of the internal coupling.

(2) The magnetic coupling of the electron spin to the magnetic moment of another electron spin, $\mathbf{S_2}$. This **internal** coupling is called the **spin-spin dipolar fine** coupling and its contribution to the spin Hamiltonian is $H_{DP} = D_e\mathbf{S_1}\cdot\mathbf{S_2}$. The dipolar interaction, as discussed above, averages to zero if the spin system tumbles rapidly because all dipolar interactions averages to 0 for rapidly tumbling systems.

(3) The magnetic coupling of the electron spin to the magnetic moment of a nuclear spin, **I**. This **internal** coupling is called the **spin-nuclear hyperfine** coupling and its contribution to the spin Hamiltonian is $H_{HF} = a\mathbf{S_1}\cdot\mathbf{I}$. There may be a dipolar contribution or contact interaction leading to hyperfine coupling, although in solution the dipolar interaction usually averages to 0 because of rapid tumbling. The major contribution to a for radicals in solution is usually the Fermi contact interaction, which depends on the amount of s character in the orbital containing the unpaired electron. This interaction is distance independent, since the electron and nucleus are in the same radical.

(4) The magnetic coupling of the electron spin to the magnetic moment due to orbital motion of the electron, **L**. This **internal** coupling is called **spin-orbit** coupling and it contribution to the spin Hamiltonian is $H_{SO} = \zeta\mathbf{S_1}\cdot\mathbf{L}$. This coupling depends on overlap of the orbital involving the unpaired spin with other orbitals and is distance dependent for radical pairs and biradicals, but distance independent for molecular triplets and individual radicals.

We note that each term in the Hamiltonian is of the form $H_B = k\mathbf{S_1}\cdot\mathbf{X}$, where k represents a constant which is a measure of the strengths of the magnetic couplings and $\mathbf{S_1}\cdot\mathbf{X}$ represents the vector coupling of the magnetic moments.

In addition to these interactions, the electron spin can also experience a magnetic coupling to the oscillating magnetic fields resulting from molecular motions of the environment. This coupling is called **spin-lattice coupling** and its contribution to the Hamiltonian is mainly in causing transitions between spin states. The magnetic coupling of the electron spin to the fluctuating magnetic moment due to fluctuating magnetic fields due to random motion of molecules in the vicinity of $\mathbf{S_1}$. The frequency of these fluctuations and the intensity of the fluctuation at any given frequency determine the extent of the coupling. Spin-lattice coupling is not strictly expressable in an analogous form to the other internal couplings. However, to a rough approximation this term can be expressed as $H_{SL} = \mathbf{S_1}\cdot\boldsymbol{\rho}_L$, where $\boldsymbol{\rho}_L$ is the "spectral density" of frequencies in the environment (lattice) that are at the Larmor frequency of $\mathbf{S_1}$ and therefore capable of coupling to the spin.

Finally, the electron spin is influenced by the oscillating magnetic field associated with an electromagnetic field and is termed **spin-photon coupling**. This coupling is responsible for radiative transitions between magnetic states. To a rough approximation this coupling can be expressed as $H_{\backslash\nu} = \mathbf{S_1} \cdot \rho_{\backslash\nu}$

The Electron Exchange Interaction.

The exchange of electrons is a non-classical effect resulting in a splitting of singlet and triplet states as discussed in the previous section as responsible for splitting the singlet state from triplet states. The form of J in a spin Hamiltonian is given by eq. 21. The splitting energy is defined as 2J (a splitting of J above and below the energy corresponding to no exchange). The sign of J may be positive or negative, but in most cases of interest it is negative. In these cases, the singlet state is lower in energy than the triplet.

$$H_{ex} = J\mathbf{S}_1 \cdot \mathbf{S}_2. \tag{21}$$

Although electron exchange is a Coulombic (electrostatic) effect and not a magnetic effect, it influences magnetic couplings in two important ways: (1) the exchange interaction causes the singlet and triplet states to be different in energy; and (2) for the two electrons in a strong exchange situation the spins are tightly electrostatically coupled to each other. When the energy gap, J, is much larger than available magnetic energy, singlet triplet interconversions are said to be "quenched" by J. In addition, since exchange electrostatically correlates the motions of electrons and electron spins, this tight coupling makes it difficult for magnetic couplings to operate on either of the spins and cause intersystem crossing. In this case we view the two spin vectors to be precessing about each other to produce a resultant and it is not longer meaningful to think of the individual spins as components!

The magnitude of J depends on the "contact" region of orbital overlap of the electron spins. This overlap region of two orbitals is usually well approximated as an exponential function such as eq. 22, where J_0 is a parameter which depends on the orbitals and R is the separation of the orbitals in space.

$$J = J_0 e^{-R} \tag{22}$$

Vector Representation of Coupling.

Although there are many different magnetic couplings that can influence the energy levels associated with an electron spin and its transitions, **in each case the specific case of interest can be analyzed in terms of the vector model and the cylindrical symmetry of a coordinate system for which the z axis is the symmetry axis of the cylinder.** In this coordinate system, magnetic interactions along the z axis are effectively **static** and magnetic interactions along the x and y axes are effectively **oscillating.** This means that the magnetic field in the z direction (termed H_Z) is static and the magnetic field in the x or y direction (termed H_x or $H_{y)}$ is oscillating.

The essence of understanding the transitions between magnetic states is relating molecular structure and dynamics to the magnitudes of H_Z and H_x (H_y), and to the frequency of oscillation of H_x (H_y). We will now attempt to relate the external and internal magnetic interactions operating on the electron spin to molecular structure.