and spins may be app ful for understanding the qualitative aspects of organic photochemistry. The electronic wave function and the energies of orbital configurations and associated states have been visualized in terms of the distribution of one-electron wave functions, ϕ_i, in space (i.e., MOs). The vibrational wave function (χ) has been visualized in terms of a PE curve with quantized vibrational levels whose energies depend on the quantum number, v. Upon these quantized energy levels, we picture the form of the wave function as the representative point moves along the PE curve. Chapter 3 uses this quantum intuition to examine how vibrational wave functions influence the rates of transitions between the vibrational levels of different electronic states. We have one wave function left to visualize, namely, the electron spin wave function, S. In the following sections, we will see that our quantum intuition for the energetic characteristics of the spin wave function will come from the visualization of classical vectors in space.

2.22 Electron Spin: A Model for Visualizing Spin Wave Functions

Electron spins play an important role in many photochemical reactions (e.g., Scheme 1.3). Consequently, in addition to visualizing the orbital nature of electrons and vibrating nuclei, we also need to visualize the nature of the electron's spin wave function, **S**, in order to determine the expectation values for important quantities, such as the energies of the spin quantum system and the ranking of the relative energies of spin states in a magnetic field. In Chapter 3, we use our model of **S** to develop an understanding of the mechanisms of intersystem crossing (electron spin change) transitions between singlet states (S_n) and triplet states (T_n), and vice versa. Since electron spin is generally covered only briefly, if at all, in elementary chemistry texts, we develop a relatively detailed model of the electron spin wave function (**S**) that is in the pictorial spirit of the electronic orbital model, Ψ_0, and the harmonic oscillator model for the vibrational wave function, χ. Our model[7] of electron spin is based on the properties of classical *vectors* and should provide a great deal of quantum intuition about the properties of the spin wave function (**S**). The language of the vector model for electron spin is readily transferable for the description of structures that are probably more familiar, namely, nuclear spins, the key objects of interest for nuclear magnetic resonance (NMR) spectroscopy.

In quantum mechanics, spin is a manifestation of an unremovable property of electrons that is at the same fundamental level as the electron's mass and charge. *Spin corresponds to the inherent angular momentum of an electron.* As we have done previously for orbiting electrons and vibrating atoms, we develop a quantum mechanical picture of electron spin angular momentum by first appealing to a classical model of angular momentum and then modifying this model with the appropriate quantum mechanical and wave characteristics. An important connection between an electron's spin and its magnetic moment resulting from the electron's angular momentum provide a way to rank the relative energies of spin states and to thereby produce a state energy diagram for electron spins.

The two most important classes of classical angular momentum involve (1) the circular "spin" motion of a point on the surface of a rotating sphere (or a rotating cylinder) about a defined axis (arbitrarily called the z-axis), and (2) the circular "orbital" motion of a particle rotating at a fixed distance from the center of a circle that contains an axis (arbitrarily called the z-axis) perpendicular to the plane of the circle. We begin to describe the electron spin by considering the angular momentum of a rotating sphere (case 1), then discuss the angular momentum of a rotating particle (case 2) in Section 2.31.

We can use the classical model of the angular momentum of a rotating sphere as a concrete physical model to describe the electron spin. Although electron spin, like electron exchange, is fundamentally a quantum mechanical phenomenon that has no classical analogue, chemists nevertheless accept the convenient fiction that electron spin is the angular momentum arising from the electron behaving like a negatively charged sphere that rotates without friction about an axis. Remarkably, *this concrete physical model allows chemists to visualize most of the critical quantum mechanical properties of electron spin.* In particular, *this model makes it possible to understand why an electron possesses not only a spin but also a magnetic moment, which is expected of a charged particle that is spinning.* The model of a magnetic moment, in turn, allows chemists to consider the energies of two interacting spins through their magnetic moments.

If we take a concrete physical model of an electron as a sphere of negative electricity, the *spin* of an electron is the angular momentum resulting from the electron's spin motion about the z-axis. Although a classical spinning electron would possess a continuous range of the angular momentum values, depending on the velocity and direction of its spinning motion, quantum mechanics demands that *electron spin has a fixed and fundamental characteristic value of exactly* $\hbar/2$. Recall that $\hbar$ is a fundamental quantity of angular momentum and is equal to Planck's constant (h), the fundamental quantum mechanical unit of angular momentum, divided by 2π (a characteristic mathematical quantity that occurs when you are dealing with circular motion). The value of the electron's spin is $\hbar/2$, whether it is a "free" electron that is in interstellar space and is unassociated with any nucleus (i.e., not bound to any positive nucleus), or whether the electron is associated with a nucleus in an atom, a molecule, an electronically excited state, or a free radical. Furthermore, the spin angular momentum of an electron is *always* the same, *exactly* $\hbar/2$, regardless of the orbital (e.g., n, π, or π^*) that the electron happens to occupy. Thus, an electron in the n orbital of an n, π^* state has the same spin as the electron in a π^* orbital of an n, π^* state: both have a spin of $\hbar/2$. If two electrons occupy the same orbital, they both still possess a spin of $\hbar/2$; however, because the two spins must be spin paired to satisfy the Pauli exclusion principle, the angular momentum of the two spins cancel each other for a net angular momentum of 0 and a net spin of 0. (*Note: For the remainder of the text, when dealing with spin,* **S**, *the units of* $\hbar$ *will be assumed and may not be shown explicitly except when required for clarity.*)

Recall from Section 2.8 that electronically excited states (*R) that possess orbital *configurations* consisting of two half-filled orbitals may exist with different spin configurations of the orbitally unpaired electrons (i.e., a singlet-spin or a triplet-spin configuration). For a $(\mathrm{HO})^1(\mathrm{LU})^1$ electron configuration, for example, there exists an S_1 state in which the electron spins are "antiparallel" (↑↓), and for which there is no net spin (i.e., one electron spin cancels the other). There is also a T_1 state in which the electron spins are "parallel" (↑↑), for which there is a net spin of $1\hbar$ (i.e., each electron spin contributes $\hbar/2$ to the total spin of the state). In the following sections, we explain how to visualize the antiparallel and parallel configurations of two electron spins *by appealing to the classical vectorial properties of an object executing a spinning motion about an axis, such as a top or a gyroscope*. We review the fundamental classical properties of vectors that are important for an understanding of electron spin and then describe the quantum mechanics of spin in terms of this vector description.

Since we are interested in the relative energies associated with different spin configurations and states, we also describe the interactions between electron spins as being analogous to those between *spin magnetic moments* (given the symbol μ), which we directly relate to the *spin angular momentum* (**S**). The idea behind this strategy is that we can build a classical intuition for the energy of interactions of two magnets and then relate that energy to the interactions of two electron spins. For simplicity, we use the same symbol (**S**) to describe the spin wave function and the associated quantity, the spin angular momentum. In the case of the spin angular momentum, the unit $\hbar$ is assumed.

2.23 A Vector Model of Electron Spin

Physical quantities are classified as *scalars* if they can be completely described by a magnitude (i.e., a single number and a unit). Examples of scalar quantities are energy, mass, volume, time, wavelength, temperature, and length. Physical quantities that require both a magnitude and a *direction* in order to be fully defined, on the other hand, are called *vectors*. Examples of vector quantities are velocity, electric dipoles, angular momentum, magnetic fields, and magnetic dipoles. If required by the context, we represent *scalar* quantities in *italics* and **vector** quantities in **boldface.**

Spin angular momentum[7] is a vector quantity (as is any form of angular momentum) and is represented by the boldface symbol **S**. The *magnitude* of the spin angular momentum is a scalar quantity and is represented by the italicized symbol, S. The scalar S is mathematically equal to the absolute value of the vector **S**; that is, $S = |\mathbf{S}|$. The spin quantum number is a pure number (no units) and is represented by the roman symbol, S. The parameter S is the symbol for the *total* spin quantum number of a collection of two or more coupled spins (the most common in organic photochemistry being collections of two, three, or four spins), and the symbol s is to be used for the quantum number of a single spin. For example, an electron possessing a spin quantum number $\mathrm{s} = 1/2$ (pure number) is described by a spin vector **S**, which is the symbol for the mathematical representation of the spin angular momentum of the electron, $\mathbf{S} = \hbar/2$ (vector). In experimental measurements, the angular momentum along the z-axis, $\mathbf{S}_z$, is measured. The value (length) of the spin angular momentum on the arbitrary z-axis is $\mathrm{S}_z = |\mathbf{S}_z|$. The uppercase letter "es" (S) is used for a number of representations in organic photochemistry, including S_n, which symbolizes the singlet states of molecules. The meaning, though, should be clear from the context of the discussion for each case.

2.24 Important Properties of Vectors

In this section we review briefly some properties of vectors that are used repeatedly to describe the properties of electron spin and the interactions of electron spins. Vectors are conveniently represented by an arrow. The arrowhead (the "head") of a vector indicates its direction relative to a reference axis (conventionally designated as the Cartesian z-axis), and the length of the arrow represents the magnitude of the physical quantity represented by that vector. The orientation of the vector in space is defined in terms of the angle (θ) that the vector makes with the z-axis. Interacting vectors must all relate to the same z-axis system. *If the vectors do not interact, each will have its own arbitrary axis system; when they do interact, a single arbitrary z-axis must be used to describe all vectors.* Thus, for two uncoupled spins the vectors representing each spin can be oriented to any arbitrary z-axis; whereas for two spins that are coupled by some interaction (e.g., electron exchange or magnetic moments), each spin must possess a well-defined orientation relative to each other and to the reference z-axis.

2.25 Vector Representation of Electron Spin

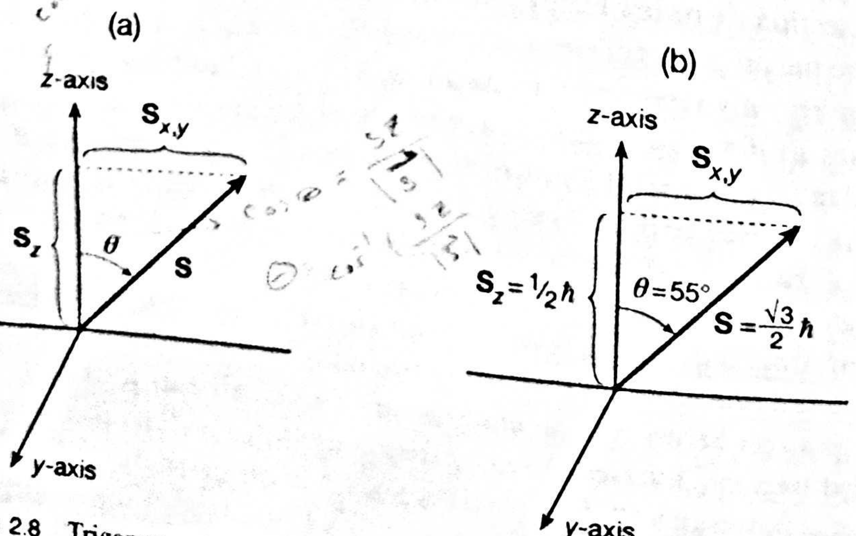
In this section we consider some important properties of all vectors, with a vector representation of the spin angular momentum **S** as a concrete exemplar. Figure 2.8 summarizes the trigonometric relationships of a spin vector, **S**, that makes an angle θ with the z-axis. The important vectorial properties are (1) the spin vector **S** possesses a component $\mathbf{S}_z$ on the z-axis; (2) the spin vector **S** possesses a component $\mathbf{S}_{x,y}$ in the x–y plane; and (3) the magnitude of the component $\mathbf{S}_z$ on the z-axis is related to the magnitude of the total spin, **S**, by the trigonometric relationship given in Eq. 2.28, where $|\mathbf{S}_z|$ is the magnitude (the absolute value) of the vector on the z-axis and $|\mathbf{S}|$ is the absolute magnitude of the spin vector.

$$\boxed{\cos\theta = |\mathbf{S}_z|/|\mathbf{S}|} \tag{2.28}$$

According to the uncertainty principle, the precise value of the vector **S** cannot be precisely measured in any experiment. There is a way, however, to circumvent the uncertainty principle. *The uncertainty principle allows one component* ($\mathbf{S}_z$ *or* $\mathbf{S}_{x,y}$) *of the spin vector to be specified exactly (typically the z-component is the component selected) if the other components are completely unknown.* In this way, if the position of **S** in the x–y plane (i.e., $\mathbf{S}_{x,y}$, called the azimuth of the vector **S**) is completely undetermined, then the magnitude of $\mathbf{S}_z$ on the z-axis can be determined precisely in an experiment. This finding explains why only the z-axis is employed and specified when discussing the energies of interacting spin states, which are, by convention, defined as the value of **S** on the z-axis.

Now, let us consider the magnitude of an arbitrary spin vector **S** and its value on the z-axis, $\mathbf{S}_z$. Recall from quantum mechanics that it is the square of the wave function, Ψ^2, and not Ψ, that corresponds to the magnitude of physical quantities. Thus, it is S^2 that is the starting point for the discussion of the measurement of the magnitude of electron spin. From the laws of quantum mechanics, the possible values of S^2 are

component



$\cos\theta = \frac{S_z}{|S|}$

$\theta = \cos^{-1}\left(\frac{S_z}{|S|}\right)$

Figure 2.8 Trigonometric relationships between any spin vector, **S**, and its orientation θ and value, $\mathbf{S}_z$, with respect to the z-axis (left).

given by applying the allowed spin quantum numbers, S (i.e., the eigenvalues from the solution of the appropriate wave equation). The allowed values of S^2 are limited to those given by Eq. 2.29a. Thus, for a given value of S, there is an associated square of the spin angular momentum (S^2) that can be computed from Eq. 2.29a. The values of S are given by Eq. 2.29b.

$$\mathbf{S}^2 = [S(S+1)] \tag{2.29a}$$

$$\mathbf{S} = [S(S+1)]^{1/2} \tag{2.29b}$$

As a concrete example, consider the spin quantum number of a single electron: S = 1/2 (S is a pure number). According to Eq. 2.29a, the value of the magnitude of $\mathbf{S}^2$ (in units of $\hbar$) is $1/2(1/2+1) = 3/4$, and according to Eq. 2.29b, the value of $\mathbf{S}$ for a single electron is given by $[1/2(3/2)]^{1/2} = (3/4)^{1/2}$. Electrons possess the same value of the spin angular momentum, exactly 1/2, as other spin 1/2 particles, such as a ^{1}H or a ^{13}C nucleus, so the vector representation of the electron spin as an exemplar can also be applied to discussions of nuclear spins. Although the magnitude of the spin is identical for electrons and all nuclei of spin 1/2, the magnitude of the magnetic moments associated with electron and nuclear spin are very different (see Section 2.33).

Figure 2.8 shows the vector model for the case of S = 1/2. Although the value of the vector $\mathbf{S} = (3/4)^{1/2}$, the value of $\mathbf{S}_z$ must equal 1/2 on the *z*-axis. As a result, from Eq. 2.28, the value of θ must be 55°.

Now, we consider the vector representation of *quantized* electron spin in some detail for the two most important cases in photochemistry, namely, a single spin and two interacting spins that are coupled and therefore must behave as parallel (↑↑) or antiparallel (↑↓) spins. The latter description is essentially two-dimensional (2D), so for the three-dimensional (3D) representation of interacting spins, these two cases require a modification and reinterpretation of the terms "parallel" and "antiparallel."

2.26 Spin Multiplicities: Allowed Orientations of Electron Spins

The allowed values of the electron spin (or coupled electron spins) are given by Eq. 2.29, and the corresponding values of the electron spin on the *z*-axis are given by Eq. 2.28; that is, $\mathbf{S} = [S(S+1)]^{1/2}$ and $|\mathbf{S}|\cos\theta = |\mathbf{S}_z|$. The allowed values for the quantum number for electron spin (S) are 0, 1/2, 1, 3/2, 2, and so on, so the values of $|\mathbf{S}_z|$ are $0\hbar, \hbar/2, \hbar, 3\hbar/2, 2\hbar$, and so on. A remarkable principle of quantum mechanics is that angular momentum can take up a number of quantized orientations in space. It turns out that this spatial orientation of the angular momentum causes a very important spatial orientation of the magnetic moment associated with an electron spin in a magnetic field.

Now, we need to expand our model of electron spin to take into account the fact that quantum mechanics only allows certain orientations of the electron spin vector in space in a magnetic field. The *multiplicity* (M) of a given state of spin angular momentum is the *number* of quantum mechanically allowed orientations of a spin of magnitude S in a magnetic field. The multiplicity of a spin state is computed from S, the spin angular momentum quantum number:

Spin multiplicity = M = 2S + 1 = number of allowed spin orientations in space

Each allowed orientation is assigned a spin orientation quantum number, M_S, where the subscripted S is related to the quantum number for the orientation of the spin and the value of the projection for the spin on the *z*-axis. The value of the spin remains the same for a given multiplicity, but the value of the spin projection can take on the values of M_S.

The multiplicities for a single electron and for two coupled electrons are of greatest interest in organic photochemistry. For a single electron, the spin quantum number is 1/2, so $M = [2(1/2) + 1] = 2$. Since M = 2, there are *two* and *only two* allowed orientations of the electron spin vector in a magnetic field, corresponding to $M_S = +1/2$ and $M_S = -1/2$. These two allowed orientations of the electron spin are shown in Fig. 2.9. One of the orientations has a value of $S_z = +1/2$ (referred to as the α orientation of a single electron spin), and the other orientation has the value of $S_z = -1/2$ (referred to as the β orientation of a single electron spin). Because there are two and only two allowed orientations of a single electron in a magnetic field, the S = 1/2 state is called a *doublet* state and is given the symbol D. The doublet state corresponds to the spin state of a radical that possesses a single unpaired electron. Once again we have redundancy in the use of a symbol. The symbol D that is used for a doublet spin state is also used to denote a reactive diradical intermediate I(D) (i.e., a radical pair, or a biradical) that possesses two half-filled orbitals, each orbital being occupied by a single electron. [Multiple uses of the same symbol for different entities are an unavoidable fact of the scientific literature. You must be sure of the context when a symbol that refers to different entities is used. In this text we try to be careful to indicate such contexts.]

Figure 2.9 shows the angular momentum vector pointing perpendicular to the plane of rotation of a spinning spherical electron, a feature based on analogy to the classical angular momentum of a spinning sphere. Although a specific arbitrary orientation

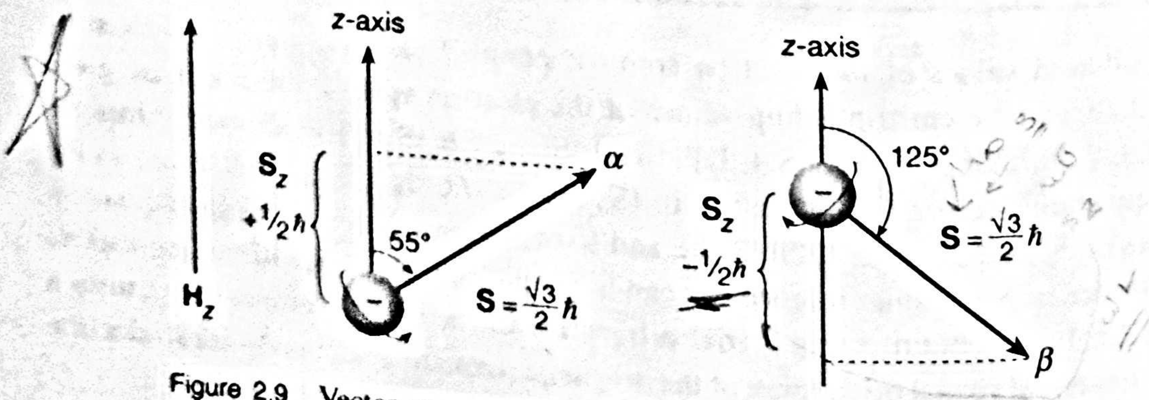


Figure 2.9 Vector representation of a spin −1/2 particle (e.g., an electron, a proton, or a ^{13}C nucleus). The symbol α refers to the spin wave function of a spin with $M_S = +1/2$, and the symbol β refers to the spin wave function of a spin with $M_S = -1/2$.

of the spin 1/2 vector is shown in Fig. 2.9, the vector may lie anywhere in a cone of possible orientations (see Section 2.28) that make an angle θ of either 55° (α-orientation) or 125° (β-orientation) with the z-axis.

2.27 Vector Model of Two Coupled Electron Spins: Singlet and Triplet States[7]

Perhaps the most important coupled spin systems in organic photochemistry correspond to those situations involving the coupling of two electron spins, each of which occupies a separate orbital. The quantum mechanical rule for the possible couplings of two 1/2 spins of the two orbitally uncoupled electrons is as follows: The final *total* spin angular momentum (in units of $\hbar$) of a two-spin system is either 0 or 1. For total spin $S = 0$, the multiplicity of the state is $M = (2S + 1) = 1$, and for total spin $S = 1$, the multiplicity of the state is $M = (2S + 1) = 3$. We are now in a position to understand the origin of the terms "singlet state" and "triplet state," which refer to the multiplicity of a state based on its spin and which has its origin in the study of the number of spin states of molecules in a magnetic field. Recall from Scheme 1.3 that both $^*R$ and I(D) can be either singlet or triplet states.

Now, we use the vector model of spin to visualize the singlet and triplet states that result from the coupling of two electron spins occupying separate orbitals. The singlet state results from the coupling of two electron spins in such a way that the spin vectors are antiparallel (↑↓) and collinear; the angle between the heads of the vectors is 180° (Fig. 2.10a) for a singlet state. Such an orientation of vectors results in the *exact cancellation of the net spin angular momentum of each of the spin vectors*, so the net spin vector length $|S|$ is 0. This means that the net spin of the singlet state, as well as its projection on the z-axis, is exactly equal to $0\,\hbar$ (Fig. 2.10a). Although a specific arbitrary orientation of the two spin 1/2 vectors is shown in Fig. 2.10a, there is no preferred orientation in the cone of possible orientations (see Section 2.28) at all, since all orientations of the two spins that are 180° apart yield zero-spin angular momentum.

We conclude, therefore, that the singlet state has no net spin because of vectorial cancellation of the spin momentum of the two spins, and no preferred orientation of the component spin vectors in a magnetic field, even though the singlet state is composed of two electrons, each of which possesses a spin of 1/2 and each of which possesses a magnetic moment. This situation is analogous to the cancellation of two bond dipole moments in a linear molecule, such as $O{=}C{=}O$, which has two polar bonds but no net dipole moment. All electrons that are paired in an orbital are required by the Pauli exclusion principle to be in a singlet state, and therefore will have their spin vectors oriented as shown in Fig. 2.10a. Since nearly all organic molecules possess two electrons in each orbital in their ground states, organic molecules typically possess singlet ground states.

The triplet state ($S = 1$) also results from the coupling of two electron spins, but this time the coupling is such that the spin vectors make an angle of ~70° between the two spin 1/2 vectors (Fig. 2.10b). The angle of 70° is required by trigonometry

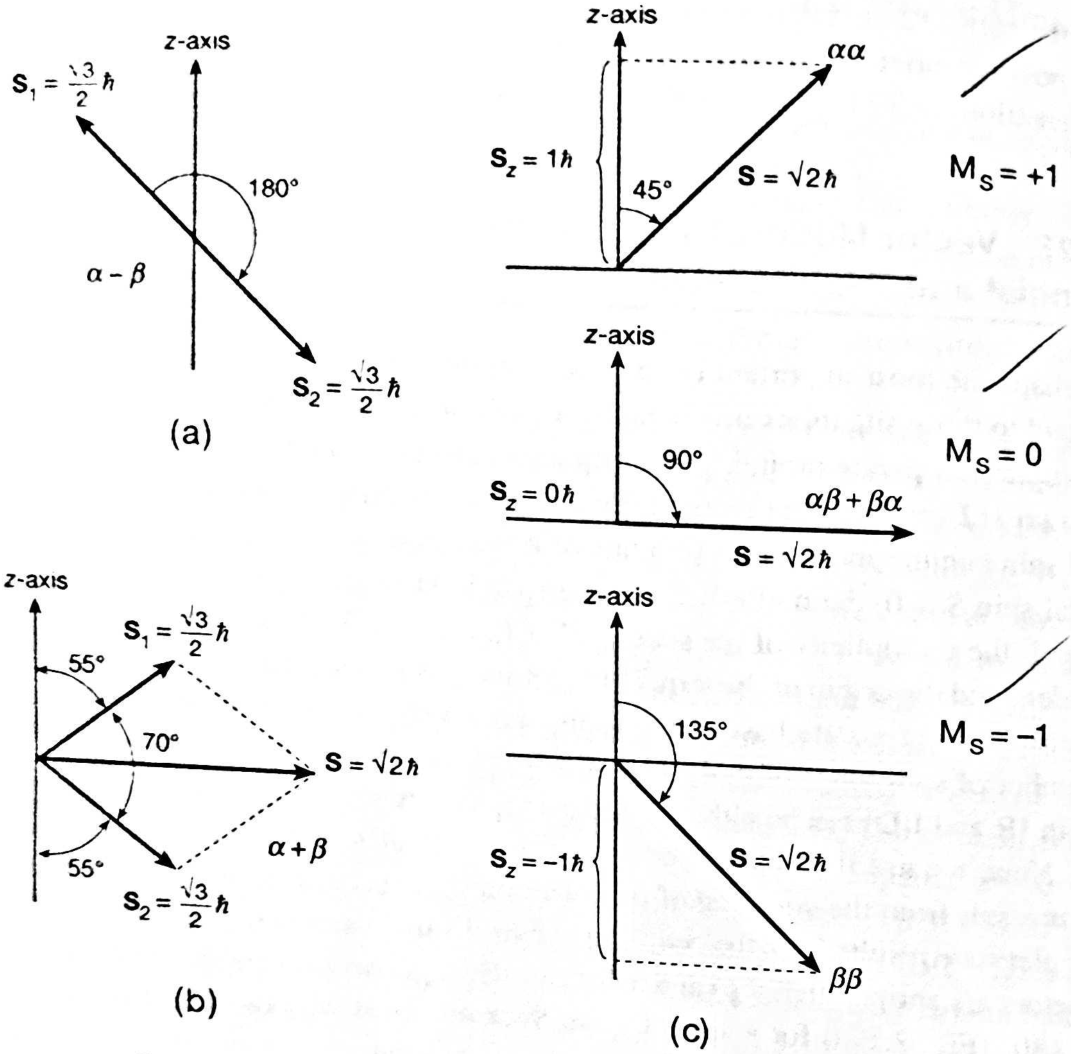


Figure 2.10 Subtraction and addition of two spin 1/2 particles.

so that the two spin 1/2 vectors will add vectorially to produce a single spin vector, $S = (2)^{1/2}$. A vector of this length produces a value of $S_z = 1$ on the z-axis when the vector is at an angle of 45° relative to the z-axis (Fig. 2.10c). Since M = 3 for an S = 1 state, there are three values for the quantum numbers for the orientation of the spin on the z-axis of an S = 1 system: $S_z = +\hbar$, $S_z = 0$, or $S_z = -\hbar$ (Fig. 2.10c). These three spin states are assigned the quantum numbers $M_S = +1$, $M_S = 0$, and $M_S = -1$, respectively, and are called the sublevels of a triplet state, T. Thus, the origin of the term "triplet state" is based on the quantum mechanical requirement that an S = 1 spin state must possess three energy sublevels corresponding to the three quantum numbers, $M_S = +1$, $M_S = 0$, and $M_S = -1$, when the spin system is placed in a magnetic field. From trigonometry (Eq. 2.28), the angle θ that the vector **S** for an S = 1 spin state must make with the z-axis to achieve the values of $+\hbar$, 0, $\hbar$, or $-\hbar$ is 45°, 90°, or 135°, respectively (Fig. 2.10c). The spin vectors **S** for $M_S = +1$ and $M_S = -1$ are shown as lying in some arbitrary position in the possible cone of orientations. For $M_S = 0$, the spin vector **S** is shown as a *circle* of possible orientations lying in the x–y plane. The possible cone of orientations that the spin vector may assume is discussed in Section 2.28.

We can now see how the vector model and trigonometry provide a very convenient and vivid means of visualizing singlet and triplet spin states based on the rules of quantum mechanics. For $\mathbf{S} = 0$, two coupled spins are collinear and oriented at 180° relative to one another and exactly cancel each other's spin angular momentum. As a result, there is no net spin anywhere in space; only *one* spin state, a *singlet* state (quantum number $M_S = 0$) results, and this state remains a singlet state in a magnetic field because it lacks a magnetic moment. For $\mathbf{S} = 1$, the coupled spins add to one another in a manner (with a relative angle in the cone of orientation of 70°) to form a vector of length $|\mathbf{S}| = 2^{1/2}$. The coupled spins have a fixed value of $(2^{1/2})\hbar$, but can possess one of three allowed orientations in a magnetic field (Fig. 2.10), corresponding to the quantum numbers $M_S = +1$, $M_S = 0$, and $M_S = -1$.

Let the spin wave function α represent an "up" spin ($M_S = +1/2$), and the spin wave function β that represents a "down" spin ($M_S = -1/2$). *Both* the singlet state (Fig. 2.10a) and the triplet component with $M_S = 0$ possess one α spin and one β spin (Fig. 2.10c, middle). Thus, a simple 2D up–down "arrow" notation (↑↓) would make the singlet state ($M_S = 0$) and the $M_S = 0$ level of the triplet state appear to be identical in terms of spin characteristics, even though the singlet has no net spin and the $M_S = 0$ level of the triplet possesses a net spin of $\hbar$. This distinction between the $M_S = 0$ for the singlet and triplet is made only in a vector representation relative to the z-axis (Fig. 2.10) or, even better, in the 3D representation in Section 2.28.

In closing this section, we comment on an interesting mathematical modification of our α and β label of spins that must be made to provide proper wave functions for both the singlet state and the $M_S = 0$ level of the triplet state. This modification is imposed by the Pauli exclusion principle and electron exchange (Section 2.9), which states that all of the properties of exchanged electrons must be identical. Suppose, for example, that we labeled the wave functions of the two states (i.e., the singlet and triplet with $M_S = 0$) with one spin up and one spin down as either $\alpha_1\beta_2$ or $\beta_1\alpha_2$ (where the subscripts refer to electrons 1 and 2). However, such an assignment would imply that we could distinguish electron 1 and electron 2 as being in a specific and differentiable spin state. *This distinction violates the Pauli exclusion principle, which states that two electrons must be indistinguishable upon exchange.* Quantum mechanics allows that an acceptable modification of the spin wave function for the singlet state is $\mathbf{S} = (\alpha_1\beta_2 - \beta_1\alpha_2)$, where the minus sign signifies that the two spins are exactly 180° *out of phase* [a mathematical "normalization" factor of $(1/2)^{1/2}$ is of no interest for our qualitative discussion and is therefore ignored]. The spin wave function for the triplet state ($M_S = 0$) is $\mathbf{S} = (\alpha_1\beta_2 + \beta_1\alpha_2)$, where the plus sign signifies that the two spins are *in phase* and couple to generate a net spin of 1. Thus, we will let the singlet state (S) be represented by the symbols $\alpha\beta - \beta\alpha$, and the triplet state (T_0, where the subscript 0 refers to the spin quantum number $M_S = 0$) will be represented by the symbols $\alpha\beta + \beta\alpha$. Both of these states have the same quantum number ($M_S = 0$) but possess different wave functions and correspond to different vectorial orientations of the α and β spins. We can think of the minus sign in the singlet function $\alpha\beta - \beta\alpha$ as representing the "out-of-phase" character of the two spin vectors, causing the spin angular momentum of the individual spin vectors to exactly cancel (Fig. 2.10a), and the plus sign in the triplet wave function as representing the "in-phase" character, causing the individual spin vectors to add together and reinforce each other (Fig. 2.10b).

There is no Pauli restriction with respect to the interchange of spin if we label the wave function for the triplet state for which $M_S = +1$ as $T_+(\alpha\alpha)$ or if we label the triplet state for which $M_S = -1$ as $T_-(\beta\beta)$. For the state with $M_S = +1$, the spin function $\alpha\alpha$ is acceptable because both electrons possess the same orientation, so they are indistinguishable upon exchange. The same holds for the $M_S = -1$ state, for which the spin function $\beta\beta$ is acceptable according to the Pauli exclusion principle.

2.28 The Uncertainty Principle and Cones of Possible Orientations for Electron Spin

So far, we have discussed the spin vectors in terms of a 2D representation relative to a z-axis. Now, we proceed to a more realistic model of the spin vector in 3D relative to a z-axis. In 3D, the directional angle of **S** in the x–y plane is called the azimuthal angle. According to the uncertainty principle of quantum mechanics,[10] *if the value of S_z on the z-axis is measured precisely, then the azimuthal angle's position in space will be completely indeterminable.* Thus, only S_z can be measured precisely if we accept that there is no information at all that can be obtained experimentally concerning the azimuthal angle of **S**. In terms of the vector model, this means that an α spin, which makes a specific angle of 55° with the z-axis and a value of $S_z = 1/2$, must project to an unknown azimuthal angle in the x–y plane for any measurement of S_z (Fig. 2.9). Thus, there is an infinite set of positions that the spin vector can assume in space making an angle of 55° with the z-axis, any one of which could correspond to the actual position of the spin vector. *This set of possible positions constitutes a cone such that, whatever the specific position the spin vector takes on the cone, the angle of the vector with the z-axis and the projection of the vector on the z-axis are always the same, namely, 55° and $+\hbar/2$; however, the x and y components of the vector are completely undetermined in any experiment that measures S_z precisely.* Such a cone is called the *cone of possible orientations of an α spin ($M_S = +1/2$)*. Fig. 2.11 (left, top) shows the cone of possible orientations of an α spin with one possible arbitrary orientation being shown explicitly. Although we can be sure that an α spin will lie somewhere in this cone, we cannot specify at all where it is located in the cone. A corresponding cone of possible orientations (Fig. 2.11, left, middle) also exists for a β spin ($M_S = -1$), with one possible arbitrary orientation being shown explicitly.

In the absence of an interacting magnetic field, the vector representing the spin angular momentum is imagined as being stationary and "resting" somewhere in the cone of possible orientations. If a coupling magnetic field is applied (e.g., a static applied laboratory field, an oscillating applied laboratory field, or fields due to the magnetic moments generated by the motion of spins in the environment, etc.), the coupling will cause the spin vector to sweep around the cone with the direction of the coupling field serving as the z-axis. This sweeping motion about the cone is called *spin precession*. We discuss spin precession in the cone of possible orientations in Chapter 3 when we consider transitions between magnetic states. Here we only describe the "static" magnetic states and the energies associated with them.

2 possible orientation

S = ½

S = 1 there 3 possible orientation

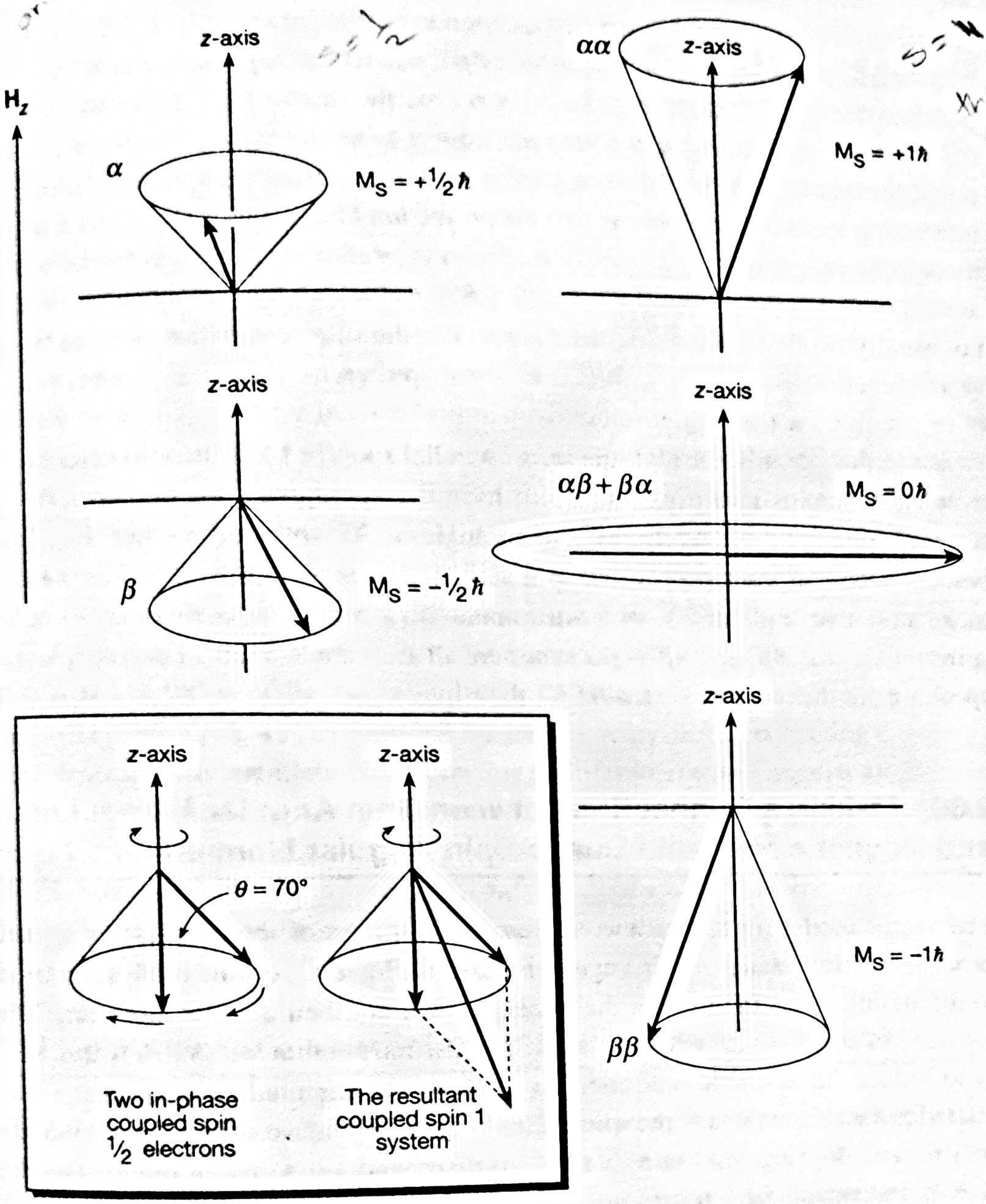


Figure 2.11 Cones of possible orientation for a spin 1/2 (left) and a spin 1 (right) system of angular momentum. An arbitrary position of the spin vectors is shown for each of the possible cones.

2.29 Cones of Possible Orientations for Two Coupled 1/2 Spins: Singlet and Triplet Cones of Orientation as a Basis for Visualizing the Interconversion of Spin States

Let us consider *R, which may be an excited singlet or a triplet state possessing an electronic configuration that is approximated by two singly occupied orbitals, such as an n,π^* or a π,π^* configuration. For *R, the two electron 1/2 spins can be viewed as being coupled to produce a net spin of 1, *R(T_1), or a net spin of 0, *R(S_1).

Now, consider the possible orientations of the spin vector **S** in the case of the triplet of **S** = 1 (Fig. 2.11, right). The situation with respect to a cone of possible orientations of the spin = 1 case is analogous to that for the spin = 1/2 case in the cases of $M_S = +1$ ($\alpha\alpha$) and $M_S = -1$ ($\beta\beta$), for which "up" and "down" cones of possible orientations exist (Fig. 2.11). However, the case of $M_S = 0$ (wavefunction = $\alpha\beta + \beta\alpha$), the spin vector S does not define a cone but instead defines a *circle* of possible orientations for the vector in the x–y plane (Fig. 2.11, right, middle). An interesting feature of this case is that the projection of the spin on the z-axis is 0, even though the length of S is $2^{1/2} = 1.4\hbar$. The magnitudes of the spin vectors for S = 1 are larger ($1.4\hbar$) than those for S = $1/2(0.87\hbar)$, although by convention the units are not usually explicitly shown in the figures. For the singlet state that also has $M_S = 0$ (wave function = $\alpha\beta - \beta\alpha$), the value of the spin vector is zero, so there is no cone of orientation for the singlet state.

Up to this point in the text, the term "parallel spins" (↑↑) is used to describe two coupled 1/2 spins in a triplet state. To have the appropriate resultant of $1.4\hbar$, two coupled spin 1/2 systems must make an angle of 70° with one another (Fig. 2.11). Now, we see that the term parallel spin actually refers to the condition that the spins make a relative angle of 70° with one another on a cone of possible orientation. The spins for the $\alpha\alpha$, $\beta\beta$, and $\alpha\beta + \beta\alpha$ states are all at an angle of 70°. Thus, only loosely speaking are the two spins *parallel* for the triplet state.

2.30 Making a Connection between Spin Angular Momentum and Magnetic Moments Due to Spin Angular Momentum

The vector model for spin allows a clear visualization of the coupling of spins to produce different states of spin angular momenta. However, chemists are accustomed to discussing states in terms of their energies and not their angular momenta. Now, we need to connect the vector model of angular momentum with models that allow us to deduce the magnetic state energies and how the magnitude of these energies are related to the orientations of the spin vector in space. Then, we will be in a position not only to rank the magnetic states in terms of their energies (a goal of this chapter) but also to understand the interactions that control the dynamics of transitions between magnetic states (a goal of Chapter 3).

2.31 The Connection between Angular Momentum and Magnetic Moments: A Physical Model for an Electron with Angular Momentum

Now, we consider a physical model for electron spin that concentrates on the *magnetic properties* and the *magnetic energies* associated with the spin angular momentum.[8] Electrons and certain nuclei (e.g., ^{1}H and ^{13}C), which possess both electrostatic charge and spin angular momentum, also possess magnetic moments μ (i.e., magnetic dipoles, which are vectors analogous to electric dipoles and spin angular momentum). These magnetic moments may interact with each other and with applied laboratory magnetic fields. Now, we examine the connection between spin angular momentum

(S) and the magnetic moments (μ) associated with **S**. First, we apply the vector model to a familiar physical model of a magnetic moment resulting from the orbital motion of an electron in a Bohr orbit. *This concrete physical model allows us to compute the magnetic moment of the orbiting electron in terms of its orbital angular momentum.* With a connection between electron *orbital* angular momentum and magnetic moments in hand, we shall see how this result can be used to deduce a connection between electron *spin* angular momentum and the magnetic moment due to spin.

In Section 2.7, we described how to qualitatively rank the relative energies of electronic orbitals and electronic states based on the filling of a set of energy-ranked electron orbitals following the aufbau principle and the Pauli exclusion principle. In addition, in Section 2.19, we learned how to qualitatively rank the relative energies of vibrational levels based on their quantum numbers and the number of nodes in their wave functions. It is now our goal to develop a model that allows us to rank the relative energies of *electronic spins and spin states*. The importance of magnetic moments is that the energy of their interactions with a magnetic field can be estimated and ranked in terms of a *magnetic energy diagram*, analogous to the electronic state energy diagram for orbitals (and the vibrational energy diagram for vibrations). Therefore, through an evaluation of the magnetic moments associated with electron spin in an applied magnetic field, we can construct magnetic energy diagrams ranking the energy of the various spin orientations corresponding to different states of angular momentum and thus to different magnetic moments. An important property of such magnetic energy diagrams is that, in contrast to the orbital and vibrational energy diagrams, *the separation between the energy levels depends on the strength of the coupled magnetic fields that interact with the electron spin's magnetic moment.*

[illegible] Pragraph

2.32 The Magnetic Moment of an Electron in a Bohr Orbit

The Bohr model of an electron orbiting about a nucleus provides a concrete physical model (i.e., an electron as a negatively charged particle moving in a circular orbit) for showing how a magnetic moment (μ) is associated with the orbital angular momentum (**L**).[8] Through the model of the Bohr atom, we can connect the electron's **L** with the μ_L associated with orbital motion. After developing this model, we can use it as a basis for deducing the relationship between the quantum mechanical *spin angular momentum* (**S**) and the *magnetic moment* (μ_S) associated with spin motion.

To compute the magnetic motion associated with an electron in a circular Bohr orbit of radius *r*, first we suppose that an electron is a point of negative charge orbiting at constant velocity, **v**, in the plane of the circular orbit. Figure 2.12 presents a vectorial description of the relationship between μ_L and **L** (the figure is schematic to the extent that the sizes of the vectors are unitless and not to any particular scale). The circular motion of the electron generates orbital angular momentum, **L**, whose axis of rotation is perpendicular to the plane of the circular motion and passes through the nucleus (Fig. 2.12, left). The orbital motion of an electron of charge $-e$ generates a magnetic field (in fact, any charge moving in a circle generates a magnetic field). The magnetic field generated by the orbiting electron may be represented (Fig. 2.12,

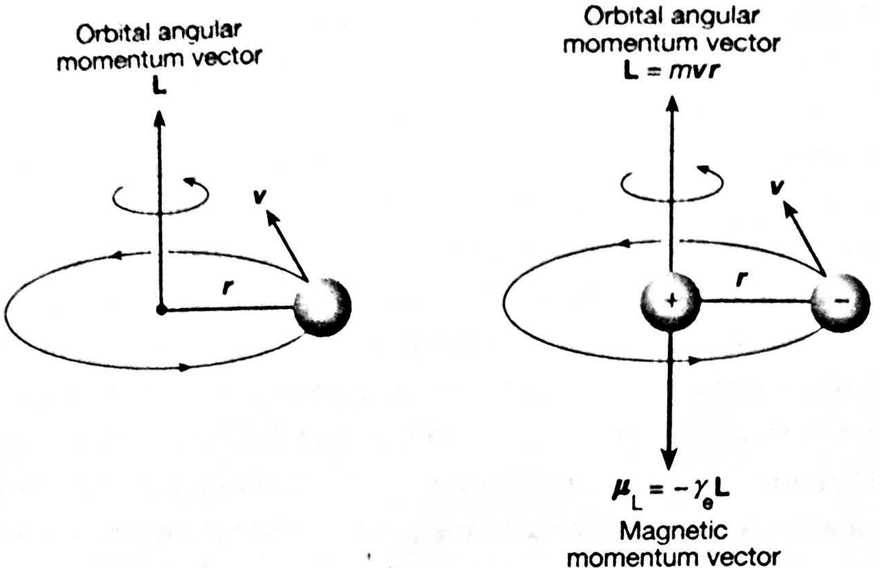


Figure 2.12 The vector model for the orbital angular momentum and the magnetic moment due to the circular motion of an electron in a Bohr orbit. The direction of the magnetic moment vector is opposite to that of the angular momentum vector for an electron. The units of **L** are $\hbar$ and the units of μ_L are joule per gauss (JG^{-1}).

right) as a magnetic dipole μ_L (a vector quantity analogous to an electric dipole) with a magnitude proportional to the angular momentum and a direction perpendicular to the plane of the orbit. For a constant circular velocity **v**, and fixed orbital angular momentum **L**, an orbiting Bohr electron generates a fixed magnetic moment, μ_L, that can be represented by a vector coinciding with the axis of rotation (Fig. 2.12). The direction of the head of the arrow representing the angular momentum vector follows the "right-hand-thumb rule" and points above the plane of rotation for the direction of motion in the orbit shown. This behavior is completely analogous to the classical picture of an electric current flowing in a circular wire and producing a magnetic moment positioned at the center of the motion and perpendicular to the plane of the wire.

From classical physics, the magnetic moment due to orbital motion of the electron, μ_L, is directly proportional to the magnitude of the orbital angular momentum, **L**. *This relationship is the important link connecting the value of angular momentum (in general) to the magnetic moment associated with the angular momentum.* From the model of the electron in the Bohr orbit, the proportionality constant between **L** and μ_L is $-e/2m$, the negative of one-half of the ratio of the unit of electric charge (e) to the electron's mass (m), as shown in Eq. 2.30a. Thus, the simple relationship expressed in Eq. 2.30b exists between the fundamental constants of an electron's charge and mass and the vectors μ_L and **L**.

$$\mu_L = -(e/2m)\mathbf{L} \tag{2.30a}$$

$$-\mu_L/\mathbf{L} = e/2m = \gamma_e \tag{2.30b}$$

The proportionality constant $(-e/2m)$ reflects a fundamental relationship between the magnetic moment $\boldsymbol{\mu}_L$ and angular momentum **L** of a Bohr orbit electron and is therefore a fundamental quantity of quantum magnetism. This constant is called the *magnetogyric ratio* of the electron and is given the symbol γ_e, as shown in Eq. 2.30b. Thus, Eq. 2.30b may be rewritten in terms of γ_e, as shown in Eq. 2.31 (where γ_e is defined as a positive quantity).

$$\boldsymbol{\mu}_L = -\gamma_e \mathbf{L} \tag{2.31}$$

If the electron possesses a single unit of *orbital* angular momentum $(\mathbf{L} = \hbar)$, the magnitude of its magnetic moment, $\boldsymbol{\mu}_L$ is defined as exactly equal to $e/2m$. This fundamental unit of quantum magnetism is called the *Bohr magneton* and is given the symbol, μ_e. Its numerical value is 9.3×10^{-20} JG^{-1}. The symbol μ_e is the magnetic moment generated by an electron possessing an angular momentum of exactly $\hbar$.

The following important concepts can be deduced from Eqs. 2.30 and 2.31:

same direction

1. The vectors representing the magnetic moment $(\boldsymbol{\mu}_L)$ and the orbital angular momentum (**L**) are collinear (i.e., parallel in orientation).
2. The vector representing $\boldsymbol{\mu}_L$ is *opposite (antiparallel) in direction* to that of **L** (the negative sign in Eq. 2.31 relating vectors means that the collinear vectors possess orientations 180° apart). [illegible]
3. The proportionality factor γ_e reveals that the magnitude of the magnetic moment $\boldsymbol{\mu}_L$ due to orbital motion is directly proportional to the charge of the electron (e) and inversely proportional to its mass (m). (2-30b)

Equations 2.30 and 2.31 are very important because they allow us to visualize both the electron's orbital angular momentum (**L**) and magnetic moment $(\boldsymbol{\mu}_L)$. We use these visualizations to understand the rankings of the energies of the magnetic states of electrons.

Now, we need to deduce how a spin magnetic moment $(\boldsymbol{\mu}_S)$ is associated with the electron spin angular momentum (**S**). We begin with the quantum mechanical results deduced previously from the interactions of **L** and $\boldsymbol{\mu}_L$. Then, we can transfer these ideas to electron spin, which can be modeled as resulting from a rotating sphere of negative charge. Finally, we can determine what quantum mechanical modifications of the model are necessary to apply our vector model to qualitatively visualize spin and its associated magnetic moment.

2.33 The Connection between Magnetic Moment and Electron Spin

The electron is a quantum particle, so it possesses many properties that are not understandable from observations of classical particles. Nonetheless, a clear and appealing visualization is possible if we start with a model that considers the electron as a classical particle of definite mass and of a spherical shape that possesses unit negative electric charge distributed uniformly over its surface. The classical properties of mass and charge are articulated in this simple physical model. It is natural to assume, therefore, that since the mass of the electron is fixed, and since its spin angular momentum is quantized (and therefore also a fixed quantity equal to $\hbar/2$), the spherical electron must spin about an axis with a fixed velocity, **v** (Fig. 2.13, left), in order to obey the fundamental law of the conservation of angular momentum. In other words, *because the electron's mass and charge are fixed, and since the electron possesses a fixed quantum unit of angular momentum (i.e., $\hbar/2$), the spinning velocity of the rotating electron must be constant for all electrons.* It is quite straightforward now to apply the results from the Bohr atom, discussed previously, to infer the relationship between the spin angular momentum (**S**) of an electron to the magnetic moment (μ_S) due to its spin motion.

Analogous to a charged particle executing orbital motion, an electron executing spinning motion also generates a magnetic moment (also called a magnetic dipole) as shown in Fig. 2.13 (left). Accordingly, due to its spinning motion, the charged electron generates a magnetic moment (μ_s) in analogy to the magnetic moment (μ_L) generated by an electron in a circular Bohr orbit. The issue to be addressed is the relationship between μ_s and **S**.

It is tempting to start with a direct analogy to Eq. 2.31, the relationship between orbital angular momentum (**L**) and the associated magnetic moment (μ_L), which would suggest that $\mu_S = -\gamma_e \mathbf{S}$ (Eq. 2.32a). In other words, if the analogy of the magnetic moment due to orbital motion of a Bohr atom and the magnetic moment due to electron spin motion is valid, the magnetic moment due to spin (μ_S) should be directly proportional to the value of the spin (**S**) and the proportionality constant should be γ_e. This simple analogy has the correct form qualitatively, but it has been shown experimentally that the expression is not quite correct quantitatively. Although a direct proportionality between μ_s and **S** exists, for a free electron a "correction factor" g_e must be applied to relate μ_s and **S** quantitatively. This quantitative relationship is thus given by Eq. 2.32b.

$$\mu_s = -\gamma_e \mathbf{S} \longrightarrow \text{negative mag mom opposite direction} \qquad \underline{(2.32a)}$$

$$\mu_s = -g_e \gamma_e \mathbf{S} \qquad \underline{(2.32b)}$$

In Eq. 2.32b, g_e is a dimensionless constant (a correction factor) called the *g* factor (or *g* value) of the free electron. The *g* factor has an experimental value close to 2 for a free electron in a vacuum. Thus, the simple model that attempts to transfer the properties of an orbiting electron to a spinning electron is correct qualitatively but is incorrect quantitatively by a factor very close to 2. This factor of 2 is fully justified by a more rigorous theory of the electron, which considers relativistic effects, but this rather subtle issue is of no concern for the qualitative features of spin that interest us in this text.

Fig. 2.13 uses the vector model to summarize the relationships between the spin angular momentum and the magnetic moment associated with electron spin. Fig. 2.13

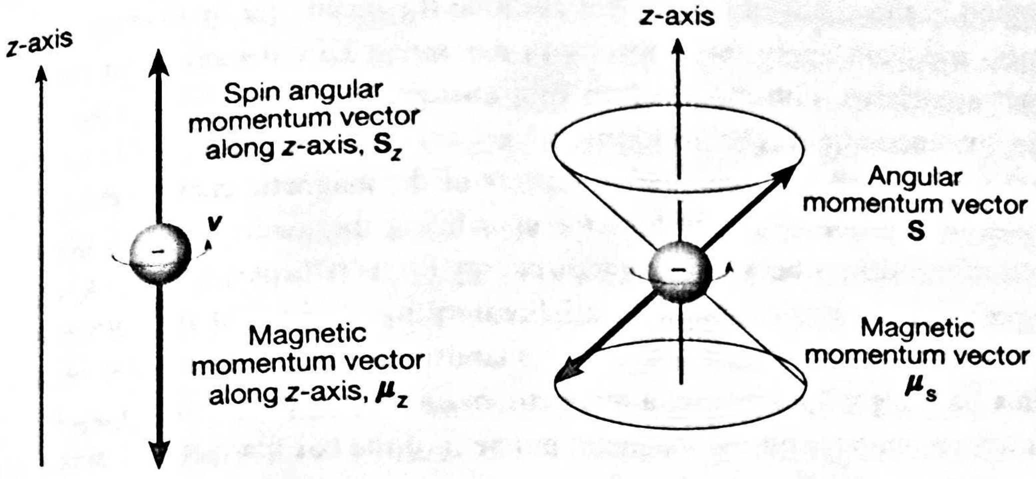


Figure 2.13 Vector representation of the spin angular momentum (S) and of the magnetic moment associated with spin (μ_S). The two vectors (S and μ_S) are collinear but antiparallel. The lengths shown are only schematic.

should be compared to the analogous form of the orbital angular momentum and its associated magnetic moment in Fig. 2.12.

Based on Eq. 2.32b and Fig. 2.13, the following important conclusions can be made concerning the relationship between electron spin and the magnetic moment due to spin:

1. Since electron spin is quantized and the spin vector and the magnetic moment vectors are directly related, *the magnetic moment associated with spin* (μ_S), *just as the angular momentum* (S) *from which it arises, is quantized in magnitude and orientation.*
2. Since the energy of a magnetic moment depends on its orientation in a magnetic field, *the energies of quantized spin states depend on the orientation of the spin vector in a magnetic field.*
3. In analogy to the relationship between the orbital angular momentum and the magnetic moment derived from orbital motion, the vectors μ_S and S are antiparallel (Fig. 2.13, left).
4. The vectors μ_S and S are both positioned in a cone of orientation that depends on the value of M_S [Fig. 2.13 (right) shows the case for S for $M_S = +1/2$].

2.34 Magnetic Energy Levels in an Applied Magnetic Field for a Classical Magnet

We have developed a model, specified in Eq. 2.32, that allows the association of a specific value of the magnetic moment (μ_S) with a specific value of spin angular momentum (S). Our next goal is to develop a model for the magnetic energy levels associated with different values (M_S) of spin for electrons in an applied magnetic field. First, let us consider what happens to the magnetic energy levels when a magnetic field is applied in the classical model. We examine the results for an exemplar classical magnet, and then apply these results to determine how the quantum mechanical magnet associated with the electron spin changes its energy when coupled to an applied magnetic field. The vector model not only provides an effective tool to deal with the qualitative and quantitative aspects of the magnetic energy levels but also provides us with an excellent tool for visualizing the qualitative and quantitative aspects of transitions between magnetic energy levels (Chapter 3).

According to classical physics, a laboratory magnetic field is characterized by its magnetic moment, which is a vector quantity we represent with the symbol $\mathbf{H}_z$. When a bar magnet possessing a magnetic moment μ is placed in a magnetic field $\mathbf{H}_z$, a torque operates on the magnetic moment of the bar magnet and twists it with a force that tries to align the direction of the moment with the direction of the field determined by $\mathbf{H}_z$. The precise equation describing the energy relationship of the bar magnet at various orientations in $\mathbf{H}_z$ is given by Eq. 2.33, where μ and $\mathbf{H}_z$ are the magnitudes of the magnetic moments of the bar magnet and the applied field in the z direction (defined as the direction from the south to north pole of the laboratory magnetic field), respectively. According to classical mechanics, any orientation of the bar magnet in the magnetic field is possible. However, the energy of a bar magnet depends on its orientation relative to the z-axis. Three important limiting orientations of the bar magnet relative to the magnetic field, namely, parallel (0°), perpendicular (90°), and antiparallel (180°), are shown schematically in Fig. 2.14. The values for these three orientations are $-\mu\mathbf{H}_z$, 0, and $\mu\mathbf{H}_z$, respectively.

$$E_z(\text{magnetic}) = -\mu\mathbf{H}_z\cos\theta \tag{2.33}$$

In Eq. 2.33, the negative sign before the quantity on the right side of the equation means that the system is *more stable* if the product $\mu\mathbf{H}_z \cos\theta$ is a positive quantity.

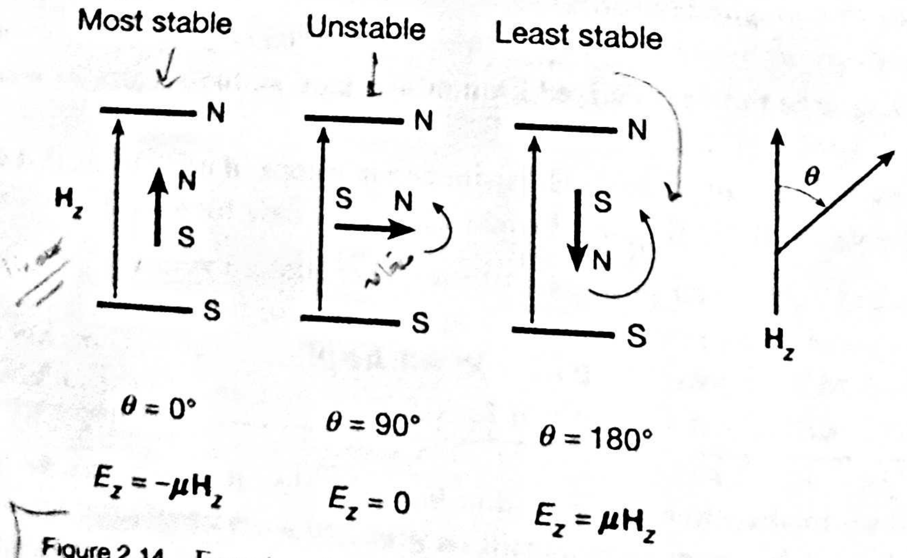


Figure 2.14 Energies of a classical bar magnet in a magnet field $\mathbf{H}_z$. The curved arrow indicates the force acting to rotate the magnet to align it with the direction of the field.

By definition, the magnitudes (lengths) of the vector quantities $\boldsymbol{\mu}$ and $\mathbf{H}_z$ are always positive, so whether the energy of the system is positive (less stable than the situation in zero field) or negative (more stable than the situation in zero field) depends on the sign of $\cos\theta$ (which is positive for θ between 0° and 90° and negative for θ between 90° and 180°).

Consider the situations when $\boldsymbol{\mu}$ and $\mathbf{H}_z$ are two parallel vectors ($\theta = 0^\circ$ or 0π), two perpendicular vectors ($\theta = 90^\circ$ or $\pi/2$), or two antiparallel vectors ($\theta = 180^\circ$ or π). For these cases, $\cos\theta = 1$, 0, and -1, respectively (Fig. 2.14). Thus, any orientation of the bar magnet with θ between 0 and just $< 90^\circ$ is stabilizing (the energy E_z in Eq. 2.33 is negative) and any orientation of the bar magnet with θ between 90° and up to 180° is destabilizing (the energy E_z is positive). At an orientation of 90°, the magnetic interaction between the applied magnetic field and the bar magnet is zero ($\cos 90^\circ = 0$ in Eq. 2.33), that is, the same as in the absence of a field, when $\mathbf{H}_z = 0$. A more detailed discussion of the effect of the orientation of a bar magnet in a magnetic field is given in Section 2.39 for the interactions of two magnetic dipoles.

2.35 Quantum Magnets in the Absence of Coupling Magnetic Fields

In contrast to the classical magnet, which can assume any orientation in a magnetic field, the quantum magnet can only assume a set of orientations that depend on the value of the magnetic quantum number (M_S). We now review the notations and vector representations that are convenient for describing the most important spin situations that arise in organic photochemistry, namely, a single electron spin and two coupled electron spins. Table 2.4 summarizes the notations and vector representations for a single spin and two coupled spins; these conventions can be used to describe spin systems at both zero and high applied magnetic fields. We use the symbol D (doublet) to describe the state of a single spin, $\mathbf{S} = 1/2$. For the case of $M_S = +1/2$ (α, or up spin pointing in the *positive* direction along the *z*-axis), we label the state D_+; for the case of $M_S = 1/2$ (β, or down spin pointing in the *negative* direction along the *z*-axis), we label the state D_-. In the case of two coupled spins, we use the symbol S to denote the singlet state (one α spin and one β spin; wave function $\mathbf{S} = \alpha\beta - \beta\alpha$). This spin state has the quantum number $M_S = 0$. For the triplet state we use the symbols T_+ (two α spins), T_0 (one α spin and one β spin; wave function $\mathbf{S} = \alpha\beta + \beta\alpha$), and T_- (two β spins) to label the states with quantum numbers $M_S = +1$, 0, and -1, respectively.

In the absence of magnetic interactions operating on the magnetic moments associated with the electron spins, all six of the states (D_+, D_-, S, T_-, T_0, and T_+) have exactly the same energy; that is, the magnetic energy levels of all these states are degenerate (of identical energy), since there are no magnetic interactions to split the energy levels ($\mathbf{H}_z = 0$ in Eq. 2.33). In the absence of any magnetic interactions, the vector model of electron spin views the spin vector representing the angular momentum and magnetic moment as stationary and possessing random arbitrary orientations

Table 2.4 Conventional Representations of the Singlet, Doublet, and Triplet States in an Applied Magnetic Field ($\mathbf{H}_z$)[a]

State	State Symbol	M_s	Magnetic Energy (E_z)	Spin Function	Vector Representation
Doublet	D_+	$+1/2$	$+(1/2)g\mu_e\mathbf{H}_z$	α	
Doublet	D_-	$-1/2$	$-(1/2)g\mu_e\mathbf{H}_z$	β	
Singlet	S	0	0	$\alpha\beta - \beta\alpha$	
Triplet	T_+	$+1$	$+(1)g\mu_e\mathbf{H}_z$	$\alpha\alpha$	
Triplet	T_0	0	0	$\alpha\beta + \beta\alpha$	
Triplet	T_-	-1	$-(1)g\mu_e\mathbf{H}_z$	$\beta\beta$	

S=½

a. The mathematical normalizing factor is not shown for the spin function.

in space. There is no pertinent M_S quantum number in zero field, because there is *no preferred* axis of orientation. However, even at zero field the total spin angular momenta for the singlet, doublet, and triplet (S = 0, 1/2, and 1) are well defined, but M_S is not. When $\mathbf{H}_z = 0$, therefore, the quantum number for total spin **S** is still a valid quantum number, but the quantum number M_S is not. In other words, a D or T state is magnetic and an S state is not, whether or not an applied magnetic field is present.

2.36 Quantum Mechanical Magnets in a Magnetic Field: Constructing a Magnetic State Energy Diagram for Spins in an Applied Magnetic Field

The magnetic energy resulting from the interaction of a magnetic moment μ and an applied field $\mathbf{H}_z$ (Fig. 2.14) is known as the *Zeeman energy* (E_z). Eq. 2.34 relates the energy of the quantum mechanical magnet to the strength of the applied field along the z-axis ($\mathbf{H}_z$), the magnetic quantum number for a given spin orientation (M_S), the g-value of the electron (g_e), and the magnetic moment of a free electron (μ_e).

$$E_z = M_S g \mu_e \mathbf{H}_z \tag{2.34}$$

The ranking of magnetic energies (relative to those in zero field) of the singlet, doublet, and triplet states are listed in Table 2.4.

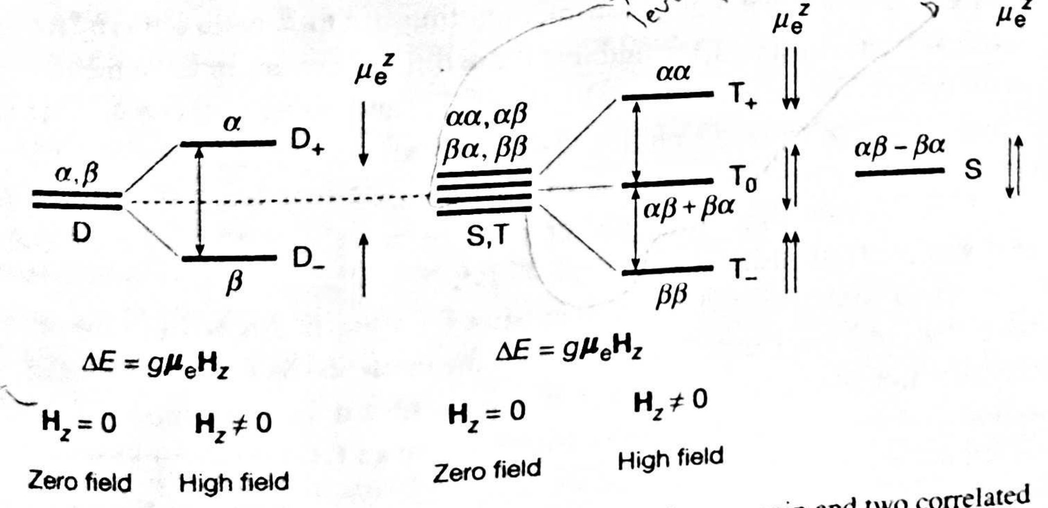
2.37 Magnetic Energy Diagram for a Single Electron Spin and for Two Coupled Electron Spins

Fig. 2.15 displays the magnetic (Zeeman) energy-level state diagram[10] at zero magnetic field ($\mathbf{H}_z = 0$ G) and in the presence of a strong magnetic field ($\mathbf{H}_z \gg 0$ G) for the two fundamental cases: (1) a single electron spin, a doublet (D) state, and (2) two correlated electron spins, which may be either a triplet (T) or singlet (S) state. In zero field (for now we ignore the electron-exchange interaction (J) and only consider the magnetic interactions in the energy diagram), all of the magnetic energy levels are degenerate, because there is no preferred orientation of the angular momentum and therefore no preferred orientation of the magnetic moment due to spin. Although these states are all of the same energy, they are shown with levels slightly separated in Fig. 2.15 so that the number of degenerate states is clear. All of these states have identical energies in the absence of magnetic (and electron exchange) interactions.

The relative ordering of the magnetic states is always the same in an applied magnetic field ($\mathbf{H}_z$) : $D_+ > D_-$ and $T_+ > T_0 > T_-$ (Fig. 2.15). The energy separation between adjacent levels depends, moreover, on the magnitude of the applied field ($\mathbf{H}_z$) (Eq. 2.34).

The zero-field situation is a benchmark for the calibration of the magnetic coupling energy in devising a magnetic energy diagram. The concept is the same as using the energy of a nonbonding p orbital as a benchmark of energy (set at $E = 0$) and then to treat bonding orbitals as lower in energy than a p orbital (i.e., negative energy relative to $E = 0$), and antibonding orbitals as higher in energy than a p-orbital (i.e., positive energy relative to $E = 0$). The magnitude of the exchange interaction, J (Section 2.12 and 2.13), is typically much larger (several to tens of kcal mol^{-1}) than

therre level energy in Triplet but single in SL



magnetic field

Figure 2.15 Magnetic energy diagram for a single electron spin and two correlated electron spins. The magnetic energy of T_0 and S are the same at $\mathbf{H}_z = 0$ or $\mathbf{H}_z \gg 0$. For these examples, $J = 0$, so the energy of T_0 and S are identical (i.e., there is no T_0 and S splitting when $J = 0$).

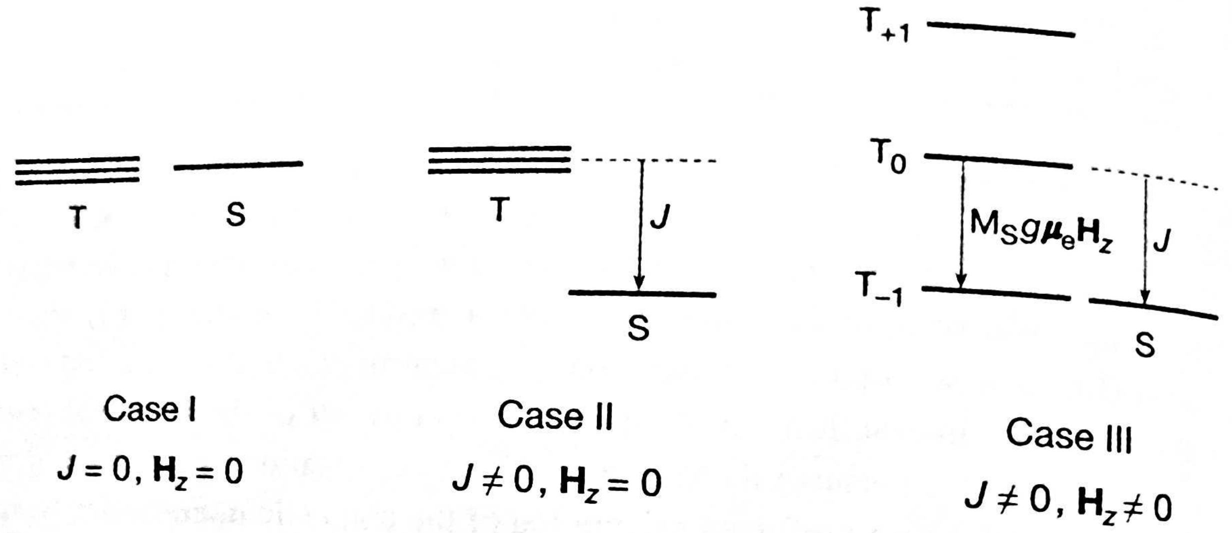


Figure 2.16 The effect of electron exchange on the magnetic energy levels of a triplet and singlet state.

that of magnetic interactions (much less than 1 kcal mol^{-1}). However, the exchange interaction is Coulombic (i.e., an electrostatic interaction between charged particles) and is not magnetic. This finding allows us to consider the magnetic interactions first and independently, as shown in Fig. 2.15, and to later "turn on" the electrostatic exchange interactions J after considering the magnetic interactions (see Fig. 2.16).

2.38 Magnetic Energy Diagrams Including the Electron Exchange Interaction, J

The energy diagrams shown in Fig. 2.15 must be modified in the presence of electron exchange, J (Section 2.7). We saw in Section 2.14 that there is a significant difference between the magnitude of the singlet–triplet splittings for molecules (*R) and for reactive diradical intermediates, I(D), and that these differences are in large measure due to J. In the case discussed in Section 2.14, the singlet and triplet states being compared were S_1 and T_1, both derived from a HO–LU orbital configuration corresponding to *R. Even in the case of *R = n,π^*, the value of the exchange integral is on the order of several kilocalories per mole or greater. In these cases, $J \gg E_z$, so the value of E_z can be considered independent of the value of J.

However, the situation is very different when the value of J is on the same order as the value of E_z. Review Fig. 2.3, which shows the influence on orbital orientation and the separation of two radical centers. Let us now review the important conclusions in Section 2.14 concerning the singlet–triplet splittings for a diradical species, I(D), for which the value of J is small and close to zero. W

I(D) have two important consequences: (1

between electrons become on th

between electrons fo

for som