## 3. Angular Momentum States.

We now employ the vector model to enumerate the possible number of spin angular momentum states for several commonly encountered situations in photochemistry. We shall give examples for the important situations involving the coupling of several electron spins, since these examples will capture the most important features of cases commonly observed in photochemical sytems. Of these the most important is the coupling of two electron spins with one another. After deducing the number of states that result from coupling of individual spins, we shall be interested in the relative energy ranking of these spin states when magnetic interactions and couplings are present. These interactions and couplings will be connected to molecular structure through the relationship of spin angular momentum and magnetic moments due to spin. The coupling of magnetic moment due to spin with other magnetic moments will be the basis for the understanding of both magnetic resonance spectroscopy and intersystem crossing. For magnetic resonance spectroscopy, the influence of an applied laboratory magnetic field on the energy levels is of particular importance. For intersystem crossing, couplings of the electron spin with other sources of angular momentum are important.

Before counting angular momentum states for the important commonly encountered cases, we shall briefly review the principles of both classical angular momentum and quantum angular momentum and relate these quantities to the vector model.

### Classical Angular Momentum. The Physics of Rotational Motion.

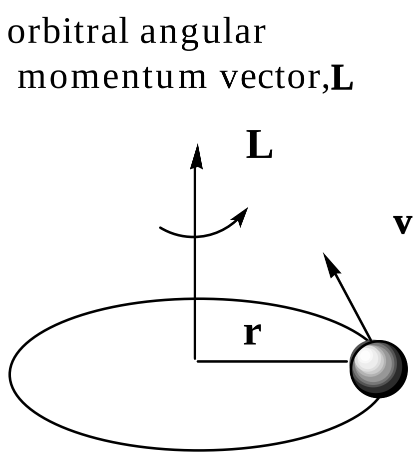
Classical angular momentum refers to the rotation motion of of an object around a fixed point or about a fixed axis. The two most important models of angular momentum for chemistry are (1) a particle constrained to move in a circular path with a fixed radius about a point (Figure 4, left) and (2) a spherical body rotating about a fixed axis that passes through a point at the center of the sphere (Figure 4, right). These two simple models capture the essence of the origin of electron orbital angular momentum and to electron spin angular momentum.

We choose two definite physical models to visualize (1) **orbital** angular momentum in terms of **an electron of mass $m_e$ travelling in a circular Bohr orbit or radius r with angular velocity v**, and (2) **spin** angular momentum in terms of **a spherical top or gyroscope spinning about an axis with a moment of inertia, I, and an angular velocity, v** (the moment of inertia is related to a radius of gyration, r, rotating about the center of mass). Let the orbital angular momentum be symbolized by **L** and the spin angular momentum of a single electron be symbolized by **S**. According to classical mechanics the values of **L** and **S** are given by equations 1 and 2, respectively.

$$\mathbf{L} = m\mathbf{v}r \quad (1)$$

$$\mathbf{S} = I\mathbf{v} \quad (2)$$

According to classical mechanics, both the orbital and spin angular momentum of a particle undergoing circular motion (as an electron in a Bohr orbit) or a rotating top or gyroscope (as an electron spinning on its axis) may be represented as a **vector**. To visualize this vector we employ the "right hand thumb rule" which states the angular momentum vector points in the direction that a right-hand thumb points when the fingers of the right hand are turned in the same sense as the rotation. Figure 4 shows the vector representation of the orbital angular momentum of an electron, **L**, in a Bohr orbit and of the spin angular momentum, **S**, of a single electron spinning on its axis. From classical mechanics, the direction of the angular momentum vector is always perpendicular to the plane defined by the circular motion of the electron in its orbit or the rotation of the spherical electric charge. The length of the vector represents the magnitude of the angular momentum. The important features of the classical representation of angular momentum are: **(1) that angular momentum can be represented by a vector whose direction is related to the sense of the direction of rotation; (2) that the representation of the vector can be conveniently placed on the axis of rotation; and (3) that the length of the vector is proportional to the absolute magnitude of the angular momentum.** In these diagrams the vector sizes are generally schematic and not to scale.



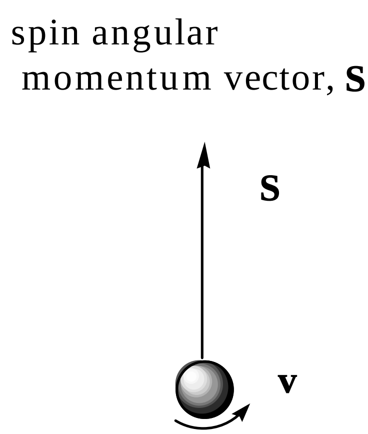




Figure 4. Classical representation of the angular momentum of an electron in a Bohr orbit (left) and of an electron spinning about an axis (right). The important features to note are the angular momentum in both cases possesses a characteristic circular motion: in one case the mass of the particle is at a distance,

r, from the axis of rotation, and in the other case the center of mass is at a distance, r, from the axis of rotation.

**Quantum Electron Spin Angular Momentum**

The results of classical angular momentum provide a clear physical model for representation of orbital and spin angular momentum in terms of the vector model. Let us now consider the new features that are introduced by the laws of quantum mechanics which spin angular momentum (both electronic and nuclear) must obey.

The elementary components of an atom (electrons and protons) behave as if they were spinning on an axis. The motion of the electron spin (or a nuclear spin) can be considered to be a "zero point" motion. It is eternal and cannot be stopped. The spinning electron is like a ltoy top that is simultaneously provided with a pulse of rotational energy and magically freed from friction or other means of dissipating the rotational energy. Thus, the magnitude of an electron spin is fixed and constant in time and cannot be changed. These qualities are all subsumed in the statement that an electron possesses exactly 1/2\ worth of spin angular momentum. Recall that \ is Planck's constant divided by 2 $\pi$. The factor $2\pi$ is a natural consequence of the **circular** motion implicit in all forms of angular momentum. No matter where the electron resides, in bonds with a partner of opposite spin orientation, as an entity in a half occupied orbital, as a member of a cluster of spins of the same orientation, or in orbitals of different angular momentum (s, p, d, etc.), *the spin of the individual electron is always 1/2\ exactly*. We shall see that the fact that the proton, $^{13}$C and other nuclei also possess exactly 1/2 \ of spin angular momentum will allow them to couple with electron spins and thereby be actively involved in magnetic resonance and intersystem crossing. This coupling will allow the conservation of angular momentum to be maintained as angular momentum is exchanged between the coupled partners. The situation will be completely analogous to maintaining conservtion of energy while energy is being exchanged between coupled partners.

According to the laws of classical mechanics the angular momentum of a rotqting body may assume any value or any direction of the angular momentum, consistent with torques applied to the body. This means that in a Cartesian coordinate system, the angular momentum of a body around each of the three perpendicular axes may take any value consistent with the magnitude of the angular momentum. Thus, if electron spin were a classical quantity, the magnitude and direction of the vector representing the spin angular momentum could assume any length, S, and any angle $\theta$ relative to the z-axis. The situation is quite different for a quantum mechanical particle, such as an electron or a proton. In the quantum case t**he amount of angular momentum is quantized**

**and can achieve only certain definite values for any given value of the angular momentum. This means that only certain orientations of the angular momentum can occur in physical space**. This in turn implies that only certain orientations of the spin angular momentum vector are allowed in spin space. What we mean by this is that for all measurable (stable) situations, the quantum mechanical rules must be followed. In certain, unstable, situations the rules are temporarily modified and transition between states of different spin may occur. Let us now review the rules for stable situations, i.e., the situations which will determine the measurable magnetic energy levels from which transitions between spin states can occur. Then we will investigate how a given spin state may become unstable and undergo radiative or radiationless transitions to another spin state.

## Quantum Rules of Spin Angular Momentum

According to the laws of quantum mechanics, an electron or group of electrons can be characterized completely by certain quantum numbers. When we say that an electron or a proton has a spin of 1/2 we usually are referring to the electron's **spin quantum number**, S, rather than the magnitude of the spin angular momentum. However, when we say we are dealing with any particle with spin of 1/2 we also mean that the particle has an inherent, irremovable angular momentum of 1/2\ **which can be measured in an experiment.** (The quantum number for total spin will be represented by the plain type and care will be taken to distinguish this unitless quantity from the magnitude of the spin, which has the units of angular momentum). For electron spin there are only two pertintent quantum numbers: S, the quantum number associted with **the length of the total spin** and $M_S$ the quantum number assoicated with the **orientation of the total spin** relative to the z axis. The relationship between the quantum number, S (unitless), and the magnitude of the total spin angular momentum **S** (in units of \) is given by eq. 3a. The pecular square root relationship of eq. 3a will be discussed below.

Magnitude of **S** (units of \) = $[S(S + 1)]^{1/2}$ (3a)

The possible values of S, the total electron spin angular momentum quantum number, are given by eq. 3b, where n is 0 or a positive integer.

Possible values of S (unitless) = n/2 (3b)

From eq. 3a and 3b we deduce that the total spin quantum number may be equal to 0, 1/2, 1, 3/2, 2, etc. and that the magnitude of the spin angular momentum may be equal to 0 \, $(3/4)^{1/2}$ \, $(2)^{1/2}$ \, $(15/4)^{1/2}$ \, $(5)^{1/2}$ \, etc. We shall see below that we need not deal with the square root quantities because the measuarble values of the spin on the z axis will bear a simple relationship to the quantum number $M_S$.

According to the laws of quantum mechanics spin angular momentum is not only quantized in magnitude, but in orientation relative to the z axis in physical space. Therefore, **the vector representing spin can only assume certain orientations relative to the z axis in spin vector space**. The quantum number $M_S$ specifies the possible orientation of a given angular momentum in space. This quantum number is analogous to the familiar quantum number for orientation of orbitals in space, e.g., a p-orbital along the x, y or z-axis. The measurable values of the possible orientations of spin angular momentum on the z axis are given the quantum numbers, $M_S$, where the possible values of $M_S$ are given by eq. 4a. The values of $M_S$ each correspond to an allowed measurable value of $\mathbf{S}_z$.

$$\text{Possible values of } M_S \text{ (unitless)} = S, (S-1), \ldots, (-S) \qquad (4a)$$

The values of $M_S$ (unitless) are the same as the value of the angular momentum of the spin (units of \) on the z-axis . As a result of this relationship, it is convenient to refer to the values of the spin angular momentum on the z axis rather than the total spin angular momentum (which has the peculiar square root character given in eq. 3a). For example, for S = 1/2, the possible values of $M_S$ are + 1/2 and -1/2 and for S = 1, the possible values of $M_S$ are +1, 0 and -1, respectively. The positive sign means that the head of the vector is pointing in the positive direction of the z axis, and the negative sign means that the head of the vector is pointing in the negarive direction of the z axis. For these values of $M_S$ the values of $\mathbf{S}_z$ are + 1/2 \ , -1/2 \, +1 \ , 0 \ and -1 \, respectively. These important cases will be considered in greater detail below. We shall see that nearly all cases of interest will only involve the coupling of only a few spins with each other or with an applied field and can readily be extended conceptually to more complicated cases.

From Eq. 4a we can conclude that for any given value for the total quantum number of spin, S, there are exactly 2S + 1 allowed orientations of the total spin. This important conclusion is expressed in Eq. 4b, where M is termed the **multiplicity** of a given state of angular momentum.

$$\text{Multiplicity, M, of state with quantum number S} = 2S + 1 \qquad (4b)$$

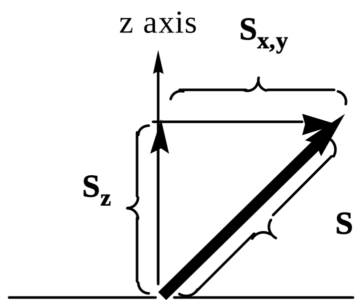
Let us consider three simple, but common examples of S = 0, 1/2 and 1. According to Eq. 4b, for S = 0, M = 1. Thus, when there is only one spin state when S = 0 and this is termed a **singlet state**. For S = 1/2, M = 2. Thus, when there are two spin states when S = 1/2 and this is termed a **doublet state**. For S = 1, M = 3. Thus, when there are three spin states when S = 1 and this is termed a **triplet state**. In the absence of a magnetic field the two doublet states and the three triplet states have the same energy (are degenerate). However, the application of a magnetic field (internal or external) removes the degeneracy as we shall soon see.

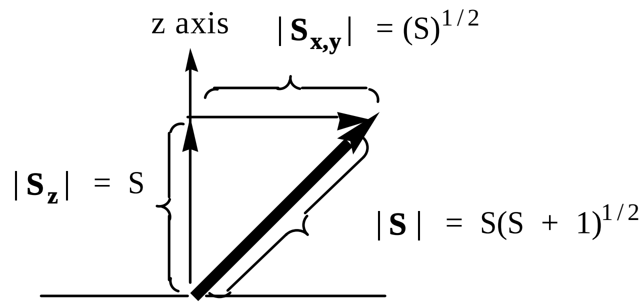
## Pythagorean Relationships and Spin Angular Momentum

The peculiar square root relationship of eq. 3a is embedded in the remarkable trigonometric features of all vectors. The triangular relationship among vectors in 2 dimensions is shown in Figure 5. From the familar Pythagorean theorem, Eqs. 5 a and 5 b provide a relationship between the **square** of the total angular momentum $\mathbf{S}^2$ and the components on the z and x (or y) axis. Note that the lengths $|S_x| = |S_y|$ because of the cylindrical symmetry of the x,y plane about the z axis. This cylindrical symmetry has a profound influence on the vector properties of spin.

$$\mathbf{S}^2 = \mathbf{S_z}^2 + \mathbf{S_{x,z}}^2 \qquad (5a)$$

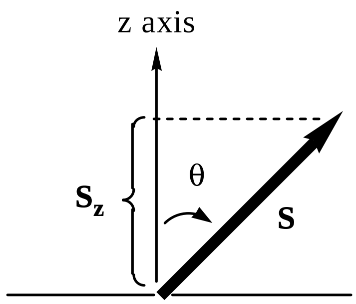
$$\mathbf{S} = (\mathbf{S_z}^2 + \mathbf{S_{x,z}}^2)^{1/2} \qquad (5b)$$




Angular Momentum (Vector Quantity):
**S** is the total angular momentum
$\mathbf{S_z}$ is the component on the z axis
$\mathbf{S_{x,y}}$ is the component on the x or y axis. The units are in \.

Vector Length (Scalar Quantity):
|**S**| is the total **length** of the angular momentum; $|\mathbf{S_z}|$ is the length of the component on the z axis; $|\mathbf{S_{x,y}}|$ is the length of the component on the x or y axis.




Vector Direction: The **direction** of the angular momentum vector is given by the angle θ made by the vector with the z axis. The value of θ is given by $\cos\theta = |\mathbf{S_z}| / |\mathbf{S}|$.

Figure 5. Trigonometric relationships between the angular momentum vector and the geometric axes.

By inspection of the vector diagram and use of trigonometry, if we require the value of $\mathbf{S_z}$ to follow the quantum mechanical rules then the value of **S** must also be constrained to values determined by the Pythagorean theorem through eq. 5b! Furthermore, the allowed values of the angle, θ, between **S** and $\mathbf{S_z}$, will be given by elementary trigometric relationships through eq. 6, where the magnitudes of **S** and $\mathbf{S_z}$ conform to the allowed values of θ are those for which the $|\mathbf{S_z}|$ and $|\mathbf{S}|$.

$$\cos\theta = |S_z| / |S| \qquad (6)$$

For example, for the case of S = 1/2 (Figure 6 below), the possible values of θ are: (1) for $M_S = 1/2$, θ = 55 º, for $M_S = -1/2$, θ = 125 º. For the case of S = 1

(Figure 7 below) , the possible values of θ are: (1) for $M_S$ = 1, θ = 45 º, for $M_S$ = 0, θ = 90º and for $M_S$ = -1, θ = 135 º.

Let us now consider the vector representation of spin quantization in some detail for the two most important cases in photochemistry: a single spin and two coupled spins.

**Vector Model of a Single Electron Spin**

Figure 6 shows the vector model for a single electron spin. In the Figure we show the angular momentum vector pointing perpendicular to the plane of rotation of a rotating spherical electron. Since the spin quantum number, S, of a single electron is 1/2, according to eq. 3a, the value of the length of **S** for a single electron is $[S(S + 1)]^{1/2}$ = $(3/4)^{1/2}$ (values of **S** will always be in units of \). Thus the length of a single electron spin is **independent of its orientation** and is = $(3/4)^{1/2}$. What are the possible orientations of **S** allowed by quantum mechanics? From equation 4a and 4 b, we deduce that there are two such states (a doublet state) and that the possible values of $\mathbf{S}_z$ are +1/2 \ and -1/2 \. From eq. 6 we have computed that the possible angles these two states are θ = 55º and 125º relative to the z-axis (the direction parallel to the positive direction along the z-axis is defined as 0º). Thus, from Figure 6 we can readily visualize the two possible orientations or an electron spin in terms of the vector model in **two dimensional** spin space. At this point the coordinates in the x,y plane are not specified. We shall return to this important issue when we deal below with the uncertainty principle and cones of orientation of spin vectors.

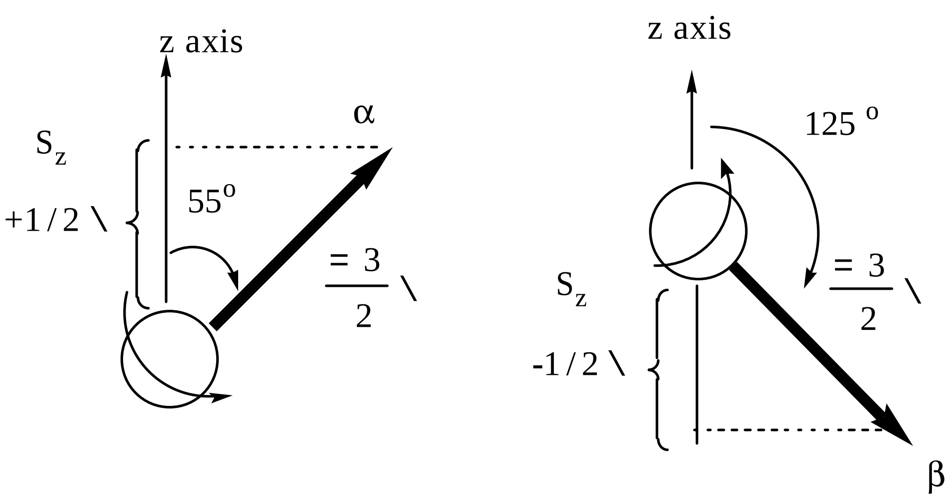



Figure 6. Vector representation of a spin 1/2 particle (an electron, a proton, a 13C nucleus). The symbol α refers to the spin wave function of a spin with $M_s$=

+1/2 and the symbol β refers to the spin wave function of a spin with $M_s$ = -1/2. See text for discussion.

In quantum mechanics spin is represented by a wave function (the mathematical details of which will not concern us). The symbols α and β are employed to represent the spin wave functions corresponding to the $M_S$ = 1/2 and -1/2 quantum numbers, respectively. Thus, the spin vector with the 55º value of θ is related to an α spin function and the spin vector with the 125º value of θ is related a β spin function. The α spin is said to be pointing "up" (relative to the z-axis) and the β spin is said to be pointing "down" relative to ther z-axis. The α and β representations of spin wave functions will be useful in describing spin states which are strongly mixed.

**Vector Model of Two Coupled Electron Spins. Singlet and Triplet States.**

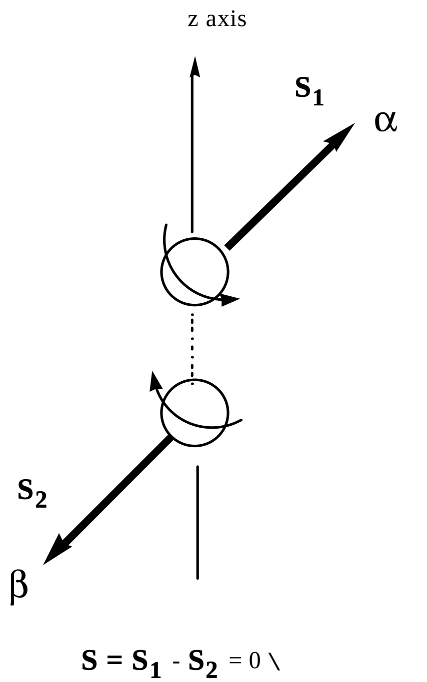
When two particles possessing angular momentum interact or couple, how many different states of **total angular momentum** can result from the coupling? Knowledge of the rules for coupling of angular momentum is very important in photochemistry since various steps in most photochemical processes will involve the coupling of one electron spin with another or the coupling of one electron spin with some other form of angular momentum intramolecularly or intermolecularly. Evidentally, from eq. 3a and 3 b, quantum mechanics constrains the number of angular momentum states that can exist, so the number of states that can result from coupling must also be constrained! The rules for coupling of angular momentum are very simple if the vector model is employed.

<u>Rule 1</u> is that the final **total** angular momentum (units of \) of a coupled system can take on only three possible types of allowed values (eq. 3b): (1) 0; (2) a positive half integer; or (3) a whole integer.

<u>Rule 2</u> is that the allowed values of the spin **differ from the maximum value of the spin by one less fundamental unit of angular momentum**, \, to produce as many states as possible consistent with rule 1.

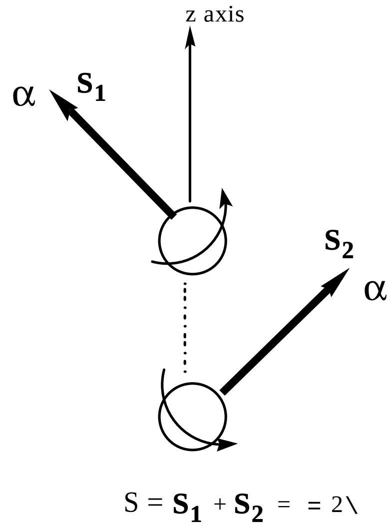
Let us apply these rules for the most important case of two electron spins coupling with one another. We start with the value of a single electron spin as 1/2 \. From the rules, we first find the **maximum** value of the coupled angular momentum on the z axis, which is simply the sum of the individual values, i.e., (1/2 + 1/2)\ = 1 \. Thus, one of the possible coupled states will have a total angular momentum of 1. All other possible states will differ from the state of maximum angular momentum by one unit of \ and must be positive or zero (rule 2). Clearly there is only one such state that follows the rules: the state for which the total angular momentum is 0. *Any other states would possess a negative value for the total angular momentum, which is not allowed by the rules of quantum mechanics.* Thus, from these simple considerations we conclude that the only possible spin states that can result from the coupling of two individual electron spins (or coupling of two spin 1/2 particles of any kind) correspond to total spin angular momentum of 1 or 0. These states possess the spin quantum number for projection on the z axis of S = 1 and S = 0, respectively.

In Figure 7, the vector representation of the two possible state for two coupled spins is shown. In one case the two spins are antiparallel (S = 0) and so that the angular momenta exactly cancel and the resulting spin is 0. In this case the only possible value of S is equal to 0, so this is a singlet state. Notice that this spin state possesses one $\alpha$ spin and one $\beta$ spin. When we consider electron exchange we cannot label this state as $\alpha_1\beta_2$ or $\beta_1\alpha_2$ because this would imply that we can distinguish electrton 1 and eletron 2. However, an acceptable spin function for the singlet state turns out to be $(1/2)^{1/2}(\alpha_1\beta_2 - \beta_1\alpha_2)$, i.e., a mixture of the two spin states (From this point on, we shall ignore a mathematically required "normalization" factor of $(1/2)^{1/2}$ when discussing the sin wave function of the singlet state and shall drop the labels 1 and 2 which will be implicit). We can think of the - sign in the function $\alpha\beta - \beta\alpha$ as representing the "out of phase" character of the two spin vectors which causes the spin angular momentum of the individual spin vectors to exactly cancel.



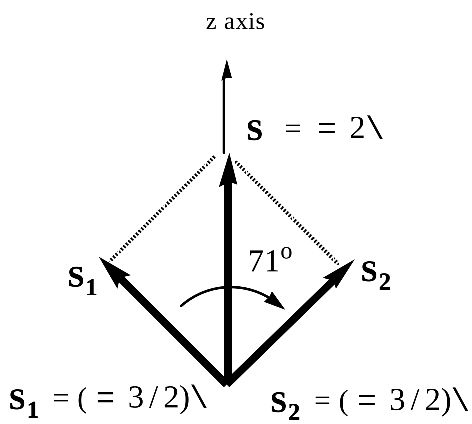
z axis
S1
α
S2
β
S = S1 - S2 = 0 \


(a)



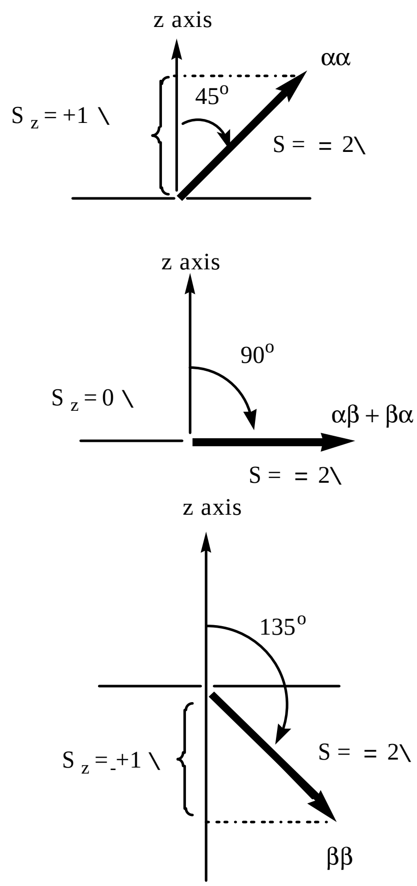
z axis
α
S1
S2
α
S = S1 + S2 = = 2\


(b)



z axis
S = = 2\
71o
S1
S2
S1 = ( = 3/2)\
S2 = ( = 3/2)\


(c)



z axis
αα
45o
S z = +1 \
S = = 2\
z axis
90o
S z = 0 \
αβ + βα
S = = 2\
z axis
135o
S z = -+1 \
S = = 2\
ββ


(d)

<u>Figure 7</u>. Subtraction and addition of two spin 1/2 particles. Upon addition, the spin vectors add up (middle) to a total length of $(2)^{1/2}$, but have a projections (right) of 1, 0 and -1 on the z axis (right). These representations apply to the coupling of an two spin 1/2 particles, electrons with electrons, electrons with nuclei and nuclei with nuclei.

The second possible state possesses S = 1 and is therefore a triplet state. The angular momentum of the state can take three possible orientations in physical space, as can the vector representing the angular momentum in spin space. The vector model of the triplet state reveals some rather interesting features which result from the rules of quantum mechanics and the rules of vector additions. In order to arrive at a resultant angular momentum corresponding to a vector length of 1 \ on the z axis (i.e., a total spin vector length of $(1/2)^{1/2}$ \ ), using individual component vectors whose lengths are $(3/4)^{1/2}$ \ , the individual vectors cannot lie at an arbitrary orientation, but must make a definite angle with one another. Have a definite angle to one another is equivalent to having a definite **phase** (angular) relationship of the two vectors. From triogonometry, if the value of the angle between the two vectors (termed the azimuthal angle) is $71^{o}$ then the resultant of addition of the two vectors is the required $(1/2)^{1/2}$ \ (Figure 7c). The common, and less precise description of two 1/2 spins coupling to produce a spin 1 system is to say that the spins are "parallel", i.e. colinear. The vector model reveals that this description is not correct, although the use of the term is acceptable to make the qualitative point that there is a net spin. In the vector diagrams representing the triplet state, we shall show the vectors separated at an angle which will be understood to be that required to satisfy the phase relationship required by quantum mechanics. We shall return to this point when discussing the cones of possible orientations of electron spins.

In the case of S = 1, the vector model of the three allowed orientations of the spin vector (Figure 7 d) shows several important features: (1) the <u>length</u> of the vector **S** is = $(2)^{1/2}$ for each of three allowed orientations; (2) the three allowed orientations of **S** relative to the z-axis are $45^{o}$, $90^{o}$, and $135^{o}$ (Eq. 6), corresponding to the value of $M_S$ of +1, 0 and -1, respectively (values of 1 \, 0 \ and -1 \ on the z axis). As in the case of the state for which coupling produces **S** = 0, the $M_S$ state for S = 1 possesses an $\alpha$ spin and a $\beta$ spin relative to the z-axis. Upon introduction of electron exchange we shall cannot label the electrons and distinguish them, so that the true state must be a mixture of the two spins, $\alpha$ and $\beta$, but different from the S = 0 state with no net spin. The appropriate spin function for the triplet state is $\alpha\beta + \beta\alpha$ (again the normalization constant of $(1/2)^{1/2}$ will be ignored throughout the text). We can interpret the + sign to mean that the spin vectors are in phase (with $\theta = 71^{o}$). For the state with $M_S$ = +1, the spin function αα is acceptable because since both electrons possess the same orientation, we need not attempt to distinguish them. The same holds for the $M_S$ = -1, for which the spin function ββ is acceptable.

It is interesting to note (compare Figures 6 and 7) that the component length of the angular momentum on the x or y axes, $S_{x,y}$ , grows smaller as the value of S gets larger. At the same time, the angle θ gets smaller as the size of the vectors **S** and $\mathbf{S_z}$ approach the same value. This is a feature of the so-called correspondence principle, which states that as the angular momentum of a system increases (i.e., as the angular momentum quantum number increases) the quantum system approaches the classical limit for which it is allowed that $S = S_z$. At this limit both the magnitude ($S_z$) and the direction ($90^o$) of the vector $\mathbf{S} = \mathbf{S_z}$ would be precisely measurable.

**Consequences of the Uncertainty Principle. The Cones of Possible Orientations**

We have seen that according to quantum mechanics, the angular momentum vector representing a rotating particle or a spinning body can take up only a specific discrete set of orientations in space. Moreover, the Uncertainty Principle states that the length and the direction of the angular momentum vector are conjugate quantities which means that if one is measured precisely, the other cannot be measured with any precision. So far we have for simplicity considered a two dimensional representation of the spin vectors. Let us now consider the more realistic situation in three dimensional spin space. From the Uncertainty Princple, if the value of the angular momentum is precisely measured on the z axis, the x and y components in three dimensional space are completely uncertain. This means that we can measure the value of $\mathbf{S}_z$ precisely and also means that we give up all precision in the measurement of $\mathbf{S}_x$ or $\mathbf{S}_y$.

This restriction of the the Uncertainty Principle is represented in the vector description by indicating the set of possible orientations that the angular momentum vector can assume relative to the z axis, since this corresponds to the range of possible component vectors that exist in the x,y plane. **This set of possible vectors constitutes a cone such that whatever the specific position the 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; however, the x and y components or the vector are completely undetermined.** Such a cone is termed the **cone of possible orientations of the spin**.

**Cone of Possible Orientations for Spin 1/2**

There is one cone associated with each possible orientation of the spin angular momentum; thus, once cone exists for each value of the quantum number $M_S$. For example, for a single spin of 1/2, there are two such cones, one associated with $M_S$ = 1/2 ($\alpha$ spin) and the other associated with $M_S$ = -1/2 ($\beta$ spin). Figure 8 (left) shows a representation of the two cones for an $\alpha$ spin and for a $\beta$ spin. An arbitrary possible position of the spin vector in the cone is shown for each case. We emphasize that it is impossible to measure such a position within the cone, although the existence of the vector somewhere in the cone (i.e., as an $\alpha$ or as a $\beta$ spin) can be inferred. **Thus, the vector for spin = 1/2 lies in one of two cones that represents all of the possible orientations of the angular momentum which may have a projection of +1/2 \, or -1/2 \ on the z-axis. The cones possess a side whose length is $(3/4)^{1/2}$ = 0.87 and an angle $\theta$ of either 55 º or 125 º** (units of length of the spin vector are always \).

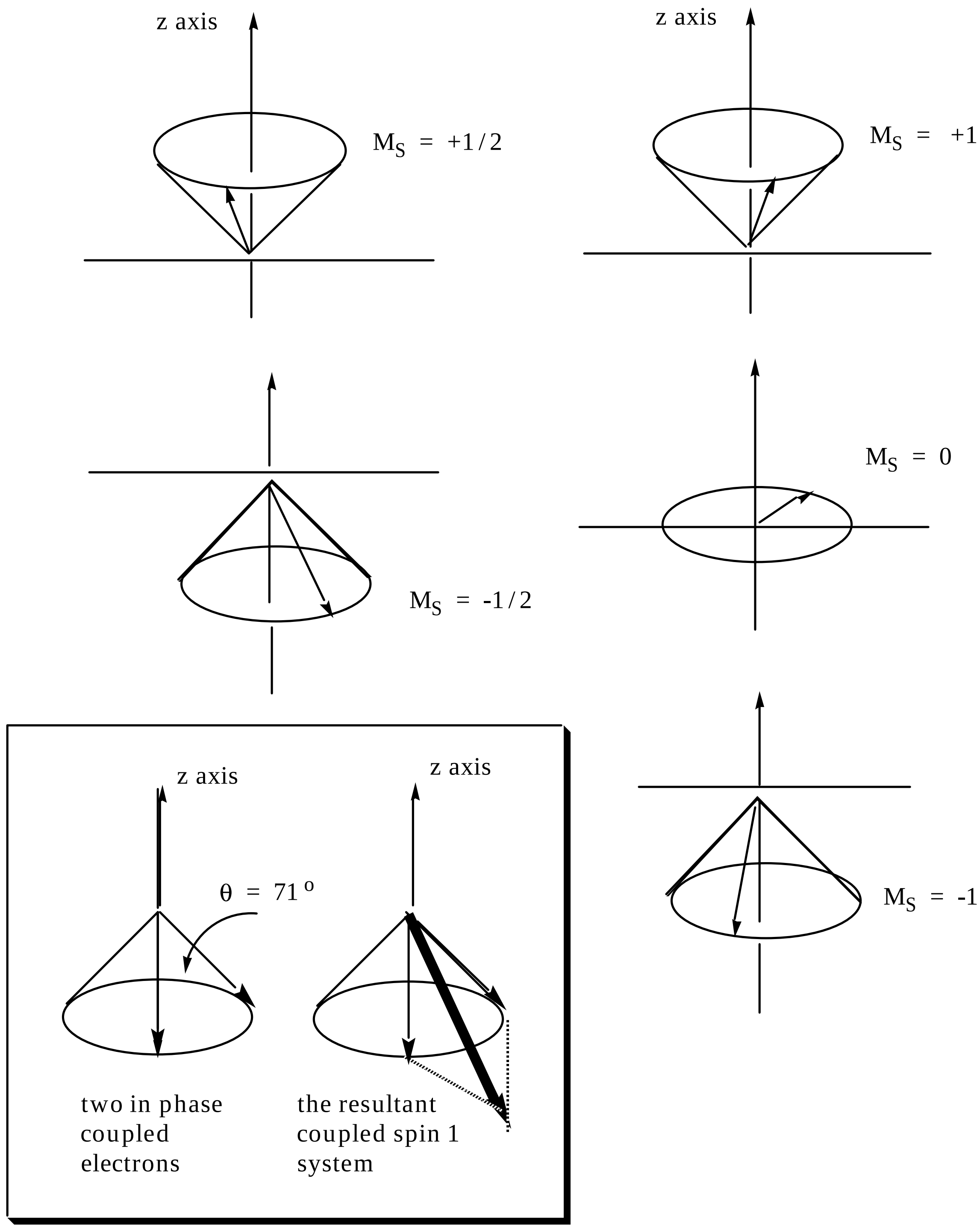



Figure 8. Cones of possible orientation for a spin 1/2 (left) and spin 1 (right) system of angular momentum. An arbitrary position of the spin vectors is shown for each of the possible cones. See text for discussion of the insert.

The above discussion shows that although we can have no knowledge of their precise position within a cone, we can determine whether a vector lies in one or the other of the two possible cones for a spin 1/2 system, i.e., that the projection of the angular momentum on the z-axis is exactly -1/2 \ or +1/2 \. Each cone has a definite projection of $M_s$ units of angular momentum on the z-axis and this projection represents the precise values of $S_z$. The $S_x$ and $S_y$ projections are indefinite, but the vector representing the angular momentum can be imagined as stationary and "resting" somewhere in the cone. In the absence of an external torque (magnetic field) the vector is "at rest" and does not move around in the cone. If any magnetic field is applied (as the result of a static applied laboratory field, an oscillating applied laboratory field, fields due to the magnetic moments generated by the motion of spins in the environment, etc.) the vector will begin to sweep around the cone, a motion that we shall refer to as precession. At this point, we simply consider that the spin vector is motionless and located somewhere in the cone.

**Cone of Possible Orientations for Spin 1**

Let us next consider the cones for the orientations of the case of S = 1 Figure 8, right). The situation is analogous to that for the spin = 1/2 case in that cones of orientation for the spin vector exist. In this case there are three cones of possible orientation for $M_S$ = +1, 0 and -1. Thus, t**he vector for spin = 1 lies in a cone that represents all of the possible orientations of the angular momentum which may have a projection of 1 \, 0 \ or -1 \ on the z-axis. Each of the cones possess a side whose length is $(2)^{1/2}$ = 1.7, but differ with respect to the angle θ that the side of the cone makes with the z axis**. 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 1.7 \. It should be noted that the magnitude of the spin vectors for S = 1 are larger than those for S = 1/2, although by convention the units are not explicitly shown in the figures. We note that for the singlet state, since the value of the spin vector is zero, there is no cone of orientation since the vector length is zero.

Finally, we can employ the cone of possible orientations to represent two coupled 1/2 spins and to clarify the point mentioned above concerning the requirement that two 1/2 spins must be in phase in order to produce a triplet. In the box in the lower left of Figure 8, a representation of two β spin 1/2 vectors ($M_S$ = 1) at the azimuthal angle (angle between vectors on the cone) of 77° are shown. Also shown is the resultant S = 1 system. The resultant length **on the cone of orientation** is exactly $[S(S + 1)]^{1/2}$ = 1.7 \, the angle, θ, relative to the z axis is 45 ° and the component on the z axis is -1. Upward rotation of this representation by 45 ° produces the represenation of the $M_S$ = 0 state and upward rotation of the latter representaion by another 45 ° produces the representaion of the $M_S$ = +1 state.

**Summary**

The angular momentum of a rotating or spinning particle is conveniently and mathematically represented by a vector. For an electron spin the vector possesses a length of $[S(S + 1)]^{1/2}$ where S is the electron spin quantum number of the system. Following the rules of quantum mechanics, the vector representing the angular momentum due to electron spin can only possess certain observablevalues and any particular value can only possess specific orientaitons in space. Sionce only one component of a spin vector (conventionally the z axis) can be observed, the aximuth of the vectro (its orientation in the xy plane) is completely unknown. However, the vector must be oriented in one of the cones of orientation allowed by quantum mechanics.

The vector model for spin angular momentum allows a clear visualization of the coupling of spins to produce different states of angular momenta. We now need to connect the vector model of angular momentum with models that allow us to deduce the magnetic energies and dynamics of transitions between magnetic states. This is done in the following sections.