## 2. Spin Chemistry and the Vector Model

The story of magnetic resonance spectroscopy and intersystem crossing is essentially a choreography of the twisting motion which causes reorientation or rephasing of electron spins. We can visualize this choreography wonderfully through the concept of **vectors**. Vectors are a tool for understanding spin structure, as the Lewis formulae are to understanding molecular structure. Vectors provide both a vivid and simple physical basis for visualizing the intersystem crossing processes and magnetic resonance phenomena (NMR and ESR) and in addition provide us with an economical and precise mathematic shorthand for keeping track of the structure and dynamics of spin systems. For example, the precessional motions associated with the choreography of spin in intersystem crossing are readily and elegantly handled by vector mechanics in which we will visualize transitions between spin states occurring as the result of changes in the relative precessional motions or orientations of two or more vectors representing the spins or the magnetic moments associated with spins.

We now consider some of the simple mathematical properties of vectors, after which we will relate the concept of vectors to the structure and dynamics of classical angular momentum and then to quantum mechanical spin angular momentum. After connecting vectors to spin angular momentum, we shall make a connection between spin angular momentum and magnetic moments directly associated with spin angular momentum. From knowledge of the properties of magnetic moments in a magnetic field, we shall be able to deduce qualitatively the magnetic energy diagram corresponding to the angular momentum states. We will then show how the vector model nicely depicts the precessional motion of the magnetic moment associated with spin, and how both radiative and radiationless transitions between magnetic states can be visualized as the result of coupled magnetic moments.

### Vectors and Angular Momentum and Magnetic Moments.

In order to gain or renew familiarity with the properties of classical angular momentum and vectors, we shall present a brief review of some important principles involving both, by referring to a **vector model for angular momentum**. Some physical quantities are completely described by a magnitude , i.e., a single number and a unit. Such quantities are termed **scalars**. Examples of scalar quantities are energy, mass, volume, time, wavelength, temperature, and length. However, other quantities have a **directional quality** and their complete description requires both a magnitude and a direction. Examples of vector quantities are electric dipoles, angular momentum, magnetic fields and magnetic moments. Such quantities are termed **vectors**. In discussing vector quantities we must always be concerned **not only with the magnitude of the**

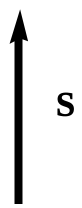
**quantity but a direction**. Scalar quantities will be represented in normal type and **vectors** will be represented in **bold face type.** For example, the magnitude of spin angular momentum is defined as a scalar, and therefore does not refer to direction and is represented by the symbol S. Similarly, the magnitude of a magnetic moment is a scalar and is represented by the symbol μ. When both magnitude and direction are condsidered, the spin angular momentum is a vector and is represented by the symbol **S**. The magnetic moment is a vector and is represented by the symbol **μ**.

The importance of vectors is that the characteristics of many physical quantities such as angular momentum, spin angular momentum, magnetic moments, magnetic fields, etc., can be faithfully represented by vectors. When this is the case, the powerful and simple shorthand, rules and algebra of vector mathematics can be employed to describe and to analyze the physical quantities in a completely general manner independent of the specific quantity the vectors represent. We may think of vectors as existing in a "vectorial space" that is independent of the physical space occupied by the physical object. Vector notation often clarifies the meanings of many equations whose physical and chemical bases are hidden by obscure mathematical symbolism. Thus, one motivation for using vectors is to simplify higher mathematical equations. Vectors are also closely related to the fundamental ideas of symmetry and their use can lead to valuable insights into the possible forms of fundamental scientific laws. We shall review the fundamental features of vectors and introduce a vector model of angular momentum and magnetic moments that will help to visualize the spin angular momentum states, the transitions between spin angular momentum states and the mechanisms of magnetic resonance spectroscopy, spin relaxation and spin chemistry.

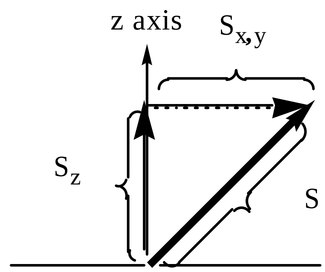
## Definition and Important Properties of a Vector.

There is perhaps no more natural and obvious way to represent a direction than an arrow. Similarly, a natural and obvious way to represent a **magnitude** is with the **length** of a line segment. Vectors combine these two intuitive and universal means of representation: **a vector is simply a mathematical object representing simultaneously a distance and a direction**. It is the fact that vectors are conveniently represented by an "arrow", which makes quantities represented by the vectors and the interactions between vector quantities readily visualizable. The arrowhead indicates the sense of the direction and the length of the arrow represents the magnitude of a physical quantity. In general, since direction must be specificed for all vector quantities, an axis is needed to serve as reference (Cartesian axis x, y, z) coordinate system for direction. This **reference axis**, by convention, will always be termed the **z**

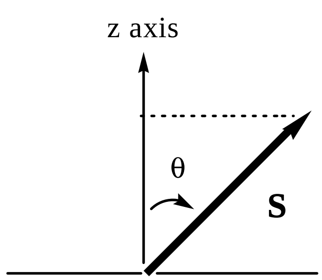
**axis**. The orientation of the vector in space is defined in terms of the angle, $\theta$, that the arrow or vector makes with the z-axis. Examples of vector notation for length and direction are given below in Figure 2 with spin angular momentum **S** as examples. In Figure 2 is depicted (a) an arbitrary spin vector with an undefined reference axis, **S**; (b and c) a spin vector with a specific length, S, and orientation in space, $\theta$, relative to a reference axis; and (d) a representation of two equivalent spin vectors $\mathbf{S}_1$ and $\mathbf{S}_2$, i.e., $\mathbf{S_1}$ and $\mathbf{S_2}$ possess identical lengths, i.e., $S_1 = S_2$.



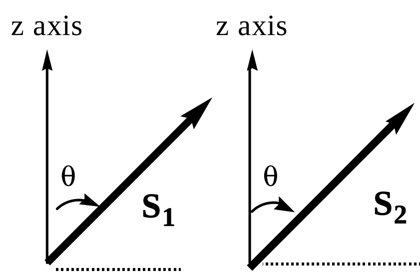

(a) An arbitrary Spin Vector is represented by the symbol , **S,** and by an arrow.




(b) Vector Length: S is the total **length** of the spin angular momentum vector **S**; $S_z$ is the length of the component on the spin angular momentum on the z axis; $S_{x,y}$ is the length of the component on the x or y axis.




(c) Vector Direction: The **direction** of the spin angular momentum vector is given by the angle $\theta$ made by the vector with the z axis.




$$\mathbf{S_1} = \mathbf{S_2}$$

(d) Equivalent Vectors $\mathbf{S_1}$ and $\mathbf{S_2}$. The two spin vectors show are identical (congruent) in spin space because they differ only by a parallel translation. They possess the same length, S, and direction, $\theta$.

Figure 2. Some simple properties of vectors with electron spin as an example. See text for discussion.

We must emphazise that vectors are mathematical objects and that represent physical objects. As a result, the vectors shown in Figure 2 refer not to real space, but to mathematical objects in a **spin space**. It is important not to confuse the "spin space" of vectors, with the real space of electons, nuclei and molecules. Furthermore, the lengths of the vectors represent the magnitude of spin, not distances. For example, the units of spin are angluar momentum (units, e.g., erg-s or J-s) and are not distance (units, e.g., Å or nm). We will attempt, however, to establish a relationship between the Euclidean space or molecules and radicals to the spin space of vectors when we discuss magnetic resonance and intersystem crossing.

## Vector Representation of Electron Spin

Now let us consider some important properties of all vectors, again with a vector representation of spin angular momentum **S** as a particular example.

*Property (1).* If two spin vectors have the same length and direction they are defined as equal and equivalent vectors, **no matter where they are located in <u>spin</u> space**. This property is similar to that of congruence of geometric figures, except that the reference axis must remain fixed. Thus, a **parallel** translation does not change a vector and all vectors of the same length which are parallel to each other represent the same vector, i.e., they are equivalent. For example (Figure 2, d), the two **spin** vectors, $\mathbf{S}_1$ and $\mathbf{S}_2$ have the same length (S) and direction (angle $\theta$ relative to the z-axis), therefore they are completely equivalent, i.e., they represent the same vector in the same way that molecules are equivalent if they have the identical molecular structures. Put mathematically, if two vectors possess identical length and direction: $\mathbf{S}_1 = \mathbf{S}_2$.

*Property (2).* The length of a spin vector is termed the magnitude of its spin angular momentum. Planck's constant, *h*, possesses the units of angular momentum (J-s) and the magnitude of spin is always expressed in units of$h/2\pi$ (which is commonly abbrebriated as \). By definition the magnitude of a vector quantity is a scalar (a single number) and is always positive (the absolute value of the number). Occasionally, because the magnitude of a vector is defined as a positive quantity, the symbol representing the magnitude of a vector may also represented by vertical bars (absolute value sign, | |) or the same letter as the vector except in plain type. For example, the symbol $|\mathbf{S}_1|$ and $S_1$ represents the magnitude of the vector $\mathbf{S}_1$. Since $\mathbf{S}_1$ and $\mathbf{S}_2$ are equivalent vectors, their lenghts are exactly identical: $|\mathbf{S}_1| = S_1 = S_2 = |\mathbf{S}_2|$. In Figure 2, the lengths of all of the spin vectors shown are the same in all instances (equal to S or $|\mathbf{S}|$).

It is important to note that any rotation of a vector of fixed length in vector space changes the vector to a different one, even though the magnitude of the vector does not change, because the angle θ with respect to the reference axis changes upon rotation.

*Property (3).* The orientation of a vector in space may be unambiguously defined by an angle, θ, that the vector makes with respect to the z axis (Figure 2 c). Thus, for full characterizaiton the x and y coordintes must be specified. In refering to molecular structures, the z axis is usually taken as the molecular axis of highest symmetry (or pseudosymmetry). For example, in a linear molecule this is the internuclear axis. In a strong laboratory magnetic field the z-axis is taken as the direction of the magnetic field (north to south pole).

We now consider two important procedures involving vectors that are commonly employed in describing **couplings** of spin angular momenta:

(1) Vector addition and subtraction
(2) Resolution of vectors into components

**Vector Addition and Subtraction. Resultants and Spin Space.**

Two spin vectors, $\mathbf{S}_1$ and $\mathbf{S}_2$ can be added or subtracted to produce new vectors (Figure 3). The addition is symbolized by $\mathbf{S_1} + \mathbf{S_2}$, where boldface symbols emphasizing that vectors, not scalars, are being added. Each of the vectors make a definite angle with the z axis. The addition of two vectors may be accomplished by applying the parallelogram law of vector adition: **the addition or sum of two vectors, $S_1 + S_2$ is the diagonal of the parallelogram of which $S_1$ and $S_2$ are the adjacent sides.** Figure 3 b shows an example of the addition of the vectors $\mathbf{S_1}$ and $\mathbf{S_2}$ according to the parallelogram law, for convenience referenced to the z axis. The new vector, **S**, representing the addition of $\mathbf{S_1}$ and $\mathbf{S_2}$ is termed the **resultant** of the addition and is shown as a heavier arrow in the Figure. An equivalent method (Figure 3 c) of adding two vectors is to place the tail of $\mathbf{S_1}$ at the head of $\mathbf{S_2}$ and draw a new vector from the tail of $\mathbf{S_1}$ to the head of $\mathbf{S_2}$. The new vector, **S**, can be seen to be identical to the resultant from the parallelogram method. Since both methods are mathematically equivalent, which representation employed will be a matter of convenience.

Two vectors, $\mathbf{S_1}$ and $\mathbf{S_2}$ can be also be subtracted to produce a new vector. The subtraction is symbolized by $\mathbf{S_1} - \mathbf{S_2}$. The vector $-\mathbf{S}_1$ is simply the vector $\mathbf{S}_1$ multiplied by -1, which in vector notation corresponds to rotating $\mathbf{S}_2$ by $180^o$ in space. In other words, $\mathbf{S}_1$ has the same length as $-\mathbf{S}_1$, and the two vectors are colinear but are antiparallel to one another. In spin chemistry the coupling between two spins or more generally between a spin and some other angular momentum can be characterized as a vector addition or subtraction. We shall soon see how the rules of "counting" possible spin states that result from interacting spins can be formulated in terms of vector additions and subtractions. Figure 3 d shows an example of the subtraction of the vectors $\mathbf{S_1}$ and $\mathbf{S_2}$. As in the case of vector additon, the subtraction of $\mathbf{S_1}$ from $\mathbf{S_2}$, can be achieved by placing the tail of -$\mathbf{S_1}$ at the head of $\mathbf{S_2}$ (figure 3d) or by the parallelogram method.

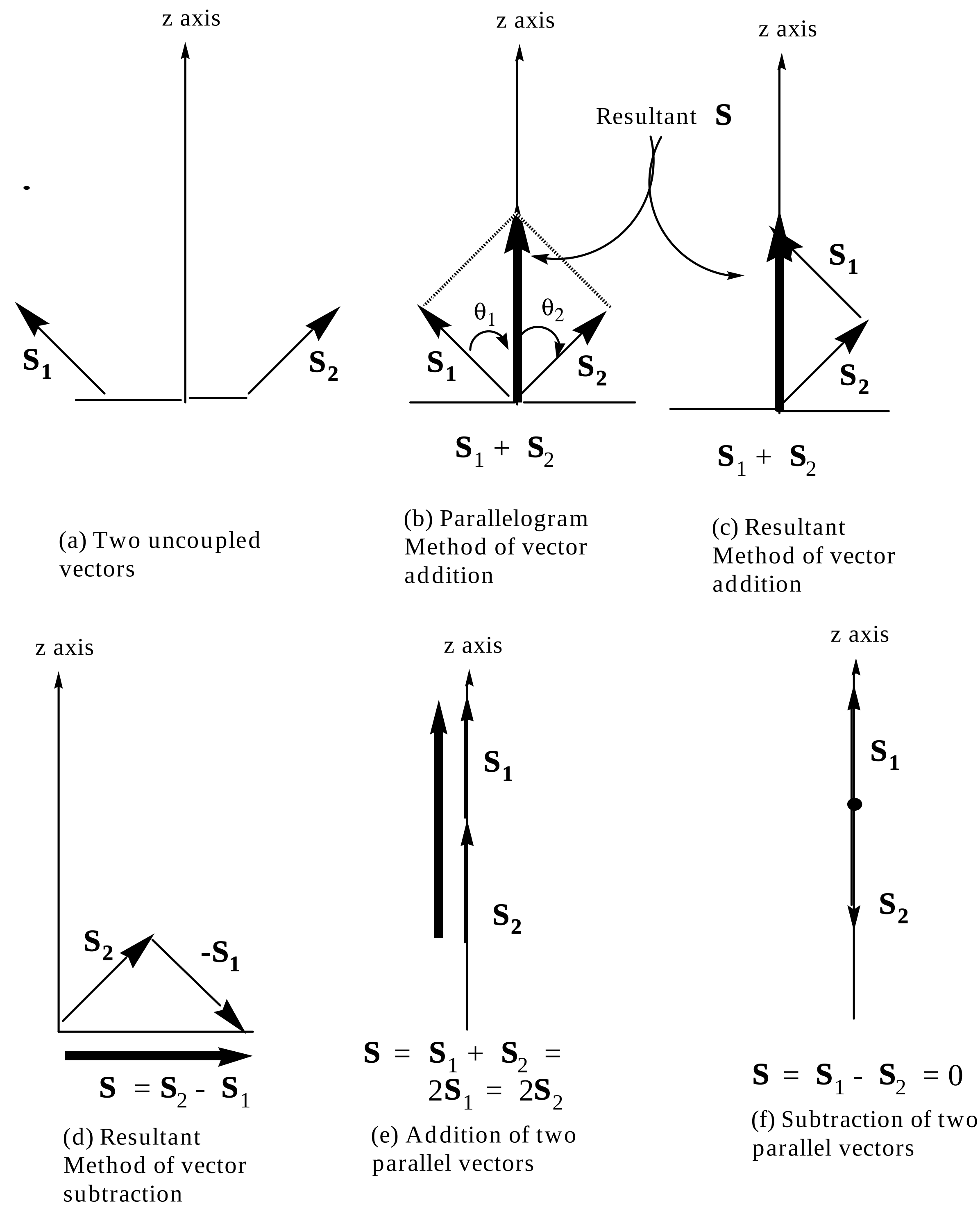



Figure 3. Examples of addition and subtraction of vectors with spin as an example.

A special case of vector addition occurs when the two vectors are parallel or antiparallel. For parallel vectors it is convenient to display the vectors as parallel or antiparallel to the z axis (Figure 3 e and f). If the vectors are parallel ($\mathbf{S_1}$ + $\mathbf{S_2}$), the magnitude of the vector sum is simply equal to the sum of the magnitudes of the individual vectors. If the vectors are antiparallel, the magnitude of the vector addition equals the absolute value of the difference of the magnitudes of the vectors and the resultant is parallel to the component vectors. In Figure 3 e and f examples of the addition and subtraction of two parallel and antiparallel spin vectors of equal length are shown. For the case of addition, the resultant is parallel to the original components ($\theta = 0$) and twice the magnitude of an individual component. (The resultant has been displaced slightly sidewise to show it more clearly).

**Vector Resolution into Components**

Just as two vectors may be added together to produce a new single vector, a given vector can be considered to be the sum of two or more component vectors, each of which has a specific magnitude and direction. These component vectors are conveniently resolved as the x-, y- and z-components of the vector on the Cartesian coordinates in 3 dimensions. For example, components of a vector are defined in a Cartesian coordinate axis system such that any vector lying in the xz plane can be represented as the sum of a vector parallel to the x axis and one parallel to the z axis (Figure 2 b, $\mathbf{S_{x,y}}$ and $\mathbf{S_z}$). The magnitude of a component in the z direction is positive when the vector points in the positive z direction and the component in the z direction is negative when the vector points in the negative z direction. The component method has a very simplifying effect in calculating vector sums, because it involves the use of right triangles and well known geometric principles such as the use of trigonometric functions and the Pythagorean theorem. Its most important use will be in dealing with angular momentum and magnetic moments. The quantized nature of angular momentum of elementary particles and the Uncertainty Principle require that only one component of angular momentum (by convention the component on the z axis) can be measured accurately in any experiment. The vector model will assist in clarifying this rather non-intuitive principle of quantum mechanics.

It is important to note that although two vectors may be added or subtracted to produce a non-zero resultant, the component on one or more of the principle axes may be zero. For example, in Figure 3 d, the resultant of subtracting $\mathbf{S_2}$ from $\mathbf{S_1}$ in non-zero, but its component on the z axis is zero. This feature of a finite sized vector with a zero component on the z axis will be important when we consider the vector model of the triplet state.

**Summary**

In quantum mechanics, angular momenta in general and spin angular momenta in particular, behave according to the rules of vectors. The total angular momentum of a system can therefore be regarded as the *resultant vector* of contributing vectors. The vector model of spin angular momenta provides insight into the physical significance of various coupling schemes, sparks and guides the imagniation to interpret many phenomena which depend on spin mechanics and places a ring of concrete geometry on the abstract operators of angular momentum quantum mechanics.