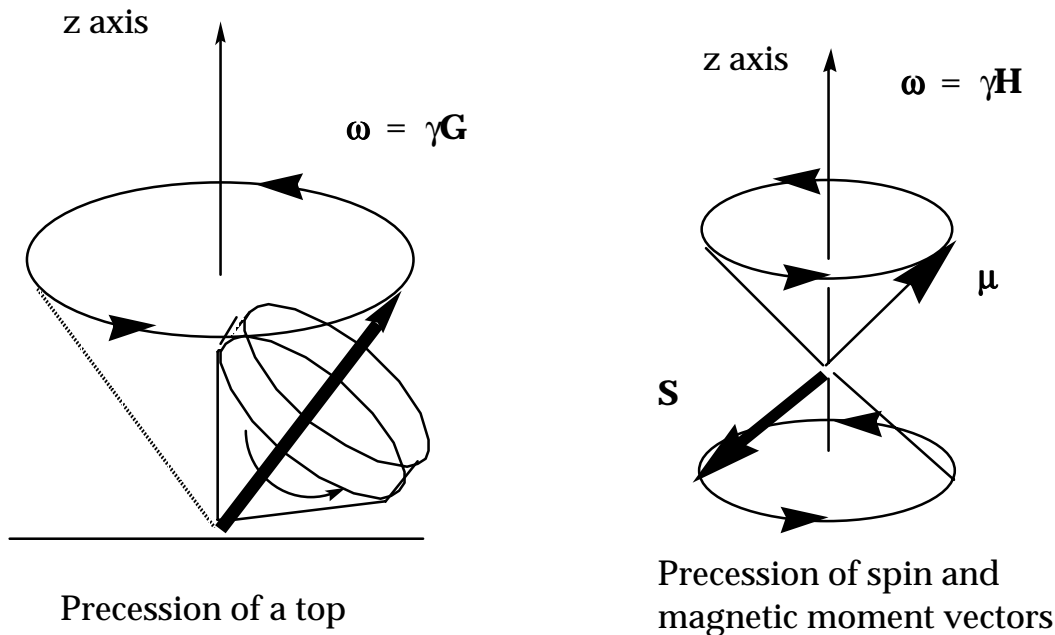## 6.   Classical Precession of the Angular Momentum Vector

A classical bar magnet (Figure 11) may lie motionless at a certain orientation in a magnetic field. However, if the bar magnet possesses angular momentum, it would not lie motionless, but would execute a precessional motion about the axis defined by the applied magnetic field. A classical analogue of the expected motion of a magnet possessing angular momentum in a magnetic field is available from the classical precessional motion of a rotating or spinning body such as a toy top or gyroscope. The angular momentum vector of a spinning top sweeps out a cone in space as it makes a **precessional** motion about the axis of rotation and the tip of the vector sweeps out a circle (Figure 12 left). The cone of precession of a spinning top possesses a geometric form identical to the cone of possible orientations that are possible for the quantum spin vector, so that the classical model cans serve as a basis for understanding the quantum model. A remarkable, and non-intuitive, feature of a spinning top is that it appears to defy gravity and precess, whereas a non-spinning gyroscope falls down! The cause of the precessional motion and the top's stability toward fallin is attributed to the external force of gravity, which pulls downward, but exerts a torque "sideways" on the angular momentum vector. This torque produces the non-intuitive result of precession. By analogy, in the presence of an applied field, the coupling of the magnetic moment with the field produces a torque that "grabs" the vectors and causes them to precess about the field direction.

Precession of a top

Precession of spin and magnetic moment vectors

<u>Figure 12</u>. A vector diagram comparing the precessional motion of a spinning top to the precessional motion of spin angular momentum vector **S** and the

precessional motion of the magnetic moment, μ_S in the presence of an applied magnetic field.

The classical vector properties of the angular momentum of a toy top or gyroscope are analogous to many of the important characteristics of the vector properties of the quantum mechanical magnetic moment. The reason for the close analogy is due to the important and **critical connection between the electron's magnetic moment and the angular momentum due to the electron's spin**. For example, the rotating mass of a gyroscope possesses angular momentum which can be represented by a vector whose direction is along the symmetry axis of rotation. A gyroscope in a gravitational field precesses, i.e., the axis of its rotation rotates about the direction of the gravitational field (figure 12 left). What factors determine the **rate of precession** of the gyroscope? The answer is the **force or gravity and the inherent angular momentum of the gyroscope**. If the angular momentum, which is determined by the angular velocity of spin and the mass of the gyroscope, is constant, the rate of precession ω is determined only by the force of gravity, so that there is a proportionality between the rate of precession and the force of gravity, **G**, as shown in eq. 12, where γ (compare to the magnetogyric ratio in eq. 8 and eq. 9) is the scalar proportionality constant between the precessional frequency and the force of gravity.

$$\omega = \gamma\mathbf{G} \qquad\qquad (12)$$

Since the mechanics of the precessional motion of a gyroscope in the presence of gravity are of the same mathematical form as the mechanics of a magnetic moment associated with a spinning charged body in the presence of a magnetic field, we postulate that the vector due to the magnetic moment of the quantum magnet undergoes precessional motion in an applied magnetic field.

Precession of a Quantum Magnetic Moment in an Applied Magnetic Field.

There are several features of the vector representation of a quantum mechanical magnetic moment that are critical for an understanding of how electron spin manifests itself in photophysical and photochemical processes. The first is the **magnitude** of the magnetic moment; second is the **orientation** of the magnetic moment with respect to a defined axis of quantization; the third is the **coupling strength** of the magnetic moment associated with electron spin to other magnetic moments; and the fourth is the **angular frequency** and **direction** of precessional motion made by the magnetic moment about a defined axis of quantization. In order to understand the quantum model, we shall first consider the concrete features of a classical model of a spinning electron and then move to

determine the new features that are imposed on an electron and its spin by the laws of quantum mechanics.

Application of a magnetic field has the effect of producing a torque on the magnetic moment vector in the same way that the force of gravity produces a torque on the angular momentum of a spinnig top (Eq. 12). According to Newton's classic Laws, this torque is equal to the rate of change of angular momentum. For a single electron in a given orbit, the absolute magnitude of the spin angular momentum is fixed, so that a magnetic torque can only be produced by changing the direction of the angular momentum vector, and not its magnitude. The conclusion is that the quantum magnetic moment vector, together with the angular momentum vector (whose motions are identical except for direction in space) must precess about the axis of the applied field because precession allows the direction of the angular momentum to change continuously without changing the magnitude of the angular momentum. If the amount of angular momentum is $\hbar$, the fundamental unit of angular momentum in the quantum world (i.e., the value of the angular momentum for $S = 1$) then the angular momentum vector and the magnetic moment vector precess about the field direction with a characteristic angular frequency, ω, given by eq. 13, where γ_e is the magnetogyric ration of the electron and H is the strength of the magnetic field (one unit of angular momentum is assumed).

$$\omega \text{ (Larmor frequency)} = \gamma_e H \qquad\qquad (13)$$

For a fixed unit of angular momentum of $\hbar$, the rate of precession, ω, of the spin and magnetic moment vectors about the magnetic field **H depends on the magnitude of both γ_e and H** and is termed the **Larmor** frequency (Figure 12). As mentioned above, this precessional motion is directly analogous to that of the motion of a gyroscope under the influence of gravity. We should remind the reader that the value of ω also depends on the amount of angular momentum, which was assumed to be one unit ($\hbar$) in the example.

The second important feature differentiating the classical magnet from the quantum magnet is that a classical magnet may achieve any arbitrary position in an applied field (of course, the energy will be different for different positions), but the quantum magnet can only achieve a finite set of orientations with respect to the applied field, i.e., **the orientations of the quantum magnet with respect to the applied field are quantized.** This result is due to the principle of quantization of angular momentum, which can possess only the following values on the z axis, depending on the value of M_S: $0\hbar$, $\hbar/2$, $\hbar$, $3\hbar/2$, $2\hbar$, etc., each value of which corresponds to a cone or possible orientations about the z axis. We now show that this feature leads to the conclusion that **the cones of possible**

orientations become cones of possible precess ion for the angular momentum and magnetic moment vectors in the presence of a coupling magnetic fields.

The Quantum Magnet. Precession in the Cone of Orientations.

Individual spin vectors are confined to cones which are oirented to cones which are oriented along the quantization axis. The **cone of possible orientations** (for each value of M_S) of the angular momentum vector also represents a **cone of precession** when the vector is subject to a torque from some magnetic field. When a magnetic field is applied along the z axis, the quantum states with different values of M_S will possess different energies because of the different orientations of their magnetic moments in the field (recall from eq. 9 that the direction of the magnetic moment vector is colinear with that of the angular momentum, so if the angular momentum possesses different orientations, so will the magnetic moment). These different energies, in turn, correspond to different angular frequencies of precession, ω, about the cone of orientations. The energy of a specific orientation of the anglar momentum in a magnetic field is directly proportional to M_S, μ_e and $\mathbf{H}_z$ (eq. 11, previous section).

$$E_Z \ = \ \backslash\omega_S \ = \ M_S g\mu\mathbf{H}_z \qquad\qquad (14a)$$

Thus, the value of the spin vector precessional frequency, ω_S, is given by Eq. 14b.

$$\omega_S \ = \ [M_S g\mu\mathbf{H}_z]/\backslash \qquad\qquad (14b)$$

From Eq. 14b, the values of ω are directly related to the same factors as the magnetic energy associated with coupling to the field. For two states with the same absolute value of M_S, but different signs of M_S, the precessional rates are identical in magnitude, but opposite in the sense of precession (if the tips of the vectors in Figure 12 were viewed from above, they either trace out a circle via a clockwise motion or via a counterclock wise motion). This opposite sense corresponds to differing orientations of the magnetic moment vector and therefore different energies, E_Z.

From classical physics, the rate of precession about an axis is proportional to the strength of coupling of the angular momentum to that axis. The same ideas hold if the coupling is due to sources other than an applied field, i.e., coupling with other forms of angular momentum. For example, if spin-orbit coupling is strong, then the vectors **S** and **L** precess rapidly about their resultant and are strongly coupled. The precessional motion is difficult for other magnetic torques to break up. However, if the coupling is weak, the precession is slow about the coupling axis and the coupling can be broken up by relatively weak

forces. These ideas will be of great importance when we consider transitions, such as intersystem crossing, between magnetic states.

Since the magnetic moment vector and the spin vector are colinear, these two vectors will faithfully follow each other's precession, so that we do not need to draw each vector, since we can deduce from one vector the characteristics of the other. We must remember, however, that one vector has the units of angular momentum (\) and the other has the units of magnetic moment (J/G). Figure 13 shows the vector model of the different rates of precession for a spin 1/2 and spin 1 state for the possible cones of orientation.
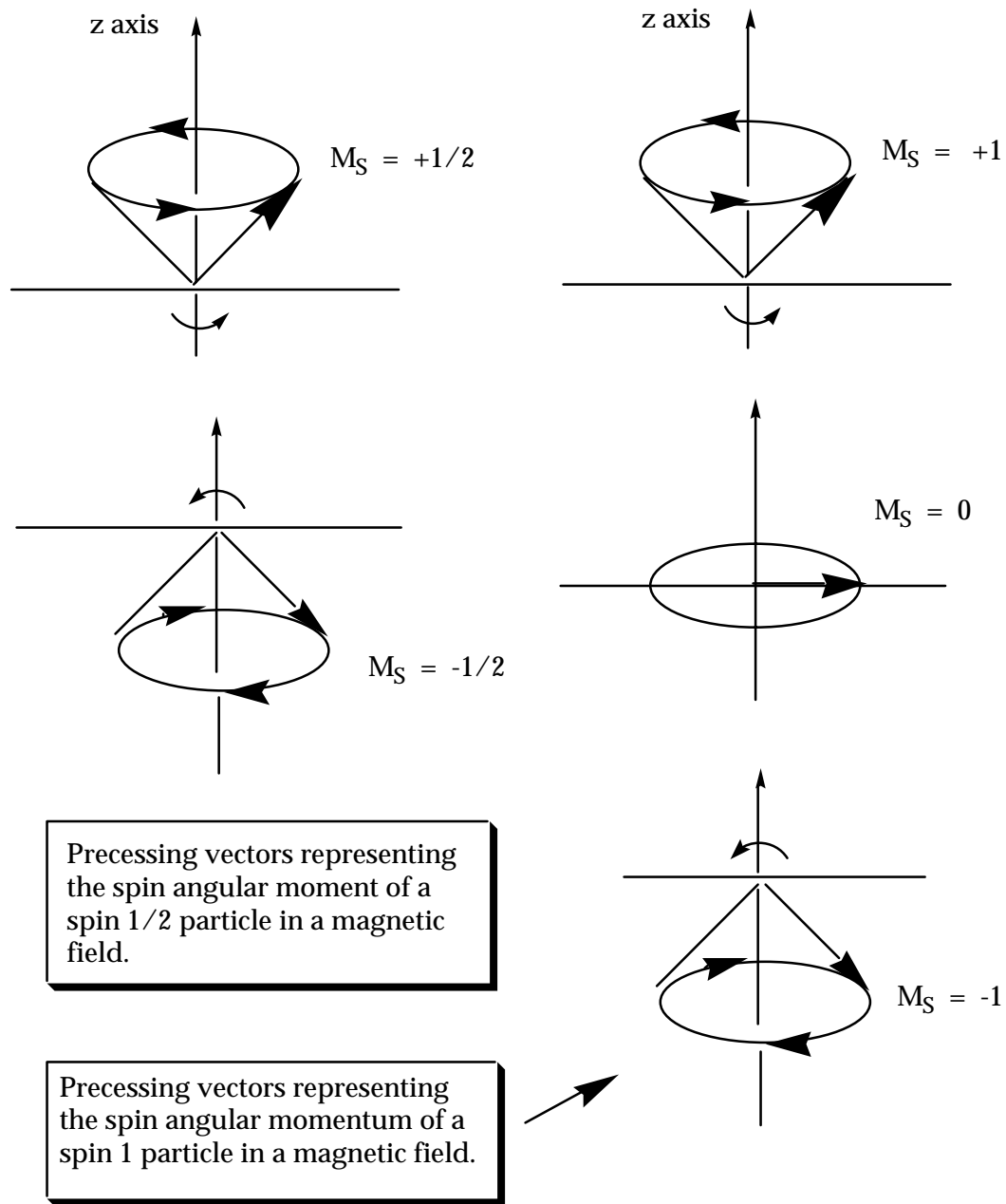
Figure 13. Vector model of vectors precessing in the possible cones of orientation. Only the spin angular momentum vectors are shown. The magnetic moment vectors (μ) (see Figure 11) precess at the same angular frequency as the angular momentum vectors (**S**), but are oriented colinear and 180° with respect to the spin vector. The magnitude of the angular momentum vector for the $S = 1$ system (right) is twice the magnitude of the angular momentum vector of the $S = 1/2$ system (left).

Summary

The process of rotation of the quantum magnet's vector about an axis is termed **precession** and the specific precessional frequency of a given state under the influence of a specific field is termed the **Larmor precessional frequency, ω.** We note the following characteristics of the Larmor precession, all of which are implied by eq. 14b:

(1)   The value of the precessional frequency ω is proportional to the magnitude of M_s,, g, μ and $\mathbf{H_z}$, where $\mathbf{H_z}$ is the value of a magnetic field interacting with the spin magnetic moment.

(2)   For a given orientation and magnetic moment, the value of ω decreases with decreasing field, and in the limit of zero field, the model requires recession to cease and the vector to lie motionless at some indeterminate value on the cone of possible orientations.

(3)   For a given field strength, a state with several values of M_S, the vector precesses fastest for the largest absolute values of M_S and is zero for states with $M_S = 0$.

(4)   For the same absolute value of M_S different signs of M_S correspond to different directions of precession, which have identical rates, but different energies.

(4)   A high precessional rate corresponds to a high energy because a high ω implies a strong coupling field **H** and the magnetic energy corresponds to the strength of the coupling field.

(5)   For the same field strength and quantum state, the precessional rate is proportional to the value of the g factor.

Some Quantitative Relationships Between the Strength of a Coupled Magnetic Field and Larmor Frequency.

From eq. 14b and the measured value of γ_e (1.7 x 10^7 rad s^{-1}) the following quantitative relationship exists between the precessional frequency and the coupling magnetic field for a "free" electron:

ω = 1.7 x 10^7 rad s^{-1} **H,** where **H** is in the units of Gauss   (15a)

It is also useful to consider the frequency of oscillation, ν (the frequency for which the precessing angular momentum vector sweeps a single circle). The relationship between ω and ν is ν = ω/2π or ω = 2πν. The latter relationships lead to eq. 16:

ν = 2.8 x 10^6 s^{-1} **H,** where **H** is in the units of Gauss   (15b)

Since one complete cycle is equivalent to 2π radians, for a fixed field the value of ω is always greater than the value of ν. The frequency ν is the same frequency associated with the oscillations of a light wave. Through the relationship (Eq. 16) of ΔE. ω and ν, we can readily associate the precessional frequency, ω with the resonance oscillational frequency of radiative transitions, ν and the energy gap between the states undergoing transitions, ΔE.

$$\Delta E \;=\; h\nu \;=\; \backslash\omega \qquad\qquad (16)$$

From eqs. 15 and 16, we can therefore compute that the frequency of precession ω for fields of 1 G, 100 G, 10,000 G and 1,000,000 G is: 1.7×10^7 rad s^{-1}, 1.7×10^9 rad s^{-1}, 1.7×10^{11} rad s^{-1}, and 1.7×10^{13} rad s^{-1} (for oscillation frequency, ν, the values are 2.8×10^6 s^{-1}, 2.8×10^8 s^{-1}, 2.8×10^{10} s^{-1}, and 2.8×10^{12} s^{-1}), respectively. Practically speaking, applied laboratory fields whose strengths can be varied from 0 to about 100,000 G are readily achievable, so that precessional rates ω of the order of 1.7×10^{11} rad s^{-1} ($\nu = 2.8 \times 10^9$ s^{-1}) are achievable by applying laboratory magnetic fields to a free electron spin. Internal magnetic fields resulting from interactions with other electron spins or nuclear spins typically correspond to magnetic fields in the range from a fraction of a G to several hundreds of G. In certain cases, however, strong spin-orbit coupling interactions or strong coupling of two electron spins, can produce magnetic fields of the order of 1,000,000 G or larger, causing precessional frequencies of the order of 10^{12} s^{-1} and greater.

Precession of Electron and Nuclear Spins

The value of the electron's magnetic moment μ_ε is proportional to the magnitude of the gyromagnetic ratio, γ_e (eqs. 8 and 9). An analogous expression holds for the magnetic moment of a nucleus, $\boldsymbol{\mu}_n$ (eq. 17, where γ_n is the magnetogyric ratio for a specific nucleus, g_n is the nuclear g factor and $\mathbf{I}$ is the value os the nuclear spin).

$$\boldsymbol{\mu}_n \;=\; g_n\gamma_n\mathbf{I} \qquad\qquad (17)$$

Since the value of ω is proportional to μ, it is also proportional to γ. From these relationships, we can deduce that the precessional rate of an electron spin is much faster than that of a nuclear spin of a proton, since γ_e is ca 1000 times larger than γ_p, the gyromagnetic ratio for a proton. The differences can be traced to the difference in the mass of the nucleus and the electron (they both have the same absolute value of charge and angular momentum). To achieve the same angular momentum as an electron, the more massive nucleus need achieve a much smaller angular velocity. Because of this slower velocity, the spinning nucleus

"carries less current" as a spinning charge and therefore generates a smaller magnetic moment. From the definition of γ as $e/2m$ (eq. 7 and 8), it is readily deduced that the magnetic moment of a proton is nearly 1000 times smaller than the magnetic moment of an electron, i.e., the ratio of magnetic moments is proportional to the ratio of the masses for particles of the same spin (1/2 \) and electric charge (one unit).

Eq. 18 gives the quantitative relationship of the precessional frequency, ω_p, of a proton's magnetic moment in a field $\mathbf{H}_z$. For a ^{13}C nucleus, the precessional frequency is approximately 4 times less than that of a proton (which possesses the largest value of γ_n of any nucleus.

$\omega_p = 2.4 \times 10^4$ rad s^{-1} $\mathbf{H}$, where $\mathbf{H}$ is in the units of Gauss   (18)

For example, at a field of 10,000 G the precessional frequency of the proton's magnetic moment is 2.4×10^8 rad s^{-1}, which can be compared to the precessional frequency of 1.7×10^{11} rad s^{-1} at the same field strength.