## 5. Classical Magnetic Energy Levels in a Strong Applied Field

In the absence of a coupling magnetic field (zero field situation), the magnetic energy levels due to spin angular momentum are degenerate, i.e., they all have the same (zero) magnetic energy. Let us now consider what happens to the degenerate magnetic energy levels at zero field when a strong field magentic field is applied. We shall examine the results for a classical magnet and then apply these results to determine how the quantum magnet associated with the electron spin changes its energy when it couples with a 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 will also provides us with an excellent tool for dealing with the qualitative and quantitative aspects of transitions between magnetic energy levels.

According to classical physics, when a bar magneti is placed in a magnetic field, $H_0$, the torque acting on the magnetic moment of the bar magnet is proportional to the product of the magnitude of the magnetic moment, $\boldsymbol{\mu}$, of the bar magentic, the magnitude of the magnetic moment of the magnetic field, $\mathbf{H}_Z$, and the angle $\theta$ between the vectors describing the moments. Three important orientations of bar magnetic are shown schematically in Figure 11.

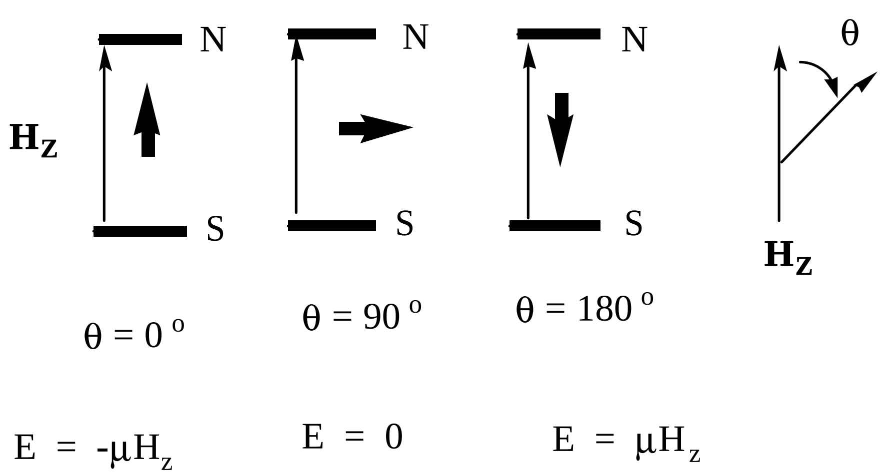



Figure 11. Energies of a classical bar magnet in a magnet field, $H_Z$.

The precise equation describing the energy relationship of the bar magnetic at various orientations is given by equation 10, where $\boldsymbol{\mu}$ and $\mathbf{H}_Z$ are the magnitudes of the magnetic moments of the bar magnet and the applied field in the Z direction.

$$E\,(\text{magnetic}) = -\mu H_Z \cos\theta \qquad (10)$$

In eq. 10 the negative sign before the quantity on the right of the equation means that the system becomes more stable if the product of $\mu H\cos\theta$ is a positive quantity. The magnitudes (lengths) of the vector quantities $\boldsymbol{\mu}$ and **H** are always positive by definition. 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 q between $0^o$ and $90\ ^o$ and negative for $\theta$ between $90\ ^o$ and $180\ ^o$. Let us consider the situation for two parallel vectors ($\theta = 0$), two perpendicular vectors ($\theta = 90^o$ or $\pi/2$), and two antiparallel vectors ($\theta = 180^o$ or $\pi$). For these cases, $\cos\theta = 1$, 0 and -1, respectively (Figure 11). Thus, we can make the important conclusions that any orientation of the bar magnet with $\theta$ between 0 and less than $90^o$ is stabilizing (the E in Eq. 10 is negtive relative to the zero of magnetic energy) and any orientation of the bar magnet with $\theta$ between $90^o$ and up to $180^o$ is destabilizing (the E in Eq. 10 is positive relative to the zero of magnetic energy). Importantly, at an orientation of $90^o$ the magnetic interactions between the applied magnetic field and the bar magnet are zero ($\cos 90^o = 0$), i.e., the same as they are in the absence of a strong field!

## From Spin Angular Momentum States to Magnetic Energy Levels

From the classical model for a bar magnet in a magnetic field, we can proceed to deduce the energies of the quantum magnets. To do this, we now proceed to translate the spin states for one, two and three spins into magnetic energy diagramss that will show the relative energetic ordering of the magnetic energy levels. From magnetic energy level diagrams, just as for the electronic energy level diagrams, all possible transitions between different magnetic energy levels can be readily deduced by inspection. The paradigm of selection rules and plausible mixing mechanisms will then provide a means of analyzing magnetic resonance phenomena such as magnetic resonance spectroscopy and intersystem crossing.

We shall consider the energy level diagrams for two extreme situations: (1) zero (or "low") applied magnetic field, i.e., the usual situation under which photochemical reactions are conducted; and (2) a strong ("high") applied field, i.e. the conditions under which magnetic resonance spectrosopy is conducted. The terms high and low will refer to the strength of the applied magnetic field compared to inherent magnetic interactions between the spin states and internal magnetic fields.

## Quantum Magnets in the Absence of Coupled Magnetic Fields

In the absence of any magnetic interactions, the vector model of a single electron spin views the angular momentum and magnetic moment as stationary in space and possessing random orientations in space. There is no pertinent $M_S$ quantum number in this case, because there is no preferred axis of orientation. However, the spin angular momentum of the electron (1/2\) and the quantum number for the total spin, S, are still a good quantum numbers.

As for the case of a single electron spin, at zero field it is convenient to consider a system containing spin correlated electron spins as a mixture of singlet (S) and triplet states (T). Thus, the spin functions given in Table 1 cans be used to describe the system at both zero and high fields. In the absence of magnetic interactions operating on the paired spins, the four states have exactly the same energy, i.e., all four of the magnetic energy levels are degenerate.

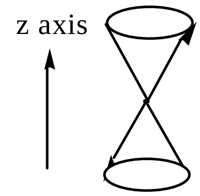
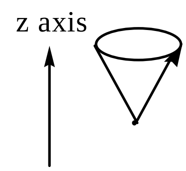
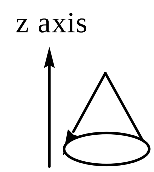
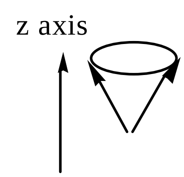
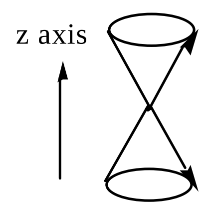
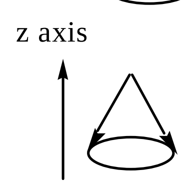
**Quantum Magnetic Energy Levels in a Strong Applied Field. Zeeman Magnetic Energies**

We are now in position to determine the energies of magnetic sublevels and the precession rates assoicated with spins in magnetic sublevels as a function of their g-factors and the strength of applied fields. The magnetic energy of interaction of a magnetic moment and an applied field is known as the **Zeeman energy**. Eq. 9 relates the magnetic moment of the quantum magnet with the value of the g factor and the spin. Eq. 11 relates the energy of the quantum magnet to the strength of the applied field, $H_0$, the magnetic quantum number for the spin orientation, $M_S$, the g-value of the electron and the universal constant $\mu_e$.

$$E = M_s g \mu_e H_Z \qquad (11)$$

Thus, the magnetic energies (relative to those in zero field) of the singlet, doublet and triplet states are readily computed and are shown in Table 2.

Table 1. Important facets of singlet, doublet and triplet states in an applied magnetic field $H_Z$.

| **State** | **State Symbol** | **$M_S$** | **Magnetic Energy** | **Spin Function** | **Vectror Representation** |
|---|---|---|---|---|---|
| Singlet | S | 0 | 0 | $\alpha\beta - \beta\alpha$ |  |
| Doublet | $D_+$ | +1/2 | $+(1/2)g\mu_e H_Z$ | $\alpha$ |  |
| Doublet | $D_-$ | -1/2 | $-(1/2)g\mu_e H_Z$ | $\beta$ |  |
| Triplet | $T_+$ | +1 | $+(1)g\mu_e H_Z$ | $\alpha\beta + \beta\alpha$ |  |
| Triplet | $T_0$ | 0 | 0 | $\alpha\beta + \beta\alpha$ |  |
| Triplet | $T_-$ | -1 | $-(1)g\mu_e H_Z$ | $\alpha\beta + \beta\alpha$ |  |