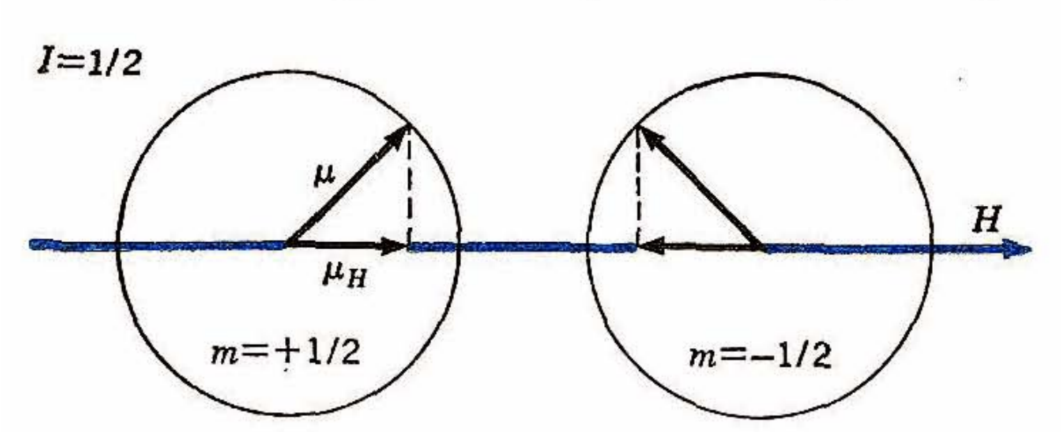
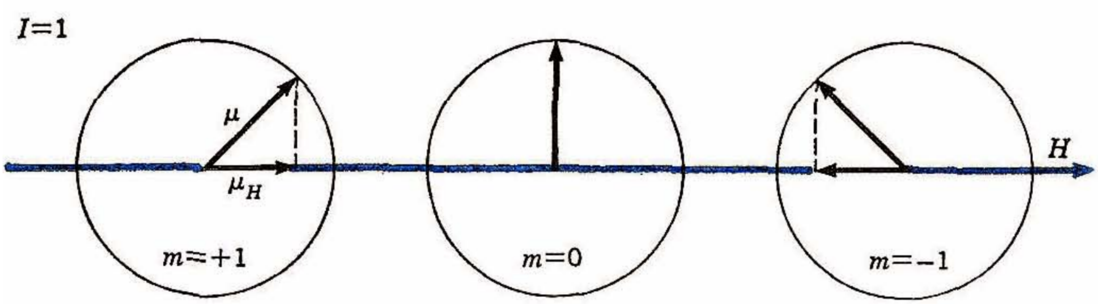
1.4: Magnetic Quantum Numbers

An important property of spinning nuclei is that their magnetic moment vectors appear to have only certain specified average values in any given direction, such as along the axis of the principal magnetic field. The permitted values of the vector moment along the direction of interest can be described with the aid of a set of magnetic quantum numbers m, which are derivable from the nuclear spin I and the relation m = I, (I - 1) (I - 2), . . . , -I. Thus, if I is 1/2, the possible magnetic quantum numbers are +1/2 and -1/2, and if the magnetic moment is p, the possible values of the vector components of the moment in the direction of the principal magnetic field H will be +/mu x and -mu x, as shown below.



If I is unity, then the possible magnetic quantum numbers are +1,0, and -1, and the vector along the field direction will have possible values corresponding to the nucleus being oriented so as to have a component in the same direction as the field vector, perpendicular to the field vector, or opposite in direction to the field vector.



In the absence of a magnetic field there will be no preference for one or the other of the two possible magnetic quantum numbers for a nucleus with I equal to 1/2. In a large assemblage of such nuclei, there will be then exactly equal numbers with rn equal to +1/2 and m equal to -1/2. In a magnetic field, the nuclei will tend to assume the magnetic quantum number (+1/2) which represents alignment with the field in just the same way as compass needles tend to line up in the earth's magnetic field. Thus, in the presence of a magnetic field, m = +1/2 represents a more favorable energy state than m = -1/2 [provided the gyromagnetic ratio y (see Sec. 1-5) is positive]. However, the tendency of the nuclei to assume the magnetic quantum number +1/2 is opposed by thermal agitation. The nuclear moment, field strength, and temperature can be used to calculate the equilibrium percentages of the nuclei in each quantum state by the Boltzmann distribution law. At room temperature, even in rather high magnetic fields such as 10,000 gauss, thermal agitation is so important relative to the energy gained by alignment of the nuclei that only a very slight excess of the nuclei go into the more favorable quantum state, as shown by the following:

$$N = Apexp\frac{-\epsilon}{kT}$$

(Boltzmann equation)

$$\epsilon = -\mu_H H = -\frac{\gamma h}{2\pi} mH$$

For protons at 300°K in a field of 9,400 gauss

$$\frac{N(+\frac{1}{2})}{N(-\frac{1}{2})} = exp(\frac{\gamma hH/2\pi}{kT}) = 1.0000066$$

This situation is analogous to an assemblage of compasses on a table subjected to violent agitation. The movements of the table tend to throw the compass needles out of alignment with the earth's magnetic field, so that on the average only a very slight excess of the needles may be actually pointing north.

Nuclear magnetic resonance spectroscopy is primarily concerned with transitions of the nuclei in a magnetic field between energy levels which are expressed by the different magnetic quantum numbers. These energy changes are analogous to electronic and vibrational-rotational energy changes in other forms of spectroscopy. There is no direct magnetic interaction between the nuclei and the electrons which surround them. Thus, a problem is posed with regard to the transfer of energy from the nuclei to and from their surroundings. The energy-transfer problem may be restated in the following way. Consider an assemblage of nuclei in the absence of a magnetic field. As stated before, there will be exactly equal numbers of nuclei with the magnetic quantum numbers +1/2 and -1/2 In the presence of a magnetic field, this distribution corresponds to an infinitely high temperature because the state with the magnetic quantum number -1/2 is now energetically less favorable than the +1/2 state and only an infinitely high temperature could produce sufficient thermal agitation to keep the nuclear magnets from having some net alignment in the field direction. In order to achieve the equilibrium distribution of nuclei between the two possible spin states at a lower temperature, it is necessary that energy be lost to the surroundings by nuclear "relaxation." Relaxation is hardly expected to be a simple process, since the nuclei are not easily able to collide with one another or the surrounding electrons and convert their energy due to an external magnetic field into molecular vibrational, rotational, or translational energy. Transfer of energy back and forth among nuclei in various magnetic quantum states and their surroundings can be achieved with the aid of another property which might be ascribed to magnetic nuclei, called "nuclear precession."
