1.6: Nuclear Relaxation

The property of magnetic nuclei which corresponds to precession provides a means whereby energy may be transferred back and forth between the nuclei and their surroundings. Consider a magnetic field vector arranged so as to rotate perpendicular to a magnetic field in which are immersed magnetic nuclei precessing at the angular velocity mo (Fig. 1-4). If the rotating vector has a quite different angular velocity from the precessing nuclei, the rotating field vector and the precessing nuclear magnetic vectors cannot remain in phase and there will be no effective interaction between them. On the other hand, if the rotating field vector has the same angular velocity as the precessing nuclear vectors, it will remain in phase with them and can exert a magnetic torque tending to flip over the orientation of the nuclei and thence change their magnetic quantum numbers. Of course, if the nuclear magnetic quantum numbers change, energy is transferred to or from the agency producing the rotating field vector. Thus, an assemblage of nuclear magnets immersed in a magnetic field can come to thermal equilibrium with its surroundings.

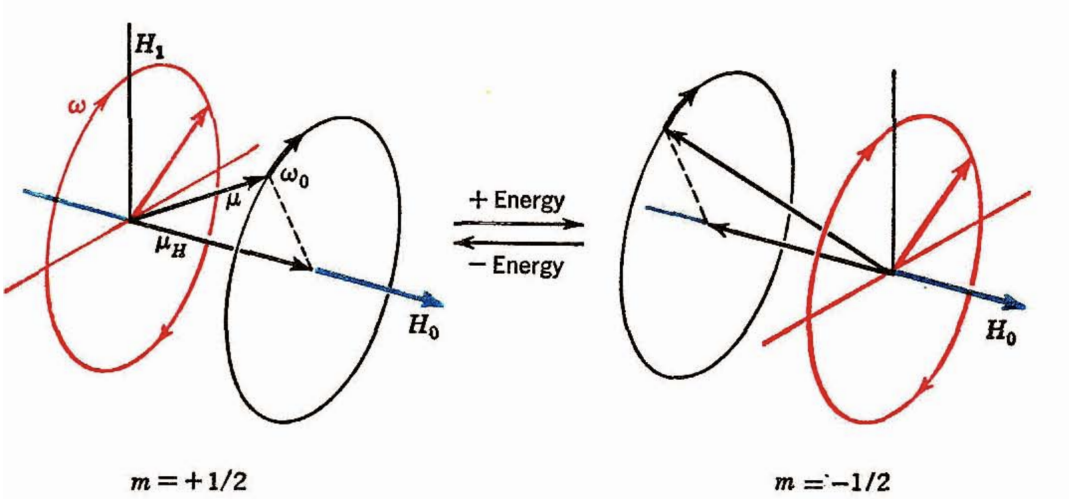

Fig. 1-4. Interaction between a rotating magnetic vector H_1 and nuclei precessing in an applied magnetic field H_0.

An important mechanism for relaxation of a group of nuclei at a nonequilibrium spin temperature utilizes atomic and molecular thermal motions as follows. Suppose a magnetic nucleus is surrounded by others of its type contained in atoms undergoing violent thermal motions. The thermal motions of the nuclei produce random oscillatory magnetic fields which can have frequency components with frequencies equal to the precession frequencies of the relaxing nuclei and can act as a rotating magnetic field vector so as to permit the magnetic orientation energy to be converted to thermal energy. The rate of relaxation by this mechanism depends on the temperature, the concentration of magnetic nuclei, and the viscosity of the medium. It is kinetically a first-order process and can be expressed in terms of a "relaxation time," which is the mean lifetime of the excess of nuclei in the nonrelaxed state. Thermal relaxation is often slow, on the order of seconds to weeks. A vivid example is provided by $_{13}C$ of natural abundance located at the central atom of neopentane molecules. The natural abundance of $_{13}C$ is SO low that such atoms will usually be connected only to nonmagnetic $_{12}C$ atoms and thus are sterically shielded from other magnetic nuclei such as the methyl protons in the same or surrounding molecules. As a result, the rotating field components produced by the thermal motions of the surrounding magnetic nuclei are not very effective at aiding the relaxation of the central $_{13}C$ nucleus, and the mean lifetime before relaxation is very long.

As might be expected, thermal motions of substances with unpaired electrons are particularly effective in inducing thermal relaxation, and such paramagnetic substances present as impurities may spoil high resolution spectra by making the relaxation times very short, which, as will be seen later, results in line-broadening.

In summary, transitions between states with various magnetic quantum numbers which have different energies because of an applied magnetic field may be induced by thermal motions of magnetic nuclei or paramagnetic substances or else by an external rotating magnetic field which has a frequency equal or very nearly equal to the precession frequency of the nuclei.