However, quantum mechanical magnetic nuclei differ from classical bar magnets in several important ways. First, a proton (for example) is so small that it would have to spin faster than the speed of light to produce its observed magnetic moment by the classical model of a spinning charge. Thus, we are forced to accept that the proton has a nuclear magnetic moment, even though we cannot account for its magnitude by classical arguments. Second, although both classical and quantum mechanical magnetic moments may point in arbitrary direction with respect to an applied magnetic field, the direction of a quantum mechanical magnetic moment is experimentally *observed* to point only along the magnetic field direction. Third, the z-component of μ_n is quantized (i.e., is observed to have only $2I+1$ values, where I denotes the "nuclear spin quantum number"), as shown in Figure 8.3. Thus, one commonly hears that the magnetic moment of a proton (for which $I = 1/2$, so that the (observable) z-component of μ_n has only two possible values) can point only "up" or "down" with respect to $\boldsymbol{B}_0$. In fact, a proton magnetic moment can point anywhere, but in a given experiment can only be *observed* to point "up" or "down" along $\boldsymbol{B}_0$.

A classical bar magnet has a fixed "strength" (i.e., fixed magnetic moment), and therefore only one possible energy for a given orientation of the magnet in a magnetic field (Eq. 8.7). In contrast, an individual quantum mechanical nucleus of spin, I, can have any of $2I+1$ possible z-components of angular momentum, $I(h/2\pi)$, $(I-1)(h/2\pi)$, $\cdots$, $-(I-1)(h/2\pi)$, $-I(h/2\pi)$, and hence $2I+1$ possible energies, E_m.

$$E_m = -\frac{\gamma h m}{2\pi} B_0, \quad m = -I, -I+1, \ldots, I-1, I \tag{8.9}$$

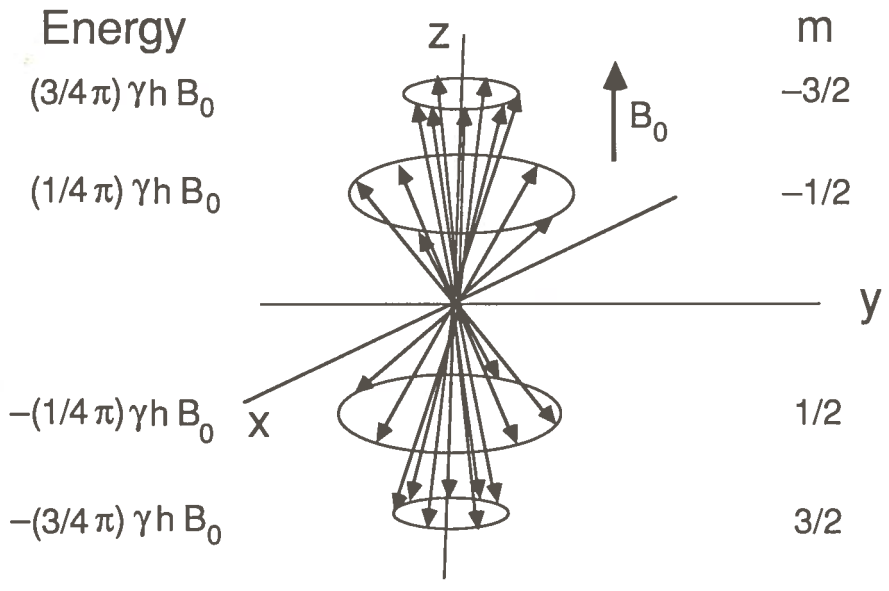

Figure 8.3 Discrete observable energies for a quantum mechanical magnetic nucleus of spin, $I = 3/2$, in a static magnetic field, $B_0\,\mathbf{k}$. The $2I+1 = 4$ possible energies are determined by the quantum number, m, of the z-component of nuclear spin angular momentum (see text), and are independent of ϕ.

At thermodynamic equilibrium, the relative probability $P(m)$ that a given nucleus will be observed with magnetic energy, E_m, is given by the Boltzmann factor:

$$P(m) = \frac{\exp\left(\frac{-E_m}{kT}\right)}{\sum_{m=-I}^{I} \exp\left(\frac{-E_m}{kT}\right)} \tag{8.10}$$

in which k is the Boltzmann constant and T is temperature in Kelvin. For typical NMR experiments, $E_m \ll kT$, so that

$$\exp\left(\frac{-E_m}{kT}\right) \cong 1 - \frac{E_m}{kT} \tag{8.11}$$

An *individual* quantum mechanical magnetic nucleus can be observed to point only along or opposed to $\boldsymbol{B}_0$. However, a *macroscopic ensemble* of quantum mechanical magnetic nuclei will have a net magnetic moment given by the (vector) sum of the magnetic moments of the individual nuclei. For example, for an ensemble of N_0 protons, for which the individual angular momentum z-components are $\pm(h/4\pi)$, Eqs. 8.9 to 8.11 can be combined to yield an equilibrium macroscopic magnetic moment, $\boldsymbol{M}_0 = M_0\,\mathbf{k}$. For spins, $I = 1/2$ (see Problems),

$$\boldsymbol{M}_0 = M_0\,\mathbf{k}\,; \quad M_0 = N_0\,\gamma^2 \left(\frac{h}{2\pi}\right)^2 \frac{B_0}{4\,k\,T} \tag{8.12}$$

Because the magnetic energy is independent of the azimuthal angle, ϕ, the ϕ-angles of the *individual* nuclear magnetic moments are randomly distributed around the z-axis (see Figure 8.3), so that the resultant net *macroscopic* magnetic moment, $\boldsymbol{M}_0$, lies along the z-axis. Finally, M_0 is proportional to N_0; thus, NMR spectral peak relative areas (see below) provide a direct measure of the relative numbers of nuclei at each Larmor frequency.

8.2 NMR parameters

The enormous practical value of FT/NMR is based on the direct relationship between various spectrally measurable NMR parameters and molecular structure, motions, and chemical reactivity: e.g., chemical bond type, number, and pattern; dihedral angle about a given bond; and intramolecular distances between atoms not directly bonded to each other. Modern FT/NMR experiments can be designed to detect particular chemically bonded groups of atoms (e.g., CH_3) or even to trace out the whole carbon-bonded skeleton of a molecule from a single experiment. In this section, we describe briefly the principal FT/NMR spectral parameters.

8.2.1 Chemical shift: identification of chemical bonds

The Larmor frequencies of some common magnetic nuclei are shown in Figure 8.4. Since FT/NMR spectral peak width is typically < 1 Hz for nuclei of spin, $I = 1/2$, it is clear that chemically different nuclei are readily distinguishable (e.g., ^1H and ^{13}C, whose Larmor frequencies differ by ~375 MHz at 11.75 tesla).