Bloch equations

Consider a nucleus that possesses a magnetic moment μ and angular momentum $I\hbar$. The torque experienced by the magnetic moment vector μ in a static magnetic field is $\mu \times B$. As the rate of change of angular momentum is equal to the torque acting on the system

$$\frac{d}{dt}(I\hbar) = \mu \times B$$

since $\mu = \gamma I \hbar$

$$\frac{d\mu}{dt} = \gamma(\mu \times B) \quad \text{---------} \quad (1)$$

The nuclear magnetization M is $\sum_i \mu_i$ over all the nuclei in unit volume. Therefore eqn (1) is summed over all nuclei gives

$$\frac{dM}{dt} = \gamma(M \times B) \quad \text{---------} \quad (2)$$

If the applied magnetic field is along the z direction $B = B_0 \hat{z}$, where $\hat{z}$ is the unit vector along the z axis.

Under thermal equilibrium magnetization will be along z axis

$$M_x = 0, \quad M_y = 0, \quad M_z = M_0 = \chi_0 B_0$$

$\chi_0 = C/T$ C - Curie constant, T absolute temperature

Equation (2) gives the magnetization of the specimen due to the interaction of the nuclear spin with the magnetic field B

In addition to this, there can be contributions to $\left(\frac{dM}{dt}\right)$ that arise from interactions non included in the magnetic field B.

Let us assume that the magnetization M_z approaches the equilibrium value M_0 at a rate given by

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \quad \text{———} \quad (3)$$

T_1 is the spin-lattice relaxation time

Including the additional interaction the z-component of the equation of motion becomes

$$\frac{dM_z}{dt} = \gamma (M \times B)_z + \frac{M_0 - M_z}{T_1} \quad \text{———} \quad (4)$$

The x and y components of the equation of motion

$$\frac{dM_x}{dt} = \gamma (M \times B)_x - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma (M \times B)_y - \frac{M_y}{T_2}$$

where T_2 is the spin-spin relaxation time

If i, j, k be the unit vectors along the x, y and z axes respectively

$$M \times B = \begin{vmatrix} i & j & k \\ M_x & M_y & M_z \\ B_x & B_y & B_z \end{vmatrix}$$

$$= i(M_y B_z - B_y M_z) - j(M_x B_z - B_x M_z) + k(M_x B_y - B_x M_y)$$

$$= i(M_y B_z - B_y M_z) + j(B_x M_z - M_x B_z) + k(M_x B_y - B_x M_y)$$

$\therefore$ The x, y, and z component of equation of motion becomes

The magnetic vector in the combined r-f and static fields

$$\frac{dM_x}{dt} = \gamma(M_y B_z - M_z B_y) - \frac{M_x}{T_2} \quad \text{--- (5)}$$

$$\frac{dM_y}{dt} = \gamma(M_z B_x - M_x B_z) - \frac{M_y}{T_2} \quad \text{--- (6)}$$

$$\frac{dM_z}{dt} = \gamma(M_x B_y - M_y B_x) + \frac{M_0 - M_z}{T_1} \quad \text{--- (7)}$$

The induction in eqn (1) and (2) consists of B_0 together with the magnetic vector of the applied radio-frequency B_1 which is equivalent to an induction rotating in the xy plane at an angular frequency ω rad s^{-1}. The components of B can be easily deduced

$$B_x = B_1 \cos \omega t$$

$$B_y = -B_1 \sin \omega t$$

$$B_z = B_0$$

Substituting the value of B_y, B_y and B_z in eqn (5), (6) and (7)

$$\frac{dM_x}{dt} = \gamma(M_y B_0 + M_z B_1 \sin\omega t) - \frac{M_x}{T_2} \quad \text{--- (8)}$$

$$\frac{dM_y}{dt} = \gamma(M_z B_1 \cos\omega t - M_x B_0) - \frac{M_y}{T_2} \quad \text{--- (9)}$$

$$\frac{dM_z}{dt} = -\gamma(M_x B_1 \sin\omega t + M_y B_1 \cos\omega t) + \frac{M_0 - M_z}{T_1} \quad \text{--- (10)}$$

The above three equations (8), (9), and (10) are called the Bloch equations.

10.8 CHEMICAL SHIFT

According to the resonance condition, Eq. (10.5), all protons should absorb energy at the same magnetic field. However, it is not the case even under low resolution. The spectrum of acetaldehyde (CH_3CHO) showed two lines with intensity ratio 1:3 whereas ethanol (CH_3CH_2OH) showed 3 lines in the ratio 1:2:3 (Figure 10.5). Moving electrons in a molecule constitute effective currents within the molecule and this produces a secondary magnetic field which acts in a direction opposite to the externally applied magnetic field.

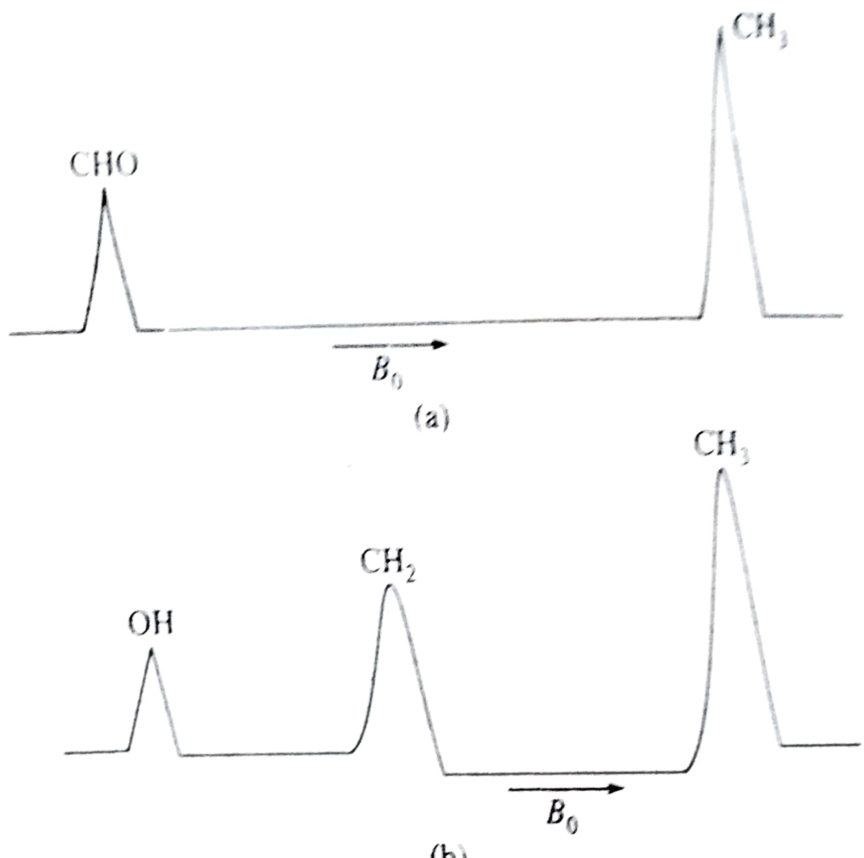

Figure 10.5 The NMR spectrum of (a) CH_3CHO, (b) CH_3CH_2OH under low resolution

That is, the nucleus finds itself in an effective field less than the actual field applied. In other words, the nucleus is screened by the surrounding electrons. Thus,

$$B_{eff} = B_0 - \sigma B_0 = B_0 (1 - \sigma) \quad (10.35)$$

where σ is a dimensionless constant called the **screening constant** or **shielding parameter.** The value of σ ($\sim 10^{-5}$) depends on the electron density around the proton. Figure 10.6 illustrates the situation for a shielded spin 1/2 nucleus.

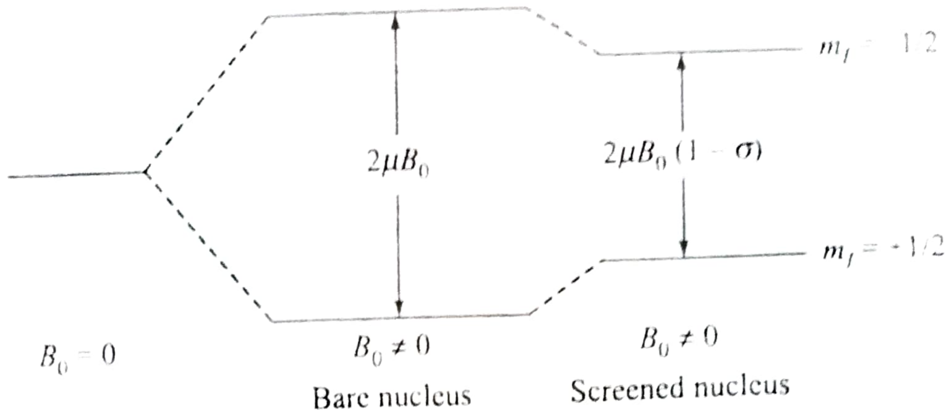

Figure 10.6 Bare and screened, spin 1/2 nucleus in a magnetic field B_0.

Acetaldehyde has two types of protons, CHO and CH_3 protons. The three protons in CH_3 are equivalent. Since the oxygen atom is more electronegative, the electron density around the proton in CHO is less than that around the CH_3 protons. Therefore, the screening is more for the methyl protons, $\sigma CHO < \sigma CH_3$. For a given external field B_0, B_{eff} for CHO proton will be greater than that for CH_3. Consequently, to bring CHO proton into resonance at a fixed frequency, a lesser magnetic field is sufficient. As a result the NMR spectrum of acetaldehyde shows two peaks, the CHO resonance occurring at a lower magnetic field. We can now view the situation in a different angle, that is, when the applied field B_0 is kept constant. At a fixed field B_0, the CHO proton finds itself in a greater B_{eff} than the CH_3 protons. Therefore, a higher frequency is required to bring the CHO proton into resonance.

The shift of the resonance line of a given compound from that of a standard reference sample is called the **chemical shift** (δ) of the compound. The absolute magnitude of the shift is extremely small. Let B_r and B_s be the magnetic fields at which resonance occurs for the reference and given compound/group. Then

$$B_r = B_0\,(1 - \sigma_r), \qquad B_s = B_0\,(1 - \sigma_s)$$

$$\delta = \frac{B_r - B_s}{B_0} = \sigma_s - \sigma_r \tag{10.36}$$

Since σ_s and σ_r are extremely small, a different unit is usually selected (in terms of field or frequency) for expressing the chemical shift.

$$\delta = \frac{B_r(\text{reference}) - B_s(\text{sample})}{B_0} \times 10^6 \text{ ppm} \tag{10.37a}$$

$$\delta = \frac{\nu_s(\text{sample}) - \nu_r(\text{reference})}{\nu_0} \times 10^6 \text{ ppm} \tag{10.37b}$$

In general, the reference is selected in such a way that it gives the resonance at a very high field. This leads to a positive δ in most of the cases. A different chemical shift τ which is the one commonly used by chemists, is sometimes employed.

$$\tau = 10.00 - \delta \tag{10.38}$$