Chapter 10: Spin angular momentum

Until this point, we have only discussed quantities that have a classical analogue. More specifically, we took systems that one can describe in terms of classical mechanics, such as the free particle, harmonic oscillator, rigid rotor, and a particle subject to a central potential, and examined their quantum analogues. In this chapter we encounter, for the first time, a quantity, called the spin, which does not have a classical analogue! **We know that it exists because we can measure it**. In fact, several extremely powerful modern technologies in chemistry, biology and medicine are based on such measurements. In this chapter, we introduce the spin operators and learn how to work with them.

The spin operators

Until this point, we found the operators that represent physical quantities by applying the **quantization rules** to the corresponding classical expressions (see chapter 3). More specifically, any classical quantity can be expressed in terms of positions and momenta, and the corresponding operator can be obtained by replacing them with the position and momentum operators. How do we know what operators represent a quantity like the spin that has no classical analogue? The answer is surprisingly simple (at least in principle!)– We determine them empirically, by requiring that the operators we choose lead to predictions which are consistent with experimental observations. The spin operators that we will define below were determined in this manner.

The first observation is that the spin is a 3D vector quantity (like position, momentum and angular momentum in 3D). We will denote the spin vector by $\vec{S}$, and the operators that correspond to its Cartesian components by $\hat{S}_x, \hat{S}_y, \hat{S}_z$. We will also define the operator that corresponds to the square of the spin vector amplitude: $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$.

As it turns out, the spin is observed to be similar to orbital angular momentum, in the sense that the commutators of $\hat{S}_x, \hat{S}_y, \hat{S}_z, \hat{S}^2$ are identical to those of $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$, namely:

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar \hat{S}_z \quad, \quad \left[\hat{S}_y, \hat{S}_z\right] = i\hbar \hat{S}_x \quad, \quad \left[\hat{S}_z, \hat{S}_x\right] = i\hbar \hat{S}_y$$

$$\left[\hat{S}_x, \hat{S}^2\right] = \left[\hat{S}_y, \hat{S}^2\right] = \left[\hat{S}_z, \hat{S}^2\right] = 0$$

(1)

For this reason, we refer to the spin as an angular momentum (although, it does not correspond to a specific type of orbital angular momentum!). Only based on those commutators, one can then show that (stated without proof):

The eigenvalues of $\hat{S}^2$ are given by $s(s+1)\hbar^2$, with $s = 0, \dfrac{1}{2}, 1, \dfrac{3}{2}, ...$ (2)

The eigenvalues of $\hat{S}_z$ are given by $m_s\hbar$, with $m_s = -s, -s+1, ..., s-1, s$ (3)

It should be noted that the orbital angular momentum operators, which satisfy the same commutation relations, has eigenvalues of a similar form (with the quantum numbers

denoted by l and m, rather than by s and m_s).However, there are two important differences between spin and orbital angular momenta:

1. While the orbital angular momentum quantum number l can only obtain **integer** values, that is $l = 0, 1, 2, 3, ...$, **spin angular momentum quantum number s can be half-integer**, that is $s = 0, 1/2, 1, 3/2, ...$

2. The orbital angular momentum of a particle can be increased indefinitely, by changing the state of the particle to that corresponding to a larger value of l. However, the spin quantum number s of an elementary particle such as the electron, proton or neutron, is **fixed** (this is an empirical observation)!

Those differences reveal why the spin **cannot** and should **not** be thought about as a type orbital angular momentum. Furthermore, the fact that s is fixed implies the spin vanishes at the classical limit (which is why it does not have a classical analogue).

Spin-1/2 particles

In chemistry, we are mostly concerned with the spins of electrons and protons. As it turns out, electrons and protons are **spin-1/2 particles**, that is they correspond to $s = 1/2$ (this is an empirical observation!). We will therefore restrict our discussion to the spin-1/2 case.

Eigenfunctions and eigenvalues

For a spin-1/2 particle, $s = 1/2$, such that the value of S^2 is always known with certainty, and is given by $s(s + 1/2)\hbar^2 = (1/2)(1 + 1/2)\hbar^2 = 3\hbar^2/4$. This means that the wave function that describes the state of the particle must be an eigenfunction of the operator $\hat{S}^2$, with the eigenvalue $3\hbar^2/4$. Since $\hat{S}^2$ commutes with $\hat{S}_z$, we know that the value of S_z can also be known with certainty (note that we could have chosen any component of the spin angular momentum vector, and that the choice of the z component is arbitrary, although it follows the standard convention). According to Eq.(3), $\hat{S}_z$ has two possible eigenvalues: $\hbar/2$ and $-\hbar/2$. Those two eigenvalues correspond to two distinctly different eigenfunctions that we will denote by α and β, respectively:

$$\hat{S}_z \alpha = \frac{\hbar}{2}\alpha \; ; \; \hat{S}_z \beta = -\frac{\hbar}{2}\beta \qquad (4)$$

It is important to note that α and β are fundamentally different from the wave functions of the form $\psi(\vec{r})$ that we have encountered until this point. As was discussed in Chapters 2 and 3, $\psi(\vec{r})$ is actually a representation, in terms of the $\{\delta(\vec{r} - \vec{r}_0)\}$ continuous basis, of a vector in an infinitely dimensional Hilbert space. In the case of the spin-1/2, $\{\alpha, \beta\}$ is a basis of the corresponding state space, which means that in this case, the Hilbert space is two-dimensional, rather than infinitely dimensional! Thus, α and β cannot be represented by functions of the coordinates!

Because $\{\alpha, \beta\}$ is a basis of the spin state space, any spin state can be written as a linear combination of those two states, $\psi = c_+\alpha + c_-\beta$. Although this is just one possible basis, we are going to stick with it from now on (only for the sake of simplicity). Different spin states will be characterized by different values of the two coefficients c_+ and c_-, which are complex numbers. The inner product of two states $\psi = c_+\alpha + c_-\beta$ and $\chi = d_+\alpha + d_-\beta$ is defined in the usual way by:

$$\langle \psi | \chi \rangle = \begin{pmatrix} c_+^* & c_-^* \end{pmatrix} \begin{pmatrix} d_+ \\ d_- \end{pmatrix} = c_+^* d_+ + c_-^* d_- \tag{5}$$

For example:

$$\langle \alpha | \alpha \rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1 \times 1 + 0 \times 0 = 1$$

$$\langle \beta | \beta \rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0 \times 0 + 1 \times 1 = 0$$

$$\langle \alpha | \beta \rangle = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 1 \times 0 + 0 \times 1 = 0$$

$$\langle \beta | \alpha \rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 \times 1 + 1 \times 0 = 0$$

$$\tag{6}$$

Thus, we see that α and β are normalized and orthogonal (orthogonality is also implied by the fact that α and β are eigenfunctions with different eigenvalues of the Hermitian operator $\hat{S}_z$). Also, a spin state is normalized if

$$\langle \psi | \psi \rangle = \begin{pmatrix} c_+^* & c_-^* \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = |c_+|^2 + |c_-|^2 = 1 \quad . \tag{7}$$

Operators

Based on the discussion above, we can immediately construct the 2×2 matrices that represent the operators $\hat{S}^2$ and $\hat{S}_z$ in terms of the $\{\alpha, \beta\}$ basis:

$$\hat{S}_z \doteq \begin{pmatrix} \langle \alpha | \hat{S}_z | \alpha \rangle & \langle \alpha | \hat{S}_z | \beta \rangle \\ \langle \beta | \hat{S}_z | \alpha \rangle & \langle \beta | \hat{S}_z | \beta \rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar}{2} \langle \alpha | \alpha \rangle & -\frac{\hbar}{2} \langle \alpha | \beta \rangle \\ \frac{\hbar}{2} \langle \beta | \alpha \rangle & -\frac{\hbar}{2} \langle \beta | \beta \rangle \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{8}$$

$$\hat{S}^2 \doteq \begin{pmatrix} \langle \alpha | \hat{S}^2 | \alpha \rangle & \langle \alpha | \hat{S}^2 | \beta \rangle \\ \langle \beta | \hat{S}^2 | \alpha \rangle & \langle \beta | \hat{S}^2 | \beta \rangle \end{pmatrix} = \begin{pmatrix} \frac{3\hbar^2}{4} \langle \alpha | \alpha \rangle & \frac{3\hbar^2}{4} \langle \alpha | \beta \rangle \\ \frac{3\hbar^2}{4} \langle \beta | \alpha \rangle & \frac{3\hbar^2}{4} \langle \beta | \beta \rangle \end{pmatrix} = \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{9}$$

We will utilize the raising and lowering operators in order to obtain the matrices that represent $\hat{S}_x$ and $\hat{S}_y$. Following the same procedure as in the case of orbital angular momentum, we define

$$\begin{cases} \hat{S}_+ = \hat{S}_x + i\hat{S}_y \\ \hat{S}_- = \hat{S}_x - i\hat{S}_y \end{cases} \Leftrightarrow \begin{cases} \hat{S}_x = \left(\hat{S}_+ + \hat{S}_-\right)/2 \\ \hat{S}_y = \left(\hat{S}_+ - \hat{S}_-\right)/2i \end{cases} \tag{10}$$

Based on the commutators (which are the same as for orbital angular momentum!), we can show that

$$\hat{S}_+\alpha = 0 \; ; \; \hat{S}_+\beta = \hbar\alpha$$
$$\hat{S}_-\alpha = \hbar\beta \; ; \; \hat{S}_-\beta = 0 \tag{11}$$

which means that (verify that !)

$$\hat{S}_x\alpha = \frac{\hbar}{2}\beta \; ; \; \hat{S}_x\beta = \frac{\hbar}{2}\alpha$$
$$\hat{S}_y\alpha = \frac{i\hbar}{2}\beta \; ; \; \hat{S}_y\beta = \frac{-i\hbar}{2}\alpha \tag{12}$$

Thus, the matrices that represent $\hat{S}_+, \hat{S}_-, \hat{S}_x$ and $\hat{S}_y$ in terms of the $\{\alpha, \beta\}$ basis are given by

$$\hat{S}_+ \doteq \begin{pmatrix} \langle\alpha|\hat{S}_+|\alpha\rangle & \langle\alpha|\hat{S}_+|\beta\rangle \\ \langle\beta|\hat{S}_+|\alpha\rangle & \langle\beta|\hat{S}_+|\beta\rangle \end{pmatrix} = \begin{pmatrix} 0 & \hbar\langle\alpha|\alpha\rangle \\ 0 & \hbar\langle\beta|\alpha\rangle \end{pmatrix} = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\hat{S}_- \doteq \begin{pmatrix} \langle\alpha|\hat{S}_-|\alpha\rangle & \langle\alpha|\hat{S}_-|\beta\rangle \\ \langle\beta|\hat{S}_-|\alpha\rangle & \langle\beta|\hat{S}_-|\beta\rangle \end{pmatrix} = \begin{pmatrix} \hbar\langle\alpha|\beta\rangle & 0 \\ \hbar\langle\beta|\beta\rangle & 0 \end{pmatrix} = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$\hat{S}_x \doteq \begin{pmatrix} \langle\alpha|\hat{S}_x|\alpha\rangle & \langle\alpha|\hat{S}_x|\beta\rangle \\ \langle\beta|\hat{S}_x|\alpha\rangle & \langle\beta|\hat{S}_x|\beta\rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar}{2}\langle\alpha|\beta\rangle & \frac{\hbar}{2}\langle\alpha|\alpha\rangle \\ \frac{\hbar}{2}\langle\beta|\beta\rangle & \frac{\hbar}{2}\langle\beta|\alpha\rangle \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{13}$$

$$\hat{S}_y \doteq \begin{pmatrix} \langle\alpha|\hat{S}_y|\alpha\rangle & \langle\alpha|\hat{S}_y|\beta\rangle \\ \langle\beta|\hat{S}_y|\alpha\rangle & \langle\beta|\hat{S}_y|\beta\rangle \end{pmatrix} = \begin{pmatrix} \frac{i\hbar}{2}\langle\alpha|\beta\rangle & -\frac{i\hbar}{2}\langle\alpha|\alpha\rangle \\ \frac{i\hbar}{2}\langle\beta|\beta\rangle & -\frac{i\hbar}{2}\langle\beta|\alpha\rangle \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

It should be noted that the matrices that represent $\hat{S}_x$ and $\hat{S}_y$ are not diagonal, which is due to the fact that those operators do not commute with $\hat{S}_z$ (remember that $\{\alpha, \beta\}$ are the eigenstates of $\hat{S}_z$). Also note that the off-diagonal elements of the matrices which represent $\hat{S}_x$ and $\hat{S}_y$ are complex conjugates of each other, which testifies to the fact that those are Hermitian operators. The matrices that represent $\hat{S}_+, \hat{S}_-$ do not satisfy this condition, which is consistent with the fact that they are not hermitian.

Spin-orbital states

Until this chapter, we have described the state of spin-1/2 particles like electrons and protons by a wave function $\phi(\vec{r})$, which depends on the particle's actual position. This wave function contained all the information one needs regarding measurements of quantities that have a classical analogue, such as position, momentum and orbital angular momentum. However, we now know that a complete description of the particle's state must also include a specification of its spin state, which is completely missing from $\phi(\vec{r})$. We therefore have to extend the definition of what is meant by a "quantum state" in order to address this issue.

Consider, for example, an electron in a Hydrogen atom, which occupies the $\phi_{n,l,m}(r,\theta,\varphi)$ orbital. This electron also has a spin. Assume that the spin state of the electron is described by the spin state function α (the so called "spin-up state"). A complete description of the state of the particle is given by $\phi_{n,l,m}(r,\theta,\varphi)\alpha$, which is called a spin-orbital state, or simply a **spin-orbital**. Similarly, if the spin state is given by β, then the electron is described by the spin-orbital $\phi_{n,l,m}(r,\theta,\varphi)\beta$ ("spin down"). In fact, the spin state can be given by a linear combination of α and β, such that the spin-orbital is given by $\phi_{n,l,m}(r,\theta,\varphi)\left[c_{+}\alpha+c_{-}\beta\right]$. The state of the electron can also be given by a linear combination of two spin-orbitals with opposite spins, for example $\left[\phi_{1S}(r,\theta,\varphi)\alpha+\phi_{2S}(r,\theta,\varphi)\beta\right]/\sqrt{2}$. In those cases, the state is a superposition of spin-up and spin-down states.

The normalization of spin-orbital states must include the two types of inner product (spin and orbital). For example:

$$\left\langle \phi_{n,l,m}\alpha \middle| \phi_{n,l,m}\alpha \right\rangle = \left\langle \alpha | \alpha \right\rangle \left\langle \phi_{n,l,m} \middle| \phi_{n,l,m} \right\rangle = 1 \times 1 = 1$$

$$\left\langle \frac{1}{\sqrt{2}}\left[\phi_{1s}\alpha+\phi_{2s}\beta\right] \middle| \frac{1}{\sqrt{2}}\left[\phi_{1s}\alpha+\phi_{2s}\beta\right] \right\rangle$$

$$= \frac{1}{2}\left\{ \left\langle \alpha|\alpha\right\rangle \left\langle \phi_{1s}|\phi_{1s}\right\rangle + \left\langle \beta|\beta\right\rangle \left\langle \phi_{2s}|\phi_{2s}\right\rangle + \left\langle \alpha|\beta\right\rangle \left\langle \phi_{1s}|\phi_{2s}\right\rangle + \left\langle \beta|\alpha\right\rangle \left\langle \phi_{2s}|\phi_{1s}\right\rangle \right\}$$

$$= \frac{1}{2}\left\{ 1\times 1 + 1\times 1 + 0\times 0 + 0\times 0 \right\} = 1$$

(14)

Similarly, expectation values that only involve the spin or orbital degrees of freedom only depend on the spin and orbital components of the spin-orbital, respectively. For example:

$$\left\langle \phi_{n,l,m}\alpha \middle| \hat{S}_z \middle| \phi_{n,l,m}\alpha \right\rangle = \left\langle \alpha \middle| \hat{S}_z \middle| \alpha \right\rangle \left\langle \phi_{n,l,m} \middle| \phi_{n,l,m} \right\rangle = \left\langle \alpha \middle| \hat{S}_z \middle| \alpha \right\rangle = \frac{\hbar}{2}$$

$$\left\langle \phi_{n,l,m}\alpha \middle| \hat{L}_z \middle| \phi_{n,l,m}\alpha \right\rangle = \left\langle \alpha | \alpha \right\rangle \left\langle \phi_{n,l,m} \middle| \hat{L}_z \middle| \phi_{n,l,m} \right\rangle = \left\langle \phi_{n,l,m} \middle| \hat{L}_z \middle| \phi_{n,l,m} \right\rangle = m\hbar$$

(15)

$$\left\langle \phi_{n,l,m}\alpha \middle| \hat{S}_z\hat{L}_z \middle| \phi_{n,l,m}\alpha \right\rangle = \left\langle \alpha \middle| \hat{S}_z \middle| \alpha \right\rangle \left\langle \phi_{n,l,m} \middle| \hat{L}_z \middle| \phi_{n,l,m} \right\rangle = \frac{\hbar}{2} \times m\hbar = \frac{m}{2}\hbar^2$$

$$\left\langle \frac{1}{\sqrt{2}}[\phi_{1s}\alpha + \phi_{2s}\beta] \middle| \hat{S}_z \middle| \frac{1}{\sqrt{2}}[\phi_{1s}\alpha + \phi_{2s}\beta] \right\rangle = \frac{1}{2}\{\langle \alpha | \hat{S}_z | \alpha \rangle \langle \phi_{1s} | \phi_{1s} \rangle + \langle \beta | \hat{S}_z | \beta \rangle \langle \phi_{2s} | \phi_{2s} \rangle$$

$$+ \langle \alpha | \hat{S}_z | \beta \rangle \langle \phi_{1s} | \phi_{2s} \rangle + \langle \beta | \hat{S}_z | \alpha \rangle \langle \phi_{2s} | \phi_{1s} \rangle\} = \frac{1}{2}\left\{\frac{\hbar}{2} - \frac{\hbar}{2}\right\} = 0 \tag{16}$$

Magnetic resonance

The Zeeman Hamiltonian

We know about the existence of the spin because we can measure it. But how exactly can we measure it? The most direct way of measuring the spin is based on its interaction with magnetic fields. This interaction also forms the foundation of nuclear and electron magnetic resonance techniques that are among the most powerful in chemistry, biology and medicine.

The interaction of the spin $\vec{S}$ with a magnetic field $\vec{B} = (B_x, B_y, B_z)$ is given by the **Zeeman Hamiltonian**:

$$\boxed{\hat{H} = -\gamma \vec{B} \bullet \hat{\vec{S}} = -\gamma \left(B_x \hat{S}_x + B_y \hat{S}_y + B_z \hat{S}_z \right)} \tag{17}$$

The constant γ is called the **magnetogyric ratio**. It is usually written as a product of two other constant:

$$\gamma = g\beta \tag{18}$$

where g is called the **g-factor** and β is called the **magneton** (and should be clearly distinguished from the state β in Eq. (4)). The values of g and β differ from one elementary particle to another, and are obtained empirically. For the electron $g_e = 2.0023$ and $\beta_e = -e/2m_e = -8.793 \times 10^{10} C/kg$, while for the proton $g_p = 5.5854$ and $\beta_p = e/2m_p = 4.789 \times 10^7 C/kg$ (the values for other elementary particles and heavier nuclei are tabulated in many books).

Now, assume that a spin-1/2 particle, such as the electron or proton, is subject to a constant magnetic field of amplitude B_0 that lies along the z axis, $\vec{B} = (0, 0, B_0)$. The Zeeman Hamiltonian in this case is given by:

$$\hat{H} = -\gamma B_0 \hat{S}_z = \omega_0 \hat{S}_z \tag{19}$$

where $\omega_0 = -\gamma B_0$ is called the **Larmor (angular) frequency**. Since this Hamiltonian is proportional to $\hat{S}_z$, it has the same eigenfunctions as $\hat{S}_z$. Thus, the eigenstates of $\hat{H}$ (i.e. the stationary states) are simply α and β, and the energy levels are $\hbar\omega_0/2$ and $-\hbar\omega_0/2$, respectively:

$$\boxed{\begin{aligned}\hat{H}\alpha &= \omega_0 \hat{S}_z \alpha = \frac{\hbar\omega_0}{2}\alpha \\ \hat{H}\beta &= \omega_0 \hat{S}_z \beta = -\frac{\hbar\omega_0}{2}\beta\end{aligned}}$$

(20)

In conclusion, a constant magnetic field splits the, otherwise degenerate, energy levels of a spin-1/2 particle, and the energy gap between them is given by $\hbar\omega_0 = -\gamma B_0 \hbar$.
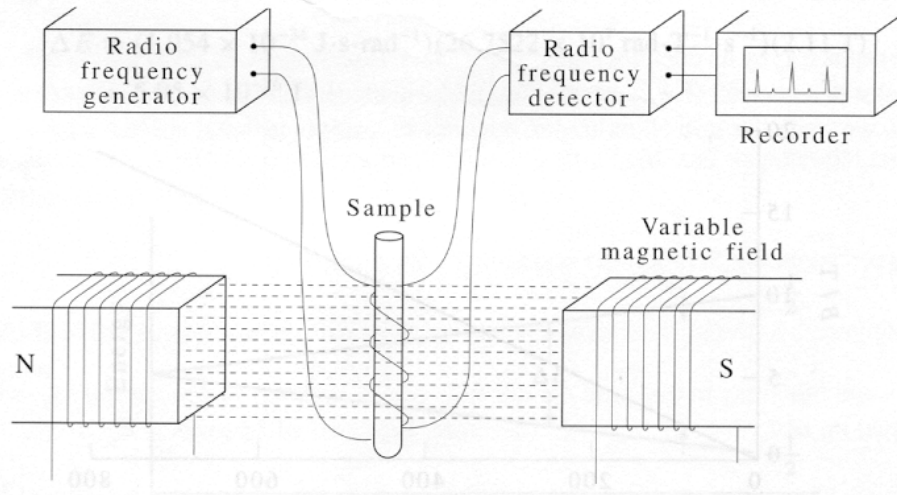

Figure 1:Schematic view of NMR spectrometer

Modern commercial magnetic resonance spectrometers are often classified according to the maximal strength of the magnetic field that they can produce. The main point is that the Larmor frequency increases with the amplitude of the magnetic field, and therefore leads to a more accurate (better resolved) determination of the corresponding spectroscopic transitions. The strongest fields in commercially available NMR (nuclear magnetic resonance) machines are at around $21T$ ($T = Tesla = JsC^{-1}m^{-2}$ is the SI unit for measuring the strength of a magnetic field). This implies that the transition frequency between the two spin states of a free proton is given by:

$$\nu_0 = \frac{\omega_0}{2\pi} = \frac{\gamma_p B_0}{2\pi} = \frac{g_p \beta_p B_0}{2\pi} = \frac{5.5854 \times 4.789 \times 10^7 \times 21}{2\pi} \simeq 9 \times 10^8 \, Hz = 900 MHz$$

Such an NMR spectrometer will be often referred to as a "900MHz machine". Low field NMR spectrometers are classified as leading to splits of around 200MHz and below. It should be noted that those frequencies correspond to radio waves (the wavelength is $\sim 30cm$ in the case of a 900MHz machine), and are smaller than those involved in electronic, vibrational and rotational transitions.

The magnetogyric ratio of a free electron is about three orders of magnitude larger than that of the proton, which implies that the same magnetic field would produce a much bigger splitting. Commercially available ESR (electron spin resonance, also known as EPR, for electron paramagnetic resonance), come with fields of around $1T$, which corresponds to the following transition frequency between the two spin levels of a free electron:

$$\nu_0 = \frac{\omega_0}{2\pi} = \frac{\gamma_e B_0}{2\pi} = \frac{g_e \beta_e B_0}{2\pi} = \frac{2.0023 \times 8.793 \times 10^{10} \times 1}{2\pi} \simeq 3 \times 10^{10} \, Hz = 3 \, GHz$$

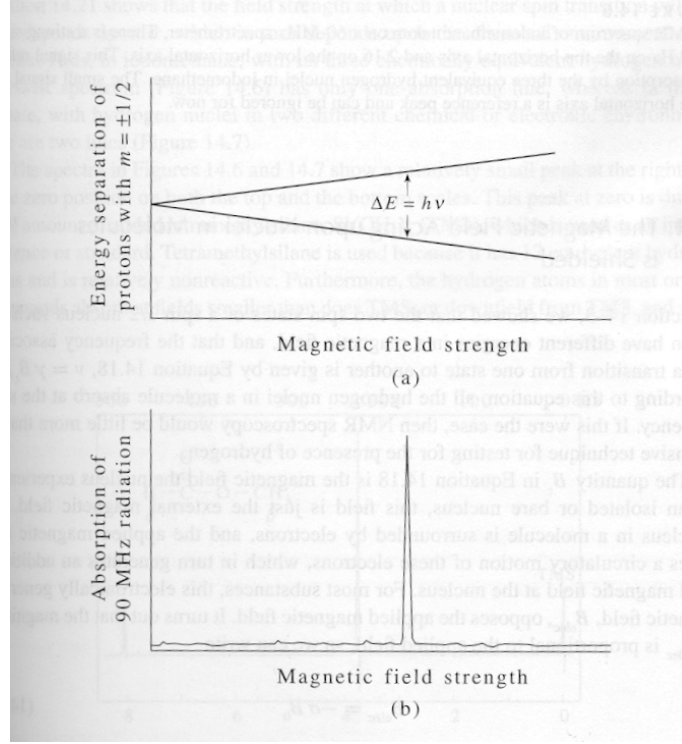This is a higher frequency (the wavelength is $\sim cm$) and corresponds to microwave radiation.

Figure 2: The energy gap between the spin levels as a function of magnetic field strength (a), and the corresponding spectral line (b).

Magnetic resonance spectroscopy and selection rules

We have already seen that a strong and **static** magnetic field along the z axis is needed in order to split the spin energy levels. Magnetic resonance spectroscopy is based on applying a weak and explicitly time-dependent magnetic field which is polarized in a direction which is perpendicular to the z axis. For example, consider such a monochromatic driving field along the x axis, $B_1 \sin(\omega t)$. The Zeeman Hamiltonian is now given by:

$$\hat{H} = -\gamma B_z \hat{S}_z - \gamma B_1 \sin(\omega t) \hat{S}_x = \omega_0 \hat{S}_z + \omega_1 \sin(\omega t) \hat{S}_x \tag{21}$$

where $\omega_1 = -\gamma B_1$ (sometimes referred to as Rabi's Frequency). We see that in this case, $\hat{S}_x$ plays the role of the (magnetic) dipole moment operator, such that the selection rules are dictated by the following matrix element: $\langle \alpha | \hat{S}_x | \beta \rangle = \hbar / 2$ [see Eq. (13)]. Thus, the transition between the energy levels split by the static field is allowed, and can be induced by a weaker monochromatic magnetic field, at resonance (i.e., when $\omega = \omega_0$).

Shielding and chemical shifts

From this point on we will focus on NMR, which is a more powerful and more widely utilized technique. At first sight NMR looks like nothing more than a very expensive way of detecting protons. However, as we will see below, NMR is such a powerful technique because of the great sensitivity of the Larmor frequency (and in more advanced applications other characteristics of the absorption line) to the chemical environment of the proton.

The discussion above referred to the rather ideal case of an isolated proton. However, NMR is usually applied to molecular samples where the protons are surrounded by electrons. The latter are charged particles, and subjecting them to an external magnetic field will make them move in a circular motion[1]. This circular motion corresponds to inducing electrical current, which in turn generates a local magnetic field[2] This local magnetic field generally opposes the external magnetic field, such that the overall magnetic field felt by the proton is somewhat **lower** than the external field and is given by:

$$B = (1-\sigma)B_0 \tag{22}$$

Here $-\sigma B_0$ is the local field and $\sigma > 0$ is called the **shielding constant**, which is usually much smaller than 1 ($\sigma \sim 10^{-5}$ in most organic compounds). The most important point is that the shielding coefficient is very sensitive to the environment of the proton. Thus, protons in different chemical environments are subject to different local magnetic fields and therefore absorb at different frequencies.

In order to compare spectra taken with different spectrometers, that correspond to different strengths of the static magnetic field, one defines the **chemical shift**, which corresponds to the location of the line relative to the line of a standard (tetramethysilane (TMS), $Si(CH_4)_4$, which is relatively non-reactive, produces a strong line, and absorbs at a frequency which is lower than that of most molecules), divided by the frequency of the spectrometers:

$$\delta_H = \left(\frac{\nu_H - \nu_{TMS}}{\nu_0} \right) \times 10^6 \quad . \tag{23}$$

The 10^6 factor is added so that the chemical shift is given in terms of parts-per-million (ppm).

The value of σ reflects the electron density in the vicinity of the proton and increases with it. Thus, a **large chemical shift** is indicative of a chemical environment with a **small electron density, and vice versa.**

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[1] This phenomenon, where a magnetic field induces an electrical field, which in turn induces a current, is called **electromagnetic induction**. For example, it is the operating principle of the electric generator, where mechanical energy is converted into electrical one by rotating a wire loop in a constant magnetic field.

[2] The operating principle is opposite to that of the electric generator, and is similar to that of the electric motor, where electrical energy is converted into mechanical motion.
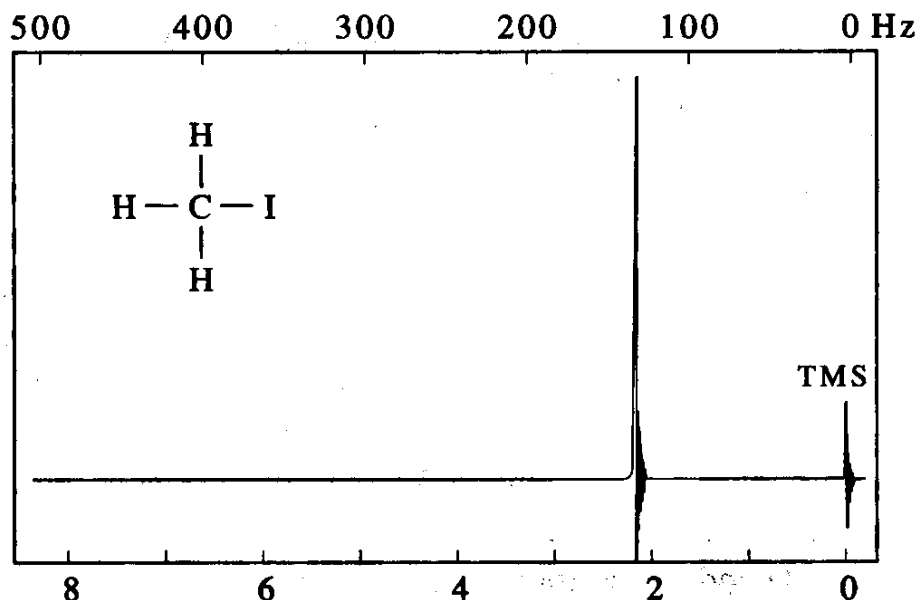
Figure 3: NMR spectrum of CH_3I (note that the chemical shift increases from left to right).

Example 1: The NMR spectrum of $CH_4, CH_3Cl, CH_2Cl_2, CHCl_3$ consists of a single line at $\delta = 0.23, 3.05, 5.33, 7.26$, respectively. The fact that we see a single line in a molecule that has more than one proton is due to the fact that those protons are equivalent that is they feel the same chemical environment. The chemical shift increases as we substitute the Hydrogen atoms by Chlorine atoms. This is explained by the electronegativity of Chlorine, which implies that it can pull electrons from the close vicinity of the protons (see discussion above).

Example 2: The NMR spectrum of a molecule with the molecular formula $C_3H_6O_2$ has two lines of the same height. This means that the six protons are separated into two groups with the same number of three equivalent protons in each (in order to explain the fact that the two lines are of the same height). This molecule has several isomers, and one of them, methyl acetate, CH_3COOCH_3, is consistent with the observed spectrum. We can also associate the peak with the larger chemical shift with the protons on the right-hand-side methyl group, due to the closer proximity to the electronegative oxygen.

A complete analysis of NMR spectra is much more involved and can supply far more information than may be suggested by the discussion above. For example, the lines that correspond to equivalent groups are often seen to be split into doublets, triplets, quartets, etc, which is due to spin-spin interactions. We leave this and other important phenomena that have to do with NMR to a more advanced course on this topic.[3]

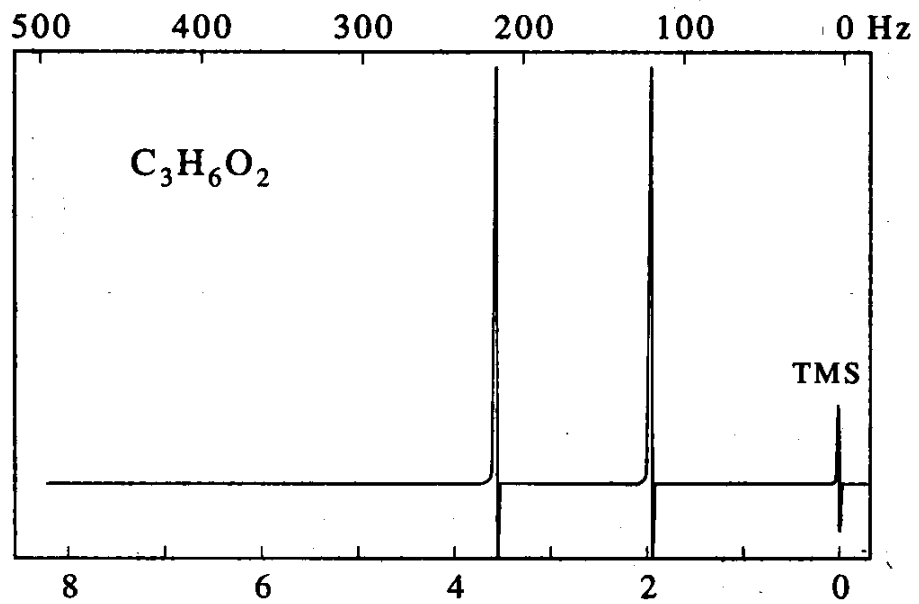[3] See, for example, Chapter 14 in "Physical Chemistry: A molecular approach", by McQuarrie and Simon.

Figure 4: NMR spectrum of CH_3COOCH_3