5.2: Nuclear Magnetic Resonance (NMR) - Turning on the Field

Spin is a type of angular momentum. Nuclear spin angular momentum was first reported by Pauli in 1924 and will be described here. Analogous to the angular momentum commonly encountered in electron, the angular momentum is a vector which can be described by a magnitude L and a direction, m. The magnitude is given by

$$L = \hbar\sqrt{I(I+1)}$$

The projection of the vector on the z axis (arbitrarily chosen), takes on one of $2I+1$ discretized values according to m, where

$$m_I = -I, -I+1, -I+2, \ldots +I$$

The angular momentum along the z-axis is now

$$I_z = m\hbar$$

Pictorially, this is represented in Figure $5.2.1$ for three values of I.

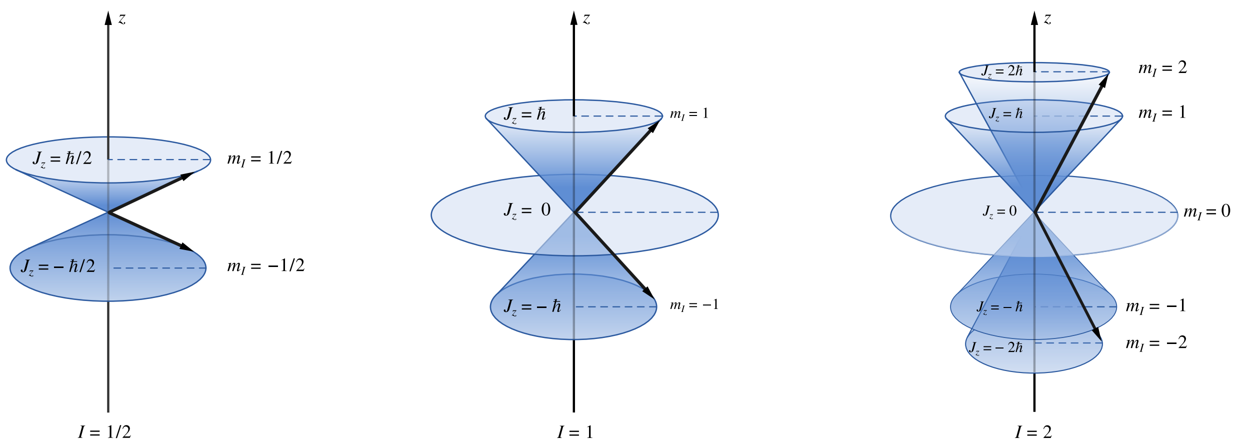


Figure $5.2.1$: The quantized angular momentum values for a I=1/2 (left) I=1(middle) and I=2 (right). The magnitude is denoted by the arrow while the projection along the z-axis is denoted by the circle.

The quantum numbers of the nucleus are denoted below.

Interaction	Symbol	Quantum Numbers
Nuclear Spin Angular Momentum	I	$0 < I < 9/2$ by unites of $1/2$
Spin Angular Momentum Magnitude	L	$L = \hbar\sqrt{I(I+1)}$
Spin Angular Momentum Direction	m	$m = -I, -I+1, -I+2, \ldots +I$

Field Effects

The absence of external fields, there is no preferred orientation for a magnetic moment. That is, the different m values of the orientation of the spin are degenerate. However, since a nucleus is a charged particle in motion, it will develop a magnetic field. Randomly oriented nuclear spins are aligned when a magnetic field applied on it. Hence, in the presence of a magnetic field, the energy of a magnetic moment depends on its orientation relative to the applied field lines. Classically, this is the Zeeman interaction:

$$E = -\vec{\mu} \cdot \vec{B}_o \tag{5.2.1}$$

where B_0 is the external magnetic field.

The Zeeman interaction is the physical phenomenon underlying the coupling of magnetic moments to magnetic fields. Apply an external magnetic field to nuclei with $I=1/2$ spin, and the different orientations split into **two** depending on if the nuclei are parallel or antiparallel with the applied field ($\vec{B}_o$ or $\vec{H}$).

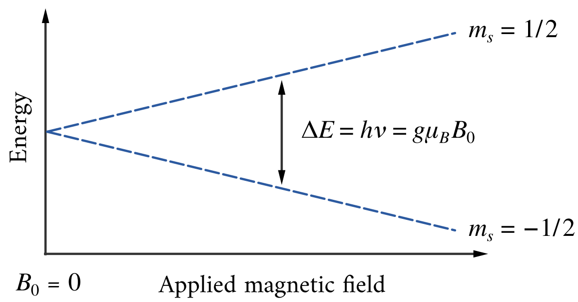


Figure 5.2.2: Energy levels for a I = -1/2 in an applied magnetic field B_o.

We now understand why the nucleus has a magnetic moment associated with it. Now we are getting to the crux of NMR, the use of an external magnetic field. Initially, the nucleus is in the nuclear ground state which is degenerate. The degeneracy of the ground state is $2I+1$. The application of a magnetic field splits the degenerate $2I+1$ nuclear energy levels via Equation 5.2.1, which we will simplify assuming the magnetic field is aligned with the z-direction, so Equation 5.2.1 becomes

$$E=-\mu B_0$$

by substitution with the definition of magnetic moment μ

$$E=-m\hbar\gamma B_0$$

The magnitude of the splitting therefore depends on the size of the magnetic field. In most labs this magnetic field is somewhere between 1 and 21T. Those spins which align with the magnetic field are lower in energy, while those that align against the field are higher in energy.

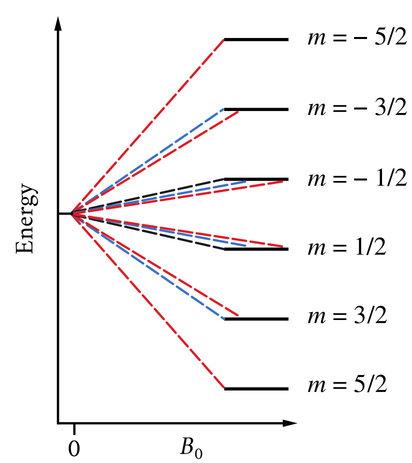


Figure 5.2.3: Splitting of the energy levels for a I=1/2 (black dashed lines), I= 3/2 (blue dashed lines), and I=5/2 (red dashed lines). Note how the energy level is dependent on the applied magnetic field. The offset of the red and blue lines is for illustrative purposes only.

Selection Rules

The selection rule in NMR is

$$\Delta m = \pm 1$$

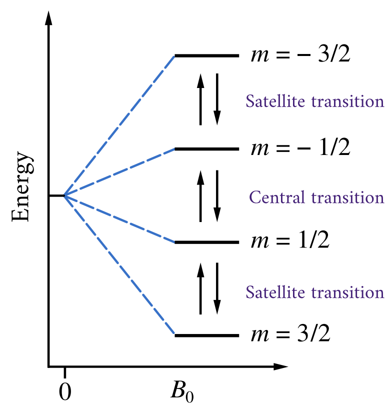
For a nucleus with $I = 1/2$ there is only one allowed transition since there are only two states. However, for nuclei with $I > 1/2$, multiple transitions may take place. Consider the case of $I = 3/2$. The following transitions can take place

$$-\frac{3}{2} \leftrightarrow -\frac{1}{2}$$

$$-\frac{1}{2} \leftrightarrow \frac{1}{2}$$

$$\frac{1}{2} \leftrightarrow \frac{3}{2}$$

which is illustrated below.



The transition from

$$-\frac{3}{2} \leftrightarrow -\frac{1}{2}$$

$$\frac{1}{2} \leftrightarrow \frac{3}{2}$$

are known as satellite transitions, while the

$$-\frac{1}{2} \leftrightarrow \frac{1}{2}$$

transition is known as the central transition. The central transition is primarily observed in an NMR experiment. For more information about satellite transitions please look at quarupole interactions.

The NMR Experiment

During the NMR experiment several things happen to the nucleus, the bulk magnetization is rotated from the z axis into the xy plane and then allowed to relax back along the z-axis. A full theoretical explanation for a single atom was developed by Bloch into a set of equations known as the Bloch equations. From the NMR experiment chosen a variety of information can be gleaned by studying different interactions.

References

1. Claude H. Yoder, Charles D. Schaeffer,Introduction to multinuclear NMR : theory and application, Benjamin/Cummings Pub. Co., Menlo Park, Calif., 1987.
2. Robin K. Harris, Nuclear magnetic resonance spectroscopy : a physicochemical view, Pitman, Marshfield, Mass., 1983.

3. Jeremy K.M. Sanders and Brian K. Hunter, Modern NMR spectroscopy : a guide for chemists, Oxford University Press, New York, 1993.
4. David A.R. Williams ; editor, David J. Mowthorpe, Nuclear magnetic resonance spectroscopy, Published on behalf of ACOL, London, by J. Wiley, New York, 1986.
5. Frank A. Bovey, Lynn Jelinski, Peter A. Mirau, Nuclear magnetic resonance spectroscopy, Academic Press, San Diego, 1988.
6. R.J. Abraham, J. Fisher and P. Loftus, Introduction to NMR spectroscopy, Wiley, New York, 1988.
7. J.W. Akitt, NMR and chemistry : an introduction to modern NMR spectroscopy, Chapman & Hall, London; New York, 1992.