III.4 Nuclear Magnetic Resonance

Radiofrequency (rf) spectroscopy on nuclear spin states in a uniaxial constant magnetic field

\[ \mathbf{B} = B_0 \mathbf{z} \]  

(III.4.1)

B\(_0\) is on the order of 1-25 T

The rf frequencies vary between 1 and 1000 MHz.

Advantages of radiofrequency spectroscopy: Easy control over timing, amplitudes, and phases

Disadvantage of radiofrequency spectroscopy: low sensitivity

Prelude: Short History of NMR

A. Understanding of Magnetism – Late 19\(^{\text{th}}\) century
B. Discovery of Spin – 1920’s
C. WWII – Development of RF technology
D. First Observation of NMR Signal in paraffin:
   3. Nobel Prize in Physics - 1952
E. Discovery of Chemical Shift (1949)
F. First Commercial NMR Spectrometer – 1953 (Varian)
G. 50’s and 60’s: Spin Echoes, Nuclear Overhauser Effect, ENDOR, Magic Angle Spinning
I. 70’s:
   1. 2D NMR:
      a. J. Jeener – 1971
J. 80’s
   1. Magnetic Resonance Imaging (Paul Lauterbur – University of Illinois)
H. 90’s: Protein Structure Determination in Solid-state (Membrane Proteins) (Griffin, Opella, McDermott, Oschkinaat)
Quantization of Angular Momentum

Nuclear Spin is a form of angular momentum just like what is found in rotation. Classically, angular momentum is:

\[ \mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times m\mathbf{v} \quad (\text{III.4.2}) \]

The angular momentum vector is perpendicular to the page.

Angular momentum is always quantized, that is it has discrete values. This is only of consequence when it has small values, as it does in nuclei, atoms, and molecules. The eigenvalues for the operator \( L^2 \) are:

\[ \hbar^2 [l(l+1)] \quad (\text{III.4.3}) \]

where \( l \) is an integer (cf. Eqs. III.2.12 and III.3.5).

Angular momentum is a vector. Its value is defined or quantized along only one spatial axis and is not defined along the other spatial axes. For magnetic resonance, this axis is typically the direction of the external magnetic field. We typically label this as the \( z \) axis and have eigenvalues for the projection of \( \mathbf{L} \) along the \( z \) axis (\( L_z \)):

\[ \hbar m_l \quad (\text{III.4.4}) \]

where

\[ m_l = l, l-1, l-2, \ldots, -l \quad (\text{cf. Eq. III.2.13}) \quad (\text{III.4.5}) \]

\( L_x \) and \( L_y \) do not have definite values. There is uncertainty in the determination of \( \phi, L_x, \) and \( L_y \).

Electron and Nuclear Spin

I briefly discussed spin in Section I. The existence of electron and nuclear spin angular momentum was inferred from atomic physics experiments in magnetic fields and from relativistic quantum mechanical theory. In atoms and molecules to a good approximation, spin angular momentum is not coupled to spatial angular momenta such as orbital motion of electrons.
or rotational motion of molecules. There are however small fine and hyperfine couplings between spin and spatial angular momenta which are observable in highly resolved atomic and molecular spectra.

We tend to think classically about angular momentum like in the first figure. The word ‘spin’ confuses us because we think of the planetary model for the atom with the nucleus and electrons spinning about their respective axes. It is best to think of spin as another angular momentum associated with the electron or nucleus but not associated with spinning motion.

The S (nuclear spin l) value for the electron, proton, and neutron are all ½. For nuclei composed of multiple protons and neutrons, the following even/odd general rules apply

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Charge</th>
<th>S</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odd</td>
<td>Odd or Even</td>
<td>Half-Integer</td>
<td>$^{13}$C, $^{15}$N, $^{29}$Si (S=1/2), $^{27}$Al (S=3/2)</td>
</tr>
<tr>
<td>Even</td>
<td>Even</td>
<td>Zero</td>
<td>$^{12}$C, $^{16}$O, $^{32}$S</td>
</tr>
<tr>
<td>Even</td>
<td>Odd</td>
<td>Integer</td>
<td>$^2$H, $^{14}$N (S=1), $^{10}$B (S=3)</td>
</tr>
</tbody>
</table>

Spin S can be half-integer or integer whereas spatial l can only be integral.

**Nuclear Magnetic Moments**

For nuclei with non-zero spin, there is an associated *magnetic dipole moment* $\mu$. I discussed this in Eqs. I.2.15 – 20. The spin angular momentum and magnetic dipolar moments are proportional and colinear.

$$\mu = g_N \mu_N \frac{L}{h}$$  \hspace{1cm} (III.4.6)

The constant $\mu_N = e/2M$ where $e$ is the electron charge and $M$ is the mass of the proton. The nuclear $g_N$ factor is specific to a given nucleus and varies between ~ -5 and +5. The proton $g_N$ factor is 4.83724. Eq. (III.4.6) can also be expressed in terms of the *gyromagnetic ratio* $\gamma$ defined by:

$$\gamma = g_N \mu_N / h$$  \hspace{1cm} (III.4.7)

so that

$$\mu = \gamma L$$  \hspace{1cm} (III.4.8)

Since the magnitude of $L$ is $\hbar[l(l+1)]^{1/2}$, the scalar version of Eq. (III.4.8) is:

$$\mu = \gamma \hbar [S(S+1)]^{1/2}$$  \hspace{1cm} (III.4.9)
Nuclei in a Magnetic Field

In the presence of a magnetic field, the magnetic dipoles experience the Zeeman interaction:

\[ H_{\text{Zeeman}} = -\mu \cdot B \]  

(III.4.10)

This can be derived from classical electrodynamics and is intuitive if you’ve ever played with small bar magnets. These magnets want to align in one direction but not in the other. In the presence of a uniaxial field of constant magnitude \( B_0 = B_0\mathbf{z} \):

\[ H_{\text{Zeeman}} = -\mu_z B_0 = -\gamma B_0 L_z = -\gamma h B_0 S_z \]  

(III.4.11)

We have introduced the spin operator \( S \) which is a unitless spin angular momentum operator:

\[ S = L/\hbar = S_x x + S_y y + S_z z \]  

(III.4.12)

The eigenvalue of \( S^2 \) is \( S(S+1) \) and the eigenvalues (\( m_S \)) of \( S_z \) are \( S, S-1, \ldots, -S \). For \( S = \frac{1}{2} \), the eigenvalues of \( S_z \) are \( \frac{1}{2} \) and \( -\frac{1}{2} \). The selection rule for magnetic dipole transitions is \( \Delta m_S = \pm 1 \).

Resonant absorption will take place with rf radiation of energy

\[ \Delta E_{\text{abs}} = |\gamma h B_0| \]  

(III.4.13)

The quantities \( \omega_L = |\gamma B_0| \) and \( \nu_L = |\gamma B_0|/2\pi \) are known as Larmor frequencies with \( \omega_L \) an angular frequency and \( \nu_L \) a real frequency. For a 9.4 T magnet, \( \nu_L \) for \(^1\text{H} \) is 400 MHz. All other nuclei will have lower \( \nu_L \) in this field (\(^{19}\text{F} \) – 370 MHz, \(^{13}\text{C} \) – 100 MHz, \(^{15}\text{N} \) – 40 MHz, \(^{109}\text{Ag} \) – 14 MHz)

Nuclei with \( S \geq 1 \) also have an electric quadrupole moment in addition to their magnetic dipole moment. The electric quadrupole moment can make an important contribution to the NMR spectrum. Dipoles interact with fields while quadrupoles interact with field gradients or the derivative of the field with respect to position. In particular, the nuclear electric quadrupole interacts with the electric field gradient at the nucleus. This field gradient is determined by the electronic environment at the nucleus which is in turn determined by the chemical bonding of the nucleus.

Even in the absence of an external magnetic field, the nuclear spin states are quantized by the quadrupole/electric field gradient interaction, that is different values of \( m_S \) have different quadrupolar energies. Transitions between these \( m_S \) states can be observed in the absence of an external magnetic field by pure nuclear quadrupole resonance. In the presence of the external magnetic field, the quantization and energy levels of the quadrupolar \( m_S \) states are complex and depend on the relative strengths and orientations of the magnetic dipole/external magnetic field and electric quadrupole/electric field gradient interactions. We will only focus on spin \( \frac{1}{2} \) nuclei which do not have quadrupolar moments.
**Larmor Precession**

This section contains a model which provides a different insight into magnetic resonance. The model is a mix of classical and quantum mechanics. The quantum mechanical input is to consider the magnetic dipole moment as being tilted with respect to the external magnetic field with angle \( \theta = \cos^{-1}\left\{ \frac{m_S}{\sqrt{S(S+1)}} \right\} \). Classically, the external magnetic field will exert a torque \( \mathbf{N} \) on the magnetic dipole which results in precessional motion of the dipole about the external magnetic field. This can be derived from:

\[
\mathbf{N} = \mu \times \mathbf{B}_0 \quad \text{(III.4.14)}
\]

This torque is perpendicular to both \( \mu \) and \( \mathbf{B}_0 \). We use relationships between torque, angular momentum, and magnetic moment to derive:

\[
\mathbf{N} = \frac{d\mathbf{L}}{dt} = (1/\gamma)\frac{d\mu}{dt} = \mu \times \mathbf{B}_0 \quad \text{(III.4.15)}
\]

\[
\frac{d\mu}{dt} = \gamma \mu \times \mathbf{B}_0 = \mu \times \gamma \mathbf{B}_0 \mathbf{z} = \gamma \mathbf{B}_0 (\mu \times \mathbf{z}) \quad \text{(III.4.16)}
\]

\[
\frac{d\mu}{dt} = -\omega_L (\mathbf{z} \times \mu) \quad \text{(III.4.17)}
\]

So, the dipole moment precesses about the external magnetic field with angular Larmor frequency \( \omega_L \). Note that this precession frequency is the same as the angular resonant frequency for absorption.

Radiative energy at the Larmor frequency will have an oscillating \( \mathbf{B} \) field. This field will provides an additional torque on \( \mu \) to change its direction relative to \( \mathbf{z} \), that is to change its \( m_S \) state. In this semiclassical way, we can then understand the absorption of radiation by the magnetic dipole. Although we specifically derived these equations for magnetic dipoles interacting with radiation, it is also a useful picture to think about electric dipoles interacting with radiation.

**Electronic Shielding**

The actual magnetic field experienced by the nucleus is *different* than the external field because of the magnetic fields of the electrons. Because the NMR frequency is linearly proportional to the magnetic field *at the nucleus*, there can be a distribution of frequencies for the same nucleus type. This frequency dependence is known as the *chemical shift*. In NMR spectra, the resonant linewidths are often much smaller than the differences in chemical shifts so we can obtain well-resolved spectra with resolved signals for each chemically different nucleus in the compound.

The electronic magnetic fields which cause the chemical shift are the results of electronic currents *induced* by the external magnetic field. Calculation of the actual induced currents is complicated so we try to understand them with a simple example. We consider the *cyclotron* motion of the electrons about the external magnetic field direction. This is circular motion of the
In order for there to be cyclotron motion, there has to be a force pushing in on the electron. This force is:

\[ \mathbf{F} = -e\mathbf{v} \times \mathbf{B} \]  

(III.4.18)

This is the Lorentz Force Law for motion of electrons in an external magnetic field.

If the electrons move counterclockwise then the force points inward and one gets cyclotron motion. Note that protons would move clockwise. In the uniform uniaxial NMR magnetic field, \( \mathbf{B} = B_0 \mathbf{z} \), so \( F_{\text{mag}} = evB_0 \). In order to get circular motion, the magnetic force has to be equal to the centrifugal force:

\[ evB_0 = mv^2/r \]  

(III.4.19)

where \( r \) is the radius of the circular orbit and \( m \) is the electron mass. Using Eq. (III.4.19), we calculate that the angular frequency of the motion is:
\[ \omega = \frac{v}{r} = \frac{eB_0}{m} \]  

(III.4.20)

The key thing is that the cyclotron frequency is independent of radius and velocity. Also, remember that \( I = \frac{e\omega}{2\pi} \) so that the induced current is proportional to \( B_0 \).

So, we have an induced current loop and there is an associated induced magnetic moment. If you use equation III.4.8 and take into account the negative charge of the electron, you will see that the induced electronic magnetic dipole moment lies antiparallel to the external magnetic field direction. Because the induced moment is proportional to the induced current, the induced moment and its associated dipolar magnetic field are proportional to \( B_0 \). If the nucleus lies along the axis of cyclotron orbit, then the induced field will be antiparallel to the external field and hence reduce the field experienced by the nucleus. This effect is known as chemical shielding, where the chemical comes in because the magnitude of the shielding depends on the particular bonding (that is chemical) environment of the nucleus. So, the true field experienced by the nucleus is:

\[ B = B_0(1-\sigma) \]  

(III.4.21)

where \( \sigma \ll 1 \). The NMR frequency will be \( \gamma B_0 / 2\pi \). In diamagnetic molecules, (that is molecules with no unpaired electrons), \( \sigma \) is always positive. Typically, \( \sigma \) is quoted in ppm, that is parts per million. One multiplies the true \( \sigma \) by \( 10^6 \) to get ppm. For \( ^1H \), the range of shieldings is about 10 ppm. For \( ^13C \), it is about 200 ppm. The particular shielding depends of functional group. For example, the difference in average shielding for the ketone carbonyl \( ^13C \) and methyl \( ^13C \) is about 200 ppm.

Because the NMR frequency is linearly proportional to the magnetic field at the nucleus, the NMR frequency linearly decreases with increasing shielding. This frequency dependence is known as the chemical shift. In NMR spectra, the resonant linewidths are often much smaller than the differences in chemical shifts so we can obtain well-resolved spectra.

In materials with unpaired electrons, the induced field from the unpaired electron can be significantly larger than that in diamagnetic materials. For example, in metalloproteins, the nuclei near the metal center(s), will be have significantly different shielding (and NMR frequencies) than the other nuclei. This effect allows one to determine which nuclei are close to the metal center. If the metal ion can be removed, the NMR spectra with and without the metal ion can be compared. In conductive materials, like metals, the induced conduction electron fields are parallel to the external field and \( \sigma < 0 \). For example, the total magnetic field experienced by Cu is 0.23% (2300 ppm) greater in metallic copper than in CuCl2.

Shifts and shieldings are anisotropic, that is they depend on the orientation of the chemical bonds of the nucleus relative to the external magnetic field direction. In liquids, the molecules tumble rapidly and NMR signals are only observed at the average chemical shift. In solids, the molecules are fixed in space and anisotropy is important. To understand this, let’s consider a simple case of a C-H bond. We assume that the induced electronic magnetic dipole moment is antiparallel to the external field and at the center of the bond. Because of the angular nature of
the dipolar field, the dipolar field will subtract (add) to the external field when the C-H bond is parallel (perpendicular) to the external field.

If we understand how the NMR frequency depends on functional group or chemical bond orientation relative to the external magnetic field direction (as can be measured from NMR on single crystals of model compounds where this orientation is known), then the solid state NMR spectrum contains a great deal of information. Each NMR frequency can be associated with a particular functional group orientation in the magnetic field. This information can be used in structural analysis, for example to determine the relative orientation of two functional groups in the molecule.

The range of chemical shift anisotropy (CSA) for a particular nucleus can be large (for example about 200 ppm for $^{13}$C in a C=O group) and in solid state NMR spectra, this can lead to rather broad lines. In general, nuclei in more symmetric electronic environments will have smaller CSAs because many different functional group orientations will have equivalent induced fields and chemical shifts.

**Spin-Spin Coupling**

Nuclei which are separated by $\leq 3$ chemical bonds can exert small fields on one another through their bonding electrons. This leads to the J-coupling or spin-spin interaction which can often split spectral peaks. These splittings can be used to assign NMR resonances to particular nuclei (i.e. $^{13}$C with or without directly bonded $^1$H.) It can also be used to figure out whether two nuclei are connected through chemical bonds and thus can be useful as a structural tool. The general J-coupling Hamiltonian for nuclei 1 and 2 is:

$$H_J = \hbar J (S_1 \cdot S_2) = \hbar J (S_{x1}S_{x2} + S_{y1}S_{y2} + S_{z1}S_{z2})$$

(III.4.22)

where the $S_x$, $S_y$, and $S_z$ are the x, y, and z spatial components of nuclear spin angular momenta. Note that there are no vectors in the final expression and hence no spatial or angular dependence. The value of $J$ typically ranges between 1 – 150 Hz. Numerical calculations of the J-coupling are difficult. This interaction is mediated through bonds and bonding electrons. When the two nuclei are separated by more than three bonds, the J-coupling is generally negligible, less than 1 Hz.

The $S$’s in Eq. (III.4.22) can be the same type of nucleus (homonuclear – e.g. $^1$H, $^1$H) or different types of nuclei (heteronuclear – e.g. $^{13}$C, $^1$H).
Consider two spin ½ whose difference in NMR frequency is much larger than their J-coupling. Because of the small magnitude of the J-coupling, this case always holds in the heteronuclear J-coupling. It will also hold for homonuclear J-coupling when there is a significant chemical shift difference. We write the mathematical expression for this case as:

$$|\nu_1 - \nu_2| >> J$$

(III.4.23)

where $\nu_1$ and $\nu_2$ are the NMR frequencies in the absence of J-coupling. Eq. III.4.23 may not hold when the two nuclei are chemically equivalent, for example the $^1$H’s in a methyl group. For this case, we will have do a different calculation.

Let’s consider the specific case of two $^1$H which are J-coupled and which for which Eq. III.4.23 holds. When Eq. III.4.23 holds, we can neglect the $J(S_x1S_x2 + S_y1S_y2)$ energy term in Eq. (III.4.23) and only consider the $JS_z1S_z2$ term. We denote the individual spin states $m_S = +1/2$ and $m_S = -1/2$ as $\alpha$ and $\beta$, respectively. The coupled spin states for nuclei 1 and 2 will be: $\alpha_1\alpha_2$, $\alpha_1\beta_2$, $\beta_1\alpha_2$, $\beta_1\beta_2$. The chemical shift of nucleus 1 is $\delta_1$, the chemical shift of nucleus 2 is $\delta_2$, and their spin-spin coupling constant is $J$. The total Hamiltonian will be:

$$H = h[-\nu_{ref}(1 + \delta_1)S_{z1} - \nu_{ref}(1 + \delta_2)S_{z2} + JS_{z1}S_{z2}]$$

(III.4.24)

Our coupled spin states are all eigenstates of this Hamiltonian. In this Hamiltonian, $\nu_{ref}$ refers to a chemical shift reference frequency. In NMR calculations, we typically neglect the $h$ factor so that energy has units of frequency. Because of unit confusion, remember to distinguish energy from transition frequency. The minus sign in front of the $\nu_{ref}$ is true when we are dealing with a positive $\gamma$ nucleus such as $^1$H. Typically (although not always) $\delta_1$, $\delta_2$, and $J$ are positive. We consider this specific case and draw the energy level diagram for two $^1$H’s under three different conditions: (a) no chemical shift and no J-coupling ($\delta_1 = \delta_2 = J = 0$) (b) chemical shift and no J-coupling ($J = 0$) and (c) chemical shift and J-coupling. In our example, $\delta_1 > \delta_2 > 0$. NMR transitions only allow one spin to change its spin state and these allowed single quantum transitions are drawn in the figure.
The NMR spectrum in the three cases is:

(a) \( \nu_1 = \nu_2 = \nu_{\text{ref}} \)
(b) \( (\delta_1 - \delta_2) \nu_{\text{RF}} \)
(c) \( J \)

\( \nu_1 = \nu_2 = \nu_{\text{ref}} \quad \nu_1 \quad \nu_2 \quad \nu_{\text{ref}} \quad \nu_1 \quad \nu_2 \)

**Matrix Approach to Spectroscopic Problems**

Magnetic resonance and other spectroscopic problems can often be solved using a matrix approach.

For example, we can describe the nuclear spin by a unitless operator \( S \):

\[
S = S_x x + S_y y + S_z z
\]  

(III.4.25)

where \( x, y, \) and \( z \) are unit vectors along these three spatial directions. \( S_x, S_y, \) and \( S_z \) are scalar operators. \( S \) is proportional to the nuclear spin magnetic moment \( \mu \) and to the nuclear spin angular momentum \( L \).

\[
S = \frac{L}{\hbar} = \frac{(2M/g_N e h) \mu}{\hbar}
\]  

(III.4.26)

In a uniform axial magnetic field \( B_0 z \), the Hamiltonian operator for this system is:

\[
H = -\mu \cdot B_0 z = -(\gamma B_0) S_z = -(h \beta) S_z
\]  

(III.4.27)

where \( \beta \) is the angular Larmor frequency.

For a spin \( \frac{1}{2} \) such as \( ^1H \) or \( ^{13}C \), the system can be described by a complete set of two orthonormal energy eigenstates which we denote as \( |+\rangle \) and \( |-\rangle \). These states are eigenstates of the \( S_z \) operator and are the same as the \( \alpha \) and \( \beta \) states in the first part.

\[
S_z |+\rangle = \frac{1}{2} |+\rangle
\]  

(III.4.28a)

\[
S_z |-\rangle = -\frac{1}{2} |-\rangle
\]  

(III.4.29b)

These states are not eigenstates of the \( S_x \) and \( S_y \) operators. It is easiest to understand the effects of \( S_x \) and \( S_y \) after introduction of the raising operator \( S_+ \) and lowering operator \( S_- \). The raising
and lowering operators are linear combinations of \( S_x \) and \( S_y \) and are the NMR equivalents of the angular momentum operators in III.2.16 and III.2.17

\[
S_+ = S_x + iS_y \quad \text{(III.4.30a)}
\]
\[
S_- = S_x - iS_y \quad \text{(III.4.30b)}
\]

where \( i \) is \((-1)^
\frac{1}{2}\) . The raising and lowering operators have the properties:

\[
S_+ \vert + \rangle = 0 \quad \text{(II.4.31a)}
\]
\[
S_+ \vert - \rangle = \vert + \rangle \quad \text{(II.4.31b)}
\]
\[
S_- \vert + \rangle = \vert - \rangle \quad \text{(III.4.31c)}
\]
\[
S_- \vert - \rangle = 0 \quad \text{(III.4.31d)}
\]

We set out to calculate the eigenvalues and eigenstates of the \( S_x \) operator. Because the \( \vert + \rangle \) and \( \vert - \rangle \) states form a complete set (\textit{cf.} Section II, Postulate 4), we know that the eigenstates of \( S_x \) will be some linear combinations of \( \vert + \rangle \) and \( \vert - \rangle \). We denote an eigenvalue of \( S_x \) as \( \lambda \). So, an eigenvalue/eigenstate equation for \( S_x \) will be:

\[
S_x (c_+ \vert + \rangle + c_- \vert - \rangle) = \lambda (c_+ \vert + \rangle + c_- \vert - \rangle) \quad \text{(III.4.32)}
\]

where \( c_+ \) and \( c_- \) are coefficients. We solve this equation by forming two new equations. These new equations are obtained by first \textit{projecting} the \( \langle + \vert \) and then projecting the \( \langle - \vert \) state onto both sides of Eq. III.3.32

\[
\langle + \vert S_x \vert + \rangle c_+ + \langle + \vert S_x \vert - \rangle c_- = \lambda (c_+ \langle + \vert + \rangle + c_- \langle + \vert - \rangle) \quad \text{(III.4.33a)}
\]
\[
\langle - \vert S_x \vert + \rangle c_+ + \langle - \vert S_x \vert - \rangle c_- = \lambda (c_+ \langle - \vert + \rangle + c_- \langle - \vert - \rangle) \quad \text{(III.4.33b)}
\]

The right-hand sides of these equations can be rewritten using the orthonormality of the \( \vert + \rangle \) and \( \vert - \rangle \) states.

\[
\langle + \vert S_x \vert + \rangle c_+ + \langle + \vert S_x \vert - \rangle c_- = \lambda c_+ \quad \text{(III.4.34a)}
\]
\[
\langle - \vert S_x \vert + \rangle c_+ + \langle - \vert S_x \vert - \rangle c_- = \lambda c_- \quad \text{(III.4.34b)}
\]

Eqs. III.4.34 can be rewritten in a matrix/vector form. You’ll have to put in the parentheses.

\[
\begin{pmatrix}
\langle + \vert S_x \vert + \rangle \\
\langle - \vert S_x \vert + \rangle
\end{pmatrix}
\begin{pmatrix}
c_+ \\
c_-
\end{pmatrix}
= \lambda
\begin{pmatrix}
c_+ \\
c_-
\end{pmatrix} \quad \text{(III.4.35)}
\]
The left-hand $2 \times 2$ matrix is the matrix of the $S_z$ operator in the $|+\rangle, |−\rangle$ basis. The $S_z$ matrix is composed of four scalar matrix elements, each of which is a particular integral.

We understand the $c_+, c_-$ column vector in the following way. Because the $|+\rangle$ and $|−\rangle$ states are orthonormal, we can think about them as functional equivalents of orthogonal spatial axes such as the Cartesian $x$ and $y$ axes. The eigenket $|\Psi\rangle = c_+|+\rangle + c_-|−\rangle$ can then be represented as a vector in the $|+\rangle, |−\rangle$ space with components $c_+$ and $c_-$, respectively.

Our eigenvalue/eigenket equation Eq. III.4.35 is then a matrix times a column vector equals a constant times the column vector. The operator/matrix equivalence and ket/column vector equivalence is apparent.

Along the same lines, a bra can be represented as a row vector. Complex conjugates of the individual components have to be explicitly written out in the row vector. So, the $\langle \Psi| bra$ would be represented as $(c_+^* \quad c_-^*)$.

With the ket/column vector, bra/row vector, and operator/matrix equivalences, all quantum mechanical calculations on systems with a finite number of basis states can be done in a matrix/vector format. For example, the integral $\langle \chi| A |\Phi\rangle$ could be calculated by multiplying the row vector representing the $\langle \chi| state times the matrix representing the $A$ operator times the column vector representing the $|\Phi\rangle$ state. The order of the matrices or vectors has to be the same as that of the bras, kets, or operators. Also, all matrices or vectors have to be expressed in the same basis set. As another example, the matrix representing the product operator $AB$ can be calculated from the product of the matrix representing $A$ times the matrix representing $B$.

We illustrate some of these principals by solving Eq. III.4.35.

We first need to calculate the values of the matrix elements for $S_z$ in the $|+\rangle, |−\rangle$ basis. Looking at Eqs. III.4.30, $S_z = (S_+ + S_-)/2$. Using this expression and Eqs. III.4.31,
\[ S_x = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \]  

(III.4.36)

As an exercise, we can use this representation of \( S_x \) to go back and calculate one of the matrix elements using the matrix/vector approach.

\[
\langle -| S_x |+ \rangle = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \end{pmatrix} = \frac{1}{2}
\]

(III.4.37)

We get the right answer. As another exercise, we can easily calculate the matrix representing \( S_z \).

\[
S_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}
\]

(III.4.38)

If the basis states are eigenstates of the operator, then the matrix representing the operator is diagonal.

Using Eq. III.4.36 and writing the eigenvalue \( \lambda \) as a matrix, Eq. III.4.35 can now be written as:

\[
\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = \begin{pmatrix} \lambda & 0 \\ 0 & \lambda \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix}
\]

(III.4.39)

We bring the right side of Eq. III.4.39 over to the left side.

\[
\begin{pmatrix} -\lambda & \frac{1}{2} \\ \frac{1}{2} & -\lambda \end{pmatrix} \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\]

(III.4.40)

Values of \( \lambda \) can be found by solving for the determinant of the matrix and setting it equal to 0. The determinant of a 2 \( \times \) 2 matrix is the difference between the product of the diagonal elements and the product of the off-diagonal elements. See a linear algebra book for more details.

\[
\lambda^2 - \frac{1}{4} = 0
\]

(III.4.41)

\( \lambda = \pm \frac{1}{2} \) satisfies this equation. These are the eigenvalues of \( S_x \). Note that these are the same eigenvalues as those found for \( S_z \).

The eigenstate (or equivalently eigenvector) for each of these eigenvalues is found by substituting the eigenvalue into Eq. III.4.40 and solving for \( c_+ \) and \( c_- \). For example, for \( \lambda = +\frac{1}{2} \),
We explicitly write out Eq. III.4.42 as two algebraic equations.

\[ (-\frac{1}{2})c_+ + (\frac{1}{2})c_- = 0 \]  
\[ (\frac{1}{2})c_+ - (-\frac{1}{2})c_- = 0 \]

These two equations are each solved to give \( c_+ = c_- \). Numerical values for \( c_+ \) and \( c_- \) are obtained by normalizing the eigenstate.

\[ |c_+|^2 + |c_-|^2 = 1 \]

One solution to the \( c_+ = c_- \) and the normalization conditions is \( c_+ = c_- = \frac{1}{2} \). For the \( \lambda = -\frac{1}{2} \) eigenvalue, an eigenstate solution is \( c_+ = -c_- = \frac{1}{2} \).

This matrix approach is generally applicable to many spectroscopic problems. One typically uses it to solve for energy eigenvalues and eigenstates. Spectroscopic transitions are typically between these states.

**Perturbation Theory**

Another common approach to solving quantum mechanical problems is called perturbation theory. The advantage of perturbation theory over the matrix approach is that one does not need to diagonalize matrices. If there are a large number of basis functions, matrix diagonalization can take a lot of computer time. This used to be a big deal although with faster computers, it’s becoming less of a problem.

With perturbation theory, one starts by dividing up the operator into two parts. The eigenvalue equation for the first part should be exactly soluble by analytical means. For example, the Hamiltonian for a particular vibrational motion would include a large contribution from the harmonic oscillator Hamiltonian, which is exactly soluble. Or, a magnetic resonance problem would include the Zeeman Hamiltonian, Eq. II.4.11. The effect of the rest of the Hamiltonian on the eigenvalues and eigenfunctions is solved by progressive levels of approximation.

In spectral analysis, we typically want to first solve for energy eigenvalues and eigenfunctions. The observed spectroscopic transitions are between these different eigenvalues. So, we illustrate perturbation theory for the Hamiltonian operator. We write general equations and also apply them to a specific NMR problem.

The general form for the Hamiltonian is:

\[ H = H^{(0)} + H^{(1)} \]  

(III.4.45)
where $H^{(0)}$ is the zero-order exactly soluble part of the Hamiltonian.

$$H^{(0)} |\psi_k^{(0)}\rangle = E_k^{(0)} |\psi_k^{(0)}\rangle$$  \hspace{1cm} (III.4.46)

The $E_k^{(0)}$ are the zero order energies and the $|\psi_k^{(0)}\rangle$ are the associated zero order energy eigenfunctions. Each eigenfunction (subscripted by k) is associated with a particular eigenvalue (also subscripted by k).

For example, for the nuclear spin Zeeman Hamiltonian, Eq. III.4.27,

$$H^{(0)} = -\hbar \beta S_z$$

$$|\psi_1^{(0)}\rangle = |+\rangle \hspace{1cm} |\psi_2^{(0)}\rangle = |-\rangle$$  \hspace{1cm} (II.4.47)

$E_1^{(0)} = -\hbar \beta/2 \hspace{1cm} E_2^{(0)} = \hbar \beta/2$

$H^{(1)}$ is called the perturbation. For our purposes, we simply state some results of the effect of the perturbation. The mathematical treatment of the effect of the perturbation on energy eigenvalues and eigenfunctions is found in many textbooks.

In general, the total energy of a particular state is approximated as the sum of its zero-order energy and the first and second order corrections.

$$E_k = E_k^{(0)} + E_k^{(1)} + E_k^{(2)}$$  \hspace{1cm} (II.4.48)

It is possible to calculate the third and even higher order corrections but these should be very small.

The wavefunction is typically approximated as the sum of the zero order wavefunction and the first order correction.

$$|\psi_k\rangle = |\psi_k^{(0)}\rangle + |\psi_k^{(1)}\rangle$$  \hspace{1cm} (III.4.49)

Again, it is possible to calculate higher order corrections.

The first order correction of $H^{(1)}$ on the energy eigenvalue of a particular eigenfunction $k$ is given by the following matrix element.

$$E_k^{(1)} = \langle \psi_k^{(0)} | H^{(1)} |\psi_k^{(0)}\rangle$$  \hspace{1cm} (III.4.50)

This is simply average value of $H^{(1)}$ in the zero-order eigenfunction.

Let’s do a specific example.

In NMR, the spin magnetic moment of the nucleus interacts with the applied magnetic field $B_0$. In addition, the nucleus also interacts with a much smaller internal shielding field produced by
electron currents in the vicinity of the nucleus. These electron currents are actually induced by the applied field and tend to produce magnetic fields which oppose the applied field. The Hamiltonian for the interaction of the nuclear spin with these shielding fields is approximated as:

$$H^{(1)} = -(\hbar \beta)(\delta_x S_x + \delta_y S_y + \delta_z S_z) \quad (\text{III.4.51})$$

where $\delta_x$, $\delta_y$, and $\delta_z$ are unitless chemical shifts much less than 1. For example for $^1\text{H}$, they are of the order $10^{-5}$.

For states 1 and 2, that is $|+\rangle$ and $|−\rangle$, respectively, the first order correction to the zero-order energies is given by:

$$E_+^{(1)} = -\hbar \delta_z \beta / 2 \quad (\text{III.4.52})$$

$$E_-^{(1)} = \hbar \delta_z \beta / 2$$

The first order correction of the perturbing Hamiltonian on the eigenfunction is given by:

$$|\psi_k^{(1)}\rangle = \sum_{j \neq k} \{ \langle \psi_j^{(0)} | H^{(1)} | \psi_k^{(0)} \rangle / (E_k^{(0)} - E_j^{(0)}) \} |\psi_j^{(0)}\rangle \quad (\text{III.4.53})$$

where the sum is over the other zero-order energy eigenfunctions. The effect of the perturbation is to mix in some of the other zero order energy eigenfunctions. Because of the energy difference factor in the denominator, these other eigenfunctions cannot have the same energy eigenvalue as our initial eigenfunction. If two or more zero-order energy eigenfunctions have the same eigenvalue, then perturbation effects have to be calculated using the matrix approach outlined in the previous section.

In looking at Eq. III.4.53, it is clear that the largest contributions to the correction are from states which are close in energy to state k or which have a large value of $\langle \psi_j^{(0)} | H^{(1)} | \psi_k^{(0)} \rangle$.

The first order correction by the chemical shift Hamiltonian to the $|+\rangle$ and $|−\rangle$ wavefunctions is:

$$|\psi_+^{(1)}\rangle = \frac{1}{2}(\delta_x + i \delta_y)|−\rangle \quad (\text{III.4.54})$$

$$|\psi_-^{(1)}\rangle = -\frac{1}{2}(\delta_x - i \delta_y)|+\rangle$$

Because of the size of the $\delta'$s, these are extremely small corrections. At this point, one should also normalize each of the total wavefunctions $|\psi_k^{(0)}\rangle + |\psi_k^{(1)}\rangle$.

The second order correction to the energy is given by:

$$E_k^{(2)} = \sum_{j \neq k} |\langle \psi_j^{(0)} | H^{(1)} | \psi_k^{(0)} \rangle|^2 / (E_k^{(0)} - E_j^{(0)}) \quad (\text{III.4.55})$$

As with the first order correction to the wavefunction, degenerate states with the same zero order energy eigenvalue cannot be included in the sum. Also, the largest contributions to the second
order energy correction are from states which are close in energy to the initial state \( k \) or which have large values of \( \langle \psi_j^{(0)} | H^{(1)} | \psi_k^{(0)} \rangle \). For the lowest energy state, the second order correction is always negative because each term in the sum has a positive numerator and negative denominator.

The second order energy corrections from the chemical shift perturbation are:

\[
E_+^{(2)} = -(\delta_x + \delta_y)^2(\hbar\beta/4) \\
E_-^{(2)} = (\delta_x + \delta_y)^2(\hbar\beta/4)
\]  

(III.4.56)

For this perturbation, the ratio \( |E^{(2)}/E^{(1)}| \sim \delta \), which is a very small number, \( \sim 10^{-5} \) for \(^1\text{H}\). For this reason, one typically neglects second order chemical shift corrections to the energy in NMR spectral analysis.