1 Introduction to quantum mechanics

Quantum mechanics is the basic tool needed to describe, understand and devise NMR experiments. Fortunately for NMR spectroscopists, the quantum mechanics of nuclear spins is quite straightforward and many useful calculations can be done by hand, quite literally "on the back of an envelope". This simplicity comes about from the fact that although there are a very large number of molecules in an NMR sample they are interacting very weakly with one another. Therefore, it is usually adequate to think about only one molecule at a time. Even in one molecule, the number of spins which are interacting significantly with one another (i.e. are coupled) is relatively small, so the number of possible quantum states is quite limited.

The discussion will begin with revision of some mathematical concepts frequently encountered in quantum mechanics and NMR.

1.1 Mathematical concepts

1.1.1 Complex numbers

An ordinary number can be thought of as a point on a line which extends from minus infinity through zero to plus infinity. A complex number can be thought of as a point in a plane; the x-coordinate of the point is the real part of the complex number and the y-coordinate is the imaginary part.

If the real part is $a$ and the imaginary part is $b$, the complex number is written as $(a + ib)$ where $i$ is the square root of $-1$. The idea that $\sqrt{-1}$ (or in general the square root of any negative number) might have a "meaning" is one of the origins of complex numbers, but it will be seen that they have many more uses than simply expressing the square root of a negative number.

$i$ appears often and it is important to get used to its properties:

\[
i^2 = \sqrt{-1} \times \sqrt{-1} = -1
\]
\[
i^3 = i \times i^2 = -i
\]
\[
i^4 = i^2 \times i^2 = +1
\]
\[
\frac{1}{i} = \left(\frac{1}{i}\right) \left(\frac{i}{i}\right) \{\text{multiplying top and bottom by } i\}
\]
\[
= \frac{i}{-1} = -i
\]

The complex conjugate of a complex number is formed by changing the sign of the imaginary part; it is denoted by a *

\[
(a + ib)^* = (a - ib)
\]
The square magnitude of a complex number \( C \) is denoted \( |C|^2 \) and is found by multiplying \( C \) by its complex conjugate; \( |C|^2 \) is always real

\[
|C|^2 = C \times C^* \\
= (a + ib)(a - ib) \\
= a^2 + b^2
\]

These various properties are used when manipulating complex numbers:

addition: \( (a + ib) + (c + id) = (a + c) + (b + d) \)
multiplication: \( (a + ib) \times (c + id) = (ac - bd) + i(ad + bc) \)

division:

\[
\frac{(a + ib)}{(c + id)} = \left(\frac{a + ib}{c + id}\right)^* = \left(\frac{a + ib}{c + id}\right)^* \\
= \frac{(a + ib)(c + id)^*}{c^2 + d^2} = \frac{(a + ib)(c - id)}{c^2 + d^2} = \frac{(ac + bd) + i(bc - ad)}{c^2 + d^2}
\]

Using these relationships it is possible to show that

\[
(C \times D \times E \times \ldots)^* = (C^* \times D^* \times E^* \times \ldots)
\]

The position of a number in the complex plane can also be indicated by the distance, \( r \), of the point from the origin and the angle, \( \theta \), between the real axis and the vector joining the origin to the point (see opposite). By simple geometry it follows that

\[
\text{Re}[(a + ib)] = a = r \cos \theta \\
\text{Im}[(a + ib)] = b = r \sin \theta
\]

[1.1]

Where \( \text{Re} \) and \( \text{Im} \) mean "take the real part" and "take the imaginary part", respectively.

In this representation the square amplitude is

\[
|a + ib|^2 = a^2 + b^2 \\
= r^2 \left(\cos^2 \theta + \sin^2 \theta\right) = r^2
\]
where the identity \( \cos^2 \theta + \sin^2 \theta = 1 \) has been used.

### 1.1.2 Exponentials and complex exponentials

The exponential function, \( e^x \) or \( \exp(x) \), is defined as the power series

\[
\exp(x) = 1 + \frac{1}{1!}x^2 + \frac{1}{2!}x^3 + \frac{1}{3!}x^4 + \ldots
\]

The number \( e \) is the base of natural logarithms, so that \( \ln(e) = 1 \).

Exponentials have the following properties

\[
\begin{align*}
\exp(0) &= 1 \\
\exp(A) \times \exp(B) &= \exp(A + B) \\
[\exp(A)]^2 &= \exp(2A) \\
\exp(A) \times \exp(-A) &= \exp(A - A) = \exp(0) = 1 \\
\exp(-A) &= \frac{1}{\exp(A)} \\
\frac{\exp(A)}{\exp(B)} &= \exp(A) \times \exp(-B)
\end{align*}
\]

The *complex exponential* is also defined in terms of a power series:

\[
\exp(i\theta) = 1 + \frac{1}{1!}(i\theta)^2 + \frac{1}{2!}(i\theta)^3 + \frac{1}{3!}(i\theta)^4 + \ldots
\]

By comparing this series expansion with those for \( \sin \theta \) and \( \cos \theta \) it can easily be shown that

\[
\exp(i\theta) = \cos \theta + i \sin \theta \quad [1.2]
\]

This is a very important relation which will be used frequently. For negative exponents there is a similar result

\[
\begin{align*}
\exp(-i\theta) &= \cos(-\theta) + i \sin(-\theta) \\
&= \cos \theta - i \sin \theta \quad [1.3]
\end{align*}
\]

where the identities \( \cos(-\theta) = \cos \theta \) and \( \sin(-\theta) = -\sin \theta \) have been used.

By comparison of Eqns. [1.1] and [1.2] it can be seen that the complex number \( (a + ib) \) can be written

\[
(a + ib) = r \exp(i\theta)
\]

where \( r = a^2 + b^2 \) and \( \tan \theta = (b/a) \).
In the complex exponential form, the complex conjugate is found by changing the sign of the term in $i$

$$\text{if } C = r \exp(i \theta) \quad \text{then } C^* = r \exp(-i \theta)$$

It follows that

$$|C|^2 = CC^*$$

$$= r \exp(i \theta) r \exp(-i \theta)$$

$$= r^2 \exp(i \theta - i \theta) = r^2 \exp(0)$$

$$= r^2$$

Multiplication and division of complex numbers in the $(r, \theta)$ format is straightforward

let $C = r \exp(i \theta)$ and $D = s \exp(i \phi)$ then

$$\frac{1}{C} = \frac{1}{r \exp(i \theta)} = \frac{1}{r} \exp(-i \theta)$$

$$C \times D = rs \exp(i (\theta + \phi))$$

$$\frac{C}{D} = \frac{r \exp(i \theta)}{s \exp(i \phi)} = \frac{r}{s} \exp(i \theta) \exp(-i \phi) = \frac{r}{s} \exp(i (\theta - \phi))$$

1.1.2.1 Relation to trigonometric functions

Starting from the relation

$$\exp(i \theta) = \cos \theta + i \sin \theta$$

it follows that, as $\cos(-\theta) = \cos \theta$ and $\sin(-\theta) = -\sin \theta$,

$$\exp(-i \theta) = \cos \theta - i \sin \theta$$

From these two relationships the following can easily be shown

$$\exp(i \theta) + \exp(-i \theta) = 2 \cos \theta \quad \text{or} \quad \cos \theta = \frac{1}{2} [\exp(i \theta) + \exp(-i \theta)]$$

$$\exp(i \theta) - \exp(-i \theta) = 2i \sin \theta \quad \text{or} \quad \sin \theta = \frac{1}{2i} [\exp(i \theta) - \exp(-i \theta)]$$
1.1.3 Circular motion

In NMR basic form of motion is for magnetization to precess about a magnetic field. Viewed looking down the magnetic field, the tip of the magnetization vector describes a circular path. It turns out that complex exponentials are a very convenient and natural way of describing such motion.

Consider a point \( p \) moving in the \( xy \)-plane in a circular path, radius \( r \), centred at the origin. The position of the particle can be expressed in terms of the distance \( r \) and an angle \( \theta \): The \( x \)-component is \( r \cdot \cos \theta \) and the \( y \)-component is \( r \cdot \sin \theta \). The analogy with complex numbers is very compelling (see section 1.1.1); if the \( x \)- and \( y \)-axes are treated as the real and imaginary parts, then the position can be specified as the complex number \( r \cdot \exp(i \theta) \).

In this complex notation the angle \( \theta \) is called the phase. Points with different angles \( \theta \) are said to have different phases and the difference between the two angles is called the phase difference or phase shift between the two points.

If the point is moving around the circular path with a constant speed then the phase becomes a function of time. In fact for a constant speed, \( \theta \) is simply proportional to time, and the constant of proportion is the angular speed (or frequency) \( \omega \)

\[
\theta = \omega t
\]

where \( \theta \) is in radians, \( t \) is in seconds and \( \omega \) is in radians s\(^{-1}\). Sometimes it is convenient to work in Hz (that is, revolutions per second) rather than rad s\(^{-1}\); the frequency in Hz, \( \nu \), is related to \( \omega \) by \( \omega = 2 \pi \nu \).

The position of the point can now be expressed as \( r \exp(i \omega t) \), an expression which occurs very frequently in the mathematical description of NMR. Recalling that \( \exp(i \theta) \) can be thought of as a phase, it is seen that there is a strong connection between phase and frequency. For example, a phase shift of \( \theta = \omega t \) will come about due to precession at frequency \( \omega \) for time \( t \).

Rotation of the point \( p \) in the opposite sense is simply represented by changing the sign of \( \omega \): \( r \exp(-i \omega t) \). Suppose that there are two particles, \( p \) and \( p' \), one rotating at \( +\omega \) and the other at \(-\omega \), assuming that they both start on the \( x \)-axis, their motion can be described by \( \exp(+i \omega t) \) and \( \exp(-i \omega t) \) respectively. Thus, the \( x \)- and \( y \)-components are:

<table>
<thead>
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<th>( x )-comp.</th>
<th>( y )-comp.</th>
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<tbody>
<tr>
<td>( p )</td>
<td>( \cos \omega t )</td>
<td>( \sin \omega t )</td>
</tr>
<tr>
<td>( p' )</td>
<td>( \cos \omega t )</td>
<td>( -\sin \omega t )</td>
</tr>
</tbody>
</table>

It is clear that the \( x \)-components add, and the \( y \)-components cancel. All that is
left is a component along the $x$-axis which is oscillating back and forth at frequency $\omega$. In the complex notation this result is easy to see as by Eqns. [1.2] and [1.3], $\exp(i\omega t) + \exp(-i\omega t) = 2\cos\omega t$. In words, a point oscillating along a line can be represented as two counter-rotating points.
1.2 Wavefunctions and operators

In quantum mechanics, two mathematical objects – wavefunctions and operators – are of central importance. The wavefunction describes the system of interest (such as a spin or an electron) completely; if the wavefunction is known it is possible to calculate all the properties of the system. The simplest example of this that is frequently encountered is when considering the wavefunctions which describe electrons in atoms (atomic orbitals) or molecules (molecular orbitals). One often used interpretation of such electronic wavefunctions is to say that the square of the wavefunction gives the probability of finding the electron at that point.

Wavefunctions are simply mathematical functions of position, time etc. For example, the 1s electron in a hydrogen atom is described by the function \( \exp(-ar) \), where \( r \) is the distance from the nucleus and \( a \) is a constant.

In quantum mechanics, operators represent "observable quantities" such as position, momentum and energy; each observable has an operator associated with it.

Operators "operate on" functions to give new functions, hence their name

\[
\text{operator} \times \text{function} = \text{(new function)}
\]

An example of an operator is \( \left( \frac{d}{dx} \right) \); in words this operator says "differentiate with respect to \( x \)". Its effect on the function \( \sin x \) is

\[
\frac{d}{dx}(\sin x) = \cos x
\]

the "new function" is \( \cos x \). Operators can also be simple functions, so for example the operator \( x^2 \) just means "multiply by \( x^2 \)."

It is clear from this discussion that operators and functions cannot be reordered in the same way that numbers or functions can be. For example

\[
2 \times 3 \text{ is the same as } 3 \times 2 \\
x \times \sin(x) \text{ is the same as } \sin(x) \times x \\
\text{ but } \left( \frac{d}{dx} \right) \times \sin(x) \text{ is not the same as } \sin(x) \times \left( \frac{d}{dx} \right)
\]

Generally operators are thought of as acting on the functions that appear to their right.
1.2.1 Eigenfunctions and eigenvalues

Generally, operators act on functions to give another function:

\[
\text{operator} \times \text{function} = \text{(new function)}
\]

However, for a given operator there are some functions which, when acted upon, are regenerated, but multiplied by a constant

\[
\text{operator} \times \text{function} = \text{constant} \times \text{(function)} \quad [1.4]
\]

Such functions are said to be \textit{eigenfunctions} of the operator and the constants are said to be the associated \textit{eigenvalues}.

If the operator is \(\hat{Q}\) (the hat is to distinguish it as an operator) then Eqn. [1.4] can be written more formally as

\[
\hat{Q}f_q = qf_q \quad [1.5]
\]

where \(f_q\) is an eigenfunction of \(\hat{Q}\) with eigenvalue \(q\); there may be more than one eigenfunction each with different eigenvalues. Equation [1.5] is known as the \textit{eigenvalue equation}.

For example, is \(\exp(ax)\), where \(a\) is a constant, an eigenfunction of the operator \(\left(\frac{d}{dx}\right)\)? To find out the operator and function are substituted into the left-hand side of the eigenvalue equation, Eqn. [1.5]

\[
\left(\frac{d}{dx}\right)\exp(ax) = a\exp(ax)
\]

It is seen that the result of operating on the function is to generate the original function times a constant. Therefore \(\exp(ax)\) is an eigenfunction of the operator \(\left(\frac{d}{dx}\right)\) with eigenvalue \(a\).

Is \(\sin(ax)\), where \(a\) is a constant, an eigenfunction of the operator \(\left(\frac{d}{dx}\right)\)? As before, the operator and function are substituted into the left-hand side of the eigenvalue equation.

\[
\left(\frac{d}{dx}\right)\sin(ax) = a\cos(ax)
\]

\(\neq\) constant \(\times\) \(\sin(ax)\)
As the original function is not regenerated, \( \sin(ax) \) is not an eigenfunction of the operator \( \frac{d}{dx} \).

### 1.2.2 Normalization and orthogonality

A function, \( \psi \), is said to be *normalised* if

\[
\int (\psi^*) \psi \, d\tau = 1
\]

where, as usual, the * represents the complex conjugate. The notation \( d\tau \) is taken in quantum mechanics to mean integration over the full range of all relevant variables e.g. in three-dimensional space this would mean the range \(-\infty\) to \(+\infty\) for all of \( x, y \) and \( z \).

Two functions \( \psi \) and \( \phi \) are said to be *orthogonal* if

\[
\int (\psi^*) \phi \, d\tau = 0
\]

It can be shown that the eigenfunctions of an operator are orthogonal to one another, provided that they have different eigenvalues.

If \( \hat{Q} f_q = q f_q \) and \( \hat{Q} f_{q'} = q' f_{q'} \),

then \( \int (f_q^*) f_{q'} \, d\tau = 0 \)

### 1.2.3 Bra-ket notation

This short-hand notation for wavefunctions is often used in quantum mechanics. A wavefunction is represented by a "ket" \( |\ldots\rangle \); labels used to distinguish different wavefunctions are written in the ket. For example

\( f_q \) is written \( |q\rangle \) or sometimes \( |f_q\rangle \)

It is a bit superfluous to write \( f_q \) inside the ket.

The complex conjugate of a wavefunction is written as a "bra" \( \langle \ldots | \) ; for example

\( (f_{q'})^* \) is written \( \langle q' | \)
The rule is that if a bra appears on the left and a ket on the right, integration over \( d\tau \) is implied. So

\[
\langle q' | q \rangle \text{ implies } \int (f_{q'} *) f_q \, d\tau
\]

sometimes the middle vertical lines are merged: \( \langle q' | q \rangle \).

Although it takes a little time to get used to, the bra-ket notation is very compact. For example, the normalization and orthogonality conditions can be written

\[
\langle q | q \rangle = 1 \quad \langle q' | q \rangle = 0
\]

A frequently encountered integral in quantum mechanics is

\[
\int \psi_i^* \hat{Q} \psi_j \, d\tau
\]

where \( \psi_i \) and \( \psi_j \) are wavefunctions, distinguished by the subscripts \( i \) and \( j \). In bra-ket notation this integral becomes

\[
\langle i | \hat{Q} | j \rangle
\]

as before, the presence of a bra on the left and a ket on the right implies integration over \( d\tau \). Note that in general, it is not allowed to re-order the operator and the wavefunctions (section 1.2). The integral of Eqn. [1.6] is often called a matrix element, specifically the \( ij \) element, of the operator \( \hat{Q} \).

In the bra-ket notation the eigenvalue equation, Eqn. [1.5], becomes

\[
\hat{Q} | q \rangle = | q \rangle
\]

Again, this is very compact.

1.2.4 Basis sets

The position of any point in three-dimensional space can be specified by giving its \( x \)-, \( y \)- and \( z \)-components. These three components form a complete description of the position of the point; two components would be insufficient and adding a fourth component along another axis would be superfluous. The three axes are orthogonal to one another; that is any one axis does not have a component along the other two.
In quantum mechanics there is a similar idea of expressing a wavefunction in terms of a set of other functions. For example, $\psi$ may be expressed as a linear combination of other functions

$$|\psi\rangle = a_1|1\rangle + a_2|2\rangle + a_3|3\rangle + \ldots$$

where the $|i\rangle$ are called the basis functions and the $a_i$ are coefficients (numbers).

Often there is a limited set of basis functions needed to describe any particular wavefunction; such a set is referred to as a complete basis set. Usually the members of this set are orthogonal and can be chosen to be normalized, i.e.

$$\langle i | j \rangle = 0 \quad \langle i | i \rangle = 1$$

### 1.2.5 Expectation values

A postulate of quantum mechanics is that if a system is described by a wavefunction $\psi$ then the value of an observable quantity represented by the operator $\hat{Q}$ is given by the expectation value, $\langle \hat{Q} \rangle$, defined as

$$\langle \hat{Q} \rangle = \frac{\int \psi^* \hat{Q} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

or in the bra-ket notation

$$\langle \hat{Q} \rangle = \frac{\langle \psi | \hat{Q} | \psi \rangle}{\langle \psi | \psi \rangle}$$
1.3 Spin operators

1.3.1 Spin angular momentum

A mass going round a circular path (an orbit) possesses angular momentum; it turns out that this is a vector quantity which points in a direction perpendicular to the plane of the rotation. The \( x \)-, \( y \)- and \( z \)-components of this vector can be specified, and these are the angular momenta in the \( x \)-, \( y \)- and \( z \)-directions. In quantum mechanics, there are operators which represent these three components of the angular momentum.

Nuclear spins also have angular momentum associated with them – called spin angular momentum. The three components of this spin angular momentum (along \( x \), \( y \) and \( z \)) are represented by the operators \( \hat{I}_x \), \( \hat{I}_y \) and \( \hat{I}_z \) (from now on the hats will be dropped unless there is any possibility of ambiguity).

These operators are extremely important in the quantum mechanical description of NMR, indeed just about all of the theory in these lectures uses these operators. It is therefore very important to understand their properties.

1.3.2 Eigenvalues and eigenfunctions

From now on the discussion is restricted to nuclei with nuclear spin quantum number, \( I = \frac{1}{2} \). For such a spin, it turns out that there are just \((2I + 1) = 2\) eigenfunctions of any one of the operators \( \hat{I}_x \), \( \hat{I}_y \), and \( \hat{I}_z \). As it is traditional to define the direction of the applied magnetic field as \( z \), the eigenfunctions of the \( \hat{I}_z \) operator are the ones of most interest. These two eigenfunctions are usually denoted \(|\alpha\rangle\) and \(|\beta\rangle\); they have the properties

\[
\hat{I}_x |\alpha\rangle = \frac{1}{2} \hbar |\alpha\rangle \quad \hat{I}_x |\beta\rangle = -\frac{1}{2} \hbar |\beta\rangle
\]

where \( \hbar \) is Planck’s constant divided by \( 2\pi \). These properties mean that \(|\alpha\rangle\) and \(|\beta\rangle\) are indeed eigenfunctions, with eigenvalues \( \frac{1}{2} \hbar \) and \( -\frac{1}{2} \hbar \) respectively. These functions are normalized and orthogonal to one another

\[
\langle \alpha | \alpha \rangle = 1 \quad \langle \beta | \beta \rangle = 1 \quad \langle \alpha | \beta \rangle = 0
\]
The interpretation of these two states rests on the idea of angular momentum as a vector quantity. It turns out that angular momentum of size $I$ (here $I = \frac{1}{2}$) can be represented by a vector of length $\hbar\sqrt{I(I+1)}$; for spin $\frac{1}{2}$ the length of the vector is $\left(\frac{\sqrt{3}}{2}\right)\hbar$. This vector can orient itself with respect to a fixed axis, say the $z$-axis, in only $(2I+1)$ ways such that the projection of the vector $I$ onto the $z$-axis is $Ih_z, (I-1)h_z, \ldots, -Ih_z$, i.e. integer steps between $I$ and $-I$. In the case of $I = \frac{1}{2}$, there are only two possible projections, $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. These projections are labelled with a quantum number $m_I$, called the magnetic quantum number. It has values $+\frac{1}{2}$ and $-\frac{1}{2}$.

An alternative way of denoting the two eigenfunctions of the operator $I_z$ is to label them with the $m_I$ values

$$I_z|m_I\rangle = m_I\hbar|m_I\rangle$$

i.e. $I_z|\frac{1}{2}\rangle = \frac{1}{2}\hbar|\frac{1}{2}\rangle$, $I_z|\frac{1}{2}\rangle = -\frac{1}{2}\hbar|\frac{1}{2}\rangle$

So $|\frac{1}{2}\rangle$ and $|\frac{1}{2}\rangle$ correspond to $|\alpha\rangle$ and $|\beta\rangle$ which can be thought of as "spin up" and "spin down".

The functions $|\alpha\rangle$ and $|\beta\rangle$ are not eigenfunctions of either $I_x$ or $I_y$.

### 1.3.3 Raising and lowering operators

The raising operator, $I_+$, and the lowering operator, $I_-$, are defined as

$$I_+ = I_x + iI_y \quad I_- = I_x - iI_y \quad \text{[1.7]}$$

These operators have the following properties

$$I_+|\frac{1}{2}\rangle = \hbar|\frac{1}{2}\rangle \quad I_+|\frac{1}{2}\rangle = 0$$

$$I_-|\frac{1}{2}\rangle = \hbar|\frac{1}{2}\rangle \quad I_-|\frac{1}{2}\rangle = 0 \quad \text{[1.8]}$$

Their names originated from these properties. The raising operator acts on the state $|\frac{1}{2}\rangle$, which has $m_I = -\frac{1}{2}$, in such a way as to increase $m_I$ by one unit to give $m_I = +\frac{1}{2}$. However, if $I_+$ acts on the state $|\frac{1}{2}\rangle$ there is no possibility of further increasing $m_I$ as it is already at its maximum value; thus $I_+$ acting on $|\frac{1}{2}\rangle$ gives zero.

The same rationalization can be applied to the lowering operator. It acts on $|\frac{1}{2}\rangle$, which has $m_I = +\frac{1}{2}$, and produces a state on which $m_I$ has been lowered by

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Vector representation of the spin angular momentum of a spin half and its projections onto the $z$-axis.
one i.e. \( m_l = -\frac{1}{2} \). However, the \( m_l \) value can be lowered no further so \( L \) acting on \( | - \frac{1}{2} \rangle \) gives zero.

Using the definitions of Eqn. [1.7], \( I_x \) and \( I_y \) can be expressed in terms of the raising and lowering operators:

\[
I_x = \frac{1}{2} (I_+ + I_-) \quad I_y = \frac{1}{2} (I_+ - I_-)
\]

Using these, and the properties given in Eqn. [1.8], it is easy to work out the effect that \( I_x \) and \( I_y \) have on the states \( |\alpha\rangle \) and \( |\beta\rangle \); for example

\[
I_x |\alpha\rangle = \frac{1}{2} (I_+ + I_-) |\alpha\rangle \\
= \frac{1}{2} I_+ |\alpha\rangle + \frac{1}{2} I_- |\alpha\rangle \\
= 0 + \frac{1}{2} \hbar |\beta\rangle \\
= \frac{1}{2} \hbar |\beta\rangle
\]

By a similar method it can be found that

\[
I_x |\alpha\rangle = \frac{1}{2} \hbar |\beta\rangle \quad I_x |\beta\rangle = \frac{1}{2} \hbar |\alpha\rangle \quad I_y |\alpha\rangle = \frac{1}{2} \hbar |\beta\rangle \quad I_y |\beta\rangle = -\frac{1}{2} \hbar |\alpha\rangle \quad [1.9]
\]

These relationships all show that \( |\alpha\rangle \) and \( |\beta\rangle \) are not eigenfunctions of \( I_x \) and \( I_y \).

### 1.4 Hamiltonians

The Hamiltonian, \( H \), is the special name given to the operator for the energy of the system. This operator is exceptionally important as its eigenvalues and eigenfunctions are the "energy levels" of the system, and it is transitions between these energy levels which are detected in spectroscopy. To understand the spectrum, therefore, it is necessary to have a knowledge of the energy levels and this in turn requires a knowledge of the Hamiltonian operator.

In NMR, the Hamiltonian is seen as having a more subtle effect than simply determining the energy levels. This comes about because the Hamiltonian also affects how the spin system evolves in time. By altering the Hamiltonian the time evolution of the spins can be manipulated and it is precisely this that lies at the heart of multiple-pulse NMR.

The precise mathematical form of the Hamiltonian is found by first writing down an expression for the energy of the system using classical mechanics and then "translating" this into quantum mechanical form according to a set of rules. In this lecture the form of the relevant Hamiltonians will simply be stated rather than derived.

In NMR the Hamiltonian changes depending on the experimental situation.
There is one Hamiltonian for the spin or spins in the presence of the applied magnetic field, but this Hamiltonian changes when a radio-frequency pulse is applied.

1.4.1 Free precession

Free precession is when the spins experience just the applied magnetic field, $B_0$, traditionally taken to be along the $z$-axis.

1.4.1.1 One spin

The free precession Hamiltonian, $H_{\text{free}}$, is

$$H_{\text{free}} = \gamma B_0 I_z$$

where $\gamma$ is the gyromagnetic ratio, a constant characteristic of a particular nuclear species such as proton or carbon-13. The quantity $\gamma B_0 \hbar$ has the units of energy, which is expected as the Hamiltonian is the operator for energy. However, it turns out that it is much more convenient to write the Hamiltonian in units of angular frequency (radians $s^{-1}$), which is achieved by dividing the expression for $H_{\text{free}}$ by $\hbar$ to give

$$H_{\text{free}} = \gamma B_0 I_z$$

To be consistent it is necessary then to divide all of the operators by $\hbar$. As a result all of the factors of $\hbar$ disappear from many of the equations given above e.g. they become:

$$I_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle \quad I_z |\beta\rangle = -\frac{1}{2} |\beta\rangle \quad I_+ |\beta\rangle = |\alpha\rangle \quad I_- |\alpha\rangle = \hbar |\beta\rangle$$

$$I_x |\alpha\rangle = \frac{1}{2} |\beta\rangle \quad I_x |\beta\rangle = \frac{1}{2} i |\alpha\rangle \quad I_y |\alpha\rangle = \frac{1}{2} |\beta\rangle \quad I_y |\beta\rangle = -\frac{1}{2} i |\alpha\rangle$$

From now on, the properties of the wavefunctions and operators will be used in this form. The quantity $\gamma B_0$, which has dimensions of angular frequency (rad $s^{-1}$), is often called the Larmor frequency, $\omega_0$.

**Eigenfunctions and eigenvalues**

The eigenfunctions and eigenvalues of $H_{\text{free}}$ are a set of functions, $|\beta\rangle$, which
satisfy the eigenvalue equation:

\[ H_{\text{free}} |i\rangle = \varepsilon_i |i\rangle \]
\[ \omega_i I_z |i\rangle = \varepsilon_i |i\rangle \]

It is already known that \(|\alpha\rangle\) and \(|\beta\rangle\) are eigenfunctions of \(I_z\), so it follows that they are also eigenfunctions of any operator proportional to \(I_z\):

\[ H_{\text{free}} |\alpha\rangle = \omega_\alpha I_z |\alpha\rangle = \frac{1}{2} \omega_\alpha |\alpha\rangle \]

and likewise \( H_{\text{free}} |\beta\rangle = \omega_\beta I_z |\beta\rangle = -\frac{1}{2} \omega_\beta |\beta\rangle \).

So, \(|\alpha\rangle\) and \(|\beta\rangle\) are eigenfunctions of \(H_{\text{free}}\) with eigenvalues \(\frac{1}{2} \omega_\alpha\) and \(-\frac{1}{2} \omega_\beta\), respectively. These two eigenfunctions correspond to two energy levels and a transition between them occurs at frequency \(\left(\frac{1}{2} \omega_\alpha - \left(-\frac{1}{2} \omega_\beta\right)\right) = \omega_\beta\).

**1.4.1.2 Several spins**

If there is more than one spin, each simply contributes a term to \(H_{\text{free}}\); subscripts are used to indicate that the operator applies to a particular spin

\[ H_{\text{free}} = \omega_{0,1} I_{z1} + \omega_{0,2} I_{z2} + \ldots \]

where \(I_{z1}\) is the operator for the first spin, \(I_{z2}\) is that for the second and so on. Due to the effects of chemical shift, the Larmor frequencies of the spins may be different and so they have been written as \(\omega_{0,i}\).

**Eigenfunctions and eigenvalues**

As \(H_{\text{free}}\) separates into a sum of terms, the eigenfunctions turn out to be a product of the eigenfunctions of the separate terms; as the eigenfunctions of \(\omega_{0,1} I_{z1}\) are already known, it is easy to find those for the whole Hamiltonian.

As an example, consider the Hamiltonian for two spins

\[ H_{\text{free}} = \omega_{0,1} I_{z1} + \omega_{0,2} I_{z2} \]

From section 1.4.1.1, it is known that, for spin 1
\[ \omega_{0,1} I_{1z} | \alpha_1 \rangle = \frac{1}{2} \omega_0 | \alpha_1 \rangle \quad \text{and} \quad \omega_{0,1} I_{1z} | \beta_1 \rangle = -\frac{1}{2} \omega_0 | \beta_1 \rangle \]

likewise for spin 2

\[ \omega_{0,2} I_{2z} | \alpha_2 \rangle = \frac{1}{2} \omega_0 | \alpha_2 \rangle \quad \text{and} \quad \omega_{0,2} I_{2z} | \beta_2 \rangle = -\frac{1}{2} \omega_0 | \beta_2 \rangle \]

Consider the function \( | \beta_1 \rangle | \alpha_2 \rangle \), which is a product of one of the eigenfunctions for spin 1 with one for spin 2. To show that this is an eigenfunction of \( H_{\text{free}} \), the Hamiltonian is applied to the function

\[
H_{\text{free}} | \beta_1 \rangle | \alpha_2 \rangle = \left( \omega_{0,1} I_{1z} + \omega_{0,2} I_{2z} \right) | \beta_1 \rangle | \alpha_2 \rangle \\
= \omega_{0,1} I_{1z} | \beta_1 \rangle | \alpha_2 \rangle + \omega_{0,2} I_{2z} | \beta_1 \rangle | \alpha_2 \rangle \\
= -\frac{1}{2} \omega_{0,1} | \beta_1 \rangle | \alpha_2 \rangle + \frac{1}{2} \omega_{0,2} | \beta_1 \rangle | \alpha_2 \rangle \\
= \left( -\frac{1}{2} \omega_{0,1} + \frac{1}{2} \omega_{0,2} \right) | \beta_1 \rangle | \alpha_2 \rangle 
\]

As the action of \( H_{\text{free}} \) on \( | \beta_1 \rangle | \alpha_2 \rangle \) is to regenerate the function, then it has been shown that the function is indeed an eigenfunction, with eigenvalue \( \left( -\frac{1}{2} \omega_{0,1} + \frac{1}{2} \omega_{0,2} \right) \). Some comment in needed on these manipulation needed between lines 2 and 3 of the above calculation. The order of the function \( | \beta_1 \rangle \) and the operator \( I_{2z} \) were changed between lines 2 and 3. Generally, as was noted above, it is not permitted to reorder operators and functions; however it is permitted in this case as the operator refers to spin 2 but the function refers to spin 1. The operator has no effect, therefore, on the function and so the two can be re-ordered.

There are four possible products of the single-spin eigenfunctions and each of these can be shown to be an eigenfunction. The table summarises the results; in it, the shorthand notation has been used in which \( | \beta \alpha \rangle \) is denoted \( | \beta \alpha \rangle \) i.e. it is implied by the order of the labels as to which spin they apply to

| Eigenfunctions and eigenvalues for two spins |
|---|---|---|---|---|
| eigenfunction | \( m_{11} \) | \( m_{12} \) | \( M \) | eigenvalue |
| \( | \alpha \alpha \rangle \) | \( + \frac{1}{2} \) | \( + \frac{1}{2} \) | 1 | \( + \frac{1}{2} \omega_{0,1} + \frac{1}{2} \omega_{0,2} \) |
| \( | \alpha \beta \rangle \) | \( + \frac{1}{2} \) | \( - \frac{1}{2} \) | 0 | \( + \frac{1}{2} \omega_{0,1} - \frac{1}{2} \omega_{0,2} \) |
| \( | \beta \alpha \rangle \) | \( - \frac{1}{2} \) | \( + \frac{1}{2} \) | 0 | \( - \frac{1}{2} \omega_{0,1} + \frac{1}{2} \omega_{0,2} \) |
| \( | \beta \beta \rangle \) | \( - \frac{1}{2} \) | \( - \frac{1}{2} \) | 1 | \( - \frac{1}{2} \omega_{0,1} - \frac{1}{2} \omega_{0,2} \) |
Also shown in the table are the $m_I$ values for the individual spins and the total magnetic quantum number, $M$, which is simply the sum of the $m_I$ values of the two spins.

In normal NMR, the allowed transitions are between those levels that differ in $M$ values by one unit. There are two transitions which come out at $\omega_{0,1}$, $|\beta\alpha\rangle \leftrightarrow |\alpha\alpha\rangle$ and $|\alpha\beta\rangle \leftrightarrow |\beta\beta\rangle$; and there are two which come out at $\omega_{0,2}$, $|\beta\alpha\rangle \leftrightarrow |\beta\beta\rangle$ and $|\alpha\beta\rangle \leftrightarrow |\alpha\alpha\rangle$. The former two transitions involve a flip in the spin state of spin 1, whereas the latter pair involve a flip of the state of spin 2. The energy levels and transitions are depicted opposite.

1.4.1.3 Scalar coupling

The Hamiltonian for scalar coupling contains a term $2\pi J_{ij} I_i z I_j z$ for each coupled pair of spins; $J_{ij}$ is the coupling constant, in Hz, between spins $i$ and $j$. The terms representing coupling have to be added to those terms described in section 1.4.1.2 which represent the basic Larmor precession. So, the complete free precession Hamiltonian for two spins is:

$$H_{\text{free}} = \omega_{0,1} I_1 z + \omega_{0,2} I_2 z + 2\pi J_{12} I_1 z I_2 z$$

**Eigenfunctions and eigenvalues for two spins**

The product functions, such as $|\beta_1\rangle|\alpha_2\rangle$, turn out to also be eigenfunctions of the coupling Hamiltonian. For example, consider the function $|\beta_1\rangle|\alpha_2\rangle$; to show that this is an eigenfunction of the coupling part of $H_{\text{free}}$, the relevant operator is applied to the function

$$2\pi J_{12} I_1 z I_2 z |\beta_1\rangle|\alpha_2\rangle = 2\pi J_{12} I_1 z |\beta_1\rangle I_2 z |\alpha_2\rangle$$

$$= 2\pi J_{12} I_1 z |\beta_1\rangle \frac{1}{2} |\alpha_2\rangle$$

$$= 2\pi J_{12} (-\frac{1}{2}) |\beta_1\rangle \frac{1}{2} |\alpha_2\rangle$$

$$= -\frac{1}{2} \pi J_{12} |\beta_1\rangle|\alpha_2\rangle$$

As the action of $2\pi J_{12} I_1 z I_2 z$ on $|\beta_1\rangle|\alpha_2\rangle$ is to regenerate the function, then it follows that the function is indeed an eigenfunction, with eigenvalue $(-\frac{1}{2} \pi J_{12})$. As before, the order of operators can be altered when the relevant operator and function refer to different spins.

In a similar way, all four product functions can be show to be eigenfunctions of the coupling Hamiltonian, and therefore of the complete free precession Hamiltonian. The table shows the complete set of energy levels.
There are two allowed transitions in which spin 1 flips, 1–3 and 2–4, and these appear at $\omega_{0,1} + \pi J_{12}$ and $\omega_{0,1} - \pi J_{12}$, respectively. There are two further transitions in which spin 2 flips, 1–2 and 3–4, and these appear at $\omega_{0,2} + \pi J_{12}$ and $\omega_{0,2} - \pi J_{12}$, respectively. These four lines form the familiar two doublets found in the spectrum of two coupled spins.

Transition 1–2 is one in which spin 2 flips \textit{i.e.} changes spin state, but the spin state of spin 1 remains the same. In this transition spin 2 can be said to be \textit{active}, whereas spin 1 is said to be \textit{passive}. These details are summarized in the diagram below.

The spectrum from two coupled spins, showing which spins are passive and active in each transition. The frequency scale is in rad s$^{-1}$, so the splitting of the doublet is $2 \pi J_{12}$ rad s$^{-1}$, which corresponds to $J_{12}$ Hz.

### Eigenfunctions and eigenvalues for two coupled spins

<table>
<thead>
<tr>
<th>number</th>
<th>eigenfunction</th>
<th>$M$</th>
<th>eigenvalue</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$</td>
<td>\alpha\alpha\rangle$</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>$</td>
<td>\alpha\beta\rangle$</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>$</td>
<td>\beta\alpha\rangle$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>$</td>
<td>\beta\beta\rangle$</td>
<td>1</td>
</tr>
</tbody>
</table>

### Eigenfunctions and eigenvalues for several spins

For $N$ spins, it is easy to show that the eigenfunctions are the $2^N$ possible products of the single spin eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$. A particular eigenfunction can be labelled with the $m_i$ values for each spin, $m_{1,1}$ and written as $|m_{1,1}m_{1,2}...m_{1,N}\rangle$. The energy of this eigenfunction is

$$\sum_{i=1}^{N} m_{i,j} \omega_{0,i} + \sum_{i=1}^{N} \sum_{j>i}^{N} m_{i,j} m_{j,i} (2\pi J_{ij})$$

The restricted sum over the index $j$ is to avoid counting the couplings more than once.
1.4.2 Pulses

In NMR the nuclear spin magnetization is manipulated by applying a magnetic field which is (a) transverse to the static magnetic field \( i.e. \) in the \( xy \)-plane, and (b) oscillating at close to the Larmor frequency of the spins. Such a field is created by passing the output of a radio-frequency transmitter through a small coil which is located close to the sample.

If the field is applied along the \( x \)-direction and is oscillating at \( \omega_{RF} \), the Hamiltonian for one spin is

\[
H = \omega_0 I_z + 2\omega_1 \cos \omega_{RF} t \ I_x
\]

The first term represents the interaction of the spin with the static magnetic field, and the second represents the interaction with the oscillating field. The strength of the latter is given by \( \omega_1 \).

It is difficult to work with this Hamiltonian as it depends on time. However, this time dependence can be removed by changing to a \textit{rotating set of axes}, or a \textit{rotating frame}. These axes rotate about the \( z \)-axis at frequency \( \omega_{RF} \), and in the same sense as the Larmor precession.

In such a set of axes the Larmor precession is no longer at \( \omega_0 \), but at \( (\omega_0 - \omega_{RF}) \); this quantity is called the \textit{offset}, \( \Omega \). The more important result of using the rotating frame is that the time dependence of the transverse field is removed. The details of how this comes about are beyond the scope of this lecture, but can be found in a number of standard texts on NMR.

In the rotating frame, the Hamiltonian becomes time independent

\[
H = (\omega_0 - \omega_{RF}) I_z + \omega_1 I_x
\]

\[
= \Omega I_z + \omega_1 I_x
\]

Commonly, the strength of the radiofrequency field is arranged to be much greater than typical offsets: \( \omega_1 >> |\Omega| \). It is then permissible to ignore the offset term and so write the pulse Hamiltonian as (for pulses of either phase)

\[
H_{\text{pulse},x} = \omega_1 I_x \quad \text{or} \quad H_{\text{pulse},y} = \omega_1 I_y
\]

Such pulses are described as \textit{hard} or \textit{non-selective}, in the sense that they affect spins over a range of offsets. Pulses with lower field strengths, \( \omega_1 \), are termed \textit{selective} or \textit{soft}.

1.4.2.1 Several spins

For multi-spin systems, a term of the form \( \omega_1 I_k \) is added for each spin that is
affected by the pulse. Note that in heteronuclear systems, pulses can be applied independently to nuclei of different kinds

\[ H_{\text{pulse},x} = \omega_1 I_{1x} + \omega_2 I_{2x} + \ldots \]

The product functions given above are not eigenfunctions of these Hamiltonians for pulses.

From now it, it will be assumed that all calculations are made in the rotating frame. So, instead of the free precession Hamiltonian being in terms of Larmor frequencies it will be written in terms of offsets. For example, the complete free precession Hamiltonian for two coupled spins is

\[ H_{\text{free}} = \Omega_1 I_{1z} + \Omega_2 I_{2z} + 2\pi J_{12} I_{1z} I_{2z} \]

### 1.5 Time evolution

In general, the wavefunction describing a system varies with time, and this variation can be computed using the time-dependent Schrödinger equation

\[
\frac{d\psi(t)}{dt} = -iH\psi(t) \tag{1.13}
\]

where \(\psi(t)\) indicates that the wavefunction is a function of time. From this equation it is seen that the way in which the wavefunction varies with time depends on the Hamiltonian. In NMR, the Hamiltonian can be manipulated – for example by applying radio-frequency fields – and it is thus possible to manipulate the evolution of the spin system.

As has been seen in section 1.2.5, the size of observable quantities, such as magnetization, can be found by calculating the expectation value of the appropriate operator. For example, the \(x\)-magnetization is proportional to the expectation value of the operator \(I_x\)

\[ M_x = k\langle I_x \rangle = \frac{\langle \psi(t)|I_x|\psi(t) \rangle}{\langle \psi(t)|\psi(t) \rangle} \]

where \(k\) is a constant of proportion. As the wavefunction changes with time, so do the expectation values and hence the observable magnetization.

### 1.6 Superposition states

This section will consider first a single spin and then a collection of a large
number of non-interacting spins, called an *ensemble*. For example, the single
spin might be an isolated proton in a single molecule, while the ensemble would
be a normal NMR sample made up of a large number of such molecules. In an
NMR experiment, the observable magnetization comes from the whole sample;
often it is called the bulk magnetization to emphasize this point. Each spin in
the sample makes a small contribution to the bulk magnetization. The
processes of going from a system of one spin to one of many is called ensemble
averaging.

The wavefunction for one spin can be written

$$\psi(t) = c_\alpha(t)\alpha + c_\beta(t)\beta$$

where $c_\alpha(t)$ and $c_\beta(t)$ are coefficients which depend on time and which in
general are complex numbers. Such a wavefunction is called a *superposition state*,
the name deriving from the fact that it is a sum of contributions from
different wavefunctions.

In elementary quantum mechanics it is all too easy to fall into the erroneous
view that "the spin must be either up or down, that is in state $\alpha$ or state $\beta$". This
simply is not true; quantum mechanics makes no such claim.

### 1.6.1 Observables

The $x$-, $y$- and $z$-magnetizations are proportional to the expectation values of the
operators $I_x$, $I_y$ and $I_z$. For brevity, $c_\alpha(t)$ will be written $c_\alpha$, the time dependence
being implied.

Consider first the expectation value of $I_z$ (section 1.2.5)

$$\langle I_z \rangle = \frac{c_\alpha^* \alpha + c_\beta^* \beta | I_z | c_\alpha \alpha + c_\beta \beta}{c_\alpha^* \alpha + c_\beta^* \beta | (c_\alpha \alpha + c_\beta \beta)}$$

$$= \frac{c_\alpha^* c_\alpha \alpha | I_z | \alpha + c_\beta^* c_\alpha \beta | I_z | \alpha + c_\alpha c_\beta^* \alpha | I_z | \beta + c_\beta c_\beta^* \beta | I_z | \beta}{c_\alpha^* c_\alpha \alpha + c_\beta^* c_\alpha \beta + c_\alpha c_\beta^* \alpha + c_\beta c_\beta^* \beta}$$

$$= \frac{\frac{1}{2} c_\alpha^* c_\alpha \alpha + \frac{1}{2} c_\beta^* c_\alpha \beta + (-\frac{1}{2}) c_\alpha c_\beta^* \alpha + c_\beta c_\beta^* \beta}{c_\alpha^* c_\alpha \alpha + c_\beta^* c_\alpha \beta + c_\alpha c_\beta^* \alpha + c_\beta c_\beta^* \beta}$$

$$= \frac{\frac{1}{2} c_\alpha^* c_\alpha \alpha + c_\beta^* c_\beta}{c_\alpha^* c_\alpha \alpha + c_\beta^* c_\beta}$$

$$= \frac{1}{2} \left( c_\alpha^* c_\alpha - c_\beta^* c_\beta \right)$$
Extensive use has been made of the facts that the two wavefunctions \(|\alpha\rangle\) and \(|\beta\rangle\) are normalized and orthogonal to one another (section 1.3.2), and that the effect of \(I_z\) on these wavefunctions is know (Eqn. [1.10]).

To simplify matters, it will be assumed that the wavefunction \(\psi(t)\) is normalized so that \(\langle \psi | \psi \rangle = 1\); this implies that \(c_\alpha^* c_\alpha + c_\beta^* c_\beta = 1\).

Using this approach, it is also possible to determine the expectation values of \(I_x\) and \(I_y\). In summary:

\[
\begin{align*}
\langle I_z \rangle &= \frac{1}{2} (c_\alpha^* c_\alpha - c_\beta^* c_\beta) \\
\langle I_x \rangle &= \frac{1}{2} (c_\beta^* c_\alpha + c_\alpha^* c_\beta) \\
\langle I_y \rangle &= \frac{1}{2} (c_\beta^* c_\alpha - c_\alpha^* c_\beta)
\end{align*}
\]

[1.14]

It is interesting to note that if the spin were to be purely in state \(|\alpha\rangle\), such that \(c_\alpha = 1\), \(c_\beta = 0\), there would be no \(x\)- and no \(y\)-magnetization. The fact that such magnetization is observed in an NMR experiment implies that the spins must be in superposition states.

The coefficients \(c_\alpha\) and \(c_\beta\) are in general complex, and it is sometimes useful to rewrite them in the \((r/\phi)\) format (see section 1.1.2)

\[
\begin{align*}
c_\alpha &= r_\alpha \exp(i \phi_\alpha) \\
c_\beta &= r_\beta \exp(i \phi_\beta) \\
c_\alpha^* &= r_\alpha \exp(-i \phi_\alpha) \\
c_\beta^* &= r_\beta \exp(-i \phi_\beta)
\end{align*}
\]

Using these, the expectation values for \(I_{x,y,z}\) become:

\[
\begin{align*}
\langle I_z \rangle &= \frac{1}{2} (r_\alpha^2 - r_\beta^2) \\
\langle I_x \rangle &= r_\alpha r_\beta \cos(\phi_\alpha - \phi_\beta) \\
\langle I_y \rangle &= r_\alpha r_\beta \sin(\phi_\alpha - \phi_\beta)
\end{align*}
\]

The normalization condition, \(c_\alpha^* c_\alpha + c_\beta^* c_\beta = 1\), becomes \((r_\alpha^2 + r_\beta^2) = 1\) in this format. Recall that the \(r\)'s are always positive and real.

1.6.1.1 Comment on these observables

The expectation value of \(I_z\) can take any value between \(\frac{1}{2}\) (when \(r_\alpha = 1\), \(r_\beta = 0\)) and \(-\frac{1}{2}\) (when \(r_\alpha = 0\), \(r_\beta = 1\)). This is in contrast to the quantum number \(m_I\) which is restricted to values \(\pm \frac{1}{2}\) ("spin up or spin down"). Likewise, the expectation values of \(I_x\) and \(I_y\) can take any values between \(-\frac{1}{2}\) and \(+\frac{1}{2}\), depending on the exact values of the coefficients.
1.6.1.2 Ensemble averages; bulk magnetization

In order to compute, say, the $x$-magnetization from the whole sample, it is necessary to add up the individual contributions from each spin:

$$\overline{\langle I_x \rangle} = \langle I_x \rangle_1 + \langle I_x \rangle_2 + \langle I_x \rangle_3 + \ldots$$

where $\overline{\langle I_x \rangle}$ is the ensemble average, that is the sum over the whole sample. The contribution from the $i$th spin, $\langle I_x \rangle_i$, can be calculated using Eqn. [1.14].

$$\overline{\langle I_x \rangle} = \langle I_x \rangle_1 + \langle I_x \rangle_2 + \langle I_x \rangle_3 + \ldots$$

$$= \frac{1}{2} \left( e^*_{\beta} c_{\alpha} + e^*_{\alpha} c_{\beta} \right) + \frac{1}{2} \left( e^*_{\alpha} c_{\beta} + e^*_{\beta} c_{\alpha} \right) + \frac{1}{2} \left( e^*_{\beta} c_{\alpha} + e^*_{\alpha} c_{\beta} \right) + \ldots$$

$$= r_{\alpha \beta} \cos(\phi_{\alpha} - \phi_{\beta})$$

On the third line the over-bar is shorthand for the average written out explicitly in the previous line. The fourth line is the same as the third, but expressed in the $(r, \phi)$ format (Eqn. [1.15]).

The contribution from each spin depends on the values of $r_{\alpha, \beta}$ and $\phi_{\alpha, \beta}$ which in general it would be quite impossible to know for each of the enormous number of spins in the sample. However, when the spins are in equilibrium it is reasonable to assume that the phases $\phi_{\alpha, \beta}$ of the individual spins are distributed randomly. As $\langle I_x \rangle = r_{\alpha \beta} \cos(\phi_{\alpha} - \phi_{\beta})$ for each spin, the random phases result in the cosine term being randomly distributed in the range $-1$ to $+1$, and as a result the sum of all these terms is zero. That is, at equilibrium

$$\overline{\langle I_x \rangle}_{eq} = 0 \quad \overline{\langle I_y \rangle}_{eq} = 0$$

This is in accord with the observation that at equilibrium there is no transverse magnetization.

The situation for the $z$-magnetization is somewhat different:
Note that the phases $\phi$ do not enter into this expression, and recall that the $r$'s are positive.

This is interpreted in the following way. In the superposition state $c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$, $c_\alpha c_\alpha^* = r_\alpha^2$ can be interpreted as the probability of finding the spin in state $|\alpha\rangle$, and $c_\beta c_\beta^* = r_\beta^2$ as likewise the probability of finding the spin in state $|\beta\rangle$. The idea is that if the state of any one spin is determined by experiment the outcome is always either $|\alpha\rangle$ or $|\beta\rangle$. However, if a large number of spins are taken, initially all in identical superposition states, and the spin states of these determined, a fraction $c_\alpha c_\alpha^*$ would be found to be in state $|\alpha\rangle$, and a fraction $c_\beta c_\beta^*$ in state $|\beta\rangle$.

From this it follows that

$$\langle I_z \rangle = \frac{1}{2} P_\alpha - \frac{1}{2} P_\beta$$

where $P_\alpha$ and $P_\beta$ are the total probabilities of finding the spins in state $|\alpha\rangle$ or $|\beta\rangle$, respectively. These total probabilities can be identified with the populations of two levels $|\alpha\rangle$ or $|\beta\rangle$. The $z$-magnetization is thus proportional to the population difference between the two levels, as expected. At equilibrium, this population difference is predicted by the Boltzmann distribution.

### 1.6.2 Time dependence

The time dependence of the system is found by solving the time dependent Schrödinger equation, Eqn. [1.13]. From its form, it is clear that the exact nature of the time dependence will depend on the Hamiltonian i.e. it will be different for periods of free precession and radiofrequency pulses.

#### 1.6.2.1 Free precession

The Hamiltonian (in a fixed set of axes, not a rotating frame) is $\omega_0 I_z$ and at time $t = 0$ the wavefunction will be assumed to be
\[
|\psi(0)\rangle = c_\alpha(0)|\alpha\rangle + c_\beta(0)|\beta\rangle = r_\alpha(0)\exp[i\phi_\alpha(0)]|\alpha\rangle + r_\beta(0)\exp[i\phi_\beta(0)]|\beta\rangle
\]

The time dependent Schrödinger equation can therefore be written as

\[
\frac{d\psi(t)}{dt} = -iH\psi
\]

\[
\frac{d}{dt}\left[c_\alpha(t)|\alpha\rangle + c_\beta(t)|\beta\rangle\right] = -i\omega_0\left[c_\alpha(t)|\alpha\rangle + c_\beta(t)|\beta\rangle\right] - i\omega_0\left[c_\alpha(t)|\alpha\rangle - c_\beta(t)|\beta\rangle\right]
\]

where use has been made of the properties of \(I_z\) when acting on the wavefunctions \(|\alpha\rangle\) and \(|\beta\rangle\) (section 1.4 Eqn. [1.10]). Both side of this equation are left-multiplied by \(\langle\alpha|\), and the use is made of the orthogonality of \(|\alpha\rangle\) and \(|\beta\rangle\)

\[
\frac{d}{dt}\left[\langle\alpha|c_\alpha(t)|\alpha\rangle + \langle\alpha|c_\beta(t)|\beta\rangle\right] = -i\omega_0\left[\langle\alpha|\frac{1}{2}c_\alpha(t)|\alpha\rangle - \langle\alpha|\frac{1}{2}c_\beta(t)|\beta\rangle\right] = -\frac{1}{2}i\omega_0\ c_\alpha(t)
\]

The corresponding equation for \(c_\beta\) is found by left multiplying by \(\langle\beta|\).

\[
\frac{dc_\beta(t)}{dt} = \frac{1}{2}i\omega_0\ c_\beta(t)
\]

These are both standard differential equations whose solutions are well know:

\[
c_\alpha(t) = c_\alpha(0)\exp\left(-\frac{1}{2}i\omega_0\ t\right) \quad c_\beta(t) = c_\beta(0)\exp\left(+\frac{1}{2}i\omega_0\ t\right)
\]

All that happens is that the coefficients oscillate in phase, at the Larmor frequency.

To find the time dependence of the expectation values of \(I_{x,y,z}\), these expressions for \(c_{\alpha,\beta}(t)\) are simply substituted into Eqn. [1.14]
\[
\langle I_z \rangle(t) = \frac{1}{2} \left( c^*_\alpha(t)c_\alpha(t) - c^*_\beta(t)c_\beta(t) \right) \\
= \frac{1}{2} c^*_\alpha(0)c_\alpha(0) \exp\left(\frac{i}{2} i \omega_0 t\right) \exp\left(-\frac{i}{2} i \omega_0 t\right) \\
- \frac{1}{2} c^*_\beta(0)c_\beta(0) \exp\left(-\frac{i}{2} i \omega_0 t\right) \exp\left(\frac{i}{2} i \omega_0 t\right) \\
= \frac{1}{2} c^*_\alpha(0)c_\alpha(0) - \frac{1}{2} c^*_\beta(0)c_\beta(0)
\]

As expected, the z-component does not vary with time, but remains fixed at its initial value. However, the x- and y-components vary according to the following which can be found in the same way:

\[
\langle I_x \rangle(t) = \frac{1}{2} r_\alpha(0) r_\beta(0) \cos(\omega_0 t - \phi_\beta(0) + \phi_\alpha(0)) \\
\langle I_y \rangle(t) = \frac{1}{2} r_\alpha(0) r_\beta(0) \sin(\omega_0 t - \phi_\beta(0) + \phi_\alpha(0))
\]

Again, as expected, these components oscillate at the Larmor frequency.

### 1.6.2.2 Pulses

More interesting is the effect of radiofrequency pulses, for which the Hamiltonian (in the rotating frame) is \(\omega I_z\). Solving the Schrödinger equation is a little more difficult than for the case above, and yields the result

\[
c_\alpha(t) = c_\alpha(0) \cos \frac{1}{2} \omega_0 t - ic_\beta(0) \sin \frac{1}{2} \omega_0 t \\
c_\beta(t) = c_\beta(0) \cos \frac{1}{2} \omega_0 t - ic_\alpha(0) \sin \frac{1}{2} \omega_0 t
\]

In contrast to free precession, the pulse actually causes that coefficients to change, rather than simply to oscillate in phase. The effect is thus much more significant.

A lengthy, but straightforward, calculation gives the following result for \(\langle I_y \rangle\)

\[
\langle I_y \rangle(t) = \frac{1}{2} \left( c_\alpha(0)c^*_\beta(0) - c^*_\alpha(0)c_\beta(0) \right) \cos \omega_0 t \\
- \frac{1}{2} \left( c_\alpha(0)c^*_\beta(0) - c^*_\alpha(0)c_\beta(0) \right) \sin \omega_0 t
\]  

[1.16]

The first term in brackets on the right is simply \(\langle I_y \rangle\) at time zero (compare Eqn. [1.14]). The second term is \(\langle I_z \rangle\) at time zero (compare Eqn. [1.14]). So, \(\langle I_y \rangle(t)\) can be written

\[
\langle I_y \rangle(t) = \langle I_y \rangle(0) \cos \omega_0 t - \langle I_z \rangle(0) \sin \omega_0 t
\]
This result is hardly surprising. It simply says that if a pulse is applied about the \(x\)-axis, a component which was initially along \(z\) is rotated towards \(y\). The rotation from \(z\) to \(y\) is complete when \(\omega t = \pi/2\), i.e. a 90° pulse.

The result of Eqn. [1.16] applies to just one spin. To make it apply to the whole sample, the ensemble average must be taken

\[
\langle I_y \rangle(t) = \langle I_y \rangle(0) \cos \omega t - \langle I_z \rangle(0) \sin \omega t
\]  

[1.17]

Suppose that time zero corresponds to equilibrium. As discussed above, at equilibrium then ensemble average of the \(y\) components is zero, but the \(z\) components are not, so

\[
\langle I_y \rangle(t) = -\langle I_z \rangle_\text{eq} \sin \omega t
\]

where \(\langle I_z \rangle_\text{eq}\) is the equilibrium ensemble average of the \(z\) components. In words, Eqn. [1.17] says that the pulse rotates the equilibrium magnetization from \(z\) to \(-y\), just as expected.

### 1.6.3 Coherences

Transverse magnetization is associated in quantum mechanics with what is known as a coherence. It was seen above that at equilibrium there is no transverse magnetization, not because each spin does not make a contribution, but because these contributions are random and so add up to zero. However, at equilibrium the \(z\)-components do not cancel one another, leading to a net magnetization along the \(z\)-direction.

During the pulse, the \(z\)-component from each spin is rotated towards \(y\), according to Eqn. [1.17]. The key point is that all the contributions from all the spins, although they start in random positions in the \(yz\)-plane, are rotated through the same angle. As a result, what started out as a net alignment in the \(z\)-direction rotates in the \(zy\)-plane, becoming a net alignment along \(-y\) after a 90° pulse.

Another interpretation is to look at the way in which the individual coefficients vary during the pulse

\[
c_\alpha(t) = c_\alpha(0) \cos \frac{1}{2} \omega t - ic_\beta(0) \sin \frac{1}{2} \omega t
\]

\[
c_\beta(t) = c_\beta(0) \cos \frac{1}{2} \omega t - ic_\alpha(0) \sin \frac{1}{2} \omega t
\]

In words, what happens is that the size of the coefficients at time \(t\) are related to those at time zero in a way which is the same for all spins in the sample. Although the phases are random at time zero, for each spin the phase associated
with \( c_\alpha \) at time zero is transferred to \( c_\beta \), and vice versa. It is this correlation of phases between the two coefficients which leads to an overall observable signal from the sample.

1.7 Density matrix

The approach used in the previous section is rather inconvenient for calculating the outcome of NMR experiments. In particular, the need for ensemble averaging after the calculation has been completed is especially difficult. It turns out that there is an alternative way of casting the Schrödinger equation which leads to a much more convenient framework for calculation – this is density matrix theory. This theory, can be further modified to give an operator version which is generally the most convenient for calculations in multiple pulse NMR.

First, the idea of matrix representations of operators needs to be introduced.

1.7.1 Matrix representations

An operator, \( Q \), can be represented as a matrix in a particular basis set of functions. A basis set is a complete set of wavefunctions which are adequate for describing the system, for example in the case of a single spin the two functions \(|\alpha\rangle\) and \(|\beta\rangle\) form a suitable basis. In larger spin systems, more basis functions are needed, for example the four product functions described in section 1.4.1.2 form such a basis for a two spin system.

The matrix form of \( Q \) is defined in this two-dimensional representation is defined as

\[
Q = \begin{pmatrix}
\langle \alpha | Q | \alpha \rangle & \langle \alpha | Q | \beta \rangle \\
\langle \beta | Q | \alpha \rangle & \langle \beta | Q | \beta \rangle 
\end{pmatrix}
\]

Each of the matrix elements, \( Q_{ij} \), is calculated from an integral of the form \( \langle i | Q | j \rangle \), where \(|i\rangle\) and \(|j\rangle\) are two of the basis functions. The matrix element \( Q_{ij} \) appears in the \( i \)th row and the \( j \)th column.

1.7.1.1 One spin

Particularly important are the matrix representations of the angular momentum operators. For example, \( I_z \):

\[
I_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle \\
I_z |\beta\rangle = -\frac{1}{2} |\beta\rangle \\
\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \\
\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1
\]
\[
I_z = \begin{pmatrix}
⟨α|I_z|α⟩ & ⟨α|I_z|β⟩ \\
⟨β|I_z|α⟩ & ⟨β|I_z|β⟩
\end{pmatrix}
\]
\[
= \begin{pmatrix}
⟨α|\frac{1}{2}|α⟩ & ⟨α|\frac{1}{2}|β⟩ \\
⟨β|\frac{1}{2}|α⟩ & ⟨β|\frac{1}{2}|β⟩
\end{pmatrix}
\]
\[
= \begin{pmatrix}
\frac{1}{2} & 0 \\
0 & -\frac{1}{2}
\end{pmatrix}
\]

As usual, extensive use have been made of the properties of \(I_z\) and the ortho-
normality of the basis functions (see sections 1.3.2).

The representations of \(I_x\) and \(I_y\) are easily found, by expressing them in terms
of the raising and lowering operators (section 1.3.3), to be
\[
I_x = \begin{pmatrix}
0 & \frac{1}{2} \\
\frac{1}{2} & 0
\end{pmatrix} \quad I_y = \begin{pmatrix}
0 & -\frac{i}{2} \\
\frac{i}{2} & 0
\end{pmatrix}
\]

1.7.1.2 Direct products

The easiest way to find the matrix representations of angular momentum
operators in larger basis sets is to use the direct product.

When two \(n \times n\) matrices are multiplied together the result is another \(n \times n\)
matrix. The rule is that the \(ij\)th element of the product is found by multiplying,
element by element, the \(i\)th row by the \(j\)th column and adding up all the
products. For example:
\[
\begin{pmatrix}
as & b \\
c & d
\end{pmatrix}
\begin{pmatrix}
p & q \\
r & s
\end{pmatrix} = \begin{pmatrix}
ap + br & aq + bs \\
ep + dr & cq + ds
\end{pmatrix}
\]

The direct product, symbolized \(⊗\), of two \(n \times n\) matrices results in a larger matrix
of size \(2n \times 2n\). The rule for this multiplication is difficult to express formally
but easy enough to describe:
\[
\begin{pmatrix}
as & b \\
c & d
\end{pmatrix} ⊗ \begin{pmatrix}
p & q \\
r & s
\end{pmatrix} = \begin{pmatrix}
\begin{pmatrix}a \times \begin{pmatrix}p & q \\
r & s\end{pmatrix} & b \times \begin{pmatrix}p & q \\
r & s\end{pmatrix}\end{pmatrix} \\
\begin{pmatrix}c \times \begin{pmatrix}p & q \\
r & s\end{pmatrix} & d \times \begin{pmatrix}p & q \\
r & s\end{pmatrix}\end{pmatrix}
\end{pmatrix}
\]

The right-hand matrix is duplicated four times over, because there are four
elements in the left-hand matrix. Each duplication is multiplied by the
corresponding element from the left-hand matrix. The final result is

\[
\begin{pmatrix}
  a & b \\
  c & d \\
\end{pmatrix} \otimes \begin{pmatrix}
  p & q \\
  r & s \\
\end{pmatrix} = \begin{pmatrix}
  ap & aq & bp & bq \\
  ar & as & br & bs \\
  cp & cq & dp & dq \\
  cr & cs & dr & ds \\
\end{pmatrix} \equiv \begin{pmatrix}
  ap & aq & bp & bq \\
  ar & as & br & bs \\
  cp & cq & dp & dq \\
  cr & cs & dr & ds \\
\end{pmatrix}
\]

(the lines in the central matrix are just to emphasise the relation to the 2 \times 2 matrices, they have no other significance).

The same rule applies to matrices with just a single row (row vectors)

\[(a,b) \otimes (p,q) = (ap,aq,bp,bq)\]

### 1.7.1.3 Two spins

The basis set for a single spin can be written (|\(\alpha_1\rangle,|\beta_1\rangle\); the basis set for two spins can be found from the direct product of two such basis sets, one for each spin:

\[
(|\alpha_1\rangle,|\beta_1\rangle) \otimes (|\alpha_2\rangle,|\beta_2\rangle) = (|\alpha_1\rangle,|\alpha_1\rangle,|\beta_1\rangle,|\beta_1\rangle,|\alpha_2\rangle,|\beta_2\rangle)
\]

In this basis the matrix representation of \(I_{1x}\) can be found by writing the operator as the direct product

\[I_{1x} \otimes E_2\]  \hspace{1cm} [1.18]

where \(E\) is the unit matrix

\[E = \begin{pmatrix}
  1 & 0 \\
  0 & 1 \\
\end{pmatrix}\]

The subscript 2 on the \(E\) in Eqn. [1.18] is in a sense superfluous as the unit matrix is the same for all spins. However, it is there to signify that in the direct product there must be an operator for each spin. Furthermore, these operators must occur in the correct order, with that for spin 1 leftmost and so on. So, to find the matrix representation of \(I_{2x}\) the required direct product is

\[E_1 \otimes I_{2x}\]
In matrix form $E_1 \otimes I_{2x}$ is

$$
E_1 \otimes I_{2x} = \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix} \otimes \begin{pmatrix}
0 & \frac{1}{2} \\
\frac{1}{2} & 0
\end{pmatrix}
$$

$$
= \begin{pmatrix}
0 & \frac{1}{2} & 0 & 0 \\
\frac{1}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{2} \\
0 & 0 & \frac{1}{2} & 0
\end{pmatrix}
$$

and $I_{1x} \otimes E_2$ is

$$
I_{1x} \otimes E_2 = \begin{pmatrix}
0 & \frac{1}{2} \\
\frac{1}{2} & 0
\end{pmatrix} \otimes \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
$$

$$
= \begin{pmatrix}
0 & 0 & \frac{1}{2} & 0 \\
0 & 0 & 0 & \frac{1}{2} \\
\frac{1}{2} & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0
\end{pmatrix}
$$

As a final example $I_{1x} \otimes I_{2y}$ is

$$
I_{1x} \otimes I_{2y} = \begin{pmatrix}
0 & \frac{1}{4} \\
\frac{1}{4} & 0
\end{pmatrix} \otimes \begin{pmatrix}
0 & -\frac{i}{2} \\
\frac{i}{2} & 0
\end{pmatrix}
$$

$$
= \begin{pmatrix}
0 & 0 & 0 & -\frac{i}{4} \\
0 & 0 & \frac{i}{4} & 0 \\
0 & \frac{i}{4} & 0 & 0 \\
\frac{i}{4} & 0 & 0 & 0
\end{pmatrix}
$$

All of these matrices are hermetian, which means that matrix elements related by reflection across the diagonal have the property that $Q_{ji} = Q_{ij}^*$. 

### 1.7.2 Density matrix

For a one spin system the density matrix, $\sigma$, is defined according to its elements

$$
\sigma(t) = \begin{pmatrix}
c_\alpha(t)c_\alpha^*(t) & c_\alpha(t)c_\beta^*(t) \\
c_\beta(t)c_\alpha^*(t) & c_\beta(t)c_\beta^*(t)
\end{pmatrix}
$$
where the over-bars indicate ensemble averaging. This matrix contains all the information needed to calculate any observable quantity. Formally, \( \sigma \) is defined in the following way:

\[
\sigma(t) = |\langle \psi(t) | \psi(t) \rangle|
\]

### 1.7.2.1 Observables

It can be shown that the expectation value of an operator, \( Q \), is given by

\[
\langle Q \rangle = \text{Tr}[\sigma Q]
\]

where \( \text{Tr}[A] \) means take the trace, that is the sum of the diagonal elements, of the matrix \( A \).

For example, the expectation value of \( I_z \) is

\[
\langle I_z \rangle = \text{Tr}
\begin{pmatrix}
\frac{1}{2} c_a(t)c_a^*(t) & c_a(t)c_\beta^*(t) \\
-\frac{1}{2} c_\beta(t)c_\beta^*(t) & 0
\end{pmatrix}
\begin{pmatrix}
\frac{1}{2} & 0 \\
0 & -\frac{1}{2}
\end{pmatrix}
\]

\[
= \text{Tr}
\begin{pmatrix}
\frac{1}{2} c_a(t)c_a^*(t) & \cdots \\
\cdots & -\frac{1}{2} c_\beta(t)c_\beta^*(t)
\end{pmatrix}
\]

\[
= \frac{1}{2} \left( r_\alpha^2 - r_\beta^2 \right)
\]

This is directly comparable to the result obtained in section 1.6.1.2.

The very desirable feature of this definition of the density matrix and the trace property for calculation observables is that the ensemble averaging is done before the observable is computed.

The expectation value of \( I_x \) is

\[
\langle I_x \rangle = \text{Tr}
\begin{pmatrix}
\frac{1}{2} c_a(t)c_a^*(t) & c_a(t)c_\beta^*(t) \\
-\frac{1}{2} c_\beta(t)c_\beta^*(t) & 0
\end{pmatrix}
\begin{pmatrix}
0 & \frac{1}{2} \\
\frac{1}{2} & 0
\end{pmatrix}
\]

\[
= \frac{1}{2} \left( c_a(t)c_\beta^*(t) + c_\beta(t)c_a^*(t) \right)
\]
Again, this is directly comparable to the result obtained in section 1.6.1.2.

The off-diagonal elements of the density matrix can contribute to transverse magnetization, whereas the diagonal elements only contribute to longitudinal magnetization. In general, a non-zero off-diagonal element \( c_i(t)c_j^*(t) \) indicates a coherence involving levels \( i \) and \( j \), whereas a diagonal element, \( c_i(t)c_i^*(t) \), indicates the population of level \( i \).

From now on the ensemble averaging and time dependence will be taken as implicit and so the elements of the density matrix will be written simply \( c_ic_j^* \) unless there is any ambiguity.

### 1.7.2.2 Equilibrium

As described in section 1.6.1.2, at equilibrium the phases of the super-position states are random and as a result the ensemble averages \( c_\alpha(t)c_\beta^*(t) \) and \( c_\beta(t)c_\alpha^*(t) \) are zero. This is easily seen by writing then in the \( r/\phi \) format

\[
\langle c_\alpha^*c_\beta \rangle = r_\alpha \exp(i\phi_\alpha) r_\beta \exp(-i\phi_\beta) = 0 \text{ at equilibrium}
\]

However, the diagonal elements do not average to zero but rather correspond to the populations, \( P_i \), of the levels, as was described in section 1.6.1.2

\[
\langle c_\alpha^*c_\alpha \rangle = r_\alpha \exp(i\phi_\alpha) r_\alpha \exp(-i\phi_\alpha) = r_\alpha^2 = P_\alpha
\]

The equilibrium density matrix for one spin is thus

\[
\sigma_{eq} = \begin{pmatrix} P_\alpha & 0 \\ 0 & P_\beta \end{pmatrix}
\]

As the energy levels in NMR are so closely spaced, it turns out that to an excellent approximation the populations can be written in terms of the average population of the two levels, \( P_{av} \), and the difference between the two populations, \( \Delta \), where \( \Delta = P_\alpha - P_\beta \).
\[
\sigma_{eq} = \begin{pmatrix}
P_{av} + \frac{1}{2} \Delta & 0 \\
0 & P_{av} - \frac{1}{2} \Delta
\end{pmatrix}
\]

Comparing this with the matrix representations of \( I_z \) and \( E \), \( \sigma_{eq} \), can be written

\[
\sigma_{eq} = P_{av} E + \Delta I_z
\]

\[
= P_{av} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \Delta \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}
\]

It turns out that the part from the matrix \( E \) does not contribute to any observables, so for simplicity it is ignored. The factor \( \Delta \) depends on details of the spin system and just scales the final result, so often it is simply set to 1. With these simplifications \( \sigma_{eq} \) is simply \( I_z \).

### 1.7.2.3 Evolution

The density operator evolves in time according to the following equation, which can be derived from the time dependent Schrödinger equation (section 1.5):

\[
\frac{d\sigma(t)}{dt} = -i[H\sigma(t) - \sigma(t)H]
\]

Note that as \( H \) and \( \sigma \) are operators their order is significant. Just as in section 1.5 the evolution depends on the prevailing Hamiltonian.

If \( H \) is time independent (something that can usually be arranged by using a rotating frame, see section 1.4.2), the solution to Eqn. [1.19] is straightforward

\[
\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt)
\]

where again the ordering of the operators must be preserved. All the terms in this equation can be thought of as either matrices or operators, and it is the second of these options which is discussed in the next section.

### 1.7.3 Operator form of the density matrix

So far, Hamiltonians have been written in terms of operators, specifically the angular momentum operators \( I_{x,y,z} \), and it has also been seen that these operators represent observable quantities, such as magnetizations. In addition, it was shown in section 1.1.2.2 that the equilibrium density matrix has the same form as \( I_z \). These observations naturally lead to the idea that it might be convenient also to write the density matrix in terms of the angular momentum operators.
Specifically, the idea is to expand the density matrix as a combination of the operators:

$$\sigma(t) = a(t)I_z + b(t)I_y + c(t)I_z$$

where $a$, $b$ and $c$ are coefficients which depend on time.

1.7.3.1 Observables

From this form of the density matrix, the expectation value of, for example, $I_x$ can be computed in the usual way (section 1.7.2.1).

$$\langle I_x \rangle = \text{Tr}[\sigma I_x]$$

$$= \text{Tr}[aI_x + bI_y + cI_z I_x]$$

$$= \text{Tr}[aI_x I_x] + \text{Tr}[bI_y I_x] + \text{Tr}[cI_z I_x]$$

where to get to the last line the property that the trace of a sum of matrices is equal to the sum of the traces of the matrices has been used.

It turns out that $\text{Tr}[I_p I_q]$ is zero unless $p = q$ when the trace is $= \frac{1}{2}$; for example

$$\text{Tr}[I_x I_x] = \text{Tr}\left[\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}\right]$$

$$= \text{Tr}\left[\begin{pmatrix} \frac{1}{4} & \cdots \\ \cdots & \frac{1}{4} \end{pmatrix}\right] = \frac{1}{2}$$

$$\text{Tr}[I_x I_z] = \text{Tr}\left[\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}\right]$$

$$= \text{Tr}\left[\begin{pmatrix} 0 & \cdots \\ \cdots & 0 \end{pmatrix}\right] = 0$$

In summary it is found that

$$\langle I_x \rangle = \frac{1}{2}a \quad \langle I_y \rangle = \frac{1}{2}b \quad \langle I_z \rangle = \frac{1}{2}c$$
This is a very convenient result. By expressing the density operator in the form
\[ \sigma(t) = a(t)I_x + b(t)I_y + c(t)I_z \]
the x-, y- and z-magnetizations can be deduced just by inspection as being proportional to \( a(t) \), \( b(t) \), and \( c(t) \) respectively (the factor of one half is not important). This approach is further developed in the lecture 2 where the product operator method is introduced.

### 1.7.3.2 Evolution

The evolution of the density matrix follows the equation
\[
\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt)
\]

Often the Hamiltonian will be a sum of terms, for example, in the case of free precession for two spins \( H = \Omega_1I_{1z} + \Omega_2I_{2z} \). The exponential of the sum of two operators can be expressed as a product of two exponentials provided the operators commute

\[
\exp(A + B) = \exp(A)\exp(B) \quad \text{provided } A \text{ and } B \text{ commute}
\]

Commuting operators are ones whose effect is unaltered by changing their order: i.e. \( AB\psi = BA\psi \); not all operators commute with one another.

Luckily, operators for different spins do commute so, for the free precession Hamiltonian

\[
\exp(-iHt) = \exp\left(-i\left[\Omega_1I_{1z} + \Omega_2I_{2z}\right]t\right)
\]
\[= \exp(-i\Omega_1I_{1z}t)\exp(-i\Omega_2I_{2z}t)\]

The evolution of the density matrix can then be written

\[
\sigma(t) = \exp(-i\Omega_1I_{1z}t)\exp(-i\Omega_2I_{2z}t)\sigma(0)\exp(i\Omega_1I_{1z}t)\exp(i\Omega_2I_{2z}t)
\]

The operators for the evolution due to offsets and couplings also commute with one another.

For commuting operators the order is immaterial. This applies also to their exponentials, e.g. \( \exp(A)B = B\exp(A) \). This property is used in the following

\[
\exp(-i\Omega_1I_{1z}t)I_{2x}\exp(i\Omega_1I_{1z}t) = \exp(-i\Omega_1I_{1z}t)\exp(i\Omega_1I_{1z}t)I_{2x}
\]
\[= \exp(-i\Omega_1I_{1z}t + i\Omega_1I_{1z}t)I_{2x}
\]
\[= \exp(0)I_{2x} = I_{2x}
\]
In words this says that the offset of spin 1 causes no evolution of transverse magnetization of spin 2.

These various properties will be used extensively in lecture 2.