

# 1 Quantum Mechanics

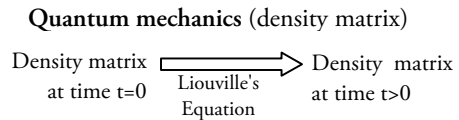
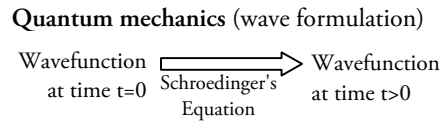
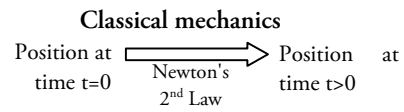
Lecture notes by Assaf Tal

NMR is a semi-classical phenomenon. On the one hand, we treat the electromagnetic fields in matter as classical, which is justified at the long wavelengths encountered<sup>1</sup>. On the other hand, the basic unit we'll be dealing with - the nuclear spin - is strictly a quantum mechanical (QM) entity. Although in certain cases we can take a classical limit in which our system of spins can be described by classical equations, for the most part NMR is best thought of in quantum mechanical terms, and cannot be explained well by classical analogies.

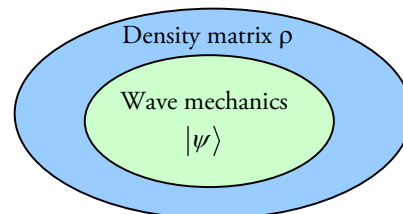
Luckily, QM is fairly benign in NMR since it deals with simple systems (mostly spin-1/2). We review here some of the basic principles which will be of use to us in explaining NMR phenomena in subsequent chapters.

1. **Kinematics:** First, I will explain how to describe a QM system. We will start with a single spin in a magnetic field. Instead of taking the "usual" view adopted by many QM textbooks which talk about wave functions and vectors, we will immediately start with the density matrix formalism, which is in fact a generalization of those concepts (and, paradoxically, easier to understand!).
2. **Dynamics:** I will show you how to "solve" any problem in quantum mechanics. That is, given the state of the system at time  $t=0$  and the electromagnetic field it's in, I'll explain how to solve - at least in theory - for its state at any time  $t>0$ .

Our philosophy will not be to "understand" quantum mechanics, which is rather ambitious, but to lay down the basic rules by which we can carry out meaningful calculations.



Most books begin by talking about "wave mechanics" using vectors to describe a pure quantum system, and generalize to statistical ensembles using the density matrix formulation. We will circumvent that step completely to simplify the discussion, which means we will be saying "just because" at a few spots where we will lack the necessary foundations to explain them. We will conclude by generalizing our notions to more than one spin.



## Wave Mechanics

### Physical Quantities of The System Are Given By Square Matrices

Physical observable quantities of a system such as energy, angular momentum and magnetic moment are given by matrices.

The simplest system in QM is possibly an isolated spin-1/2. Some atomic nuclei have non-zero angular momentum. It turns out that the magnitude of the angular momentum only appears in "steps" of  $\hbar/2$ , where  $\hbar \approx 6.62 \times 10^{-34} \frac{\text{m}^2 \cdot \text{kg}}{\text{sec}}$  is Planck's constant. So we have spin-1/2 particles (having intrinsic angular momentum  $\hbar/2$ ), spin-1

<sup>1</sup> In physics-speak we'd say we have many photons per unit volume.

particles (having intrinsic angular momentum  $\hbar$ ), spin-3/2 particles (having intrinsic angular momentum  $3\hbar/2$ ) and so forth. Some examples from nature include:

"Particle"	n	p	Spin	$\gamma$ (rad·MHz/T)
Electron	0	0	1/2	$2\pi \cdot$
Proton ( $^1\text{H}$ )	0	1	1/2	
Neutron	1	0	1/2	
Deuterium ( $^2\text{H}$ )	1	1	1	
Carbon ( $^{12}\text{C}$ )	6	6	0	
Carbon ( $^{13}\text{C}$ )	7	6	1/2	
Lithium ( $^7\text{Li}$ )	4	3	3/2	

For a spin-1/2 particle - such as the electron, or proton - the spin angular-momentum components are given by:

$$\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

For a spin-1 particle such as deuterium, the angular momentum components are  $3 \times 3$  matrices:

$$\hat{S}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$\hat{S}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

In general, for a spin  $m/2$ , the spin operators will be  $(m+1) \times (m+1)$  matrices.

### The System's Energy is Called The Hamiltonian. It Is A Matrix

We know from classical electromagnetism that the energy of a magnetic moment  $\mathbf{m}$  in an external field  $\mathbf{B}$  is given by

$$E = -\mathbf{m} \cdot \mathbf{B}.$$

It is highest when  $\mathbf{m}$  and  $\mathbf{B}$  are anti-parallel and lowest when they are parallel.

The corresponding quantum mechanical observable is called the Hamiltonian, and is obtained by swapping  $\mathbf{m}$  out for the quantum mechanical magnetization observables:

$$H = -\hat{\mathbf{M}} \cdot \mathbf{B}$$

$$= -\hat{M}_x B_x - \hat{M}_y B_y - \hat{M}_z B_z$$

Substituting the full forms for the  $M_i$ s ( $\hat{M}_i = \gamma \hat{S}_i$ ) and adding up all three matrices, we obtain:

$$H = \gamma \hbar \begin{pmatrix} -B_z & -B_{xy} \\ -B_{xy} & B_z \end{pmatrix}.$$

If the magnetic field is time dependent, so is H.

### The "Quantum" in Quantum Mechanics

A fundamental property of many quantum systems is that many of their observables (physical quantities) are quantized. This means that if we take a pure, well isolated system, and measure that quantity, we will always get an answer that belongs to a discrete set of values. This set coincides with the possible eigenvalues of the matrix<sup>2</sup>. We remind that reader that (1.) an  $m \times m$  matrix has up to  $m$  distinct eigenvalues, and (2.) a diagonal matrix's eigenvalues are simply its entries on the diagonal.

For example, the z-component of the angular momentum for a spin-1/2 particle,

$$\hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

has two eigenvalues,  $\pm \frac{\hbar}{2}$ . This means that when

<sup>2</sup> You will get to practice eigenvalues a bit more in the tutorial, but to refresh your memory, a vector  $\mathbf{v}$  is an eigenvalue of a matrix  $M$  is  $M\mathbf{v} = (\text{some number})\mathbf{v}$ . A simple example is the rotation matrix  $R_z(\theta)$  about the z-axis. It is clear that  $\hat{\mathbf{z}} = (0,0,1)$  is an eigenvector with eigenvalue 1, since it is colinear with the z-axis:  $R_z(\theta)\hat{\mathbf{z}} = \hat{\mathbf{z}}$ .

## The State Of An Ensemble is Given By A Density Matrix

A density matrix, often denoted  $\rho$ , is just a square matrix that follows a few rules. First, it is **hermitian**, just like observables:

$$\rho = \rho^\dagger.$$

It is also **positive semidefinite**, meaning that for any vector  $\mathbf{x}$ ,

$$\mathbf{x}^\dagger \rho \mathbf{x} \geq 0.$$

Finally, it has a **trace of unity**:

$$\text{tr}(\rho) = 1.$$

The density matrix has one fundamental physical property from which its entire behavior can be derived: if the system is described by a density matrix  $\rho$ , then the average value of a measured observable  $A$  is given by

$$\langle A \rangle = \text{tr}(\rho A).$$

Our next order of business will be to generalize the state vector formulation to handle statistical ensembles of particles, such as the  $\sim 10^{25}$  spin-1/2 particles in a 200 mL glass of water.

## The Entries of a Diagonal Density Matrix Represent Probabilities

In the "conventional" way of teaching QM, one first learns about wavefunctions and probabilities. It is mentioned that a spin-1/2 particle can be in either an "up" or "down" state, each having its own energy. Using these, the following interpretation is then given to the density matrix: when in a diagonal form, the elements along the diagonal represents the probability of the system of being in the up or down state, respectively:

$$\rho = \begin{pmatrix} \text{Pr}(\uparrow) & 0 \\ 0 & \text{Pr}(\downarrow) \end{pmatrix}.$$

This is also consistent with the properties of  $\rho$ , namely  $\text{tr}(\rho)=1$  (probabilities sum up to 1) and

positive-semidefiniteness (probabilities are  $\geq 0$ ). However, we will not be taking this route and will not be using this interpretation except at one point down the road, when we discuss the thermal equilibrium state of the system.

## A Simple Example: Spin-1/2 Particle

Let's take an example by looking at a general  $2 \times 2$  matrix for a spin-1/2 particle:

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix},$$

where the different elements can be complex. Let's carefully apply the conditions for  $\rho$  to be a density matrix. Hermiticity means

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = \begin{pmatrix} \rho_{11}^* & \rho_{21}^* \\ \rho_{12}^* & \rho_{22}^* \end{pmatrix} = \rho^\dagger.$$

We see that  $\rho_{11} = \rho_{11}^*$  and  $\rho_{22} = \rho_{22}^*$ , meaning both quantities are real. Let's denote them by

$$\begin{aligned} \rho_{11} &= a \\ \rho_{22} &= d \end{aligned}$$

where  $a, d$  are both real numbers. Furthermore, let's denote

$$\rho_{12} = b + ic$$

with  $b, c$  real, such that

$$\rho = \begin{pmatrix} a & b + ic \\ b - ic & d \end{pmatrix}.$$

Next, we impose the condition  $\text{tr}(\rho)=1$ , from which  $a+d=1$ , so:

$$\rho = \begin{pmatrix} a & b + ic \\ b - ic & 1 - a \end{pmatrix}.$$

Before imposing the final condition of positive-semidefiniteness, let's calculate the expectation value for the  $x, y$  and  $z$ -components of the intrinsic magnetic moment,  $\hat{M}_i = \gamma \hat{S}_i$  ( $i=x,y,z$ ):

$$M_x = \frac{\gamma\hbar}{2} \text{tr} \left( \begin{pmatrix} a & b+ic \\ b-ic & 1-a \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right) = \gamma\hbar b$$

$$M_y = \frac{\gamma\hbar}{2} \text{tr} \left( \begin{pmatrix} a & b+ic \\ b-ic & 1-a \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \right) = -\gamma\hbar c$$

$$M_z = \frac{\gamma\hbar}{2} \text{tr} \left( \begin{pmatrix} a & b+ic \\ b-ic & 1-a \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right) = \frac{\gamma\hbar}{2} (2a-1)$$

These are just enough equations to solve for the coefficients a, b & c:

$$a = \frac{1}{2} + \frac{M_z}{\gamma\hbar}$$

$$b = \frac{M_x}{\gamma\hbar}, \quad c = -\frac{M_y}{\gamma\hbar}$$

from which

$$\rho = \begin{pmatrix} \frac{1}{2} + \frac{M_z}{\gamma\hbar} & \frac{M_x - iM_y}{\gamma\hbar} \\ \frac{M_x + iM_y}{\gamma\hbar} & \frac{1}{2} - \frac{M_z}{\gamma\hbar} \end{pmatrix}$$

$$= \frac{1}{2} I + \frac{2}{\gamma\hbar^2} (M_x \hat{S}_x + M_y \hat{S}_y + M_z \hat{S}_z)$$

$$= \frac{1}{2} I + \frac{2}{\gamma\hbar^2} \mathbf{M} \cdot \hat{\mathbf{S}}$$

or

$$\boxed{\rho = \frac{1}{2} I + \frac{2}{\gamma\hbar^2} \mathbf{M} \cdot \hat{\mathbf{S}}}$$

### The Time Evolution Of The System Is Given By The Liouville Equation

Much like Newton's 2nd law,  $\mathbf{F} = m\mathbf{a}$ , dictates the dynamics of a classical system, Liouville's equation dictates the dynamics of a quantum system:

$$\frac{d\rho}{dt} = \frac{1}{i\hbar} [\hat{H}, \rho]$$

Here  $\hat{H}$  is the hamiltonian, and by definition, for any two matrices,

$$[A, B] = AB - BA.$$

If H is time independent, we can solve the Liouville formally:

$$\rho(t) = e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} = U \rho U^\dagger.$$

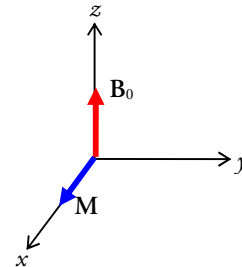
The quantity  $U(t) = e^{-iHt/\hbar}$  is called the **propagator**. To see this solves the Liouville equation, note that<sup>3</sup>  $\frac{d}{dt} U = -\frac{iH}{\hbar} U$  and differentiate:

$$\begin{aligned} \frac{d\rho}{dt} &= \dot{U} \rho(0) U^\dagger + U \overbrace{\dot{\rho}(0)}^{=0} U^\dagger + U \rho(0) \dot{U}^\dagger \\ &= -\frac{iH}{\hbar} U \rho(0) U^\dagger + U \rho(0) U^\dagger \frac{iH}{\hbar} \\ &= \frac{1}{i\hbar} (H \rho(t) - \rho(t) H) = \frac{1}{i\hbar} [H, \rho] \end{aligned}$$

so it satisfies the Liouville equation and is a solution.

### Example: Time Evolution of a Magnetic Moment In A Constant Magnetic Field

Let's use all of the machinery we've seen so far to calculate the time evolution of a spin-1/2 magnetic moment, starting along the x-axis, and placed in a constant magnetic field along the z-axis.



<sup>3</sup> For regular functions and numbers,  $\frac{d}{dt} e^{at} = a e^{at}$ .

This does not change if we discuss matrices; the only time we need to be careful when handling matrices is when we have two different matrices which don't commute. If we only have one matrix, we can treat it as a number, so:  $\frac{d}{dt} e^{\hat{A}t} = \hat{A} e^{\hat{A}t} = e^{\hat{A}t} \hat{A}$ . The last line is true because, again, we're dealing with  $\hat{A}$  and a function of  $\hat{A}$ , which commute (a matrix commutes with any function of itself).

To “solve” this problem, we will ask ourselves four questions in this order:

1. What is our density matrix at time  $t=0$ ?
2. What is our Hamiltonian?
3. What is our propagator,  $U(t)$ ?
4. What is our density matrix as a function of time? (obtained by computing  $U\rho U^\dagger$ )

Our initial density matrix is obtained by putting  $\mathbf{M}=(M_0,0,0)$  in our expression for  $\rho$ :

$$\rho = \frac{1}{2}I + \frac{2}{\gamma\hbar^2}\mathbf{M}\cdot\hat{\mathbf{S}} = \begin{pmatrix} \frac{1}{2} & \frac{M_0}{\gamma\hbar} \\ \frac{M_0}{\gamma\hbar} & \frac{1}{2} \end{pmatrix}.$$

The constant magnetic field is

$$\mathbf{B} = \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$

Our Hamiltonian is

$$\hat{H} = -\hat{\mathbf{M}}\cdot\mathbf{B} = -\gamma\hat{S}_z B_0 = \begin{pmatrix} -\frac{\hbar\omega_0}{2} & 0 \\ 0 & \frac{\hbar\omega_0}{2} \end{pmatrix}.$$

with

$$\omega_0 = \gamma B_0.$$

For a proton ( $\gamma = 2\pi \cdot 42.576 \frac{\text{rad}\cdot\text{kHz}}{\text{mT}}$ ) in a  $B_0=3$  Tesla magnetic field,  $\omega_0 \approx 2\pi \cdot 127$  MHz.

The propagator is easy to calculate because the Hamiltonian is diagonal. For any diagonal matrix,  $A$ , matrix multiplication with itself is very simple:

$$\begin{aligned} \hat{A} &= \begin{pmatrix} A_{11} & 0 \\ 0 & A_{22} \end{pmatrix} \\ \hat{A}^2 &= \begin{pmatrix} A_{11} & 0 \\ 0 & A_{22} \end{pmatrix} \begin{pmatrix} A_{11} & 0 \\ 0 & A_{22} \end{pmatrix} = \begin{pmatrix} A_{11}^2 & 0 \\ 0 & A_{22}^2 \end{pmatrix} \\ &\vdots \\ \hat{A}^N &= \begin{pmatrix} A_{11}^N & 0 \\ 0 & A_{22}^N \end{pmatrix} \end{aligned}$$

We can use this property by expanding the matrix exponential with a Taylor expansion. I remind you that Taylor expansion for  $e^x$  is

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

so for the matrix exponential  $e^{\hat{A}}$ ,

$$\begin{aligned} e^{\hat{A}} &= I + \hat{A} + \frac{\hat{A}^2}{2!} + \frac{\hat{A}^3}{3!} + \dots \\ &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} A_{11} & 0 \\ 0 & A_{22} \end{pmatrix} + \frac{1}{2!} \begin{pmatrix} A_{11}^2 & 0 \\ 0 & A_{22}^2 \end{pmatrix} \\ &\quad + \frac{1}{3!} \begin{pmatrix} A_{11}^3 & 0 \\ 0 & A_{22}^3 \end{pmatrix} + \dots \end{aligned}$$

Adding up the matrices, we get

$$e^{\hat{A}} = \begin{pmatrix} 1 + A_{11} + \frac{A_{11}^2}{2!} + \frac{A_{11}^3}{3!} + \dots & 0 \\ 0 & 1 + A_{22} + \frac{A_{22}^2}{2!} + \frac{A_{22}^3}{3!} + \dots \end{pmatrix}$$

We see that, along the diagonal, we get Taylor expansions of  $e^{A_{11}}$  and  $e^{A_{22}}$ , so

$$e^{\hat{A}} = \begin{pmatrix} e^{A_{11}} & 0 \\ 0 & e^{A_{22}} \end{pmatrix}.$$

This result is **not** true in general. For a non-diagonal matrix, in general

$$e^{\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}} \neq \begin{pmatrix} e^{A_{11}} & e^{A_{12}} \\ e^{A_{21}} & e^{A_{22}} \end{pmatrix}.$$

Using this, we can immediately write down the propagator:

$$U(t) = e^{-i\hat{H}t/\hbar} = \begin{pmatrix} e^{i\omega_0 t/2} & 0 \\ 0 & e^{-i\omega_0 t/2} \end{pmatrix}.$$

Finally, with all of this in place, we can compute the form of the density matrix as a function of time:

$$\begin{aligned}
\rho(t) &= U \rho U^\dagger \\
&= \begin{pmatrix} e^{i\omega_0 t/2} & 0 \\ 0 & e^{-i\omega_0 t/2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{M_0}{\gamma \hbar} \\ \frac{M_0}{\gamma \hbar} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} e^{-i\omega_0 t/2} & 0 \\ 0 & e^{i\omega_0 t/2} \end{pmatrix} \\
&= \begin{pmatrix} \frac{1}{2} e^{i\omega_0 t/2} & \frac{M_0}{\gamma \hbar} e^{i\omega_0 t/2} \\ \frac{M_0}{\gamma \hbar} e^{-i\omega_0 t/2} & \frac{1}{2} e^{-i\omega_0 t/2} \end{pmatrix} \begin{pmatrix} e^{-i\omega_0 t/2} & 0 \\ 0 & e^{i\omega_0 t/2} \end{pmatrix} \\
&= \begin{pmatrix} \frac{1}{2} & \frac{M_0}{\gamma \hbar} e^{i\omega_0 t} \\ \frac{M_0}{\gamma \hbar} e^{-i\omega_0 t} & \frac{1}{2} \end{pmatrix}
\end{aligned}$$

This looks simple, but we'd like to also "understand" it by recasting it in the general form  $\rho(t) = \frac{1}{2} I + \frac{2}{\gamma \hbar^2} \mathbf{M}(t) \cdot \hat{\mathbf{S}}$ . Note that, simply by inspection,

$$\begin{aligned}
\rho(t) &= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{M_0}{\gamma \hbar} \begin{pmatrix} 0 & e^{i\omega_0 t} \\ e^{-i\omega_0 t} & 0 \end{pmatrix} \\
&= \frac{1}{2} I + \frac{2M_0}{\gamma \hbar^2} \frac{\hbar}{2} \begin{pmatrix} 0 & e^{i\omega_0 t} \\ e^{-i\omega_0 t} & 0 \end{pmatrix} \\
&= \frac{1}{2} I + \frac{2M_0}{\gamma \hbar^2} \frac{\hbar}{2} \begin{pmatrix} 0 & \cos(\omega_0 t) + i \sin(\omega_0 t) \\ \cos(\omega_0 t) - i \sin(\omega_0 t) & 0 \end{pmatrix} \\
&= \frac{1}{2} I + \frac{2}{\gamma \hbar^2} \left\{ M_0 \cos(\omega_0 t) \hat{S}_x - i M_0 \sin(\omega_0 t) \hat{S}_y \right\}
\end{aligned}$$

From this we can immediately read off the components of the magnetic moment as a function of time:

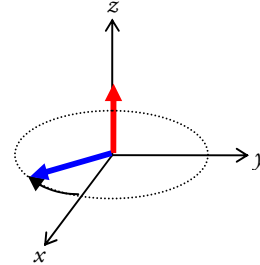
$$\begin{aligned}
M_x(t) &= M_0 \cos(\omega_0 t) \\
M_y(t) &= -M_0 \sin(\omega_0 t) \\
M_z(t) &= 0
\end{aligned}$$

We can also write this using matrix notation to make it a bit clearer:

$$\underbrace{\begin{pmatrix} M_x(t) \\ M_y(t) \\ M_z(t) \end{pmatrix}}_{\mathbf{M}(t)} = \underbrace{\begin{pmatrix} \cos(\omega_0 t) & \sin(\omega_0 t) & 0 \\ -\sin(\omega_0 t) & \cos(\omega_0 t) & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{R_z^{LH}(\omega_0 t)} \underbrace{\begin{pmatrix} M_0 \\ 0 \\ 0 \end{pmatrix}}_{\mathbf{M}(0)}$$

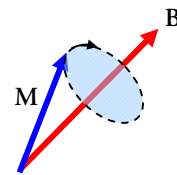
This describes a circular motion of  $M_0$  in the  $xy$ -plane about the axis along which the external constant field  $\mathbf{B}_0$  points, which is the  $z$ -axis. The rotational motion is left handed, meaning the

sense of direction is obtained by putting your left hand along  $\mathbf{B}$ , curling it and noting the direction in which your fingers curl.



## Magnetic Moments Precess About An External Field

There was nothing special about the directions chosen in the previous section. We could go back and solve for a general initial density matrix, but our physical intuition should tell us already that it shouldn't matter how we start out: if  $\mathbf{B}$  is constant in space, the magnetization will just precess around it (note the left handed sense of rotation):



We won't go back and actually solve the tedious Liouville equation with an arbitrary field and initial condition, although - aside from extremely long-winded algebra - it is quite possible to do so.

Since we know  $\mathbf{M}(t)$ , we can also immediately write down the density matrix as a function of time, using the formula

$$\rho(t) = \frac{1}{2} I + \frac{2}{\gamma \hbar^2} \mathbf{M}(t) \cdot \hat{\mathbf{S}}.$$

## A Spin-1/2 System Can Be Understood Classically: Bloch's Equations

The above quantum mechanical derivation has a completely classical analogue. To see this, we begin by proving **Ehrenfest's Theorem**, which states that the time evolution of the expectation of value an

observable,  $\langle \hat{A} \rangle = \text{tr}(\rho \hat{A})$ , evolves in time according to:

$$\frac{d\langle \hat{A} \rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle + \left\langle \frac{d\hat{A}}{dt} \right\rangle.$$

The proof is obtained simply by applying the definition of a derivative and using the fact the trace is linear in the derivative:

$$\begin{aligned} \frac{d\langle \hat{A} \rangle}{dt} &= \frac{d(\text{tr}(\rho \hat{A}))}{dt} \\ &= \text{tr} \left( \frac{d\rho}{dt} \hat{A} \right) + \text{tr} \left( \rho \frac{d\hat{A}}{dt} \right) \\ &= \text{tr} \left( \frac{[\hat{H}, \rho]}{i\hbar} \hat{A} \right) + \text{tr} \left( \rho \frac{d\hat{A}}{dt} \right) \\ &= \text{tr} \left( \frac{\hat{H} \rho \hat{A}}{i\hbar} \right) - \text{tr} \left( \frac{\rho \hat{H} \hat{A}}{i\hbar} \right) + \text{tr} \left( \rho \frac{d\hat{A}}{dt} \right) \end{aligned}$$

Now, the first term on the last line can be changed to  $\text{tr}(\frac{1}{i\hbar} \rho \hat{A} \hat{H})$  since the trace is cyclic:  $\text{tr}(ABC) = \text{tr}(BCA) = \text{tr}(CAB)$ . Using the fact that  $\langle \hat{A} \rangle = \text{tr}(\rho \hat{A})$  for any operator  $\hat{A}$ , we can write this as

$$\frac{d\langle \hat{A} \rangle}{dt} = \frac{1}{i\hbar} \langle \hat{A} \hat{H} \rangle - \frac{1}{i\hbar} \langle \hat{H} \hat{A} \rangle + \left\langle \frac{d\hat{A}}{dt} \right\rangle$$

which is precisely equivalent to the claim made.

With Ehrenfest's theorem, we can take each of the magnetization operators and write down:

$$\frac{d\langle \hat{M}_i \rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{M}_i, \hat{H}] \rangle$$

where the explicit time derivative of the operators is zero since they are time independent<sup>4</sup>. Remember what the Hamiltonian of the system looks like:

$$\hat{H} = -\hat{\mathbf{M}} \cdot \mathbf{B}.$$

Substituting in Ehrenfest's theorem, we get:

$$\begin{aligned} \frac{d\langle \hat{M}_i \rangle}{dt} &= \frac{1}{i\hbar} \langle [\hat{M}_i, -\hat{M}_x B_x - \hat{M}_y B_y - \hat{M}_z B_z] \rangle \\ &= -\frac{1}{i\hbar} \langle [\hat{M}_i, \hat{M}_x] \rangle B_x - \frac{1}{i\hbar} \langle [\hat{M}_i, \hat{M}_y] \rangle B_y \\ &\quad - \frac{1}{i\hbar} \langle [\hat{M}_i, \hat{M}_z] \rangle B_z \quad (i = x, y, z). \end{aligned}$$

I leave it to the reader to verify that

$$\begin{aligned} [\hat{M}_x, \hat{M}_y] &= i\gamma\hbar \hat{M}_z \\ [\hat{M}_y, \hat{M}_z] &= i\gamma\hbar \hat{M}_x \\ [\hat{M}_z, \hat{M}_x] &= i\gamma\hbar \hat{M}_y \end{aligned}$$

from which (along with the fact that  $[A, B] = -[B, A]$  and  $[A, A] = 0$  for any A, B) follows that

$$\begin{aligned} \frac{d\langle \hat{M}_x \rangle}{dt} &= -\gamma \langle \hat{M}_z \rangle B_y + \gamma \langle \hat{M}_y \rangle B_z \\ \frac{d\langle \hat{M}_y \rangle}{dt} &= \gamma \langle \hat{M}_x \rangle B_z + \gamma \langle \hat{M}_z \rangle B_x \\ \frac{d\langle \hat{M}_z \rangle}{dt} &= -\gamma \langle \hat{M}_y \rangle B_x + \gamma \langle \hat{M}_x \rangle B_y \end{aligned}$$

Looking closely at these three equations, we see they can be succinctly written using vector notation as:

$$\frac{d\langle \hat{\mathbf{M}} \rangle}{dt} = \gamma \langle \hat{\mathbf{M}} \rangle \times \mathbf{B}.$$

The same equation can be derived completely classically as follows: A microscopic (point-like) magnetic moment  $\mathbf{m}$  in a magnetic field  $\mathbf{B}$  will be affected in two ways: it will feel a **torque** (which is the time derivative of the angular momentum):

$$\frac{d\mathbf{L}}{dt} = \boldsymbol{\tau} = \mathbf{m} \times \mathbf{B}.$$

<sup>4</sup> Some observables can be time dependent, but that is a topic we will not touch upon in this course.

A nucleus has an intrinsic angular momentum  $\mathbf{S}$  and proportional moment  $\mathbf{M}=\gamma\mathbf{S}$ . Its derivative is

$$\frac{d\mathbf{M}}{dt} = \frac{d(\gamma\mathbf{S})}{dt} = \gamma \frac{d\mathbf{S}}{dt} = \gamma\boldsymbol{\tau} = \gamma\mathbf{m} \times \mathbf{B}.$$

The solution of the Bloch equations, which we will not pursue here, predicts - you guessed it - that the moment  $\mathbf{m}$  will precess around any constant magnetic field  $\mathbf{B}$ .

### The Initial State Of A System is Given By Boltzmann's Distribution

We now know how to solve for the time evolution of a system given its initial state. But what should that initial state be? Well, that's a question that should be answered by you: what physical state is your system in initially? However, one initial condition presents itself repeatedly: **thermal equilibrium**. I'll give you the "answer" for how  $\rho$  should look like and then we'll discuss its meaning:

$$\rho^{(TE)} = \frac{1}{Z} e^{-\frac{\hat{H}}{kT}}, \quad Z = \text{tr} \left( e^{-\frac{\hat{H}}{kT}} \right).$$

Let's assume our field is along the z-axis. The Hamiltonian is:

$$\hat{H} = -\hat{\mathbf{M}} \cdot \mathbf{B} = -\gamma \hat{S}_z B_0 = \begin{pmatrix} -\frac{\hbar\omega_0}{2} & 0 \\ 0 & \frac{\hbar\omega_0}{2} \end{pmatrix}.$$

Because it is diagonal, we can immediately write down:

$$e^{-\frac{\hat{H}}{kT}} = \begin{pmatrix} e^{\frac{\hbar\omega_0}{2kT}} & 0 \\ 0 & e^{-\frac{\hbar\omega_0}{2kT}} \end{pmatrix}$$

$$Z = \text{tr} \left( e^{-\frac{\hat{H}}{kT}} \right) = e^{\frac{\hbar\omega_0}{2kT}} + e^{-\frac{\hbar\omega_0}{2kT}}.$$

We will be working at room temperature, and can thus simplify, by noting

$$\hbar\omega_0 \approx 8 \cdot 10^{-26} \text{ J}$$

$$kT \approx 4 \cdot 10^{-21} \text{ J}$$

This means the term in the exponential is very small. Going back to our Taylor expansion, for small  $x$  we can approximate  $e^x \approx 1+x$  quite well, whence

$$e^{-\frac{\hat{H}}{kT}} = \begin{pmatrix} e^{\frac{\hbar\omega_0}{2kT}} & 0 \\ 0 & e^{-\frac{\hbar\omega_0}{2kT}} \end{pmatrix}$$

$$\approx \begin{pmatrix} 1 + \frac{\hbar\omega_0}{2kT} & 0 \\ 0 & 1 - \frac{\hbar\omega_0}{2kT} \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\omega_0}{kT} \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = I + \frac{\omega_0}{kT} \hat{S}_z$$

and

$$Z = e^{\frac{\hbar\omega_0}{2kT}} + e^{-\frac{\hbar\omega_0}{2kT}}$$

$$\approx 1 + \left( \frac{\hbar\omega_0}{2kT} \right) + 1 + \left( -\frac{\hbar\omega_0}{2kT} \right) = 2.$$

Simple! Dividing the two,

$$\rho^{(TE)} \approx \frac{1}{2} I + \frac{\omega_0}{2kT} \hat{S}_z$$

$$= \frac{1}{2} I + \frac{2}{\gamma\hbar^2} \frac{\gamma\hbar^2\omega_0}{4kT} \hat{S}_z$$

Since  $\rho^{(TE)}$  is now in the form  $\rho = \frac{1}{2} I + \frac{2}{\gamma\hbar^2} \mathbf{M} \cdot \hat{\mathbf{S}}$ , we can immediately write down the z-component of the magnetization<sup>5</sup>:

$$M_z^{(eq)} = \frac{\gamma\hbar^2\omega_0}{4kT}$$

This tells us something that's physically intuitive: when  $B_0$  is static and along z, the spins align along  $B_0$  because there is an energetic preference for them to point along the field. However, the amount of this alignment is quite small because of the thermal effects that disperse the magnetization. The x & y components of the magnetization are zero, which can also be confirmed by calculating

<sup>5</sup> We could have equally derived the thermal equilibrium components of the magnetization by first calculating  $\rho$  and then taking the traces  $\text{tr}(\rho \hat{M}_i)$ .



$\text{tr}(\rho \hat{M}_x)$ ,  $\text{tr}(\rho \hat{M}_y)$ , and this is because there is no energetic preference for the spins to point perpendicular to the main static field.

This calculation could have been repeated with any spin and yielded a similar result. For a spin  $S$  ( $S=1/2, 1, 3/2, 2, \dots$ ), the equilibrium magnetization is

$$M_z^{(eq)} = \frac{\gamma \hbar^2 \omega_0 S(S+1)}{3kT}.$$

What happens if we have  $N$  spins? If they do not interact with each other, the total magnetic moment of the ensemble will (on physical grounds) just be multiplied by a factor of  $N$ :

$$M_z^{(eq)} = \frac{N(\gamma \hbar)^2 B_0 S(S+1)}{3kT}$$

(it's written in a slightly different way – I took  $\omega_0$  and wrote it explicitly as  $\gamma B_0$ )

### The Identity Element Is Often Omitted From The Density Matrix

Remember that for a single spin-1/2, we saw that the most general density matrix has the form

$$\rho = \frac{1}{2}I + \frac{2}{\gamma \hbar^2} \mathbf{M} \cdot \hat{\mathbf{S}}.$$

In other words, it looks like this:

$$\rho = \frac{1}{2}I + \tilde{\rho}.$$

Now, whatever our propagator is,

$$U \rho U^\dagger = U \frac{1}{2}I U^\dagger + U \tilde{\rho} U.$$

The part with the identity matrix stays the same:

$$U \frac{1}{2}I U^\dagger = \frac{1}{2}I U U^\dagger = \frac{1}{2}I$$

because the propagator is unitary (so  $U U^\dagger = I$ ). This means it's "boring". Not only does it not change with time – for whatever interaction we have! – but it also usually does not even contribute

to many observables. For an observable  $\hat{A}$ , if  $\rho = I$  then<sup>6</sup>

$$\langle A \rangle = \text{tr}(\rho \hat{A}) = \text{tr}(\hat{A})$$

Many observables satisfy  $\text{tr}(\hat{A}) = 0$ . You're free to check that  $\text{tr}(\hat{S}_x) = \text{tr}(\hat{S}_y) = \text{tr}(\hat{S}_z) = 0$ , and that for a spin in an external constant magnetic field,  $\text{tr}(\hat{H}) = 0$  as well. This is why many authors simply omit it. We will do that as well and simply not write it out. One consequence of this is that the density matrix at thermal equilibrium assumes a simple form:

$$\rho^{(TE)} \propto \hat{S}_z.$$

### Product Operators

We've seen that for a single spin-1/2,

$$\rho = \frac{1}{2}I + \frac{2}{\gamma \hbar^2} \mathbf{M} \cdot \hat{\mathbf{S}}.$$

This means we can write it as a linear sum of the form:

$$\rho = a_0 I + a_x \hat{I}_x + a_y \hat{I}_y + a_z \hat{I}_z$$

where we've defined  $\hat{S}_0 = I$ , and where<sup>7</sup>  $\hat{I}_j = \frac{1}{\hbar} \hat{S}_j$  ( $j=x,y,z$ ). This is like saying that the set of operators  $\{I, \hat{I}_x, \hat{I}_y, \hat{I}_z\}$  forms a basis for the space of density matrices of spin-1/2 particles: every density matrix can be written as a linear sum of these four operators. Now,

$$\text{tr}(\hat{S}_0) = \text{tr}(I) = 2$$

$$\text{tr}(\hat{S}_1) = \text{tr}(\hat{S}_2) = \text{tr}(\hat{S}_3) = 0$$

<sup>6</sup> Of course this is not strictly a density matrix because its trace is not one. However, this reasoning holds for any part of  $\rho$  that is proportional to  $I$ , like the  $\frac{1}{2}I$  term.

<sup>7</sup> I'm dividing by  $\hbar$  to make all basis "elements" dimensionless (it would be weird to have one element of the basis have no units, while another have units of angular momentum).

The demand  $\text{tr}(\rho) = 1$  means

$$\begin{aligned}\text{tr}(\rho) &= \text{tr}\left(\sum_{n=0}^3 \alpha_n \hat{S}_n\right) \\ &= \sum_{n=0}^3 \alpha_n \text{tr}(\hat{S}_n) \\ &= 2\alpha_0 \rightarrow \alpha_0 = \frac{1}{2}\end{aligned}$$

This is of course nothing new: it means we get the  $\frac{1}{2}I$  term.

### Time Evolution of Product Operators

The interesting thing about this formulation is the way it makes us think about propagation. Given a propagator  $U$ , an initial density matrix evolves as:

$$\rho \rightarrow U \rho U^\dagger.$$

Plugging in our density matrix expression, we get

$$\begin{aligned}\rho &\rightarrow U \left( \sum_{n=0}^3 a_n \hat{I}_n \right) U^\dagger \\ &= a_0 I + \sum_{n=1}^3 a_n U \hat{I}_n U^\dagger\end{aligned}$$

So, in this **completely equivalent picture**, the coefficients are time independent and the basis vectors themselves “evolve” over time. If we know what the propagator does to each of the propagators, we can immediately write the solution down. This way of thinking will become extremely useful when trying to understand basic experiments down the line.

Let’s do an important example. For a spin-1/2 system, we want to calculate

$$U \hat{I}_n U^\dagger$$

under the influence of a general and constant magnetic field  $\mathbf{B}$ . I’ll show you that you already know the answer. We’ve said that  $\mathbf{M}(t)$  precesses about a constant magnetic field  $\mathbf{B}$ :

$$\mathbf{M}(t) = R_n^{(LH)}(\omega t) \mathbf{M}(0)$$

where  $R_n^{(LH)}(\theta)$  is a left handed rotation matrix about an axis defined by the unit vector  $\hat{\mathbf{n}}$ , which points along the direction of the constant field  $\mathbf{B}$ . The angular velocity of the precession is  $\omega = \gamma B$ . This means that the density matrix changes from

$$\begin{aligned}\rho(0) &= \frac{1}{2}I + \frac{2}{\gamma \hbar^2} \mathbf{M}(0) \cdot \hat{\mathbf{S}} \\ &= \frac{1}{2}I + \frac{2}{\gamma \hbar} \mathbf{M}(0) \cdot \hat{\mathbf{I}}\end{aligned}$$

at time  $t=0$ , to

$$\rho(t) = \frac{1}{2}I + \frac{2}{\gamma \hbar} [R(t) \mathbf{M}(0)] \cdot \hat{\mathbf{I}}.$$

Now, another way to represent the dot product is using matrices:

$$\begin{aligned}\mathbf{a} \cdot \mathbf{b} &= a_x b_x + a_y b_y + a_z b_z \\ &= \begin{pmatrix} a_x & a_y & a_z \end{pmatrix} \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} \\ &= \mathbf{a}^T \mathbf{b}\end{aligned}$$

The transpose  $T$  has a nice property<sup>8</sup>, by which it switches the order of the matrices (just like for the hermitian conjugate):  $(AB)^T = B^T A^T$ . This is true regardless of the sizes of the matrices, and they don’t even have to be square. So, for our multiplication,

$$\begin{aligned}& \left( R_n^{(LH)}(\omega t) \mathbf{M}(0) \right) \cdot \hat{\mathbf{I}} \\ &= \left( R_n^{(LH)}(\omega t) \mathbf{M}(0) \right)^T \hat{\mathbf{I}} \\ &= \mathbf{M}(0)^T \left( R_n^{(LH)}(\omega t) \hat{\mathbf{I}} \right)\end{aligned}$$

<sup>8</sup> This is easily proved. The transpose of  $A$  has elements  $(A^T)_{ij} = A_{ji}$ . For the product  $AB$ ,

$$\begin{aligned}\left( (AB)^T \right)_{ij} &= (AB)_{ji} = \sum_{k=1}^N A_{jk} B_{ki} \\ &= \sum_{k=1}^N B_{ki} A_{jk} = \sum_{k=1}^N (B^T)_{ik} (A^T)_{kj} = (B^T A^T)_{ij}\end{aligned}$$

In other words, the “basis matrices”  $\hat{I}_x, \hat{I}_y, \hat{I}_z$  themselves perform a precession around the magnetic field. For example, if our field is along the z-axis,

$$\mathbf{B} = \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$

then our Hamiltonian is

$$\hat{H} = -\hat{M}_z B_0 = -\hbar\omega_0 \hat{I}_z$$

and

$$U(t) = e^{-\frac{i\hat{H}t}{\hbar}} = e^{i\omega_0 \hat{I}_z t}$$

so

$$\begin{aligned} U(t) \hat{I}_x U^\dagger(t) &= e^{i\omega_0 \hat{I}_z t} \hat{I}_x e^{-i\omega_0 \hat{I}_z t} \\ &= \hat{I}_x \cos(\omega_0 t) - \hat{I}_y \sin(\omega_0 t) \end{aligned}$$

where in the last line we just treated  $\hat{I}_x$  as a “vector” along the x-axis and applied a left handed rotation to it with an angle  $\omega_0 t$ .

## Multiple Spin Systems

### Multiple Spin Systems Are Described By Outer (Kronecker) Products

By now we've seen how to describe the state of a system and calculate its time evolution if we know its Hamiltonian, using Liouville's equation (at least in theory, or for the simple system of a single spin-1/2). This can be extended to multiple spin systems by using the kronecker product of these spin spaces. The rules are simple and are listed below for two spin-1/2 systems; they can be generalized in a fairly straightforward manner:

1. Any operator A of system (1),

$$\hat{A} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$

is now transformed into

$$\begin{aligned} \hat{A} \otimes I &= \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &= \begin{pmatrix} a_{11} & 0 & a_{12} & 0 \\ 0 & a_{11} & 0 & a_{12} \\ a_{21} & 0 & a_{22} & 0 \\ 0 & a_{21} & 0 & a_{22} \end{pmatrix} \end{aligned}$$

where I is the identity operator of system two.

2. Any operator A of system (2),

$$\hat{A} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$

is now transformed into

$$\begin{aligned} I \otimes \hat{A} &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \\ &= \begin{pmatrix} a_{11} & a_{12} & 0 & 0 \\ a_{21} & a_{22} & 0 & 0 \\ 0 & 0 & a_{11} & a_{12} \\ 0 & 0 & a_{21} & a_{22} \end{pmatrix} \end{aligned}$$

For example, the x-component of the angular momentum for spin #1 is

$$\begin{aligned} \hat{S}_{1x} &= \hat{S}_x \otimes I = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &= \frac{\hbar}{2} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \end{aligned}$$

Another example: the y-component of angular momentum for spin #2 is:

$$\begin{aligned} \hat{S}_{2y} &= I \otimes \hat{S}_y = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ &= \frac{\hbar}{2} \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix} \end{aligned}$$

These ideas can be extended to any number of spins, by taking successive kronecker products. For

example, for three spin-1/2s, the x-component of the 2<sup>nd</sup> spin is

$$\begin{aligned}\hat{S}_{2y} &= I \otimes \hat{S}_y \otimes I \\ &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &= \frac{\hbar}{2} \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &= \frac{\hbar}{2} \begin{pmatrix} 0 & 0 & -i & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 \\ i & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & i & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i \\ 0 & 0 & 0 & 0 & i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & i & 0 & 0 \end{pmatrix}\end{aligned}$$

That is truly a frightening matrix! Down the road, we're going to come up with other ways of dealing with multiple spin systems that avoids mostly dealing with direct matrix multiplication.

## Product Operators For Multiple Spins

Can this be extended to two spin-1/2 operators easily. There are a total of 6 components of angular momentum:

$$\begin{aligned}\hat{S}_x \otimes I, \quad \hat{S}_y \otimes I, \quad \hat{S}_z \otimes I \\ I \otimes \hat{S}_x, \quad I \otimes \hat{S}_y, \quad I \otimes \hat{S}_z\end{aligned}$$

We can also form kronecker products that do not correspond to any physical observable:

$$\begin{aligned}\hat{S}_x \otimes \hat{S}_x, \quad \hat{S}_x \otimes \hat{S}_y, \quad \hat{S}_x \otimes \hat{S}_z \\ \hat{S}_y \otimes \hat{S}_x, \quad \hat{S}_y \otimes \hat{S}_y, \quad \hat{S}_y \otimes \hat{S}_z \\ \hat{S}_z \otimes \hat{S}_x, \quad \hat{S}_z \otimes \hat{S}_y, \quad \hat{S}_z \otimes \hat{S}_z\end{aligned}$$

Along with the trivial identity operator,  $I \otimes I$ , we get 16 combinations  $\hat{S}_n \otimes \hat{S}_m$  where, as before,  $n, m=0,1,2,3$  and  $\hat{S}_0 = I$ ,  $\hat{S}_1 = \hat{S}_x$ ,  $\hat{S}_2 = \hat{S}_y$ ,  $\hat{S}_3 = \hat{S}_z$ . We won't prove it mathematically, but

these form a basis for all density matrix of the combined system:

$$\rho = \sum_{n,m=0}^3 \alpha_{nm} \hat{S}_n \otimes \hat{S}_m$$

This makes sense in terms of number of constants:  $\rho$  is now a 4x4 matrix having 16 complex elements, or 32 real numbers. Hermiticity cuts this down to 16, precisely the number of coefficients in the expansion above (note the requirement  $\text{tr}(\rho)=1$  fixes  $\alpha_{00} = \frac{1}{4}$ , leaving us with 15 real coefficients).