IV
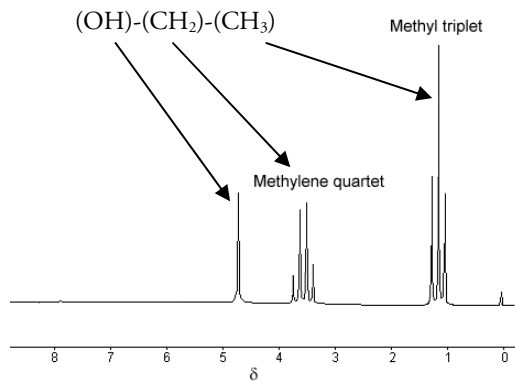# Quantum Mechanics

Lecture notes by Assaf Tal

In the previous lecture we've explained how and why ethanol should yield a spectrum having three peaks:

Today's high resolution NMR spectrometers, however, reveal fine structure, known as J-splittings. This structure and the system evolution it induces cannot be explained well by classical analogies and requires quantum mechanics. Luckily, QM is fairly benign in NMR since it deals with simple systems (spin-1/2). We review here some of the basic principles which will be of use to us in explaining J-coupling and other quantum phenomena. First, I will outline the **rules** by which quantum systems behave. Then, I will show you how to "**solve**" any problem in quantum mechanics, and finally we'll discuss **how to think about a spin-1/2** in the QM formalism. We'll conclude by talking about systems of **multiple spins**.

1. The Rules of Quantum Mechanics

1.1 The State of a System is Represented by a Vector

Quantum mechanics is just a set of rules which lets us describe a quantum system and compute how it evolves in time.

The state of the system is given by the vector $|\psi\rangle$. For a spin-1/2, this vector is 2-dimensional:

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}.$$

The coefficients a and b can be complex, but satisfy $|a|^2 + |b|^2 = 1$. I will sometimes write:

$$\langle\psi| = \begin{pmatrix} a^* & b^* \end{pmatrix},$$

for the conjugated row vector, and

$$\langle\psi|\cdot|\psi\rangle \equiv \langle\psi|\psi\rangle = \begin{pmatrix} a^* & b^* \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = |a|^2 + |b|^2.$$

So, for a state vector, we must have $\langle\psi|\psi\rangle = 1$. The two vectors

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

represent the famous "up" and "down" states of the spin: pointing with or against the external field B_0. Sometimes we'll also use the odd notation

$$|\psi\rangle\langle\varphi| = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}\begin{pmatrix} \varphi_1^* & \varphi_2^* \end{pmatrix} = \begin{pmatrix} \psi_1\varphi_1^* & \psi_1\varphi_2^* \\ \psi_2\varphi_1^* & \psi_2\varphi_2^* \end{pmatrix}$$

1.2 Physical Quantities Are Represented By Matrices

Physical observable quantities of the system such as energy or angular momentum are given by matrices. For a spin, the most important is the angular momentum

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

This means that its magnetic moment is $\mathbf{M} = \gamma\mathbf{S}$. The energy of a spin in an external magnetic field is given by

$$H = -\mathbf{M}\cdot\mathbf{B}(\mathbf{r},t).$$

Note that **B** is *not* a property of the "system" we're describing (the spin) and is therefore just a number and not a matrix. In the full quantum mechanical treatment of the world, fields are also matrices, and their treatment is called *quantum field theory*. It turns out this complexity isn't necessary for NMR, so we're going to retain fields as classical quantities.

The energy of also called the **hamiltonian** of the system. For example, the hamiltonian for a spin-1/2 in an external constant field along the z-axis is (neglecting chemical shift):

$$H = -M_z B_0 = -\gamma L_z B_0 = -\frac{\gamma \hbar B_0}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -\omega_0 I_z$$

where $\omega_0 \equiv \gamma B_0$ and

$$I_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

A word of caution: matrices behave a lot like numbers when dealing with addition, but differ considerably when it comes to multiplication. For real or complex numbers, *ab=ba*, but in general AB≠BA for two matrices A and B. We say that matrix multiplication is **not commutative**. We can define the **commutator** of A and B as:

$$[A, B] \equiv AB - BA.$$

Obviously, when $[A, B] = 0$ then $AB = BA$ and A and B *do* commute. For example, check that $\hat{S}_x, \hat{S}_y$ do not commute, so $[S_x, S_y] \neq 0$, but S_x and I (the identity) do, so $[S_x, I] = 0$. Also, every matrix naturally commutes with itself, $[A, A] = 0$.

1.4 Measurement Outcomes Are Given By An Observable's Eigenvalues

An eigenvector of a matrix A is any vector **v** for which

$$A\mathbf{v}=\lambda\mathbf{v}.$$

The number λ is called an **eigenvalue** of A corresponding to the eigenvector **v**. Obviously if **v**

is an eigenvector then a**v** is also one with the same eigenvalue, since

$$A(a\mathbf{v})=aA\mathbf{v}=a\lambda\mathbf{v}=\lambda(a\mathbf{v}).$$

So eigenvectors are only defined up to a scaling factor. An example is a rotation matrix about z by an angle θ (in 3D):

$$R_z(\theta) = \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Any vector along the z-axis will be an eigenvector with an eigenvalue 1 (since the rotation doesn't affect it). All vectors not pointing along z are obviously *not* eigenvectors. So $R_z(\theta)$ has only one eigenvalue ($\lambda=1$) with the eigenvector $\hat{\mathbf{z}}$ up to a constant.

Another example: the z-component of the angular momentum,

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

This matrix has two eigenvalues and two eigenvectors:

$$S_z\left|+\right\rangle = \tfrac{\hbar}{2}\left|+\right\rangle$$
$$S_z\left|-\right\rangle = -\tfrac{\hbar}{2}\left|-\right\rangle$$

Suppose we want to measure a physical quantity X of a system. **QM tells us the only possible results of measuring X are the eigenvalues of X.** For example, the possible results of measuring the z-component of the angular momentum are

$$\pm\frac{\hbar}{2}.$$

How does one go about finding the eigenvalues of a matrix? Let's look at the x-component of the angular momentum:

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

We're looking for its eigenvectors:

$$S_x |v\rangle = \lambda |v\rangle .$$

Shifting sides:

$$(S_x - \lambda I)|v\rangle = 0$$

The matrix $S_x - \lambda I$ turns the eigenvector $|v\rangle$ into the zero vector. This means the $|v\rangle$ is in the so-called "null space" of $S_x - \lambda I$, which from linear algebra can only be if

$$\det(S_x - \lambda I) = 0 .$$

The above equation furnishes us with an equation for finding the eigenvalues λ (there can and often is more than one). Then we substitute each eigenvalue back into the equation $S_x |v\rangle = \lambda |v\rangle$ and solve for the eigenvalues $|v\rangle$.

Example: let's look at the eigenvalues and eigenvectors of S_x. The eigenvalue equation is

$$0 = \det(S_x - \lambda I) = \det \begin{pmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{pmatrix} = \lambda^2 - \left(\frac{\hbar}{2}\right)^2$$

This has two eigenvalues:

$$\lambda_\pm = \pm \frac{\hbar}{2} .$$

This is not unexpected: why would S_x be different from S_z? They're the "same" angular momentum operator only along different axes. They should both yield the same set of possible physical outcomes if measured. We now calculate the eigenvectors associated with them. First, for λ_+:

$$S_x \begin{pmatrix} a \\ b \end{pmatrix} = \lambda_+ \begin{pmatrix} a \\ b \end{pmatrix} .$$

This yields two equations which are equivalent: a=b, so:

$$|\varphi_+\rangle = \begin{pmatrix} a \\ a \end{pmatrix}$$

If we further normalize, $|a|^2 + |a|^2 = 1$, we get $|a| = \frac{1}{\sqrt{2}}$ and so:

$$|\varphi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

This is not the only possible solution: we could multiply this by any phase, $e^{i\phi}$, and still get an acceptable eigenvector. The phase as it turns out is physically meaningless, but should be kept in mind.

Similarly, for λ_- we can solve and obtain (up to a phase $e^{i\phi}$):

$$|\varphi_-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

To sum up:
1. An N×N matrix will have, at most, N eigenvalues.
2. Each eigenvalue can have one or more **linearly independent** eigenvectors.
3. If the matrix is an observable, it will have N independent eigenvectors $|\varphi_j\rangle$ (j=1,...,N) which will constitute a **basis**, meaning every other vector can be written as a linear combination of them: $|\psi\rangle = \Sigma_{j=1}^N a_j |\varphi_j\rangle$.

1.5 Measurements Are Probabilistic

Suppose we want to measure the z-component angular momentum of a system in a state $|\varphi\rangle$. We know that the possible outcomes are the eigenvalues of S_z, which are $\pm \hbar / 2$. It turns out that if we set up the system in the state $|\varphi\rangle$ and measure S_z, we won't always get the same answer! We'll sometimes get $+\hbar / 2$ and sometimes $-\hbar / 2$, even if we repeat the experiment with the exact same state over and over! The probability of getting each is

$$\Pr(+) = |\langle + |\varphi\rangle|^2$$
$$\Pr(-) = |\langle - |\varphi\rangle|^2$$

Note that we can either get + or -, so these must sum to 1, which is indeed the case: if

$$|\varphi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$$

then

$$\Pr(+) + \Pr(-) = |a|^2 + |b|^2 = 1$$

since we've noted all state vectors are normalized.

This **lack of determinism** is a key feature of quantum mechanics. The average value of an operator A with eigenvalues A_j and eigenvectors $|\psi_j\rangle$ is therefore:

$$
\begin{aligned}
\langle A \rangle &= \sum_j A_j \left| \langle \psi_j | \varphi \rangle \right|^2 \\
&= \sum_j A_j \langle \varphi | \psi_j \rangle \langle \psi_j | \varphi \rangle \\
&= \langle \varphi | \left(\sum_j A_j |\psi_j\rangle \langle \psi_j| \right) |\varphi\rangle \\
&= \langle \varphi | A | \varphi \rangle
\end{aligned}
$$

This answers an interesting question: how come we measure continuous variables in the macroscopic world if all of the quantum variables are quantized? First, not all quantum variables quantized, as some operators/observables have a continuum of eigenvalues. However, when repeating measurements we end up averaging over all possible results, which yields a quantity that behaves macroscopically.

1.6 Dynamics are Described by The Schroedinger Equation

Just as Newton's 2nd law lets us calculate the evolution ("dynamics") of a particle's position ("state"), so does the Schroedinger equation let us calculate the dynamics of a quantum system:

$$m \frac{d^2 x}{dt^2} = F \quad \longleftrightarrow \quad i\hbar \frac{\partial |\psi\rangle}{\partial t} = H |\psi\rangle.$$

The function H ("the Hamiltonian") which is simply the system's energy plays the role of "force",

and the state vector $|\psi\rangle$ plays the role of "x", the system's state. The Schroedinger equation is difficult to solve analytically and we will not attempt to do so in this course except for some very simple cases.

The Schroedinger equation has a simple formal solution if H is time-independent:

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle.$$

The operator $U(t) = e^{-iHt/\hbar}$ is called the **propagator**. The exponential of a matrix (H is a matrix!) is defined via its Taylor expansion:

$$e^x = \sum_{k=0}^{\infty} \frac{x^k}{k!}$$

so

$$e^{-iHt/\hbar} = \sum_{k=0}^{\infty} \frac{\left(-\frac{iHt}{\hbar} \right)^n}{k!}.$$

In general it's impossible to calculate the series, but there are many approximate numerical methods that give excellent results (e.g. MATLAB's expm command, or Mathematica's MatrixExp function).

A word of caution: we are used to writing $e^{a+b} = e^a e^b = e^b e^a$ for two complex numbers a and b, but this does not necessarily hold for matrices. If A, B are matrices then e^A, e^B are matrices and they do not necessarily commute: $e^A e^B \neq e^B e^A$. Furthermore, This immediately also makes the first identity suspect: if $e^A e^B \neq e^B e^A$ then should we write

$$e^{A+B} = e^A e^B$$

or

$$e^{A+B} = e^B e^A ?$$

The truth is, neither is in general correct! However, if $[A, B] = 0$ then the usual rules for complex numbers hold as well:

$$[A, B] = 0 \quad \Rightarrow \quad e^{A+B} = e^A e^B = e^B e^A.$$

2. The Density Matrix

2.1 The Trace

The trace operation is very important so we'll spend some time on it. It equals the sum of the diagonal elements of a matrix. For example,

$$tr \begin{pmatrix} a & b \\ c & d \end{pmatrix} = a + d$$

or

$$tr \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & q \end{pmatrix} = a + e + q .$$

First, it is linear:

$$\text{tr}(aA + bB) = a \cdot \text{tr}(A) + b \cdot \text{tr}(B) .$$

An important property is that its cyclical:

$$\text{tr}(ABC) = \text{tr}(BCA) = \text{tr}(CAB) .$$

This generalizes to any number of matrices. Another important property is that:

$$\text{Tr}(|\psi\rangle\langle\varphi|) = \langle\varphi|\psi\rangle .$$

I am sure you'll take great pleasure in deriving these identities in your homework. A corollary is:

$$\text{tr}(A|\psi\rangle\langle\varphi|) = \langle\varphi|A|\psi\rangle .$$

This is simple to prove: $A|\psi\rangle$ is a vector. Call it $|\phi\rangle$. Then:

$$\text{tr}(A|\psi\rangle\langle\varphi|) = \text{tr}(|\phi\rangle\langle\varphi|) = \langle\varphi|\phi\rangle = \langle\varphi|A|\psi\rangle .$$

2.2 The Density Matrix Describes Statistical Ensembles

Consider a spin-1/2 particle which can be in any of a set of eigenstates of S_z, $|+\rangle, |-\rangle$. We've seen that

if the system is in a state $|\psi\rangle$ then the expected value of an observable A is

$$\langle A \rangle = \langle\psi|A|\psi\rangle .$$

Suppose we have a statistical **mixture** of "up" and "down" in which 50% of the particles are in the up state and 50% are in the down state. If we measure the expected value of some observable A, we should get:

$$\overline{\langle A \rangle} = \tfrac{1}{2}\langle+|A|+\rangle + \tfrac{1}{2}\langle-|A|-\rangle .$$

This is a simple statistical mean. Compare this to the expected outcome in tossing a 6-sided fair die:

$$\overline{x} = \tfrac{1}{6}\cdot 1 + \tfrac{1}{6}\cdot 2 + \ldots + \tfrac{1}{6}\cdot 6 .$$

So we're going to use a bar $\overline{A}$ to denote an ensemble mean, and $\langle A \rangle$ to denote a quantum mechanical mean. $\overline{\langle A \rangle}$ is merely an ensemble mean of quantum mechanical means (which sounds worse than it is).

In general, if we have a basis set $|\psi_1\rangle, \ldots, |\psi_n\rangle$, and our system can be in $|\psi_j\rangle$ with probability p_j ($p_1 + p_2 + \ldots + p_n = 1$), then the expected value of A is

$$\overline{\langle A \rangle} = \sum_{j=1}^{n} p_j \langle\psi_j|A|\psi_j\rangle .$$

Note that if we define the **matrix**

$$\rho = \sum_{j=1}^{n} p_j |\psi_j\rangle\langle\psi_j|$$

then

$$\text{tr}(\rho A) = \text{tr}\left(\sum_{j=1}^{n} p_j |\psi_j\rangle\langle\psi_j|A\right)$$

$$= \sum_{j=1}^{n} p_j \text{tr}\left(|\psi_j\rangle\langle\psi_j|A\right)$$

$$= \sum_{j=1}^{n} p_j \overbrace{\langle\psi_j|A|\psi_j\rangle}^{\text{QM average}} = \overline{\langle A \rangle}$$

$$\underbrace{\phantom{\sum_{j=1}^{n} p_j \langle\psi_j|A|\psi_j\rangle}}_{\text{Classical statistical average}}$$

The matrix ρ is called the **density matrix** of the system and it represents a statistical ensemble of quantum states. It generalizes the concept of a quantum mechanical state vector, $\left|\psi_j\right\rangle$.

2.3 A Spin-1/2 Example

Suppose we have a system with half the spins pointing up and half pointing down. Then it would be represented by the matrix:

$$\rho = \tfrac{1}{2}\left|+\right\rangle\left\langle+\right| + \tfrac{1}{2}\left|-\right\rangle\left\langle-\right|$$
$$= \frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}(1 \quad 0) + \frac{1}{2}\begin{pmatrix}0\\1\end{pmatrix}(0 \quad 1)$$
$$= \frac{1}{2}\begin{pmatrix}1 & 0\\0 & 0\end{pmatrix} + \frac{1}{2}\begin{pmatrix}0 & 0\\0 & 1\end{pmatrix}$$
$$= \frac{1}{2}I$$

where I is the identity matrix. Another example: if our system was in thermal equilibrium, then the p_j's would be the Boltzmann coefficients:

$$p_j = \frac{1}{Z}e^{-E_j/kT} .$$

For a spin-1/2 in an external field B_0 we saw (for kT>>ΔE, which is almost always the case):

$$p_+ = \frac{1}{2}\left(1 + \frac{\hbar\gamma B_0}{2kT}\right)$$
$$p_- = \frac{1}{2}\left(1 - \frac{\hbar\gamma B_0}{2kT}\right)$$

so a more realistic example would be:

$$\rho = p_+\left|+\right\rangle\left\langle+\right| + p_-\left|-\right\rangle\left\langle-\right|$$
$$= (1 \quad 0)\begin{pmatrix}1\\0\end{pmatrix} + \frac{1}{2}(0 \quad 1)\begin{pmatrix}0\\1\end{pmatrix}$$
$$= \frac{1}{2}\left(1 + \frac{\hbar\gamma B_0}{2kT}\right)\begin{pmatrix}1 & 0\\0 & 0\end{pmatrix} + \frac{1}{2}\left(1 - \frac{\hbar\gamma B_0}{2kT}\right)\begin{pmatrix}0 & 0\\0 & 1\end{pmatrix}$$
$$= \frac{1}{2}I + \frac{\hbar\gamma B_0}{4kT}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$
$$= \frac{1}{2}I + \frac{\gamma B_0}{2kT}\hat{S}_z$$

where

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

is just the z-component of the angular momentum.

Finally, let's see if we can deduce a "general" form of the density matrix of a single spin-1/2 moment using macroscopic parameters. Since ρ is hermitian and tr(ρ)=1, we can write it as

$$\rho = \begin{pmatrix}a & b\\b^* & 1-a\end{pmatrix}.$$

a is real, *b* is complex. Assume our system has a macroscopic magnetic moment **M**. If that system is described quantum mechanically by a density matrix ρ, and its magnetization operator is

$$\hat{\mathbf{M}} = \gamma\hat{\mathbf{S}}$$

then we would expect

$$\overline{\left\langle\hat{\mathbf{M}}\right\rangle} = \mathrm{tr}\left(\rho\hat{\mathbf{M}}\right) = \mathbf{M} .$$

This is in fact three separate equations:

$$M_x = \tfrac{\gamma\hbar}{2}\mathrm{tr}\left(\begin{pmatrix}a & b\\b^* & 1-a\end{pmatrix}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\right) = \gamma\hbar\,\mathrm{Re}(b)$$

$$M_y = \tfrac{\gamma\hbar}{2}\mathrm{tr}\left(\begin{pmatrix}a & b\\b^* & 1-a\end{pmatrix}\begin{pmatrix}0 & i\\-i & 0\end{pmatrix}\right) = \gamma\hbar\,\mathrm{Im}(b)$$

$$M_z = \tfrac{\gamma\hbar}{2}\mathrm{tr}\left(\begin{pmatrix}a & b\\b^* & 1-a\end{pmatrix}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\right) = \frac{\gamma\hbar}{2}(2a-1)$$

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

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

from which

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

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

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

2.4 THE LIOUVILLE EQUATION

How does ρ evolve in time? We need to differentiate:

$$\frac{d\rho}{dt} = \sum_{j=1}^{n} p_j \left(\frac{d|\psi_j\rangle}{dt}\langle\psi_j| + |\psi_j\rangle\frac{d\langle\psi_j|}{dt} \right)$$

$$= \sum_{j=1}^{n} \frac{p_j}{i\hbar}\left(H|\psi_j\rangle\langle\psi_j| - |\psi_j\rangle\langle\psi_j|H^\dagger \right)$$

$$= \frac{1}{i\hbar}\left(H\sum_{j=1}^{n} p_j|\psi_j\rangle\langle\psi_j| + \sum_{j=1}^{n} p_j|\psi_j\rangle\langle\psi_j|H \right)$$

$$= \frac{1}{i\hbar}\left(H\rho - \rho H\right) \equiv \frac{1}{i\hbar}[H,\rho]$$

This is called the **Liouville Equation** and it generalizes the Shroedinger equation.

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 $\frac{d}{dt}U = -\frac{iH}{\hbar}U$ and differentiate:

$$\frac{d\rho}{dt} = \dot{U}\rho(0)U^\dagger + U\overbrace{\dot{\rho}(0)}^{=0}U^\dagger + U\rho(0)\dot{U}^\dagger$$

$$= -\frac{iH}{\hbar}U\rho(0)U^\dagger + U\rho(0)U^\dagger\frac{iH}{\hbar}$$

$$= \frac{1}{i\hbar}\left(H\rho(t) - \rho(t)H\right) = \frac{1}{i\hbar}[H,\rho]$$

so it satisfies the Liouville equation and is a solution.

2.5 HOW TO SOLVE ANY PROBLEM IN QUANTUM MECHANICS

So, how do we put all of this QM to work? The most general problem in QM can be formulated as follows:

> Given a system (either $|\psi\rangle$ or a more general density matrix ρ) at time t=0, calculate its time evolution for all t>0.

This is analogous to the basic problem in classical mechanics: given a particle with position and velocity at time t=0, calculate its trajectory (using F=ma) for all t>0.

Here is a recipe that will give you the answer every single time, assuming H is time independent:

1. Write down the hamiltonian H
2. Calculate its eigenvalues E_j & eigenvectors $|\psi_j\rangle$, which constitute a basis.
3. Given an initial density matrix ρ_0, expand it in the basis of H:

$$\rho_0 = \sum_{n,m} \rho_{nm}|\psi_n\rangle\langle\psi_m|$$

4. We know $\rho(t) = e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar} = U\rho U^\dagger$. Now, $U(t)|\psi_m\rangle = e^{-iHt/\hbar}|\psi_m\rangle = e^{-iE_mt/\hbar}|\psi_m\rangle$ and therefore:

$$\rho(t) = \sum_{n,m} \rho_{nm}e^{-\frac{i(E_n - E_m)t}{\hbar}}|\psi_n\rangle\langle\psi_m|$$

Since we know how the $|\psi_j\rangle$'s look like and what the energies are, this is a full analytical solution to the problem. Often, however, this sort of brute force approach is not very revealing, nor does it supply us with physical intuition, so a great deal of QM focuses instead on approximations and trying to find more insightful ways of solving problems.

3. EXAMPLE: A SPIN-1/2

3.1 THE DENSITY MATRIX

For a single spin-1/2 in a magnetic field, the hamiltonian is:

$$\hat{H} = -\gamma \hat{S}_z B_0 = \begin{pmatrix} -\frac{\gamma \hbar B_0}{2} & 0 \\ 0 & \frac{\gamma \hbar B_0}{2} \end{pmatrix} \equiv \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}$$

This hamiltonian has two distinct energy levels $E_\pm$ with the two corresponding states (eigenvectors) termed accordingly "up" and "down":

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad H|+\rangle = -\frac{\gamma \hbar B_0}{2}|+\rangle$$

$$|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \qquad H|-\rangle = \frac{\gamma \hbar B_0}{2}|-\rangle$$

The most general coherent quantum state is spanned by the hamiltonian's eigenfunctions:

$$|\psi\rangle = a|+\rangle + b|-\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$$

and the most general density matrix:

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

The density matrix starts out from thermal equilibrium at:

$$\rho = \frac{1}{2}I + \frac{\gamma B_0}{2kT}S_z = \begin{pmatrix} \frac{1}{2} + \frac{\hbar \gamma B_0}{4kT} & 0 \\ 0 & \frac{1}{2} - \frac{\hbar \gamma B_0}{4kT} \end{pmatrix}$$

The general ρ can be written as a linear combination of these operators:

$$I, \hat{S}_x, \hat{S}_y, \hat{S}_z.$$

These are called the spin-1/2 **product operators** and constitute a **basis** for all 2×2 density matrices (prove this!).

3.2 The Effect of a Hard RF Pulse

The time evolution of the density matrix with any RF field turned on is determined by the Liouville equation, the solution to which is:

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

Any component that is proportional to the identity matrix **does not evolve in time**, since

$$e^{-iHt/\hbar}Ie^{iHt/\hbar} = e^{-iHt/\hbar}e^{iHt/\hbar}I = I$$

(this is not possible for a general ρ since in general for matrices AB≠BA). Therefore the identity matrix is often omitted and one only writes

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

although it should be kept in mind that strictly there's an identity matrix in there.

Consider a rotation about the x-axis in the rotating frame with no offset. In that frame, the effective field is

$$\mathbf{B} = B_1\hat{\mathbf{x}}$$

(assuming the RF field is applied along the x-axis.) This means that the hamiltonian is

$$H = -\gamma \mathbf{S} \cdot \mathbf{B} = -\gamma S_x B_1 \equiv -\omega_1 S_x.$$

The propagator is

$$U(t) = e^{-iHt/\hbar} = e^{i\omega_1 I_x t}$$

(where $I_x \equiv S_x/\hbar$.) We know already from the Bloch equation this represents a rotation about the x-axis and, if applied to a magnetization vector along z for a time $t = \frac{\pi}{2\omega_1}$, will rotate it by an angle $\omega_1 t = \frac{\pi}{2}$ to the x-axis (left hand rule!). So

$$\rho_0 = \frac{2}{\gamma \hbar^2}M_{z,eq}\hat{S}_z \xrightarrow{U\left(t=\frac{\pi}{2\omega_1}\right)} \frac{2}{\gamma \hbar^2}M_{z,eq}\hat{S}_x.$$

That is:

$$U\left(t = \frac{\pi}{2\omega_1}\right)\rho_0 U\left(t = \frac{\pi}{2\omega_1}\right) = \frac{2}{\gamma \hbar^2}M_{z,eq}\hat{S}_x$$

which simplifies to:

$$e^{i\hat{S}_x\omega_1 t/\hbar}\hat{S}_z e^{-i\hat{S}_x\omega_1 t/\hbar} = \hat{S}_y \,.$$

This way we can derive important identities about the action of the angular momentum operators on the density matrix. A few examples:

$$I_x \xrightarrow{\;R_x\left(\frac{\pi}{2}\right)\;} I_x$$

$$I_y \xrightarrow{\;R_x\left(\frac{\pi}{2}\right)\;} -I_z$$

$$I_z \xrightarrow{\;R_x\left(\frac{\pi}{2}\right)\;} I_y$$

$$I_x \xrightarrow{\;R_y\left(\frac{\pi}{2}\right)\;} I_z$$

> We see that the "product operators" I_x, I_y, I_z behave just like the unit vectors $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ under rotations.

3.3 MEASUREMENT

Our RF coils pick up the transverse magnetization, so the FID is proportional to

$$\begin{aligned}
\left\langle \hat{M}_{xy} \right\rangle &= \mathrm{tr}\left(\hat{M}_{xy}\rho\right) \\
&= \mathrm{tr}\left(\gamma\hat{S}_{xy}\rho\right) \\
&= 2\mathrm{tr}\left(\hat{S}_{xy}\mathbf{M}\cdot\hat{\mathbf{S}}\right) \\
&= 2\mathrm{tr}\left(\left(\hat{S}_x + i\hat{S}_y\right)\left(M_x\hat{S}_x + M_y\hat{S}_y + M_z\hat{S}_z\right)\right) \\
&= 2\left(M_x\mathrm{tr}\left(\hat{S}_x^2\right) + M_y\mathrm{tr}\left(\hat{S}_y^2\right)\right) \\
&= M_x + iM_y
\end{aligned}$$

as expected!

3.4 THE FID

Let's conclude by showing that, once the spins are excited onto the xy plane, we get the FID just as we would with the Bloch equation description.

$$U(t) = e^{-iHt/\hbar} = e^{i\omega\hat{S}_z t/\hbar} = \begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix}$$

and therefore:

$$U(t)S_x U^{\dagger}(t)$$

$$= \begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix} \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & e^{i\omega t/2} \\ e^{-i\omega t/2} & 0 \end{pmatrix}\begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & \cos(\omega t) + i\sin(\omega t) \\ \cos(\omega t) - i\sin(\omega t) & 0 \end{pmatrix}$$

$$= \cos(\omega t)\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \sin(\omega t)\frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$= \cos(\omega t)\hat{S}_x - \sin(\omega t)\hat{S}_y$$

This is in perfect accordance with our previous observation that S_j's behave just like vectors under rotations. Since the Zeeman hamiltonian merely describes a left-handed precession about the z-axis, it should come as no surprise that S_x merely seems to perform a left handed rotation in "spin operator space".

The FID is

$$\begin{aligned}
\left\langle \hat{S}_- \right\rangle &= \mathrm{tr}\left(\hat{S}_-\rho\right) \\
&= \mathrm{tr}\left(\hat{S}_x\rho\right) - i\mathrm{tr}\left(\hat{S}_y\rho\right) \\
&= \cos(\omega t)\mathrm{tr}\left(\hat{S}_x\hat{S}_x\right) - \sin(\omega t)\mathrm{tr}\left(\hat{S}_x\hat{S}_y\right) \\
&\quad - i\cos(\omega t)\mathrm{tr}\left(\hat{S}_y\hat{S}_x\right) + i\sin(\omega t)\mathrm{tr}\left(\hat{S}_y\hat{S}_y\right) \\
&= \frac{\hbar^2}{2}e^{i\omega t}
\end{aligned}$$

As expected, we observe the oscillating FID at ω, the Larmor frequency of the spin.

4. N SPIN SYSTEMS

4.1 MULTIPLE SPINS ARE DESCRIBED BY DIRECT PRODUCT SPACES

If we have two spins, we need to look at the space spanned by the **direct product** of their individual spaces. It's simpler than it sounds: the direct product of two matrices

$$A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}, \quad B = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$$

is

$$A \otimes B \equiv \begin{pmatrix} A_{11}B & A_{12}B \\ A_{21}B & A_{22}B \end{pmatrix}$$

$$= \begin{pmatrix} A_{11}B_{11} & A_{11}B_{12} & A_{12}B_{11} & A_{12}B_{12} \\ A_{11}B_{21} & A_{11}B_{22} & A_{12}B_{21} & A_{12}B_{22} \\ A_{21}B_{11} & A_{21}B_{12} & A_{22}B_{11} & A_{22}B_{12} \\ A_{21}B_{21} & A_{21}B_{22} & A_{22}B_{21} & A_{22}B_{22} \end{pmatrix}$$

Often people write just $A \otimes B \equiv AB$ out of laziness, leaving it up to the reader to understand the meaning from the context.

For two vectors this is:

$$|\psi\rangle \otimes |\varphi\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \otimes \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} = \begin{pmatrix} \psi_1\varphi_1 \\ \psi_1\varphi_2 \\ \psi_2\varphi_1 \\ \psi_2\varphi_2 \end{pmatrix}.$$

Again, people often just write $|\psi\rangle \otimes |\varphi\rangle \equiv |\psi, \varphi\rangle$. For example (verify!),

$$|++\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |+-\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |-+\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad |--\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

For operators,

$$\hat{S}_{1z}\hat{S}_{2x} \equiv \hat{S}_{1z} \otimes \hat{S}_{2x}$$

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

$$= \frac{\hbar^2}{4}\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

or

$$\hat{S}_{1z} \equiv \hat{S}_{1z} \otimes I$$

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

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

and

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

Again, people use such shorthand as $\hat{S}_{1x} \equiv S_x \otimes I$.

The Hamiltonian is simply the sum of energies of each spin (again, assuming no coupling):

$$\hat{H} = -\gamma\hat{S}_{1z}B_0 - \gamma\hat{S}_{2z}B_0$$

$$= -\hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Since the sum is diagonal we immediately see the Hamiltonian has three energy levels with the corresponding eigenfunctions:

$$E_{++} = -\hbar\omega_0 \quad \longleftrightarrow \quad |++\rangle$$
$$E_{-+} = 0 \quad \longleftrightarrow \quad |-+\rangle$$
$$E_{+-} = 0 \quad \longleftrightarrow \quad |+-\rangle$$
$$E_{--} = \hbar\omega_0 \quad \longleftrightarrow \quad |--\rangle$$

4.2 PRODUCT OPERATORS

We've seen that for a single spin-1/2, the density matrix can be written as a linear combination of $I, \hat{S}_x, \hat{S}_y, \hat{S}_z$. For two spin-1/2s, a basis can be constructed using

$$I, \qquad \hat{S}_{1x}, \qquad \hat{S}_{1y}, \qquad \hat{S}_{1z}$$
$$\hat{S}_{2x} \qquad \hat{S}_{1x}\hat{S}_{2x} \qquad \hat{S}_{1y}\hat{S}_{2x} \qquad \hat{S}_{1z}\hat{S}_{2x}$$
$$\hat{S}_{2y} \qquad \hat{S}_{1x}\hat{S}_{2y} \qquad \hat{S}_{1y}\hat{S}_{2y} \qquad \hat{S}_{1z}\hat{S}_{2y}$$
$$\hat{S}_{2z} \qquad \hat{S}_{1x}\hat{S}_{2z} \qquad \hat{S}_{1y}\hat{S}_{2z} \qquad \hat{S}_{1z}\hat{S}_{2z}$$

Basically these guys are all of the possible direct products of $I, \hat{S}_x, \hat{S}_y, \hat{S}_z$. For three spin-1/2s, you'll need all three-operator direct products of $I, \hat{S}_x, \hat{S}_y, \hat{S}_z$ (yielding a total of 4×4×4=64 basis "functions"), and for N spins you'll need 4^N such product operators.

Some of the operators make immediate sense. For example, $\hat{S}_{1y}$ describes a system in which the 1st spin is pointing along the y-axis. But what does a product like $\hat{S}_{1x}\hat{S}_{2z}$ "mean"? This is a **correlated coherent state** in which the molecules in the system have (on average) the spin of nucleus #1 pointing along y and the spin of nucleus #2 pointing along z.

4.3 Spin Subspaces Commute

It is very important to realize that operators in different subspaces commute. For example,

$$\left[A \otimes I, I \otimes B \right] = 0$$

for any A, B. This leads to major simplifications as we'll see next.

4.4 RF Pulses and 2-Spin Systems

What happens when we apply an RF pulse to a 2-spin system? First, it is very important to make a distinction between **homonuclear** spins and **heteronuclear** spins. For example, two protons in the same molecule are **homonuclear**. A proton and a carbon-13 are **heteronuclear**.

Heteronuclear systems tend to have independent transmitters, receivers, etc... meaning we can apply RF pulses to each independently (or even pulse on one and acquire on the other simultaneously!). This means we can (for an ^{1}H-^{13}C system):

Pulse on 1H, but not on 13C
Pulse on 13C, but not on 1H
Pulse on both.

Pulse on neither.
For a homonuclear system there is only one transmitter & receiver, so we can either pulse simultaneously on both (or acquire simultaneously from both), or not pulse at all. We can't pulse on one but not on the other (This excludes so-called "soft pulses" which can achieve that and which we'll briefly mention later during the course). Each of these scenarios has a different propagator. Some examples:

Heteronuclear ^{1}H-^{13}C System

Action	Propagator
Apply 90° pulse on ^{1}H, apply 180° on ^{13}C	$e^{i(\pi/2)\hat{S}_{1x}}e^{i\pi\hat{S}_{2x}}$
Apply 90° on ^{13}C	$e^{i(\pi/2)\hat{S}_{2x}}$
Apply 90° on ^{1}H	$e^{i(\pi/2)\hat{S}_{1x}}$
Do nothing	I

Homonuclear ^{1}H-^{1}H System

Action	Propagator
Apply a 90° pulse	$e^{i(\pi/2)\hat{S}_{1x}}e^{i(\pi/2)\hat{S}_{2x}}$
Apply nothing	I

How does this affect our density matrix? Let's say that our heteronuclear ^{1}H-^{13}C system is in the state:

$$\rho = \hat{S}_{1x}\hat{S}_{2z}$$

and we apply 90° pulse on ^{1}H and a 180° on ^{13}C. Our propagator is $e^{i(\pi/2)\hat{S}_{1x}}e^{i\pi\hat{S}_{2x}}$ and we can calculate the evolution of the system as follows:

$$\rho \rightarrow U\rho U^{\dagger}$$
$$= e^{i(\pi/2)\hat{S}_{1x}}e^{i\pi\hat{S}_{2x}}\hat{S}_{1x}\hat{S}_{2z}e^{-i(\pi/2)\hat{S}_{1x}}e^{-i\pi\hat{S}_{2x}}$$
$$= e^{i(\pi/2)\hat{S}_{1x}}\hat{S}_{1x}e^{-i(\pi/2)\hat{S}_{1x}}e^{i\pi\hat{S}_{2x}}\hat{S}_{2z}e^{-i\pi\hat{S}_{2x}}$$
$$\equiv \left(e^{i(\pi/2)\hat{S}_{1x}}\hat{S}_{1x}e^{-i(\pi/2)\hat{S}_{1x}} \right) \otimes \left(e^{i\pi\hat{S}_{2x}}\hat{S}_{2z}e^{-i\pi\hat{S}_{2x}} \right)$$

So what's really happening here is that each pulse (1H, 13C) acts on its own spin and commutes with the other spin. Because we know how a single spin RF pulse behaves, we can immediately say:

$$\rho = \hat{S}_{1x}\hat{S}_{2z} \rightarrow \hat{S}_{1x}\hat{S}_{2y}$$