

TA 11: The Bloch equation

Luca Teodori

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1 Introduction

In this tutorial we will introduce the Bloch equation, which deals with the spin precession properties of a particle (in applications, typically a nucleus) in the presence of magnetic field(s). The important application of the Bloch equation is in the Nuclear Magnetic Resonance (NMR). The Bloch equation can be (sort of) derived using the density matrix formalism, approximating the system of interest as a two energy level system.

How justified is such an approximation? We know that quantum systems interact continuously with the environment, plus one should take into account “unwanted” interactions with the detector as well. This mess makes such that the density matrix of the whole system becomes very complicated, in particular it lives on a possibly enormous Hilbert space. Even if experimentalists try their best to prepare a pure state, when one deals with almost degenerate energy levels, mixing is basically unavoidable. Assuming we can treat a system as a two energy level system means that we are basically considering a two dimensional Hilbert space, hence greatly simplifying the problem. This works when the dynamics which populate these levels is to a good approximation decoupled from the rest of the Hilbert space.

The prime example where such an approximation is used (and works) is the case of a spin 1/2 particle in a magnetic field \vec{B} : due to the spin, the system has two close energy levels, the one where the spin is aligned with \vec{B} , and the one where the spin direction is opposite with respect to \vec{B} . The density matrix of such a system can be decomposed as $\rho(\vec{r}, s, \vec{r}', s') \simeq \rho(\vec{r}, \vec{r}')\rho(s, s')$. $\rho(s, s')$ is a 2 by 2 matrix (for a spin n particle we have $2n + 1$ possible independent z components for example), which describes the possible two orientations of the spin plus mixing (the non-diagonal terms).

Having this example in mind, we will first build the formalism which will allow us to describe 2 by 2 matrices in this context, to then move towards the Bloch equation and some comments regarding NMR.

Most of this tutorial is based on Shimon’s lecture notes, chapter 5, section 5.

2 Pauli matrices

We need a convenient 2 by 2 matrix base to describe 2 by 2 density matrices; recalling that the density matrix is hermitian, it makes sense to look for an hermitian base as well (so that the coefficients of a density matrix expansion in this base are all real). The set which makes the job done is the following:

$$\mathbb{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (2.1)$$

then, any density matrix ρ can be expanded as

$$\rho = \rho_0 \mathbb{1} + \sum_{i=1}^3 \rho_i \sigma_i, \quad (2.2)$$

where ρ_μ , $\mu = 0, \dots, 3$ are the real coefficients of the expansion. The matrices σ_i , $i = 1, 2, 3$, are the so called Pauli matrices. They are very important, since the description of a spin 1/2 particle uses them extensively. Also for this reason, it is worth stopping a little discussing their properties. The Pauli matrices are:

- Hermitian, $\sigma_i^\dagger = \sigma_i$;

- traceless, $\text{Tr}(\sigma_i) = 0$;
- they obey $[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$; notice that ϵ_{ijk} are proportional to the $\mathfrak{su}(2)$ algebra structure constants (meaning the Pauli matrices are the generators of the $\text{SU}(2)$ group);
- they obey $\{\sigma_i, \sigma_j\} = 2\delta_{ij}\mathbb{1}$; this anticommutation relation is a “hint” of their usefulness in describing spin 1/2 particles (which obey anticommutation relations);
- one can use the previous two properties to find $\sigma_i\sigma_j = ([\sigma_i, \sigma_j] + \{\sigma_i, \sigma_j\})/2 = \delta_{ij}\mathbb{1} + i\epsilon_{ijk}\sigma_k$.

Notice that one can extract coefficients of ρ in Eq. (2.2) via traces (recall $\text{Tr}(\rho) = 1$),

$$\rho_0 = \frac{1}{2} \text{Tr}(\mathbb{1}\rho) = \frac{1}{2}, \quad \rho_i = \frac{1}{2} \text{Tr}(\sigma_i\rho). \quad (2.3)$$

Notice that, using Eq. (2.3), we can write (Greek letter here denote the matrix indices, and sum over mute indices is implied)

$$(\rho_0\mathbb{1} + \rho_i\sigma_i)_{\gamma\delta} =: \rho_{\gamma\delta} = \frac{1}{2}\rho_{\beta\alpha}\delta_{\alpha\beta}\delta_{\gamma\delta} + \frac{1}{2}\rho_{\beta\alpha}\sigma_i^{\alpha\beta}\sigma_i^{\gamma\delta} = \rho_{\beta\alpha}\delta_{\beta\gamma}\delta_{\alpha\delta} \implies \delta_{\alpha\beta}\delta_{\gamma\delta} + \sigma_i^{\alpha\beta}\sigma_i^{\gamma\delta} = 2\delta_{\beta\gamma}\delta_{\alpha\delta}, \quad (2.4)$$

which is a completeness relation.

The previous properties are what define Pauli matrices. One can ask: are there other matrices which respect those properties? In other words, are there other representations of the Pauli matrices? The answer is yes. Consider an unitary matrix U ; then the transformed set

$$\sigma'_i = U\sigma_iU^\dagger, \quad (2.5)$$

satisfies all the previous properties for every U . It turns out that we can give a nice interpretation of such a transformation. Notice that $\{\sigma_i\}$ is a base for the space of traceless matrices. So we can expand

$$U\sigma_iU^\dagger = \sum_j A_{ij}\sigma_j, \quad A_{ik} = \frac{1}{2} \text{Tr}(\sigma_kU\sigma_iU^\dagger). \quad (2.6)$$

The matrices A_{ij} are 3 by 3 matrices, and one can show that they are orthogonal, using Eq. (2.4). In fact

$$\begin{aligned} A_{ik}A_{jk} &= \frac{1}{4} \text{Tr}(\sigma_kU\sigma_iU^\dagger) \text{Tr}(\sigma_kU\sigma_jU^\dagger) = \frac{1}{4}\sigma_k^{\alpha\beta}U^{\beta\gamma}\sigma_i^{\gamma\delta}U^{\dagger\delta\alpha}\sigma_k^{\epsilon\eta}U^{\eta\theta}\sigma_j^{\theta\mu}U^{\dagger\mu\epsilon} \\ &= \frac{1}{2} \left(\delta_{\alpha\eta}\delta_{\beta\epsilon} - \frac{1}{2}\delta_{\alpha\beta}\delta_{\epsilon\eta} \right) U^{\beta\gamma}\sigma_i^{\gamma\delta}U^{\dagger\delta\alpha}U^{\eta\theta}\sigma_j^{\theta\mu}U^{\dagger\mu\epsilon} = \frac{1}{2} \text{Tr}(\sigma'_i\sigma'_j) = \delta_{ij}, \end{aligned} \quad (2.7)$$

and similar for $A_{ki}A_{kj} = \delta_{ij}$. This means that A_{ik} matrices belong to $\text{O}(3)$, the group of 3D rotations. Notice

$$\rho - \frac{1}{2}\mathbb{1} = \rho_i\sigma_i = \rho'_i\sigma'_i = \rho'_iA_{ij}\sigma_j \implies \rho_i = A_{ij}\rho'_j, \quad (2.8)$$

i.e. the components ρ_i transform as a 3D ordinary vector under this unitary transformation of Pauli matrices. All this illustrates the connection between the $\text{SU}(2)$ and $\text{O}(3)$ group. The matrices A_{ik} form the so called adjoint representation of $\text{SU}(2)$. The concept of the adjoint representation of a group will return back especially when you will study particle physics.

3 The Bloch sphere

Let's return back to our two energy level system; we now know that we can represent it as

$$\rho = \frac{1}{2}(\mathbb{1} + \vec{P} \cdot \vec{\sigma}), \quad (3.1)$$

where \vec{P} is called polarization vector; the reason of this name will become clear soon (for those of you that are not familiar with this notation, $\vec{P} \cdot \vec{\sigma} = P_i\sigma_i$, P_i are numbers whereas σ_i are matrices, hence $P_i\sigma_i$ is a matrix). $P := |\vec{P}|$ determines the eigenvalues of the density matrix; to find them, notice that $\vec{n} \cdot \vec{\sigma}$, with $\vec{n} := \vec{P}/P$, commutes with ρ , hence they have the same eigenstates (one can see \vec{n} as the “direction

in Pauli matrices space" of the polarization); also, since it is always possible to find an unitary matrix such that $\vec{n} \cdot \vec{\sigma} = U\sigma_3U^\dagger$ (rotation in Pauli matrix space, as we have seen in the previous section); hence, σ_3 and $\vec{n} \cdot \vec{\sigma}$ have the same eigenvalues (this is equivalent to diagonalization, which does not change the eigenvalues;), hence

$$\lambda_{\pm} = \frac{1}{2}(1 \pm P) . \quad (3.2)$$

Notice that, if $P = 1$, $\text{Tr}(\rho^2) = (1 + P^2)/2 = 1$, hence it is a pure state; conversely, the state with $P = 0$ is the maximally mixed state (the two levels have the same weight, hence there is no information). One can see this also by looking at the related entropy in the case $P = 0$

$$S = - \sum_i \lambda_i \ln \lambda_i = \ln 2 = \ln N , \quad (3.3)$$

where N is the number of possible configurations of the sytem. This is typical to systems with no information, or maximal entropy.

This suggests to represent the states as lying in a sphere of unitary radius. The center of the sphere, $P = 0$, is the maximally mixed state, whereas the surface of the sphere, states with $P = 1$, are the pure states. States inside the sphere are mixed states. Such a representation is called Bloch sphere.

4 Dynamical Bloch equation

Recall that the density matrix obeys the equation

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] \implies \frac{dP_i}{dt} = \frac{d}{dt} \left(\frac{1}{2} \text{Tr}(\sigma_i \rho) \right) = \frac{i}{2\hbar} \text{Tr}(\sigma_i P_k [\sigma_k, H]) ; \quad (4.1)$$

exploiting

$$\text{Tr}(\sigma_i [\sigma_k, H]) = \text{Tr}([\sigma_i, \sigma_k] H) + \underbrace{\text{Tr}(\sigma_k \sigma_i H - \sigma_i H \sigma_k)}_{=0} = 2i\epsilon_{ikl} \text{Tr}(H \sigma_l) , \quad (4.2)$$

we end up with

$$\frac{d\vec{P}}{dt} = -\frac{1}{\hbar} \vec{P} \times \text{Tr}(H \vec{\sigma}) . \quad (4.3)$$

Let's specialize our discussion for a spin 1/2 particle in a magnetic field; the Hamiltonian reads

$$H = -\vec{\mu} \cdot \vec{B} , \quad \vec{\mu} = \frac{1}{2} \hbar g \vec{\sigma} , \quad (4.4)$$

therefore

$$\frac{d\vec{P}}{dt} = g \vec{P} \times \vec{B} , \quad (4.5)$$

which is the equation of the polarization vector which precesses around the magnetic field.

We can take into account the effect of the environment by means of the relaxation time approach; for a system in a thermal bath characterized by the temperature T , the equilibrium state is

$$\rho_0 = \frac{e^{-H/T}}{\text{Tr}(e^{-H/T})} . \quad (4.6)$$

To have an explicit expression, notice that, with \vec{e} as a unit vector,

$$(\vec{e} \cdot \vec{\sigma})^2 = e_i e_j \sigma_i \sigma_j = e_i e_j (\delta_{ij} + i\epsilon_{ijk} \sigma_k) = 1 = (\vec{e} \cdot \vec{\sigma})^{2p} , \quad (\vec{e} \cdot \vec{\sigma})^{2p+1} = \vec{e} \cdot \vec{\sigma} ; \quad (4.7)$$

This means that we can split the sum on the Taylor expansion for the exponential as ($\vec{B} =: B\vec{e}$)

$$\exp\left(\frac{\hbar g B}{2T} \vec{e} \cdot \vec{\sigma}\right) =: \exp(\alpha \vec{e} \cdot \vec{\sigma}) = \mathbb{1} \sum_{k=\text{even}} \frac{\alpha^k}{k!} + \frac{\vec{B} \cdot \vec{\sigma}}{B} \sum_{k=\text{odd}} \frac{\alpha^k}{k!} = \frac{e^\alpha + e^{-\alpha}}{2} \mathbb{1} + \frac{e^\alpha - e^{-\alpha}}{2} \frac{\vec{B} \cdot \vec{\sigma}}{B} ; \quad (4.8)$$

the trace of the previous is simply $e^\alpha + e^{-\alpha}$, thus ending up in

$$\rho_0 = \frac{1}{2} \mathbb{1} + \frac{\vec{B} \cdot \vec{\sigma}}{B} \tanh \frac{g\hbar B}{2T} . \quad (4.9)$$

An easy interpretation of ρ_0 is the following: since $\lim_{x \rightarrow \infty} \tanh(x) = 1$, when $B \gg T$, the equilibrium state is basically the state with polarization vector \vec{P} aligned with \vec{B} ; in the opposite limit, we are close to the maximally mixed state (meaning that the temperature of the system is too high to give any meaningful polarization).

Returning back to Eq. (4.5), we have

$$\frac{d\vec{P}}{dt} = g\vec{P} \times \vec{B} - \frac{\vec{P} - \vec{P}_0}{\tau}, \quad \vec{P}_0 = \frac{\vec{B}}{B} \tanh \frac{g\hbar B}{2T}, \quad (4.10)$$

which is (almost) the Bloch equation. A particle with spin polarization \vec{P} will precess around \vec{B} and, in a time τ , it will relax to the equilibrium configuration given by \vec{P}_0 .

5 Nuclear magnetic resonance

The Bloch equation is applied in nuclear magnetic resonance; the setting is slightly more complicated with respect to the one discussed above, since in NMR there are typically two magnetic fields acting on a sample: a strong, static one and a time-dependent one, perpendicular to the previous. Eq. (4.10) can be phenomenologically modified as

$$\frac{d\vec{P}}{dt} = g\vec{P} \times (\vec{B} + \vec{B}_1(t)) - \frac{\vec{P}_\perp}{T_2} - \frac{\vec{P}_\parallel - \vec{P}_0}{T_1}, \quad (5.1)$$

where $\vec{P}_{\perp(\parallel)}$ is the component of the polarization vector perpendicular (parallel) to \vec{B} , and T_2 is a relaxation time related to the pulse given by $\vec{B}_1(t)$, where typically $T_2 < T_1$. Notice that \vec{P}_0 is parallel to \vec{B} as well. This is the equation that Bloch proposed back in 1946.

In applications, the spin refers to the nuclear spins of nuclei in (possibly complicate) molecules (e.g. spin of ^1H , ^{13}C , ^{15}N). One can put a sample of an unknown molecule in these perpendicular magnetic fields, together with a coil or something similar which will capture the current induced by the precession of a certain nucleus. At first, the strong static magnetic field (order of few tesla) is turned on, hence the randomly oriented nuclear spin will start precessing at a frequency given by the strength of B (the Larmor frequency $\omega = gB$, notice that g depends on the nucleus we are looking at); then, an impulse (on radio frequencies, hence no ionizing radiation) of the perpendicular magnetic field (order μT) will cause a further oscillation on the polarization vector (kicking them out of the alignment with the strong static magnetic field). If this pulse has a frequency matching the Larmor frequency, the many precessing nuclei become phase coherent, hence giving rise to a detectable signal; this phase coherence will die out with time T_2 (spin-spin relaxation, whereas T_1 may be called spin-lattice relaxation, since it mostly deals with exchange of the precessing spin energy with the environment, i.e. the lattice, until equilibrium is reached). Both relaxation times depend on the properties of the nucleus in the molecule. In fact, different nuclei will experience a different effective magnetic field, due to shielding or deshielding of neighboring electrons (more electronegative groups will feel less effective magnetic field). NMR measures these pulses, modulated by the two relaxation times, which will tell the experimentalist the molecule he has in his sample (different resonant frequencies and different relaxation times can identify nuclei in a molecule). Magnetic Resonance Imaging (MRI) is an example of a medical application of NMR (the contrast between different tissues in MRI scans is given by the rate at which nuclei relax).

For the spin-lattice relaxation, we have (focusing on the relaxation alone)

$$\vec{P}_\parallel = \vec{P}_0 - (\vec{P}_0 - \vec{P}_\parallel(0))e^{-t/T_1}, \quad (5.2)$$

whereas for the spin-spin relaxation

$$\vec{P}_\perp = \vec{P}_\perp(0)e^{-t/T_2}. \quad (5.3)$$

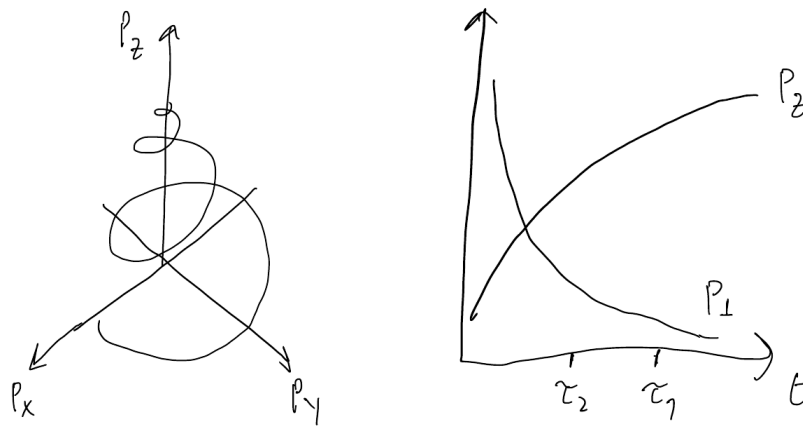


Figure 1: Visualizing the effect of the two relaxation times.