

## Density operators for spin- $\frac{1}{2}$ ensembles

So far in our discussion of spin- $\frac{1}{2}$  systems, we have restricted our attention to the case of pure states and Hamiltonian evolution. Today we'll need to move on to density operators so that we can include dissipation and dephasing to arrive at the full Bloch Equations.

We've already seen that an arbitrary pure state for a two-level system can be represented by a vector on the Bloch Sphere. If we write the quantum state vector in the form

$$|\Psi\rangle = \cos\frac{\theta}{2} \exp\left(-i\frac{\varphi}{2}\right) |+_z\rangle + \sin\frac{\theta}{2} \exp\left(i\frac{\varphi}{2}\right) |-_z\rangle,$$

then the corresponding Bloch vector connects the origin (center) of the Bloch Sphere to a surface point at polar (latitude) angle  $\theta$  and azimuthal (longitude) angle  $\varphi$ . By convention we assign the Bloch Sphere a "radius" of 1, so that the Cartesian components of the Bloch vector  $\vec{v}$  are simply

$$v_x = \sin\theta \cos\varphi, \quad v_y = \sin\theta \sin\varphi, \quad v_z = \cos\theta.$$

We have also noted that the Bloch vector is proportional to  $\langle \vec{\mathbf{S}} \rangle = (\hbar/2)\langle \vec{\sigma} \rangle = (\hbar/2)\vec{v}$ , since

$$\langle \mathbf{S}_x \rangle = \frac{\hbar}{2} \sin\theta \cos\varphi, \quad \langle \mathbf{S}_y \rangle = \frac{\hbar}{2} \sin\theta \sin\varphi, \quad \langle \mathbf{S}_z \rangle = \frac{\hbar}{2} \cos\theta.$$

When working with density operators, we can use this connection to define a generalized Bloch vector:

$$v_x = \text{Tr}[\rho \sigma_x], \quad v_y = \text{Tr}[\rho \sigma_y], \quad v_z = \text{Tr}[\rho \sigma_z].$$

In other words, we set

$$\vec{v} = \langle \vec{\sigma} \rangle = \frac{2}{\hbar} \langle \vec{\mathbf{S}} \rangle$$

for both pure states and density operators. It is worth noting that for a general mixed state,  $|\vec{v}|^2 \leq 1$ . For example, if  $\rho = \frac{1}{2}\mathbf{1}$  then  $\vec{v} = 0$  since the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

are all traceless ( $\text{Tr}[\sigma] = 0$ ).

In cases where  $\rho$  corresponds to a known ensemble

$$\rho = \sum_j p_j |\Psi_j\rangle \langle \Psi_j|,$$

then

$$\begin{aligned}
\langle \vec{\sigma} \rangle &= \text{Tr}[\rho \vec{\sigma}] = \text{Tr} \left[ \sum_j p_j |\Psi_j\rangle \langle \Psi_j| \vec{\sigma} \right] \\
&= \sum_j p_j \text{Tr}[|\Psi_j\rangle \langle \Psi_j| \vec{\sigma} |\Psi_j\rangle \langle \Psi_j|] \\
&= \sum_j p_j \langle \Psi_j | \vec{\sigma} | \Psi_j \rangle \text{Tr}[|\Psi_j\rangle \langle \Psi_j|] = \sum_j p_j \vec{v}_j,
\end{aligned}$$

where  $\vec{v}_j = \langle \Psi_j | \vec{\sigma} | \Psi_j \rangle$  and the summation is a vector sum. In other words, the generalized Bloch vector corresponding to an ensemble of pure states is the *weighted* vector sum of the Bloch vectors representing the members of the ensemble. Hence we find that for any equally-weighted two-member ensemble with  $\langle \Psi_1 | \Psi_2 \rangle = 0$ , the ensemble Bloch vector will be zero since  $|\Psi_1\rangle$  and  $|\Psi_2\rangle$  correspond to antipodal points. Indeed, we know that  $\rho = \frac{1}{2}(|\Psi_1\rangle \langle \Psi_1| + |\Psi_2\rangle \langle \Psi_2|) = \frac{1}{2} \mathbf{1}$  for any such ensemble. Similarly, we see that the generalized Bloch vector corresponding to

$$\begin{aligned}
|\Psi_1\rangle &= |+_x\rangle, & p_1 &= \alpha, \\
|\Psi_2\rangle &= |-_x\rangle, & p_2 &= \alpha, \\
|\Psi_3\rangle &= |+_z\rangle, & p_3 &= 1 - 2\alpha,
\end{aligned}$$

will simply be  $(v_x, v_y, v_z) = (0, 0, 1 - 2\alpha)$ .

It is worth noting that any density operator may be expressed in the form

$$\rho = \frac{1}{2}(\mathbf{1} + \vec{v} \cdot \vec{\sigma}),$$

by virtue of the orthogonality of the Pauli matrices:

$$\text{Tr}[\sigma_i] = 0, \quad \text{Tr}[\sigma_i \sigma_j] = 2\delta_{ij}.$$

Hence, we find that  $\vec{v}$  is just as general as  $\rho$  for the purpose of specifying mixed quantum states! The generalized Bloch vector  $\vec{v}$  has only three real parameters  $v_x, v_y, v_z$  (or  $\theta, \phi, |\vec{v}|$ ), but the same is true for  $\rho$  since Hermiticity ( $\rho = \rho^\dagger$ ) fixes

$$\text{Im}[\rho_{11}] = \text{Im}[\rho_{22}] = 0,$$

$$\text{Re}[\rho_{21}] = \text{Re}[\rho_{12}],$$

$$\text{Im}[\rho_{21}] = -\text{Im}[\rho_{12}],$$

and normalization ( $\text{Tr}[\rho] = 1$ ) gives us  $\text{Re}[\rho_{22}] = 1 - \text{Re}[\rho_{11}]$ . Hence  $\text{Re}[\rho_{11}]$ ,  $\text{Re}[\rho_{12}]$ , and  $\text{Im}[\rho_{12}]$  are the only real degrees of freedom for a density operator on a two-dimensional Hilbert space.

Furthermore,

$$\begin{aligned}
\text{Tr}[\rho^2] &= \frac{1}{4} \text{Tr}[(\mathbf{1} + \vec{v} \cdot \vec{\sigma})^2] \\
&= \frac{1}{4} \text{Tr}[(\mathbf{1} + v_x^2 \sigma_x^2 + v_y^2 \sigma_y^2 + v_z^2 \sigma_z^2)] \\
&= \frac{1}{2} (1 + |\vec{v}|^2).
\end{aligned}$$

Hence the length of the generalized Bloch vector is directly related to the purity of  $\rho$ .

Although we first introduced the density operator as a means of representing uncertain preparations for an individual quantum system, it is equally well suited to describing the “average” state of a collection of identical systems. By “identical” here we mean that each member of the ensemble lives in the same Hilbert space as every other, but the quantum states of the different members of the ensemble will vary. So if we have a collection of twenty spin- $\frac{1}{2}$  particles and prepare ten of them in the state  $|+_z\rangle$  and the other ten in  $|-_x\rangle$ , the ensemble density operator is

$$\rho = \frac{1}{2}|+_z\rangle\langle+_z| + \frac{1}{2}|-_x\rangle\langle-_x|.$$

This type of ensemble density operator can be used to compute average values of observables such as  $\langle\vec{\mathbf{S}}\rangle$ . In fact, the quantity

$$\vec{M} \equiv -N\gamma\langle\vec{\mathbf{S}}\rangle$$

corresponds to the net magnetic moment (or *magnetization*) of a collection of  $N$  spin- $\frac{1}{2}$  particles. When the magnetization vector has maximum length (here  $0 \leq |\vec{M}| \leq N\gamma\hbar/2$ ), all the spins in the ensemble must be pointing in the same direction. When  $|\vec{M}| = 0$ , the directions of the spins in the ensemble are isotropically distributed.

## Hamiltonian dynamics for a density operator

Assuming we have an ensemble representation for a given density operator  $\rho$ , we can derive its equation of motion in the following way:

$$\begin{aligned} \frac{d\rho}{dt} &= \frac{d}{dt} \left[ \sum_j p_j |\Psi_j\rangle\langle\Psi_j| \right] \\ &= \sum_j p_j \left[ \left( \frac{d}{dt} |\Psi_j\rangle \right) \langle\Psi_j| + |\Psi_j\rangle \left( \frac{d}{dt} \langle\Psi_j| \right) \right] \\ &= \sum_j p_j \left[ \left( \frac{-i}{\hbar} \mathbf{H} |\Psi_j\rangle \right) \langle\Psi_j| + |\Psi_j\rangle \left( \frac{i}{\hbar} \langle\Psi_j| \mathbf{H} \right) \right] \\ &= \frac{-i}{\hbar} \sum_j p_j [\mathbf{H} |\Psi_j\rangle\langle\Psi_j| - |\Psi_j\rangle\langle\Psi_j| \mathbf{H}] \\ &= \frac{-i}{\hbar} [\mathbf{H}, \rho]. \end{aligned}$$

Since this derivation is clearly independent of the particular ensemble representation we choose for  $\rho$ , it is valid in general.

Similarly, we know that

$$\begin{aligned} |\Psi_j\rangle &\mapsto \mathbf{T}(t,0)|\Psi_j\rangle \\ &= \exp(-i\mathbf{H}t/\hbar)|\Psi_j\rangle, \\ \langle\Psi_j| &\mapsto \langle\Psi_j|\mathbf{T}(0,t), \end{aligned}$$

so

$$\begin{aligned}
\rho(t) &= \sum_j p_j \mathbf{T}(t,0) |\Psi_j\rangle \langle \Psi_j| \mathbf{T}(0,t) \\
&= \mathbf{T}(t,0) \left[ \sum_j p_j |\Psi_j\rangle \langle \Psi_j| \right] \mathbf{T}(0,t) \\
&= \mathbf{T}(t,0) \rho(0) \mathbf{T}(0,t).
\end{aligned}$$

Hence

$$\begin{aligned}
\text{Tr}[\rho^2(t)] &= \text{Tr}[\mathbf{T}(t,0) \rho(0) \mathbf{T}(0,t) \mathbf{T}(t,0) \rho(0) \mathbf{T}(0,t)] \\
&= \text{Tr}[\mathbf{T}(t,0) \rho^2(0) \mathbf{T}(0,t)] \\
&= \text{Tr}[\rho^2(0)],
\end{aligned}$$

so Hamiltonian evolution preserves the length of the generalized Bloch vector.

In fact, we can use the above methods to derive equations of motion for the Bloch vector itself:

$$\begin{aligned}
\frac{dv_i}{dt} &= \frac{d}{dt} (\text{Tr}[\rho \sigma_i]) \\
&= \text{Tr} \left[ \sigma_i \frac{d}{dt} \rho \right] \\
&= \frac{-i}{\hbar} \text{Tr}[\sigma_i [\mathbf{H}, \rho]] \\
&= \frac{-i}{2\hbar} \text{Tr}[\sigma_i [\mathbf{H}, (\mathbf{1} + \vec{v} \cdot \vec{\sigma})]].
\end{aligned}$$

Hence the evolutions of the three components will generally be coupled. For Larmor precession in a static applied field,

$$\mathbf{H} = -\gamma \vec{\mathbf{S}} \cdot \vec{B}$$

and

$$\begin{aligned}
\frac{dv_i}{dt} &= \frac{-i}{2\hbar} \text{Tr}[\sigma_i [\mathbf{H}, (\mathbf{1} + \vec{v} \cdot \vec{\sigma})]] \\
&= \frac{i\gamma}{4} \text{Tr} \left[ \sigma_i \vec{\sigma} \cdot \vec{B} (\mathbf{1} + \vec{v} \cdot \vec{\sigma}) - \sigma_i (\mathbf{1} + \vec{v} \cdot \vec{\sigma}) \vec{\sigma} \cdot \vec{B} \right] \\
&= \frac{i\gamma}{4} \text{Tr} [(\sigma_i B_x \sigma_x + \sigma_i B_y \sigma_y + \sigma_i B_z \sigma_z) (\mathbf{1} + v_x \sigma_x + v_y \sigma_y + v_z \sigma_z)] \\
&\quad - \frac{i\gamma}{4} \text{Tr} [(\mathbf{1} + v_x \sigma_x + v_y \sigma_y + v_z \sigma_z) (B_x \sigma_x \sigma_i + B_y \sigma_y \sigma_i + B_z \sigma_z \sigma_i)] \\
&= \frac{i\gamma}{4} \text{Tr} \left[ \begin{array}{c} \sigma_i \sigma_x \sigma_y (B_x v_y - v_x B_y) + \sigma_i \sigma_x \sigma_z (B_x v_z - v_x B_z) \\ + \sigma_i \sigma_y \sigma_x (B_y v_x - v_y B_x) \end{array} \right] \\
&\quad + \frac{i\gamma}{4} \text{Tr} \left[ \begin{array}{c} \sigma_i \sigma_y \sigma_z (B_y v_z - v_y B_z) + \sigma_i \sigma_z \sigma_x (B_z v_x - v_z B_x) \\ + \sigma_i \sigma_z \sigma_y (B_z v_y - v_z B_y) \end{array} \right],
\end{aligned}$$

where the terms involving  $\mathbf{1}$  have been dropped due to cyclic property of the trace. Taking into account the orthogonality of the Pauli matrices, we are simply left with

$$\begin{aligned}
\frac{dv_x}{dt} &= \frac{i\gamma}{4} \text{Tr}[\sigma_x \sigma_y \sigma_z (B_y v_z - v_y B_z) + \sigma_x \sigma_z \sigma_y (B_z v_y - v_z B_y)] \\
&= \frac{i\gamma}{4} (B_y v_z - v_y B_z) \text{Tr}[\sigma_x \sigma_y \sigma_z - \sigma_x \sigma_z \sigma_y] \\
&= -\gamma (B_y v_z - v_y B_z), \\
\frac{dv_y}{dt} &= \frac{i\gamma}{4} (B_x v_z - v_x B_z) \text{Tr}[\sigma_y \sigma_x \sigma_z - \sigma_y \sigma_z \sigma_x] \\
&= -\gamma (B_x v_z - v_x B_z), \\
\frac{dv_z}{dt} &= \frac{i\gamma}{4} (B_x v_y - v_x B_y) \text{Tr}[\sigma_z \sigma_x \sigma_y - \sigma_z \sigma_y \sigma_x] \\
&= -\gamma (B_x v_y - v_x B_y).
\end{aligned}$$

In vector notation, we thus recover

$$\begin{aligned}
\frac{d}{dt} \vec{v} &= \gamma \vec{v} \times \vec{B}, \\
\frac{d}{dt} \langle \vec{S} \rangle &= \gamma \langle \vec{S} \rangle \times \vec{B}.
\end{aligned}$$

We can also work with density operators in the rotating frame. Just as for state vectors we applied the transformation

$$\begin{aligned}
|\Psi'\rangle &= \mathbf{O}_z |\Psi\rangle, \\
\mathbf{O}_z &= \exp(i\omega \sigma_z t / 2),
\end{aligned}$$

where  $\omega$  is the angular frequency (about  $\bar{z}$ ) of the rotating frame, for density operators we can apply

$$\rho' = \mathbf{O}_z \rho \mathbf{O}_z^\dagger$$

and use

$$\frac{d\rho'}{dt} = \frac{-i}{\hbar} [\mathbf{H}', \rho']$$

with

$$\begin{aligned}
\mathbf{H}' &= \mathbf{O}_z \mathbf{H} \mathbf{O}_z^{-1} - i\hbar \mathbf{O}_z \frac{d\mathbf{O}_z^{-1}}{dt} \\
&= \mathbf{O}_z \mathbf{H} \mathbf{O}_z^{-1} - \frac{\hbar\omega}{2} \sigma_z.
\end{aligned}$$

Let's return to our holding field  $B_0 \bar{z}$  plus rotating perturbation  $b_1(\cos(\omega t) \bar{x} + \sin(\omega t) \bar{y})$ ,

$$\mathbf{H} = \omega_L \mathbf{S}_z B_0 - \gamma b_1 (\cos(\omega t) \mathbf{S}_x + \sin(\omega t) \mathbf{S}_y),$$

$$\mathbf{H}' = \frac{1}{2} \hbar (\Delta \sigma_z - \gamma b_1 \sigma_x),$$

where  $\Delta = \omega_L - \omega$ . From this point on let's assume that we are always working in the rotating frame, so we can drop the primes ( $'$ ). Then

$$\begin{aligned}
\frac{dv_i}{dt} &= -\frac{i}{4} \text{Tr}[\sigma_i[\Delta\sigma_z - \gamma b_1 \sigma_x, (\mathbf{1} + v_x \sigma_x + v_y \sigma_y + v_z \sigma_z)]] \\
&= -\frac{i}{4} \text{Tr}[\sigma_i(\Delta\sigma_z - \gamma b_1 \sigma_x)(\mathbf{1} + v_x \sigma_x + v_y \sigma_y + v_z \sigma_z)] \\
&\quad + \frac{i}{4} \text{Tr}[\sigma_i(\mathbf{1} + v_x \sigma_x + v_y \sigma_y + v_z \sigma_z)(\Delta\sigma_z - \gamma b_1 \sigma_x)] \\
&= -\frac{i}{4} \text{Tr}[\sigma_i(\Delta\sigma_z(v_x \sigma_x + v_y \sigma_y) - \gamma b_1 \sigma_x(v_y \sigma_y + v_z \sigma_z))] \\
&\quad + \frac{i}{4} \text{Tr}[\sigma_i(\Delta(v_x \sigma_x + v_y \sigma_y)\sigma_z - \gamma b_1(v_y \sigma_y + v_z \sigma_z)\sigma_x)],
\end{aligned}$$

so

$$\begin{aligned}
\frac{dv_x}{dt} &= -\frac{i}{4} \text{Tr}[\sigma_x \Delta\sigma_z v_y \sigma_y - \sigma_x \Delta v_y \sigma_y \sigma_z] = -\Delta v_y, \\
\frac{dv_y}{dt} &= -\frac{i}{4} \text{Tr}[\sigma_y \Delta\sigma_z v_x \sigma_x - \sigma_y \Delta v_x \sigma_x \sigma_z] - \frac{i}{4} \text{Tr}[\sigma_y(-\gamma b_1 \sigma_x v_z \sigma_z) - \sigma_y(-\gamma b_1 v_z \sigma_z \sigma_x)] \\
&= \Delta v_x + \frac{i\gamma b_1 v_z}{4} \text{Tr}[\sigma_y \sigma_x \sigma_z - \sigma_y \sigma_z \sigma_x] = \Delta v_x + \gamma b_1 v_z, \\
\frac{dv_z}{dt} &= -\frac{i}{4} \text{Tr}[\sigma_z(-\gamma b_1 \sigma_x v_y \sigma_y) - \sigma_z(-\gamma b_1 v_y \sigma_y \sigma_x)] = \frac{i\gamma b_1 v_y}{4} \text{Tr}[\sigma_z \sigma_x \sigma_y - \sigma_z \sigma_y \sigma_x] = -\gamma b_1 v_y.
\end{aligned}$$

Copying out the results, we have

$$\begin{aligned}
\dot{v}_x &= -\Delta v_y, \\
\dot{v}_y &= \Delta v_x + \gamma b_1 v_z, \\
\dot{v}_z &= -\gamma b_1 v_y.
\end{aligned}$$

Given our previous results, we should not be surprised to discover that these may also be written as the vector equation

$$\frac{d}{dt} \vec{v} = \gamma \vec{v} \times \vec{B}_{\text{eff}},$$

where

$$\vec{B}_{\text{eff}} = \left( B_0 + \frac{\omega}{\gamma} \right) \vec{z} + b_1 \vec{x}.$$

Don't forget that we have defined  $\omega_L = -\gamma B_0$ .

Finally, we are ready to add relaxation (that is, damping and dephasing) terms! Phenomenologically, one can generally identify two distinct relaxation timescales for an ensemble of spins in contact with a heat bath or reservoir. These are known as the longitudinal relaxation time  $T_1$  and the transverse relaxation time  $T_2$ . Roughly speaking,  $T_1$  measures the time required for spins in the higher-energy eigenstate ( $|+_z\rangle$  if  $\gamma < 0$  as we have been assuming in these notes) to decay back down to the ground state (lower-energy eigenstate). Hence  $T_1$  is associated with energy dissipation, with longer  $T_1$  implying a lower rate of energy loss into the environment. The transverse relaxation time  $T_2$  accounts for dephasing, by which we mean the tendency of environmental interactions to randomly perturb the phase of Larmor precession. In the third term of this course we will use concrete models of the system-reservoir interaction to *derive* values for  $T_1$  and  $T_2$ , but for now we will just put them in by hand.

In terms of these two relaxation times, we can finally write down the full-blown **Bloch Equations**,

$$\begin{aligned}\dot{v}_x &= -\Delta v_y - v_x T_2^{-1}, \\ \dot{v}_y &= \Delta v_x + \gamma b_1 v_z - v_y T_2^{-1}, \\ \dot{v}_z &= -\gamma b_1 v_y - (v_z - v_z^0) T_1^{-1},\end{aligned}$$

where  $v_z^0$  is the value of  $v_z$  at thermal equilibrium.

We already understand that the Hamiltonian component of these equations (terms involving  $\Delta$  and  $\gamma b_1$ ) simply describe Larmor precession of the Bloch vector around the effective magnetic field in the rotating frame. In order to get some feeling for the role of the dissipative terms, let's look at the solutions with both  $\Delta$  and  $b_1$  set to zero. That is, we maintain a holding field  $B_0$  and work in a frame rotating at the Larmor frequency, but set the driving field to zero. The Bloch Equations become

$$\begin{aligned}\dot{v}_x &= -v_x T_2^{-1}, \\ \dot{v}_y &= -v_y T_2^{-1}, \\ \dot{v}_z &= -(v_z - v_z^0) T_1^{-1},\end{aligned}$$

for which we can easily write down the analytic solutions

$$\begin{aligned}v_x(t) &= v_x(0) \exp(-t/T_2), \\ v_y(t) &= v_y(0) \exp(-t/T_2), \\ v_z(t) &= (v_z(0) - v_z^0) \exp(-t/T_1) + v_z^0.\end{aligned}$$

Hence the components of the Bloch vector in the equatorial plane decay exponentially to zero, with time constant  $T_2$ , and the  $z$  component of the Bloch vector decays exponentially to its equilibrium value  $v_z^0$  with time constant  $T_1$ .

A typical mechanism that would contribute to  $T_1$  for a collection of spins is collisional interactions. If our spins correspond to the nuclear spins of gas-phase atoms such as  $^{129}\text{Xe}$ , then the spin of any given atom in the ensemble will be randomly perturbed through collisions with other atoms in the gas. Since each atom carries a magnetic moment, any time two atoms pass close by one another they will each experience a time-dependent magnetic field. The envelope and direction of this field "pulse" will essentially be random, as it depends on the details of the atomic spatial trajectories during the collision. If the collisions have a duration  $\tau$  that is comparable to the inverse Larmor frequency (for whatever holding field is being applied), we may expect that the  $x$  and  $y$  components of the field pulse will have Fourier components near  $\omega_L$  and collision-induced spin flips may occur. Appealing to general thermodynamic considerations, we may expect that the net effect of such spin flips will be to bring the energy distribution of the spins into equilibrium with the overall temperature of the gas (hence  $v_z^0$ ).

Dephasing can occur if the system-reservoir interaction leads to randomly varying  $B_z$ . If the individual spins in the ensemble experience small perturbing fields  $\delta B$  in addition to the holding field  $B_0$ , then they will precess around  $\bar{z}$  at slightly different frequencies. Viewed in the rotating frame at the "average" Larmor frequency  $\omega_L$ , this means that the Bloch vectors corresponding to the members of the ensemble will gradually "fan out" with respect to the longitudinal angle  $\varphi$ . After some time, we may expect that the distribution in  $\varphi$  should become uniform, meaning that the ensemble-average Bloch vector would have  $v_x = v_y = 0$ . The timescale  $T_2$  for such dephasing to occur can be derived explicitly for various models of  $\delta B$ .