

Spin state classification

Operator-state duality

The trace expression for the expectation value of the observables

$$\langle A \rangle = \text{Tr}(\mathbf{A}\boldsymbol{\rho}) \quad (1)$$

gives the density operator formalism a convenient property – the density matrix with specific expectation values of orthogonal operators is a linear combination of the corresponding operators.

For example, if a spin- $\frac{1}{2}$ particle is completely polarized along the Z axis, that is, $|\psi\rangle = |\alpha\rangle = \begin{pmatrix} 1 & 0 \end{pmatrix}^T$, then the corresponding density matrix is:

$$\boldsymbol{\rho} = |\psi\rangle\langle\psi| = |\alpha\rangle\langle\alpha| = \begin{pmatrix} 1 & \\ & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \frac{\mathbf{1}}{2} + \mathbf{L}_Z \quad (2)$$

where the unit matrix is inconsequential because it commutes with everything and does not influence the observable quantities. We can therefore simply say that $\boldsymbol{\rho} = \mathbf{L}_Z$. It can be similarly shown that $\boldsymbol{\rho}$ for the spin oriented along X and Y axes is equal to \mathbf{L}_X and \mathbf{L}_Y operators respectively. This leads to the common practice of associating spin operators with the state of the spin system. When we say that the spin system is “in the \mathbf{L}_Z state”, this means that its density operator is equal to \mathbf{L}_Z .

Treatment of composite systems

It is a standard result in quantum mechanics that, for a system composed of two non-interacting uncorrelated subsystems, the total wavefunction is a product of the wavefunctions of the subsystems. In matrix-vector representations, the corresponding operation is called *direct product*:

$$|\psi_{AB}\rangle = |\psi_A\rangle \otimes |\psi_B\rangle \quad (3)$$

It is defined in the following way:

$$\mathbf{A} \otimes \mathbf{B} = \begin{bmatrix} a_{11}\mathbf{B} & \cdots & a_{1n}\mathbf{B} \\ \vdots & \ddots & \vdots \\ a_{m1}\mathbf{B} & \cdots & a_{mn}\mathbf{B} \end{bmatrix} \quad (4)$$

The following properties are relevant:

$$(\mathbf{A} \otimes \mathbf{B})(\mathbf{C} \otimes \mathbf{D}) = (\mathbf{AC}) \otimes (\mathbf{BD}) \quad \text{Tr}(\mathbf{A} \otimes \mathbf{B}) = \text{Tr}(\mathbf{A})\text{Tr}(\mathbf{B}) \quad (5)$$

For the density matrix of the composite system we therefore have:

$$\begin{aligned} \boldsymbol{\rho}_{AB} &= |\psi_{AB}\rangle\langle\psi_{AB}| = (|\psi_A\rangle \otimes |\psi_B\rangle)(\langle\psi_A| \otimes \langle\psi_B|) = \\ &= (|\psi_A\rangle\langle\psi_A|) \otimes (|\psi_B\rangle\langle\psi_B|) = \boldsymbol{\rho}_A \otimes \boldsymbol{\rho}_B \end{aligned} \quad (6)$$

The Hamiltonian is built differently – the two parts must only affect their own subsystems, and must leave the other subsystem intact. The Hamiltonian of a non-interacting two-spin system is therefore:

$$\mathbf{H}_{AB} = \mathbf{H}_A \otimes \mathbf{1}_B + \mathbf{1}_A \otimes \mathbf{H}_B \quad (7)$$

where $\mathbf{1}$ denotes a unit matrix of the dimension matching the density matrix dimension of the subsystem indicated in the subscript. This procedure may be extended to multiple spins.

Relaxation of product states

In the case when the two spins do not interact, and the noise in the Hamiltonian that relaxes them is uncorrelated, the relaxation rate of the product state is the sum of the relaxation rates of the individual states, for example:

$$\begin{aligned}
 R_{L_z S_z} &= \frac{1}{N} \text{Tr} \left[(\mathbf{L}_z \otimes \mathbf{S}_z) \hat{\mathbf{R}} (\mathbf{L}_z \otimes \mathbf{S}_z) \right] = \\
 &= \frac{1}{N} \text{Tr} \left[(\mathbf{L}_z \otimes \mathbf{S}_z) \left(\hat{\mathbf{R}}_L \otimes \mathbf{1} + \mathbf{1} \otimes \hat{\mathbf{R}}_S \right) (\mathbf{L}_z \otimes \mathbf{S}_z) \right] = \\
 &= \frac{1}{N} \text{Tr} \left[(\mathbf{L}_z \otimes \mathbf{S}_z) \left(\hat{\mathbf{R}}_L \otimes \mathbf{1} \right) (\mathbf{L}_z \otimes \mathbf{S}_z) \right] + \\
 &\quad + \frac{1}{N} \text{Tr} \left[(\mathbf{L}_z \otimes \mathbf{S}_z) \left(\mathbf{1} \otimes \hat{\mathbf{R}}_S \right) (\mathbf{L}_z \otimes \mathbf{S}_z) \right] = \\
 &= \frac{1}{N} \text{Tr} \left[\mathbf{L}_z \hat{\mathbf{R}}_L \mathbf{L}_z \right] \text{Tr} \left[\mathbf{S}_z^2 \right] + \frac{1}{N} \text{Tr} \left[\mathbf{L}_z^2 \right] \text{Tr} \left[\mathbf{S}_z \hat{\mathbf{R}}_S \mathbf{S}_z \right] = \\
 &= R_{L_z} + R_{S_z}
 \end{aligned} \tag{8}$$

where N is the normalisation factor. In practice the noises are often correlated and the spins do interact, but the sum of the rates is a reasonable upper bound on the relaxation rate of the product state.

Spin state classification

Following the derivations given in the previous lecture, we will classify the basis of the density matrix space according to the physical meaning of the corresponding observable operators. Note that for historical reasons $\hat{L}_z \hat{S}_z \hat{I}_z$ means $\hat{L}_z \otimes \hat{S}_z \otimes \hat{I}_z$ crossed with the identity operators on any other spins that are not explicitly mentioned. The common classification identifies:

1. Identity (unit) operator: usually denoted \hat{E} . When a unit operator is supplied for a particular spin in the direct product of operators, the result corresponds to an average, with equal weights, over all possible states of that spin. Unit operators are typically included implicitly – *e.g.* in a two spin system, the $\hat{L}_z \otimes \hat{E}$ operator corresponding to the average Z-magnetization of the first spin would be abbreviated to just \hat{L}_z .
2. Longitudinal single-spin orders: $\hat{L}_z, \hat{S}_z, \text{etc.}$ These correspond to population differences between energy levels that are one spin flip away from each other, they are also known as *longitudinal magnetization*.
3. Longitudinal multi-spin orders: $\hat{L}_z \hat{S}_z, \hat{L}_z \hat{S}_z \hat{I}_z, \text{etc.}$ These also correspond to population differences across levels connected by single-spin flips, but the sign of the population difference depends on the state that other spins have in a particular pair of energy levels. The other name for these states is *longitudinal correlations*.
4. Transverse single-spin orders: $\hat{L}_x, \hat{S}_y, \hat{L}_+, \text{etc.}$ These correspond to observable transverse magnetization in the system and originate from the presence of linear combinations of Hamiltonian eigenfunctions in the wavefunction.

5. Transverse multi-spin orders: $\hat{L}_x \hat{S}_y, \hat{L}_+ \hat{S}_-,$ etc. Although they nominally involve transverse spin operators, these states do not yield observable transverse magnetization. For spin ensembles they correspond to correlations between the linear combination coefficients in wavefunctions across the ensemble.
6. Mixed spin orders: $\hat{L}_z \hat{S}_+,$ etc. These do not have a systematic classification and correspond to complicated correlations between longitudinal magnetization and time dynamics. Some mixed spin orders are interpretable ($\hat{L}_z \hat{S}_+$ is the transverse precession of the S spin with the precession phase dependent on the state of spin L), but this is rarely the case in general.

Several specific spin states and classes of spin states have historical names:

1. Coherences: a spin state $\hat{\rho}$ having the following property under the commutation action by the total spin projection operator:

$$[\hat{L}_z, \hat{\rho}] = k \hat{\rho} \quad \hat{L}_z = \sum_n \hat{L}_z^{(n)} \quad (9)$$

is often referred to as k -*quantum coherence*. If a state is written as a Kronecker product of raising and lowering operators, e.g. $\hat{L}_+ \hat{S}_- \hat{I}_z$, then the coherence order k is equal to the number of “+” operators minus the number of “-” operators in the direct product (Z operators do not contribute). Of particular note are *single-quantum coherences* (\hat{L}_+ and \hat{L}_-) because they correspond to the observable transverse magnetization. Non-Hermitian \hat{L}_\pm operators make an appearance because they correspond to quadrature-detected magnetization:

$$\langle \hat{L}_x \rangle \pm i \langle \hat{L}_y \rangle = \langle \hat{L}_x \pm i \hat{L}_y \rangle = \langle \hat{L}_\pm \rangle \quad (10)$$

2. Correlations: a spin state having k non-unit operators in its direct product representation is called a k -spin correlation because it describes the collective behaviour of those spins. High-order correlations often relax faster than low-order correlations.
3. Singlet and triplet: the following spin states are eigenfunctions of the symmetry operator that permutes the labels on the two particles:

$$\begin{aligned} |S\rangle &= \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle), & |S\rangle\langle S| &= \frac{1}{4} \hat{E} - (\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z) \\ |T_+\rangle &= |\alpha\alpha\rangle, & |T_0\rangle &= \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle), & |T_-\rangle &= |\beta\beta\rangle \end{aligned} \quad (11)$$

Because many spin interactions are symmetric with respect to the permutation of particle labels, these functions also span subspaces that are invariant under their Hamiltonians. In particular, the invariance of the singlet state under the dipolar Hamiltonian can in some cases make it very long-lived.

Practical analysis of pulse sequences is often performed in terms of coherence orders and correlation orders that the system is steered through by the sequence. Different coherence orders in particular respond differently to pulses and pulsed field gradients.