

Treatment of composite systems

For a system composed of two non-interacting and 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*:

$$|\psi_{AB}\rangle = |\psi_A\rangle \otimes |\psi_B\rangle \quad (1)$$

It is defined in the following way:

$$\mathbf{A} \otimes \mathbf{B} = \begin{bmatrix} a_{11}\mathbf{B} & \cdots & a_{1n}\mathbf{B} \\ \vdots & \ddots & \vdots \\ a_{m1}\mathbf{B} & \cdots & a_{mn}\mathbf{B} \end{bmatrix} \quad (2)$$

The following properties are relevant:

$$(\mathbf{A} \otimes \mathbf{B})(\mathbf{C} \otimes \mathbf{D}) = (\mathbf{AC}) \otimes (\mathbf{BD}) \quad \text{Tr}(\mathbf{A} \otimes \mathbf{B}) = \text{Tr}(\mathbf{A})\text{Tr}(\mathbf{B}) \quad (3)$$

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

$$\begin{aligned} \hat{\rho}_{AB} &= |\psi_{AB}\rangle \langle \psi_{AB}| = (|\psi_A\rangle \otimes |\psi_B\rangle) (\langle \psi_A| \otimes \langle \psi_B|) = \\ &= (|\psi_A\rangle \langle \psi_A|) \otimes (|\psi_B\rangle \langle \psi_B|) = \hat{\rho}_A \otimes \hat{\rho}_B \end{aligned} \quad (4)$$

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:

$$\hat{H}_{AB} = \hat{H}_A \otimes \mathbf{1}_B + \mathbf{1}_A \otimes \hat{H}_B \quad (5)$$

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.

Superoperators

Linear transformations of operators may be thought of as more general “super” operators. An example is the *commutation superoperator*, defined as:

$$\hat{H} \hat{\rho} = [\hat{H}, \hat{\rho}] = \hat{H} \hat{\rho} - \hat{\rho} \hat{H} \quad (6)$$

A useful feature of this notation is that it returns LvN equation into Schrödinger’s form:

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(t) &= -i[\hat{H}(t), \hat{\rho}(t)] \quad \Rightarrow \quad \hat{\rho}(t) = \exp[-i\hat{H}t] \hat{\rho}(0) \exp[+i\hat{H}t] \\ \frac{\partial}{\partial t} \hat{\rho}(t) &= -i\hat{H} \hat{\rho}(t) \quad \Rightarrow \quad \hat{\rho}(t) = \exp[-i\hat{H}t] \hat{\rho}(0) \end{aligned} \quad (7)$$

Important processes (notably relaxation and kinetics) are described by superoperators.

Thermal equilibrium

In an ensemble of identical systems in thermal equilibrium, there are no correlations and the probability of finding a system in the energy level n is given by Boltzmann’s law:

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle, \quad p_n = \frac{\exp(-E_n/kT)}{\sum_m \exp(-E_m/kT)} \quad (8)$$

These probabilities are the diagonal terms of the density matrix, therefore:

$$\hat{\rho}_{\text{eq}} = \frac{\sum_n |\psi_n\rangle \exp(-E_n/kT) \langle \psi_n|}{\sum_n \exp(-E_n/kT)} = \frac{\exp(-\hat{H}/kT)}{\text{Tr}[\exp(-\hat{H}/kT)]} \approx \frac{1}{\text{Tr}[\mathbf{1}]} (\mathbf{1} - \hat{H}/kT) \quad (9)$$

The high temperature approximation is valid when $\|\hat{H}\| \ll kT$, where the norm of the Hamiltonian is defined as its largest eigenvalue. The unit matrix is inconsequential: it commutes with the Hamiltonian and does not influence the observables. In practical calculations it is commonly ignored.

Spin state classification

The trace expression for the expectation value of the observables

$$\langle A \rangle = \text{Tr}(\hat{A}\hat{\rho}) \quad (10)$$

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, $|\psi\rangle = |\alpha\rangle = (1 \ 0)^T$, then the corresponding density matrix is:

$$\hat{\rho} = |\psi\rangle\langle\psi| = |\alpha\rangle\langle\alpha| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \frac{1}{2} + \hat{L}_z \quad (11)$$

where the unit matrix is inconsequential and we can simply say that $\hat{\rho} = \hat{L}_z$. It can be similarly shown that $\hat{\rho}$ for the spin oriented along X and Y axes is equal to \hat{L}_x and \hat{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 \hat{L}_z state”, this means that its density operator is equal to \hat{L}_z .

Spin states may be classified according to the physical meaning of the corresponding observable operators. The standard classification identifies (direct product signs skipped for brevity):

1. Longitudinal single-spin orders: \hat{L}_z, \hat{S}_z , etc. These are population differences between energy levels that are one spin flip away from each other. They are also known as *longitudinal magnetization*.
2. Longitudinal multi-spin orders: $\hat{L}_z\hat{S}_z, \hat{L}_z\hat{S}_z\hat{I}_z$, etc. These also correspond to population differences across levels connected by single-spin flips, but the sign of the difference depends on the state that other spins have. Also known as *longitudinal correlations*.
3. Transverse single-spin orders: $\hat{L}_x, \hat{S}_y, \hat{L}_+$, etc. These are off-diagonal terms in the density operator corresponding to observable *transverse magnetization*.
4. Transverse multi-spin orders: $\hat{L}_x\hat{S}_y, \hat{L}_+\hat{S}_-$, etc. These are off-diagonal terms in the density operator that are not directly connected to observable magnetisation.
5. Mixed spin orders: $\hat{L}_z\hat{S}_+$, etc. These do not have a systematic classification and correspond to complicated correlations between longitudinal and transverse magnetisation of different spins.

Coherences and correlations

Two specific 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 \hat{L}_Z spin projection operator:

$$[\hat{L}_Z, \hat{\rho}] = k\hat{\rho} \quad \hat{L}_Z = \sum_n \hat{L}_Z^{(n)} \quad (12)$$

is often referred to as k -quantum coherence. Of particular note are *single-quantum coherences* (\hat{L}_+ and \hat{L}_-) because they correspond to the observable transverse magnetization.

2. Correlations: any product operator involving k spins is called a k -spin correlation because it describes the collective behaviour of those spins.

Practical analysis of pulse sequences is often performed in terms of coherences and correlations that the system is steered through by the sequence.