22.3 Dynamics of Density Matrices

Since the density matrix describes in all generality the possible quantum states of a system, it is of interest to see how it evolves in time. To this end we need the Schrödinger equation written for a ket $|\psi\rangle$ as well as for a bra $\langle\psi|$:

$$\frac{\partial}{\partial t}|\psi\rangle = -\frac{i}{\hbar}\hat{H}|\psi\rangle, \qquad \frac{\partial}{\partial t}\langle\psi| = \frac{i}{\hbar}\langle\psi|\hat{H}. \tag{22.3.1}$$

Here $\hat{H}$ is the Hamiltonian. We can now compute the rate of change of the projector $|\psi\rangle\langle\psi|$:

$$\frac{\partial}{\partial t}|\psi\rangle\langle\psi| = -\frac{i}{\hbar}\hat{H}|\psi\rangle\langle\psi| + \frac{i}{\hbar}|\psi\rangle\langle\psi|\hat{H} = -\frac{i}{\hbar}\,[\hat{H}, |\psi\rangle\langle\psi|\,]. \tag{22.3.2}$$

Using the ensemble definition of the density matrix, we then get

$$\begin{aligned}\frac{\partial\rho}{\partial t} &= \frac{\partial}{\partial t}\sum_{a=1}^{n} p_a|\psi_a\rangle\langle\psi_a| = \sum_{a=1}^{n} p_a\frac{\partial}{\partial t}|\psi_a\rangle\langle\psi_a| = -\frac{i}{\hbar}\sum_{a=1}^{n} p_a[\hat{H},\, |\psi_a\rangle\langle\psi_a|\,] \\ &= -\frac{i}{\hbar}\Big[\hat{H},\, \sum_{a=1}^{n} p_a|\psi_a\rangle\langle\psi_a|\,\Big].\end{aligned} \tag{22.3.3}$$

This implies the simple result

$$\boxed{i\hbar\,\frac{\partial\rho}{\partial t} = [\hat{H},\, \rho].} \tag{22.3.4}$$

This equation determines the time evolution of the density matrix of a quantum system. It manifestly preserves the Hermiticity of ρ because it sets its derivative $\frac{\partial\rho}{\partial t}$ equal to a Hermitian operator. Indeed, $\frac{1}{i\hbar}[\hat{H}, \rho]$ is Hermitian because the commutator of Hermitian operators is anti-Hermitian, and the factor of i makes it Hermitian. Moreover, the trace of ρ is unchanged:

$$\frac{d}{dt}\mathrm{tr}\rho = \mathrm{tr}\left(\frac{\partial\rho}{\partial t}\right) = -\frac{i}{\hbar}\mathrm{tr}[\hat{H}, \rho] = 0, \tag{22.3.5}$$

since the trace of a commutator vanishes due to cyclicity. This is automatic in finite-dimensional vector spaces but must be checked carefully when working in infinite-dimensional vector spaces.

Suppose we solve for the time evolution of states by constructing the unitary operator $\mathcal{U}(t)$ that evolves states as follows:

$$|\psi(t)\rangle = \mathcal{U}(t)|\psi(0)\rangle. \tag{22.3.6}$$

It is then clear that the density matrix, which at any time is a sum of terms of the form $|\psi_a(t)\rangle\langle\psi_a(t)|$, evolves as

$$\rho(t) = \mathcal{U}(t)\rho(0)\mathcal{U}^\dagger(t). \tag{22.3.7}$$

This evolution, of course, is consistent with the differential equation (22.3.4) when we recall the differential equation satisfied by the unitary operator (see (16.3.2)). The above expression for $\rho(t)$ makes it manifest that if $\rho(0)$ is positive semidefinite, so is $\rho(t)$ for all times t. Indeed, for any vector v in the state space we see that

$$\langle v|\rho(t)|v\rangle = \langle v|\mathcal{U}\rho(0)\mathcal{U}^\dagger|v\rangle = \langle \mathcal{U}^\dagger v|\rho(0)|\mathcal{U}^\dagger v\rangle \geq 0. \tag{22.3.8}$$

We know from the Schrödinger equation that a pure state $|\psi\rangle$ remains pure under time evolution. This is also visible from the density matrix $\rho(t) = \square(t)|\psi\rangle\langle\psi|\square^\dagger(t)$. In fact, a more general result holds. We can quickly see that the purity $\zeta = \text{tr}\rho^2$ does not change over time:

$$\begin{aligned}\frac{d\zeta}{dt} &= \frac{d}{dt}\text{tr}(\rho\,\rho) = \text{tr}\Big(\frac{d\rho}{dt}\rho + \rho\frac{d\rho}{dt}\Big) = 2\text{tr}\Big(\rho\frac{d\rho}{dt}\Big)\\ &= \tfrac{2}{i\hbar}\text{tr}\big(\rho[\hat{H},\rho]\big) = \tfrac{2}{i\hbar}\text{tr}\big(\rho\hat{H}\rho - \rho\rho\hat{H}\big) = 0,\end{aligned} \tag{22.3.9}$$

by repeated use of the cyclicity of the trace. Since the purity does not change under unitary time evolution and a pure state has purity equal to one, a pure state will remain pure.

Exercise 22.4. *What we observed for the purity is in fact part of a simple pattern. Show that tr(ρ^n) is conserved under unitary time evolution for n an arbitrary positive integer.*

The considerations of time evolution in this section apply to isolated systems. They change in an interesting way when we consider the density matrix of a *subsystem* of an isolated system, as we will begin exploring next.