5.2: Time-Evolution of the Density Matrix

The equation of motion for the density matrix follows naturally from the definition of ρ and the time-dependent Schrödinger equation.

$$\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial t}[|\psi\rangle\langle\psi|] \tag{5.2.1}$$

$$= \left[\frac{\partial}{\partial t}|\psi\rangle\right]\langle\psi| + |\psi\rangle\frac{\partial}{\partial t}\langle\psi| \tag{5.2.2}$$

$$= \frac{-i}{\hbar}H|\psi\rangle\langle\psi| + \frac{i}{\hbar}|\psi\rangle\langle\psi|H. \tag{5.2.3}$$

$$= \frac{-i}{\hbar}[H,\rho] \tag{5.2.4}$$

Equation 5.2.4 is the **Liouville-Von Neumann equation**. It is isomorphic to the Heisenberg equation of motion, since ρ is also an operator. The solution to Equation 5.2.4 is

$$\rho(t) = U\rho(0)U^\dagger \tag{5.2.5}$$

This can be demonstrated by first integrating Equation 5.2.4 to obtain

$$\rho(t) = \rho(0) - \frac{i}{\hbar}\int_0^t d\tau[H(\tau),\rho(\tau)] \tag{5.2.6}$$

If we expand Equation 5.2.6 by iteratively substituting into itself, the expression is the same as when we substitute

$$U = \exp_+\left[-\frac{i}{\hbar}\int_0^t d\tau H(\tau)\right] \tag{5.2.7}$$

into Equation 5.2.5 and collect terms by orders of $H(\tau)$.

Note that Equation 5.2.5 and the cyclic invariance of the trace imply that the time-dependent expectation value of an operator can be calculated either by propagating the operator (Heisenberg) or the density matrix (Schrödinger or interaction picture):

$$\begin{aligned}\langle\hat{A}(t)\rangle &= \mathrm{Tr}[\hat{A}\rho(t)] \\ &= \mathrm{Tr}\left[\hat{A}U\rho_0U^\dagger\right] \\ &= \mathrm{Tr}\left[\hat{A}(t)\rho_0\right]\end{aligned}$$

For a time-independent Hamiltonian it is straightforward to show that the density matrix elements evolve as

$$\rho_{nm}(t) = \langle n|\rho(t)|m\rangle \tag{5.2.8}$$

$$= \langle n|U|\psi_0\rangle\left\langle\psi_0\left|U^\dagger\right|m\right\rangle \tag{5.2.9}$$

$$= e^{-i\omega_{nm}(t-t_0)}\rho_{nm}(t_0) \tag{5.2.10}$$

From this we see that populations, $\rho_{mn}(t) = \rho_{nm}(t_0)$, are time-invariant, and coherences oscillate at the energy splitting ω_{nm}.