

## 10.3: Time evolution of the density operator

The time evolution of the operator  $\rho$  can be predicted directly from the Schrödinger equation. Since  $\rho(t)$  is given by

$$\rho(t) = \sum_{\alpha=1}^Z |\Psi^{(\alpha)}(t)\rangle \langle \Psi^{(\alpha)}(t)|$$

the time derivative is given by

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \sum_{\alpha=1}^Z \left[ \left( \frac{\partial}{\partial t} |\Psi^{(\alpha)}(t)\rangle \right) \langle \Psi^{(\alpha)}(t)| + |\Psi^{(\alpha)}(t)\rangle \left( \frac{\partial}{\partial t} \langle \Psi^{(\alpha)}(t)| \right) \right] \\ &= \frac{1}{i\hbar} \sum_{\alpha=1}^Z \left[ \left( H |\Psi^{(\alpha)}(t)\rangle \right) \langle \Psi^{(\alpha)}(t)| - |\Psi^{(\alpha)}(t)\rangle \left( \langle \Psi^{(\alpha)}(t)| H \right) \right] \\ &= \frac{1}{i\hbar} (H\rho - \rho H) \\ &= \frac{1}{i\hbar} [H, \rho] \end{aligned}$$

where the second line follows from the fact that the Schrödinger equation for the bra state vector  $\langle \Psi^{(\alpha)}(t)|$  is

$$-i\hbar \frac{\partial}{\partial t} \langle \Psi^{(\alpha)}(t)| = \langle \Psi^{(\alpha)}(t)| H$$

Note that the equation of motion for  $\rho(t)$  differs from the usual Heisenberg equation by a minus sign! Since  $\rho(t)$  is constructed from state vectors, it is not an observable like other hermitian operators, so there is no reason to expect that its time evolution will be the same. The general solution to its equation of motion is

$$\begin{aligned} \rho(t) &= e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} \\ &= U(t) \rho(0) U^\dagger(t) \end{aligned}$$

The equation of motion for  $\rho(t)$  can be cast into a quantum Liouville equation by introducing an operator

$$iL = \frac{1}{i\hbar} [\dots, H]$$

In term of  $iL$ , it can be seen that  $\rho(t)$  satisfies

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -iL\rho \\ \rho(t) &= e^{-iLt} \rho(0) \end{aligned}$$

What kind of operator is  $iL$ ? It acts on an operator and returns another operator. Thus, it is not an operator in the ordinary sense, but is known as a *superoperator* or *tetradic operator* (see S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford University Press, New York (1995)).

Defining the evolution equation for  $\rho$  this way, we have a perfect analogy between the density matrix and the state vector. The two equations of motion are

$$\begin{aligned} \frac{\partial}{\partial t} |\Psi(t)\rangle &= -\frac{i}{\hbar} H |\Psi(t)\rangle \\ \frac{\partial}{\partial t} \rho(t) &= -iL\rho(t) \end{aligned}$$

We also have an analogy with the evolution of the classical phase space distribution  $f(\mathbf{\Gamma}, t)$ , which satisfies

$$\frac{\partial f}{\partial t} = -iLf$$

with  $iL = \{\dots, H\}$  being the classical Liouville operator. Again, we see that the limit of a commutator is the classical Poisson bracket.

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