12.1: Perturbative solution of the Liouville equation

As in the classical case, we assume a solution of the form

$$\rho(t) = \rho_0(H_0) + \Delta\rho(t)$$

where

$$[H_0, \rho_0] = 0 \qquad \Rightarrow \qquad \frac{\partial \rho_0}{\partial t} = 0$$

and we will assume

$$\rho_0(H_0) = \frac{e^{-\beta H_0}}{Q(N,V,T)}$$

Substituting into the Liouville equation and working to first order in small quantities, we find

$$\frac{\partial \Delta\rho}{\partial t} = \frac{1}{i\hbar}[H_0, \Delta\rho] - \frac{1}{i\hbar}[B, \rho_0] F_e(t)$$

which is a **first order inhomogeneous equation** that can be solved by using an integrating factor:

$$\Delta\rho(t) = -\frac{1}{i\hbar}\int_{-\infty}^{t} ds\; e^{-iH_0(t-s)/\hbar}[B, \rho_0] e^{iH_0(t-s)/\hbar} F_e(s)$$

(Note that we have chosen the origin in time to be $t = -\infty$, which is an arbitrary choice.)

For an observable A, the expectation value is

$$\langle A(t)\rangle = \mathrm{Tr}(\rho A) = \langle A\rangle_0 + \mathrm{Tr}(\Delta\rho(t) A)$$

when the solution for $\Delta\rho$ is substituted in, this becomes

$\langle A(t)\rangle$	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\; ds\; \mathrm{Tr}\, [Ae^{-iH_0(t-s)/hbar}[B, \rho_0] e^{iH_0(t-}$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\; ds\; \mathrm{Tr}\, [e^{iH_0(t-s)/\hbar} Ae^{-iH_0(t-s)/hbar}[B$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar} ds\; \mathrm{Tr}\, [A(t-s)[B, \rho_0]]\, F_e(s)$

where the cyclic property of the trace has been used and the Heisenberg evolution for A has been substituted in. Expanding the commutator gives

$\langle A(t)\rangle$	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\; ds\; \mathrm{Tr}\, [A(t-s)B\rho_0 - A(t-s)\rho_0 B]$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\; ds\; \mathrm{Tr}\, [\rho_0\, (A(t-s)B - BA(t-s))]$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\; ds\; F_e(s)\langle [A(t-s), B(0)]_0\rangle$

where the cyclic property of the trace has been used again. Define a function

$$\Phi_{AB}(t) = \frac{i}{\hbar}\langle [A(t), B(0)]\rangle_0$$

called the *after effect function*. It is essentially the antisymmetric quantum time correlation function, which involves the commutator between $A(t)$ and $B(0)$. Then the linear response result can be written as

$$\langle A(t)\rangle = \langle A\rangle_0 + \int_{-\infty}^{t} dsF_e(s)\Phi_{AB}(t-s)$$

which is the starting point for the theory of quantum transport coefficients. If we choose to measure the operator B, then we find

$$\langle B(t)\rangle = \langle B\rangle_0 + \int_{-\infty}^{t} ds\; F_e(s)\Phi_{BB}(t-s)$$