11.2: Quantum Linear Response Functions

To develop a quantum description of the linear response function, we start by recognizing that the response of a system to an applied external agent is a problem we can solve in the interaction picture. Our time-dependent Hamiltonian is

$$\begin{aligned} H(t) &= H_0 - f(t)\hat{A} && (11.2.1)\\ &= H_0 + V(t) && (11.2.2)\end{aligned}$$

H_o is the material Hamiltonian for the equilibrium system. The external agent acts on the equilibrium system through $\hat{A}$, an operator in the system states, with a time-dependence $f(t)$. We take $V(t)$ to be a small change, and treat this problem with perturbation theory in the interaction picture.

We want to describe the nonequilibrium response $\overline{A(t)}$, which we will get by ensemble averaging the expectation value of $\hat{A}$, i.e. $\overline{\langle A(t)\rangle}$. Remember the expectation value for a pure state in the interaction picture is

$$\begin{aligned} \langle A(t)\rangle &= \langle \psi_I(t) | A_I(t) | \psi_I(t)\rangle && (11.2.3)\\ &= \left\langle \psi_0 \left| U_I^\dagger A_I U_I \right| \psi_0 \right\rangle && (11.2.4)\end{aligned}$$

The interaction picture Hamiltonian for Equation 11.2.2is

$$\begin{aligned} V_I(t) &= U_0^\dagger(t) V(t) U_0(t)\\ &= -f(t) A_I(t)\end{aligned}$$

To calculate an ensemble average of the state of the system after applying the external potential, we recognize that the nonequilibrium state of the system characterized by described by $|\psi_I(t)\rangle$ is in fact related to the initial equilibrium state of the system $|\psi_o\rangle$ through a time-propagator, as seen in Equation 11.2.4. So the nonequilibrium expectation value $\overline{A(t)}$ is in fact obtained by an equilibrium average over the expectation value of $U_I^\dagger A_I U_I$:

$$\overline{A(t)} = \sum_n p_n \left\langle n \left| U_I^\dagger A_I U_I \right| n \right\rangle \tag{11.2.5}$$

Again $|n\rangle$ are eigenstates of H_o. Working with the first order solution to $U_I(t)$

$$U_I(t-t_0) = 1 + \frac{i}{\hbar} \int_{t_0}^{t} dt' f(t') A_I(t') \tag{11.2.6}$$

we can now calculate the value of the operator $\hat{A}$ at time t, integrating over the history of the applied interaction $f(t')$:

$$\begin{aligned} A(t) &= U_I^\dagger A_I U_I\\ &= \left\{1 - \frac{i}{\hbar}\int_{t_0}^{t} dt' f(t') A_I(t')\right\} A_I(t) \left\{1 + \frac{i}{\hbar}\int_{t_0}^{t} dt' f(t') A_I(t')\right\}\end{aligned}$$

Here note that f is the time-dependence of the external agent. It does not involve operators in H_o and commutes with A. Working toward the linear response function, we just retain the terms linear in

$$\begin{aligned} A(t) &\cong A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt'\, f(t') \{A_I(t) A_I(t') - A_I(t') A_I(t)\}\\ &= A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt'\, f(t') [A_I(t), A_I(t')]\end{aligned}$$

Since our system is initially at equilibrium, we set $t_0 = -\infty$ and switch variables to the time interval $\tau = t - t'$ and using

$$A_I(t) = U_0^\dagger(t) A U_0(t) \tag{11.2.7}$$

to obtain

$$A(t)=A_I(t)+\frac{i}{\hbar}\int_0^\infty d\tau\, f(t-\tau)\left[A_I(\tau),A_I(0)\right] \tag{11.2.8}$$

We can now calculate the expectation value of A by performing the ensemble-average described in Equation 11.2.5. Noting that the force is applied equally to each member of ensemble, we have

$$\overline{A(t)}=\langle A\rangle+\frac{i}{\hbar}\int_0^\infty d\tau f(t-\tau)\left\langle\left[A_I(\tau),A_I(0)\right]\right\rangle \tag{11.2.9}$$

The first term is independent of f, and so it comes from an equilibrium ensemble average for the value of A.

$$\langle A(t)\rangle=\sum_n p_n\left\langle n\left|A_I\right|n\right\rangle=\langle A\rangle \tag{11.2.10}$$

The second term is just an equilibrium ensemble average over the commutator in $A_I(t)$:

$$\left\langle\left[A_I(\tau),A_I(0)\right]\right\rangle=\sum_n p_n\left\langle n\left|\left[A_I(\tau),A_I(0)\right]\right|n\right\rangle \tag{11.2.11}$$

Comparing Equation 11.2.9 with the expression for the linear response function, we find that the quantum linear response function is

$$\begin{aligned} R(\tau) & =-\frac{i}{\hbar}\left\langle\left[A_I(\tau),A_I(0)\right]\right\rangle & \tau\geq 0 \\ & =0 & \tau<0 \end{aligned} \tag{11.2.12}$$

or as it is sometimes written with the unit step function in order to enforce causality:

$$R(\tau)=-\frac{i}{\hbar}\Theta(\tau)\left\langle\left[A_I(\tau),A_I(0)\right]\right\rangle \tag{11.2.13}$$

The important thing to note is that the time-development of the system with the applied external potential is governed by the dynamics of the equilibrium system. All of the time-dependence in the response function is under H_o.

The linear response function is therefore the sum of two correlation functions with the order of the operators interchanged, which is the imaginary part of the correlation function $C''(\tau)$

$$\begin{aligned} R(\tau) & =-\frac{i}{\hbar}\Theta(\tau)\left\{\left\langle A_I(\tau)A_I(0)\right\rangle-\left\langle A_I(0)A_I(\tau)\right\rangle\right\} \\ & =-\frac{i}{\hbar}\Theta(\tau)\left(C_{AA}(\tau)-C_{AA}^*(\tau)\right) \\ & =\frac{2}{\hbar}\Theta(\tau)C''(\tau) \end{aligned}$$

As we expect for an observable, the response function is real. If we express the correlation function in the eigenstate description:

$$C(t)=\sum_{n,m}p_n\left|A_{mn}\right|^2 e^{-i\omega_{mn}t} \tag{11.2.14}$$

then

$$R(t)=\frac{2}{\hbar}\Theta(t)\sum_{n,m}p_n\left|A_{mn}\right|^2\sin\omega_{mn}t \tag{11.2.15}$$

$R(t)$ can always be expanded in sines—an odd function of time. This reflects that fact that the impulse response must have a value of 0 (the deviation from equilibrium) at $t=t_o$, and move away from 0 at the point where the external potential is applied.

Readings

1. Mukamel, S., Principles of Nonlinear Optical Spectroscopy. Oxford University Press: New York, 1995; Ch. 5.

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