Linear Response Theory

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1 Response functions

we wish to find the change of observable B with a perturbation term in addition to the equilibrium Hamiltonian that is turned on at

$$H = H_0 - Af(t) \tag{1}$$

The perturbation is turned on from t_0, In Schrodinger picture, the time dependence of a state is given by:

$$|\Psi_n(t)\rangle = U(t, t_0)|\Psi_n(t_0)\rangle \tag{2}$$

with

$$\begin{aligned} U(t, t_0) &= e^{-i\frac{H_0}{\hbar}(t-t_0)} U_I(t, t_0) \\ &= e^{-i\frac{H_0}{\hbar}(t-t_0)} \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} H_I'(t')dt'\right] \\ &\approx e^{-i\frac{H_0}{\hbar}(t-t_0)} \left(1 + \frac{i}{\hbar}\int_{t_0}^{t} A_I(t')f(t')dt'\right) \end{aligned} \tag{3}$$

and $A_I(t) = \exp(iH_0t/\hbar)A\exp(-iH_0t/\hbar)$. We find the difference:

$$\begin{aligned} \langle B\rangle(t) - \langle B\rangle(t_0) &= \sum_n \langle\Psi_n(t)|\rho_0 B|\Psi_n(t)\rangle - \sum_n \langle\Psi_n(t_0)|\rho B|\Psi_n(t_0) \\ &\approx \sum_n \langle\Psi_n(t)|\rho_0 B|\Psi_n(t)\rangle - \sum_n \langle\Psi_n(t_0)|\rho_0 B|\Psi_n(t_0)\rangle \end{aligned} \tag{4}$$

where $\rho_0 = e^{-\beta H_0}/Z$ and we use the adabatic approximation to assume that the probability of the states remain the same as in the unperturbed case. so the expectation value of B at time t is given by:

$$\begin{aligned} \langle B\rangle(t) &= \sum_n \langle\Psi_n(t_0)| \left(1 - \frac{i}{\hbar}\int_{t_0}^{t} A(t')f(t')dt'\right) e^{i\frac{H_0}{\hbar}(t-t_0)}\rho_0 B e^{-i\frac{H_0}{\hbar}(t-t_0)} \left(1 + \frac{i}{\hbar}\int_{t_0}^{t} A(t')f(t')dt'\right)|\Psi_n(t_0)\rangle \\ &\approx \langle B\rangle_0 + \frac{i}{\hbar}\int_{t_0}^{t} dt' \mathrm{Tr}\rho_0[B(t-t_0), A(t')]f(t') \end{aligned} \tag{5}$$

So that the difference is given by:

$$\Delta B(t) = \frac{i}{\hbar}\int_{t_0}^{t} dt' \mathrm{Tr}\rho_0[B(t-t_0), A(t')]f(t') \tag{6}$$

The response function is defined to be the response after a unit unit impulse at $t = 0$:

$$\begin{aligned} \phi_{BA}(t) &= \frac{i}{\hbar}\int_{t_0}^{t} dt' \mathrm{Tr}\rho_0[B(t-t_0), A(t')]\delta(t' = 0) \\ &= \frac{i}{\hbar}\mathrm{Tr}\rho_0[B(t), A(0)] \end{aligned} \tag{7}$$

$$\phi_{BA}(t) = \frac{i}{\hbar}\langle[B(t), A]\rangle_0 = \frac{1}{i\hbar}\mathrm{Tr}\rho_0[A, B(t)] = \frac{1}{i\hbar}\mathrm{Tr}[\rho_0, A]B(t) \tag{8}$$

Using the identity:

$$[A, e^{-\beta H_0}] = e^{-\beta H_0} \int_0^\beta e^{\lambda H_0} [H_0, A] e^{-\lambda H_0} d\lambda = e^{-\beta H_0} \int_0^\beta e^{\lambda H_0} (-i\hbar) \dot{A} e^{-\lambda H_0} d\lambda \tag{9}$$

$$\begin{aligned} [\rho_0, A] &= i\hbar\rho_0 \int_0^\beta e^{\lambda H_0} \dot{A} e^{-\lambda H_0} d\lambda \\ &= i\hbar \int_0^\beta \rho_0 \dot{A}(-i\hbar\lambda) d\lambda \end{aligned} \tag{10}$$

so that $\exp(-iH_0 t/\hbar) \to \exp(-H_0\lambda)$ and we can arrive at the formula given by Kubo:

$$\phi_{BA}(t) = \int_0^\beta \mathrm{Tr}\rho_0 \dot{A}(-i\hbar\lambda) B(t) d\lambda = \int_0^\beta \langle \dot{A}(-i\hbar\lambda) B(t) \rangle_0 d\lambda \tag{11}$$

We define the frequency components of the response function as [1] :

$$\chi_{BA}(\omega) = \lim_{\eta\to 0^+} \int_0^\infty \phi_{BA}(t) e^{-\eta t - i\omega t} dt \tag{13}$$

We obtain the frequency response function:

$$\chi_{BA}(\omega) = \lim_{\eta\to 0^+} \int_0^\beta d\lambda \int_0^\infty dt e^{-\eta t - i\omega t} \langle \dot{A}(-i\hbar\lambda) B(t) \rangle_0 \tag{14}$$

Let's also consider the case where a (constant pertrubation) F is applied continuously from $t = -\infty$ to $t = 0$ and stops. The system then relax throught internal interaction. The observable will follow:

$$\begin{aligned} \Delta B(t) &= \int_{-\infty}^0 \phi_{BA}(t - t') dt' F \\ &= \int_t^\infty \phi_{BA}(t') dt' F \\ &= \Phi_{BA}(t) F \end{aligned} \tag{15}$$

and

$$\Phi_{BA}(t) = \lim_{\eta\to 0^+} \int_t^\infty \phi_{BA}(t') e^{-\eta t'} dt' \tag{16}$$

is called the relaxation function.

[1] this follows the definition of *Kubo 1957* Eq.2.21, in terms of the more conventional way, we have:

$$\chi_{BA}(\omega) = \lim_{\eta\to 0^+} \int_0^\infty \phi_{BA}(t) e^{i(\omega + i\eta)\tau} dt \tag{12}$$

2 Linear response formula of electrical conductivity

We consider an uniform external electric field (potential zero is arbitrary) ($V(x) = E(t)x$):

$$H'(t) = -e\sum_i x_i E(t) = -AE(t) \tag{17}$$

$$\dot{A} = e\sum_i \dot{x}_i = J \tag{18}$$

where x_i is the position operator of the i^{th} particle and e is the charge associated with that particle. The current operator is defined to be:

$$J_\mu = e\sum_i \dot{x}_i \tag{19}$$

The response function is given by:

$$\phi_{\mu\nu}(t) = \int_0^\beta \langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle_0 d\lambda \tag{20}$$

$$\chi_{\mu\nu}(\omega) = \lim_{\eta\to 0^+}\int_0^\beta d\lambda \int_0^\infty e^{-\eta t - i\omega t} dt \langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle_0 \tag{21}$$

and the conductivity is given by:

$$\sigma_{\mu\nu} = \frac{1}{V}\int_0^\beta d\lambda \int_0^\infty dt \langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle_0 \tag{22}$$

3 Linear response formula of thermal conductivity

Derivation of the expression of thermal conductivity is provided by *Allen and Feldman, 1993*. The total current operator is given by:

$$J_\alpha = \sum_{ij\beta\gamma}(R_{i\alpha} - R_{j\alpha})\Phi_{ij}^{\beta\gamma} u_{i\beta}\dot{u}_{j\gamma} \tag{23}$$

We consider the Hamiltonian of the system to be:

$$H_0 = \int h(x) d^3x \tag{24}$$

where $h(x) = \sum_i h_i \delta(x - x_i)$ consists of the vibration energy of each atom i. The local current operator $S(x)$ is related to $h(x)$ by the continuity equation:

$$\frac{\partial h(x)}{\partial t} + \nabla\cdot S(x) = 0 \tag{25}$$

$$J = \int S(x) d^3x \tag{26}$$

The density matrix can be written as:

$$\rho = \frac{1}{Z} e^{-\int \beta(x)h(x)d^3x} \tag{27}$$

and $\beta(x) \approx \beta[1 - \delta T(x)/T]$ with T the average temperature, then

$$\rho = \frac{1}{Z} e^{-\int \beta[1-\delta T(x)/T]h(x)d^3x} = \frac{1}{Z} e^{-\beta(H_0 + H')} \tag{28}$$

with H':

$$\begin{aligned} H' &= -\frac{1}{T}\int \delta T(x) h(x) d^3x \\ &= \frac{1}{T}\int d^3x \int_{-\infty}^0 dt \delta T(x) \nabla\cdot S(x,t) \\ &= -\left(\frac{1}{T}\int d^3x \int_{-\infty}^0 dt S(x,t)\right)\nabla T \\ &= -\left(\frac{1}{T}\int_{-\infty}^0 dt J(t)\right)\nabla T \end{aligned} \tag{29}$$

Using the relationship (*Allen 1993*):

$$e^{-\beta(H_0+H')} \approx e^{-\beta H_0}\left[1+\int_0^\beta d\lambda e^{\lambda H_0} H' e^{-\lambda H_0}\right] \approx e^{-\beta H_0}\left[1-\frac{1}{T}\int_0^\beta d\lambda e^{\lambda H_0}\int_{-\infty}^0 dt J(t) e^{-\lambda H_0}\right] \tag{30}$$

The expectation value of current J_μ is then:

$$\mathrm{Tr}\rho J_\mu = \mathrm{Tr}\rho_0 J_\mu - \mathrm{Tr}\rho_0 \frac{1}{T}\int_0^\beta d\lambda \int_{-\infty}^0 dt e^{\lambda H_0}(J(t)\nabla T)e^{-\lambda H_0} J_\mu \tag{31}$$

The first term is zero under equilibrium, the second term gives $-V\kappa_{\mu\nu}\nabla T$ and

$$\begin{aligned}\kappa_{\mu\nu} &= \mathrm{Tr}\rho_0 \frac{1}{VT}\int_0^\beta d\lambda \int_{-\infty}^0 dt e^{\lambda H_0} J_\nu(t) e^{-\lambda H_0} J_\mu \\ &= \frac{1}{VT}\int_0^\beta d\lambda \int_{-\infty}^0 dt \langle J_\nu(t-i\hbar\lambda) J_\mu(0)\rangle_0 \\ &= \frac{1}{VT}\int_0^\beta d\lambda \int_0^\infty dt \langle J_\nu(-i\hbar\lambda) J_\mu(t)\rangle_0 \end{aligned} \tag{32}$$

which agrees with the Kubo's formula for electrical conductivity. [2]

[2] in the case of electrical conductivity of Kubo's derivation, the pertrubation is in the Hamiltonian, but for heat conductivity, pertrubation is in the density matrix, thus the process of derivation is different, i.e. The Hamiltonian is time dependent because of $T(t)$. Specially, we previously assumed $\rho = \rho_0$, which is no longer the approximation. If I just directly apply Kubo's form with H', we have an negative sign of conductivity