Linear Response Theory

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August 21, 2021

1 Response functions

We consider a time dependent Hamiltonian H, which is acted upon by an external time dependent field $F(t)$ which couple linearly to an observable B of the system:

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

at $t \leq t_0$, the system is in its groud state, at $t = t_0$ the external field is turned on and the system begin to evolve adiabatically. In the classical theory, the phase space probability ρ evolve as:

$$\frac{\partial \rho}{\partial t} = \{H(t), \rho\} \tag{2}$$

where $\{,\}$ is the poisson bracket. In linear approximation $\rho(t) = \rho_0 + \Delta\rho$, the equation of motion is:

$$\begin{aligned}\frac{\partial \rho(t)}{\partial t} &= \{H_0, \rho(t)\} + \{H', \rho_0\} \\ \frac{\partial \Delta\rho(t)}{\partial t} &= \{H_0, \Delta\rho(t)\} - \{A, \rho_0\}F(t)\end{aligned} \tag{3}$$

The change of the observed quantity B is given by:

$$\begin{aligned}\Delta B(t) &= \int dqdp\Delta\rho(t)B(q,p) \\ &= -\int dqdp \int_{-\infty}^{t} \{A, \rho_0\}B(t-t')F(t')dt'\end{aligned} \tag{4}$$

and the time dependence of operator B is given by the Heisenburg equation:

$$\dot{B}(p,q) = \{B, H_0\} \tag{5}$$

The response function is defined by the reponse of an observable after time t of a unit pulse:

$$\begin{aligned}\phi_{BA}(t) &= -\int dqdp \int_{-\infty}^{t} \{A, \rho_0\}B(t-t')\delta(t')dt' \\ &= -\int dqdp\{A, \rho_0\}B(t)\end{aligned} \tag{6}$$

so that

$$\Delta B(t) = \int_{-\infty}^{t} \phi_{BA}(t-t')F(t')dt' \tag{7}$$

which is summed over all the past time.

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

$$\chi_{BA}(\omega) = \lim_{\eta \to 0^+} \int_0^{\infty} \phi_{BA}(t)e^{-\eta t - i\omega t}dt \tag{9}$$

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

$$\chi_{BA}(\omega) = \lim_{\eta \to 0^+} \int_0^{\infty} \phi_{BA}(t)e^{i(\omega + i\eta)\tau}dt \tag{8}$$

Let's 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:

$$\begin{aligned} \Delta B(t) &= \int_{-\infty}^{0} \phi_{BA}(t-t')dt'F \\ &= \int_{t}^{\infty} \phi_{BA}(t')dt'F \\ &= \Phi_{BA}(t)F \end{aligned} \tag{10}$$

and

$$\Phi_{BA}(t) = \lim_{\eta\to 0^+} \int_{t}^{\infty} \phi_{BA}(t')e^{-\eta t'}dt' \tag{11}$$

2 Response functions in Quantum case

In quantum case, we wish to find:

$$\begin{aligned} \langle B\rangle(t) - \langle B\rangle_0 &= \sum_n \langle n,t|\rho B|n,t\rangle - \sum_n \langle n,-\infty|\rho B|n,-\infty\rangle \\ &= \sum_n \langle n,t|\rho B|n,t\rangle - \sum_n \langle n,-\infty|\rho_0 B|n,-\infty\rangle \end{aligned} \tag{12}$$

where in the second equality, we use the adabatic approximation to assume that the probability of the states remain the same as in the unperturbed case. The states evolve according to the Schrodinger equation:

$$\begin{aligned} U(t,-\infty) &= e^{-i\frac{H_0}{\hbar}t}U_I(t,-\infty) \\ &= e^{-i\frac{H_0}{\hbar}t}\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t} H_I'(t')dt'\right] \\ &\approx e^{-i\frac{H_0}{\hbar}t}\left(1+\frac{i}{\hbar}\int_{-\infty}^{t} A(t')f(t')dt'\right) \end{aligned} \tag{13}$$

so the expectation value of B at time t is given by:

$$\begin{aligned} \langle B\rangle(t) &= \sum_n \langle n,-\infty|\left(1-\frac{i}{\hbar}\int_{-\infty}^{t} A(t')f(t')dt'\right)e^{i\frac{H_0}{\hbar}t}\rho_{eq}Be^{-i\frac{H_0}{\hbar}t}\left(1+\frac{i}{\hbar}\int_{-\infty}^{t} A(t')f(t')dt'\right)|n,-\infty\rangle \\ &\approx \langle B\rangle_0 + \frac{i}{\hbar}\int_{-\infty}^{t} dt'\left[\sum_n \langle n,-\infty|e^{i\frac{H_0}{\hbar}t}\rho_{eq}Be^{-i\frac{H_0}{\hbar}t}A(t')f(t') - A(t')f(t')e^{i\frac{H_0}{\hbar}t}\rho_{eq}Be^{-i\frac{H_0}{\hbar}t}A(t')f(t')|n,-\infty\rangle\right] \\ &= \langle B\rangle_0 + \frac{i}{\hbar}\int_{-\infty}^{t} dt'\mathrm{Tr}\rho_{eq}[B(t),A(t')] \end{aligned} \tag{14}$$

So that the difference is given by:

$$\Delta B(t) = \frac{i}{\hbar}\int_{-\infty}^{t} dt'\mathrm{Tr}\rho_{eq}[B(t),A(t')] \tag{15}$$

The response function is given by

$$\phi_{BA}(t) = \frac{i}{\hbar}\langle[B(t),A]\rangle_0 \tag{16}$$

$$= -\frac{i}{\hbar}\mathrm{Tr}\rho_0[A,B(t)] \tag{17}$$

$$= \frac{1}{i\hbar}\mathrm{Tr}[\rho_0,A]B(t) \tag{18}$$

Using the identity:

$$[A,e^{-\beta H_0}] = e^{-\beta H_0}\int_0^{\beta} e^{\lambda H_0}[H_0,A]e^{-\lambda H_0}d\lambda \tag{19}$$

$$
\begin{aligned}
[\rho_{eq}, A] &= i\hbar\rho_{eq}\int_0^\beta e^{\lambda H_0}\dot{A}e^{-\lambda H_0}d\lambda \\
&= i\hbar\int_0^\beta \rho_{eq}\dot{A}(-i\hbar\lambda)d\lambda
\end{aligned} \tag{20}
$$

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

$$
\phi_{BA}(t) = \int_0^\beta \mathrm{Tr}\rho_0\dot{A}(-i\hbar\lambda)B(t)d\lambda \tag{21}
$$

$$
\chi_{BA}(\omega) = \lim_{\eta\to 0^+}\int_0^\beta d\lambda\int_0^\infty e^{-\eta t - i\omega t}dt\mathrm{Tr}\rho_0\dot{A}(-i\hbar\lambda)B(t) \tag{22}
$$

3 Linear response formula of conductivity

We consider an uniform external electric field (potential zero is arbitrary):

$$H'(t) = -e\sum_i x_i E(t) = -AE(t) \tag{23}$$

$$\dot{A} = e\sum_i \dot{x}_i = J \tag{24}$$

where x_i is the position operator of the i^{th} particle. The current operator is defined to be:

$$J_\mu = e\sum_i \dot{x}_i \tag{25}$$

The response function is given by:

$$\phi_{\mu\nu}(t) = \int_0^\beta \langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle_0 d\lambda \tag{26}$$

$$\chi_{\mu\nu}(\omega) = \lim_{\eta\to 0^+}\int_0^\beta d\lambda \int_0^\infty e^{-\eta t - i\omega t} dt \langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle_0 \tag{27}$$

and the conductivity is given by:

$$\sigma_{\mu\nu} = \frac{1}{V}\int_0^\beta d\lambda \int_0^\infty dt\langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle_0 \tag{28}$$

4 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:

$$J_\alpha = \sum_{ij\beta\gamma}(R_{i\alpha} - R_{j\alpha})\Phi_{ij}^{\beta\gamma} u_{i\beta}\dot{u}_{j\gamma} \tag{29}$$

We consider the Hamiltonian of the system to be:

$$H = \int h(x) d^3x \tag{30}$$

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:

$$\frac{\partial h(x)}{\partial t} + \nabla \cdot S(x) = 0 \tag{31}$$

$$J = \int S(x) d^3x \tag{32}$$

The density matrix can be written as:

$$\rho = \frac{1}{Z} e^{-\int \beta(x)h(x)d^3x} \tag{33}$$

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

$$\rho = \frac{1}{Z} e^{-\int \beta[1-\delta T(x)/T]h(x)d^3x} = \frac{1}{Z}e^{-\beta(H+H')} \tag{34}$$

with H':

$$\begin{aligned} H' &= -\frac{1}{T}\int \delta T(x)h(x)d^3x \\ &= \frac{1}{T}\int d^3x \int_{-\infty}^0 dt \delta T(x) \nabla\cdot S(x,t) \\ &= -\left(\frac{1}{T}\int d^3x \int_{-\infty}^0 dt S(x,t)\right)\nabla T \\ &= -\left(\frac{1}{T}\int_{-\infty}^0 dt J(t)\right)\nabla T \end{aligned} \tag{35}$$

where we take ∇T to be uniform. Now, we can apply the Kubo's formula:

$$\kappa_{\mu\nu}(t) = \frac{1}{VT}\int_0^\beta \langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle d\lambda \tag{36}$$

$$\kappa_{\mu\nu}(\omega) = \frac{1}{VT}\int_0^\beta d\lambda \int_0^\infty e^{-i\omega t} dt \langle J_\nu(-i\hbar\lambda)J_\mu(t)\rangle \tag{37}$$

5 From Q.T.E.L.

The time evolution of the system is given by:

$$\begin{aligned}|\Psi_n(t)\rangle &= U(t,t_0)|\Psi_n(t_0)\rangle \\ &= e^{-\frac{i}{\hbar}H_0(t-t_0)}U_I(t,t_0)|\Psi_n(t_0)\rangle\end{aligned}$$

$U_I(t,t_0)$ is given by the equation of motion:

$$i\hbar\frac{\partial}{\partial t}U_I(t,t_0) = f(t)B(t-t_0)U_I(t,t_0) \tag{38}$$

with the initial condition $U_I(t_0,t_0) = 1$. Making the approximation that $U_I(t,t_0) = 1$ on the right hand side of the Eq.38 and integrate from time $t_0 \to t$, we obtain the first order approximation:

$$U_I^{(1)}(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} f(t')B(t'-t_0)dt' \tag{39}$$

The thermal average of another observable of the system A is given by:

$$\langle A\rangle_0 = \frac{1}{Z}\sum_n e^{-\beta E_n}\langle\Psi_n(t_0)|A|\Psi_n(t_0)\rangle \tag{40}$$

and since we consider adiabatic evolution, at a later time t, the thermal average is given by:

$$\langle A\rangle(t) = \frac{1}{Z}\sum_n e^{-\beta E_n}\langle\Psi_n(t)|A|\Psi_n(t)\rangle \tag{41}$$

where the probability of finding each state is kept constants (instead of $e^{-\beta H}$ as an operator). Now, inserting the evolution of states, we obtain:

$$\langle A\rangle(t) - \langle A\rangle_0 = -\frac{i}{\hbar}\int_{t_0}^{t}\langle[A(t),B(t')]\rangle_0 f(t')dt' \tag{42}$$

where is thermal average is taken at the time independent equilibrium ensemble, and the time dependence of the operator $A(t)$ and $B(t)$ is given by the Heisenburg form:

$$B(t) = e^{\frac{i}{\hbar}H_0 t}Be^{-\frac{i}{\hbar}H_0 t} \tag{43}$$

taking $\tau = t - t' > 0$, we can define:

$$\chi_{AB}(\tau) = -\frac{i}{\hbar}\theta(\tau)\langle[A(\tau),B]\rangle_0 \tag{44}$$

so that

$$\langle A\rangle(t) = \langle A\rangle_0 + \int_0^{t-t_0}\chi_{AB}(\tau)f(t-\tau)d\tau \tag{45}$$

where we changed the integral variable from t' to $\tau = t - t'$.

Because of the $\theta(\tau)$ in Eq.44, $\chi_{AB}(\tau)$ is called the retarded response function. We have previously taken the external field to turn on instantly at t_0, however, if we allow the field to switch on slowly, as $f(t) \to 0$ as $t_0 \to -\infty$, the result at time t should remain the same, so we can also take:

$$\langle A\rangle(t) = \langle A\rangle_0 + \int_0^{\infty}\chi_{AB}(\tau)f(t-\tau)d\tau \tag{46}$$

6 Frequency domain

Consider a switching on (real) periodic perturbation, which vanish for $t \to -\infty$:

$$f(t) = f_\omega e^{-i(\omega+i\eta)t} + c.c. \tag{47}$$

η is a positive and η^{-1} give a time scale that longer than period of the perturbation. We can thus apply the linear response formalism and take the limit $\eta \rightarrow 0^+$ at the end of the calculation. If this limit exist, it should describe the reponse of the system to a steady periodic field that has been applied long enough so that initial condition is ignorable.

Inserting the periodic perturbation into Eq.46 gives:

$$\langle A \rangle(t) - \langle A \rangle_0 = \chi_{AB}(\omega) f_\omega e^{-i\omega t} + c.c. \tag{48}$$

where

$$\chi_{AB}(\omega) = -\frac{i}{\hbar} \lim_{\eta \rightarrow 0^+} \int_0^\infty \langle [A(\tau), B] \rangle_0 e^{i(\omega + i\eta)\tau} d\tau \tag{49}$$

For any general perturbation, we fourier transform between t and ω is given by:

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega) e^{i\omega t} d\omega \tag{50}$$

$$f(\omega) = \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt \tag{51}$$