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Concerning the microscopic linear response theory

M.O. Cáceres[a,*,1], S.A. Grigera[b]

[a] Centro Atómico Bariloche, Instituto Balseiro, CNEA, Universidad Nacional de Cuyo, Av. E. Bustillo Km 9.5, 8400, San Carlos de Bariloche, Río Negro, Argentina

[b] School of Physics and Astronomy, The University of Birmingham Edgbaston, Birminghan, B15 2 TT, UK

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Abstract

We present a procedure for dealing with the fluctuation–dissipation theorem (Kubo) without using Liouville–Neumann phase-space evolution. Thus, our procedure clarifies some objections posed against microscopic linear-response theory. As an application of our method, we revisit the calculation of the electric conductivity, in particular emphasis is made to establish the validity of the Greenwood–Peierls DC-conductivity when compared with the fundamental Kubo's formula.

Keywords: Microscopic linear response; Fluctuation–dissipation theorem; Electric conductivity

1. Introduction

The foundation of non-equilibrium statistical mechanics is far more difficult to establish than that of equilibrium statistical mechanics [1–3]. In general, in non-equilibrium statistical mechanics there are two methods for working out the response (*the after-effect function*) of a system when it is externally perturbed. One is the kinetic approach (which can be used beyond the linear regime, as in plasma physics [4]), and the other is microscopic linear response theory (which applies even when the kinetic method is useless, as in transport in random media [5–8]).

Van Kampen [9] once made a criticism to the microscopic linear response theory of Kubo. He pointed out that the microscopic linear response theory introduces implicitly a sort of randomization by linearization, when solving perturbatively the Liouville–Neumann equation. He also asserted that this was a simulation of *stochastization* but

* Corresponding author. Fax: +54-2944-445-299.

E-mail address: caceres@cab.cnea.gov.ar (M.O. Cáceres).

[1] Senior Independent Research associated at CONICET.

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was not proper. This was, main, van Kampen's objection concerning microscopic linear response theory.

In the present paper, we calculate the *after-effect function* in the context of linear perturbation, but without using the Liouville–Neumann phase-space evolution. In this way, we can bring a new point of view to clarify where the *stochastization* is made in order to calculate the response. Our result enlightens some of the difficulties posed by van Kampen in arriving at the response function from a microscopic linear approximation, and therefore we give additional support to the Kubo approach.

Using straightforward time-dependent quantum perturbation theory (for an open system) we are able to express the susceptibility (the half Fourier transform of *the after-effect function* [10]) as the linear response approximation. The purpose of our paper is two-fold. *First*, we show an alternative derivation of the susceptibility (and consequently the Fluctuation–Dissipation theorem (FDT)) without using Liouville–Neumann density matrix evolution. It is also clearly stated where the *stochastization* comes in (see Eq. (7)). In fact, it is just the canonical equilibrium ensemble which allows one to connect the response of a non-equilibrium system with the correlations at equilibrium; so *stochastization* is clearly proper. As a matter of fact, higher approximations, for instance the second-order change of the observable at time t may also be obtained straightforwardly using our approach. In this way, we can reinterpret the assumptions made in proving Kubo's theorem, which are sometimes obscured by the Liuoville–Neumann phase-space evolution approach. *Second*, as an application of our approach, Greenwood–Peierls' formula for the DC conductivity is revisited. In this manner we can go one step further and point out equivalences and differences versus the Kubo electric conductivity.

2. The fluctuation–dissipation theorem revisited

2.1. Linear response function to an external force

Consider a system $\mathscr{S}$ which is governed by a Hamiltonian $\hat{H}_0$. An external force $F(t)$ is applied to it from the infinite past, $t=-\infty$, when the system was at thermal equilibrium. The perturbation term in the total Hamiltonian of $\mathscr{S}$, acted upon by the external force $F(t)$, can be written in the form

$$\hat{V}(t) = -\hat{A}F(t)\,, \tag{1}$$

where $\hat{A}$ is the dynamical quantity conjugate to the applied force $F(t)$. Using Kubo's notation [1–3], the response function $\phi_{BA}(t)$ of a given observable $\hat{B}$ under the influence of the operator $\hat{A}$ is defined by

$$\begin{aligned}\delta\langle\hat{B}(t)\rangle &\equiv \langle\hat{B}(t)\rangle - \langle\hat{B}_{eq}\rangle\\ &= \int_0^\infty \mathrm{d}\tau\,\phi_{BA}(\tau)F(t-\tau)\,.\end{aligned} \tag{2}$$

This equation expresses the response $\delta\langle\hat{B}(t)\rangle$ as a linear function of the external force $F(t)$, i.e., as a superposition of the delayed effects, so $\phi_{BA}(\tau)=0$ if $\tau<0$. The response function $\phi_{BA}(t)$ represents the response of the system at time t to an impulsive force $F(t)\propto\delta(t)$ exerted on the system at $t=0$. The aim of the microscopic FDT is to give an expression for the change – in mean value – of any observable of the system $\mathscr{S}$, initially at equilibrium, under the action of a given external force; or, what is equivalent, to provide an explicit expression for the response function $\phi_{BA}(t)$ of $\mathscr{S}$.

2.2. *Kubo's formula*

Here we present an alternative proof of Kubo's FDT without using the concept of Liouville's time evolution of the density matrix (i.e., without assuming a Liouville–Neumann equation for a closed system). The starting point is to consider that the Hamiltonian can be split into two terms

$$\hat{H}=\hat{H}_0+\hat{V}(t)\,, \tag{3}$$

one of which is the time-independent (equilibrium) Hamiltonian $\hat{H}_0$, while the other is a small perturbation $\hat{V}(t)$ which is switched on in the far distant past, and has the particular form given in Eq. (1).

Using the familiar time-dependent perturbation theory [11] the eigenvectors $|\psi_\alpha(t)\rangle$ of the total Hamiltonian $\hat{H}$ can be written (to first order in the external perturbation) in the form

$$|\psi_\alpha(t)\rangle=|\alpha\rangle e^{-(i/\hbar)\varepsilon_\alpha t}+\sum_\beta|\beta\rangle a_{\alpha\beta}e^{-(i/\hbar)\varepsilon_\beta t}+\mathcal{O}(\hat{V}^2)\,, \tag{4}$$

where $|\alpha\rangle$ are the eigenvectors of the unperturbed Hamiltonian, i.e., $\hat{H}_0\;|\alpha\rangle=\varepsilon_\alpha|\alpha\rangle$ and $\{|\alpha\rangle\}$ is a basis of the Hilbert space $\mathscr{H}_{\mathscr{S}}$. The time-dependent coefficients $a_{\alpha\beta}$ are given by

$$a_{\alpha\beta}=\frac{1}{i\hbar}\int_{-\infty}^{t}dt'\,e^{-(i/\hbar)(\varepsilon_\alpha-\varepsilon_\beta)t'}\langle\beta|\hat{V}(t')|\alpha\rangle\,. \tag{5}$$

The thermal statistical mean value of any observable $\hat{B}$ (in the Schrödinger picture) is given by

$$\langle\hat{B}(t)\rangle=\sum_\alpha p_\alpha\langle\psi_\alpha(t)|\hat{B}|\psi_\alpha(t)\rangle\,, \tag{6}$$

where p_α is the probability weight of the system to be in the state described by the perturbed eigenvector $|\psi_\alpha(t)\rangle$.

The crucial point in the approach is how to assign a specific probability p_α to each perturbed eigenvector. Hence, we now make the following important *thermal* assumption:

$$p_\alpha\approx p_\alpha^{eq}\,. \tag{7}$$

That is, we assume that the perturbation $V(t)$ is small enough that it leaves unchanged the thermal statistical distribution of the eigenstates (i.e., canonical particle distribution for fermions, bosons, etc.). Under this condition, we can calculate the mean value of the observable $\hat{B}$; using Eqs. (4), (6) and (7) we obtain

$$\begin{aligned}\langle\hat{B}(t)\rangle &= \sum_\alpha p_\alpha^{eq}\langle\psi_\alpha(t)|\hat{B}|\psi_\alpha(t)\rangle = \sum_\alpha p_\alpha^{eq}\langle\alpha|\hat{B}|\alpha\rangle \\ &\quad + \sum_\alpha\sum_\beta p_\alpha^{eq}[\langle\beta|\hat{B}|\alpha\rangle a_{\alpha\beta}^* e^{(i/\hbar)\varepsilon_\beta t}\, e^{-(i/\hbar)\varepsilon_\alpha t} \\ &\quad + \langle\alpha|\hat{B}|\beta\rangle a_{\alpha\beta} e^{(i/\hbar)\varepsilon_\alpha t} e^{-(i/\hbar)\varepsilon_\beta t}] + \mathcal{O}(V^2)\,. \end{aligned} \tag{8}$$

Noting that the first term of Eq. (8) is the mean value in the unperturbed state $\langle\hat{B}_{eq}\rangle$, and restricting ourselves to linear response we can write

$$\delta\langle\hat{B}(t)\rangle = \sum_{\alpha\beta} p_\alpha^{eq}[\langle\beta|\hat{B}|\alpha\rangle a_{\alpha\beta}^* e^{(i/\hbar)\varepsilon_\beta t} e^{-(i/\hbar)\varepsilon_\alpha t} + \langle\alpha|\hat{B}|\beta\rangle a_{\alpha\beta} e^{(i/\hbar)\varepsilon_\alpha t} e^{-(i/\hbar)\varepsilon_\beta t}]\,. \tag{9}$$

Now, if we replace the coefficients $a_{\alpha\beta}$ by their definition (5), and collect the exponentials we obtain

$$\begin{aligned}\delta\langle\hat{B}(t)\rangle = \sum_{\alpha\beta} p_\alpha^{eq}\Bigg[-\frac{1}{i/\hbar}\int_{-\infty}^{t} dt'[\langle\alpha|\hat{V}(t')|\beta\rangle e^{(i/\hbar)(t-t')\varepsilon_\beta}\langle\beta|\hat{B}|\alpha\rangle e^{-(i/\hbar)(t-t')\varepsilon_\alpha} \\ - \langle\beta|\hat{V}(t')|\alpha\rangle e^{(i/\hbar)(t-t')\varepsilon_\alpha}\langle\alpha|\hat{B}|\beta\rangle e^{-(i/\hbar)(t-t')\varepsilon_\beta}]\Bigg]\,. \end{aligned} \tag{10}$$

The exponentials can be entered into the quantum brackets $\langle\alpha|\cdots|\beta\rangle$ and consequently the sum over β eliminated (using the closure relation of the basis $\{|\alpha\rangle\}$), to get finally

$$\begin{aligned}\delta\langle\hat{B}(t)\rangle = \sum_\alpha\Bigg[-\frac{1}{i\hbar}\int_{-\infty}^{t} dt'\, p_\alpha^{eq}[\langle\alpha|\hat{V}(t')e^{(i/\hbar)(t-t')\hat{H}_0}\hat{B}e^{-(i/\hbar)(t-t')\hat{H}_0}|\alpha\rangle \\ - \langle\alpha|e^{(i/\hbar)(t-t')\hat{H}_0}\hat{B}e^{-(i/\hbar)(t-t')\hat{H}_0}\hat{V}(t')|\alpha\rangle]\Bigg]\,. \end{aligned} \tag{11}$$

Here we can identify the equilibrium evolution operator $e^{-(i/\hbar)(t-t')\hat{H}_0}$ and also its conjugate acting upon $\hat{B}$. Hence, $e^{(i/\hbar)(t-t')\hat{H}_0}\hat{B}e^{-(i/\hbar)(t-t')\hat{H}_0} \equiv \hat{B}(t-t')$ gives $\hat{B}$ in the Heisenberg picture (i.e., the equilibrium time evolution of the observable $\hat{B}$). Consequently, Eq. (11) becomes

$$\begin{aligned}\delta\langle\hat{B}(t)\rangle &= \sum_\alpha\left[-\frac{1}{i\hbar}\int_{-\infty}^{t} dt'\, p_\alpha^{eq}\langle\alpha|\hat{V}(t')\hat{B}(t-t') - \hat{B}(t-t')\hat{V}(t')|\alpha\rangle\right] \\ &= \int_{-\infty}^{t} dt'\, \mathrm{Tr}[\hat{\rho}^{eq}\{-\hat{V}(t'),\hat{B}(t-t')\}]_0 \\ &= \int_{-\infty}^{t} dt'\, \mathrm{Tr}[\hat{\rho}^{eq}\{\hat{A},\hat{B}(t-t')\}]_0 F(t') \\ &= \int_0^{\infty} d\tau\, \mathrm{Tr}[\hat{\rho}^{eq}\{\hat{A},\hat{B}(\tau)\}]_0 F(t-\tau)\,, \end{aligned} \tag{12}$$

where we have used the notation

$$\{\hat{A},\hat{B}\} \equiv \frac{1}{\mathrm{i}\hbar}[\hat{A},\hat{B}] . \tag{13}$$

Note that $\hat{V}(t)$ has been replaced by its explicit expression, Eq. (1). The subscript 0 in Eq. (12) is to remind us that the trace is taken using the equilibrium thermal weights $\{p_\alpha^{eq}\}$, which have been rewritten in a compact form using the equilibrium density matrix notation

$$\hat{\rho}^{eq} \equiv \sum_\alpha |\alpha\rangle\, p_\alpha^{eq} \langle\alpha| .$$

From Eqs. (2) and (12) we conclude that the response function is

$$\phi_{BA}(\tau) = \mathrm{Tr}[\hat{\rho}_{eq}\{\hat{A},\hat{B}(\tau)\}]_0 \tag{14}$$

which is Kubo's theorem.

If the perturbation is a periodic force $F(t) = \mathscr{R}_e F_0 \cos(\omega t)$, the response (2) can be expressed in the form $\delta\langle\hat{B}(t)\rangle = \mathscr{R}_e[\chi_{BA}(\omega)F_0 \exp(\mathrm{i}\omega t)]$. Using causality and the Fourier convolution theorem, the complex susceptibility (admittance) $\chi_{BA}(\omega)$ is just the half-Fourier transform of the response function $\phi_{BA}(t)$, i.e.,

$$\chi_{BA}(\omega) = \int_0^\infty \mathrm{e}^{\mathrm{i}\omega t}\phi_{BA}(t)\,\mathrm{d}t . \tag{15}$$

This is all we need to study non-equilibrium systems in the linear approach. Kubo's formula for the response function $\phi_{BA}(\tau)$ is written in terms of a canonical correlation (14), defined only for positive times t in according with causality. Another possibility is to introduce a symmetrized correlation (Green functions), thus regarding the response and its Fourier spectrum a clear relation connecting the energy dissipation and thermal fluctuations leads to the so-called FDT [1–3].

3. Conductivity: Kubo's versus Greenwood–Peierls' formula

Most solid-state books deal with the familiar Boltzmann transport theory; hence, it is not necessary to work with complicated superoperator algebra in order to obtain the DC conductivity in the semiclassical approximation. As a matter of fact, in order to go beyond Boltzmann's approach, Taylor [12] has introduced – in an elegant way – all the fundamental ideas of the Green functions to deal with the calculation of the DC conductivity (Greenwood–Peierls formula). Hence, the limitations of validity of the Boltzmann equation (kinetic approach) can be pointed out. Nevertheless, the similarities and differences between this Greenwood–Peierls formula and the linear response Kubo's approach are not immediately apparent, and we shall now enlighten them.

In solid-state physics, and in the context of a time-dependent perturbation theory to $\mathscr{O}(E)$ in the electric field, it is common to find the Greenwood–Peierls formula for DC conductivity

$$\sigma = \frac{e^2}{m^2\Omega}\left[\sum_{\beta\alpha}\langle\alpha|\hat{p}|\beta\rangle\langle\beta|\hat{p}|\alpha\rangle\,\mathrm{Im}[[\omega_{\alpha\beta}+\mathrm{i}\eta]^{-1}]\frac{\mathrm{d}f}{\mathrm{d}\varepsilon}|_{\varepsilon=\varepsilon_\alpha}\right], \quad \eta\to 0\,. \tag{16}$$

On the other hand, within the linear response picture "Kubo's formula for the conductivity" looks quite different

$$\sigma(\omega) = \frac{e}{\Omega}\int_0^\infty \mathrm{e}^{\mathrm{i}\omega\tau}\mathrm{Tr}\left[\hat{\rho}_{eq}\int_0^{1/kT}\dot{r}(-\mathrm{i}\hbar\lambda)\dot{r}(\tau)\mathrm{d}\lambda\right]_0 \mathrm{d}\tau\,. \tag{17}$$

Hence, one might be interested to *clearly* state under which conditions these two apparently very different conductivity formulas give the same DC conductivity.

So far, we have discussed a different perturbative method by which the general microscopic FDT theorem can be derived. In this section, we will first find, as a particular application of the FDT, an expression for the electric conductivity: Kubo's formula. Next, we will derive the Greenwood–Peierls formula following steps similar to those we used to derive the FDT. Using similar derivation methods will enable us to show in a natural way the differences and similarities between the two formulas.

3.1. *Kubo formula for the* AC *conductivity*

Our starting point will be to show that the AC conductivity can be written in terms of the after-effect function (susceptibility) of the position and momentum operators.

The total electric current density in the sample can be written as

$$J = \frac{e}{\Omega}\mathscr{F}_\omega\left[\left\langle\frac{\hat{p}}{m}\right\rangle\right]E(\omega)\,, \tag{18}$$

where e is the charge of the particles, Ω the volume of the sample, and $E(\omega)\equiv\mathscr{F}_\omega[F(t)]$ is the Fourier component of the time-dependent force $F(t)$ of Eq. (1). Because J is proportional to $\delta\langle\hat{p}(t)\rangle$, the conductivity is readily recognized to be

$$\sigma(\omega) = \frac{e}{\Omega}\chi_{\hat{p}\hat{r}}(\omega)\,. \tag{19}$$

Consequently, to calculate the conductivity within the FDT scheme we start by finding the response function $\phi_{BA}(t)$, when $\hat{A}=\hat{r}$ is the operator conjugate to the force and $\hat{B}=\hat{p}/m$ is the observable. From Eq. (14) it is possible to see that

$$\begin{aligned}\phi_{BA}(\tau) = \mathrm{Tr}[\hat{\rho}_{eq}\{\hat{A},\hat{B}(\tau)\}]_0 &= \mathrm{Tr}\left[\hat{\rho}_{eq}\int_0^{1/kT}\frac{\mathrm{d}\hat{A}(-\mathrm{i}\hbar\lambda)}{\mathrm{d}t}\hat{B}(\tau)\,\mathrm{d}\lambda\right]_0\\ &= \mathrm{Tr}\left[\hat{\rho}_{eq}\int_0^{1/kT}\dot{r}(-\mathrm{i}\hbar\lambda)\dot{r}(\tau)\,\mathrm{d}\lambda\right]_0\,,\end{aligned} \tag{20}$$

where Kubo's identity $\{\mathrm{e}^{-\hat{H}_0/kT},\hat{A}\} = \mathrm{e}^{-\hat{H}_0/kT}\int_0^{1/kT}(\mathrm{d}\hat{A}(-\mathrm{i}\hbar\lambda)/\mathrm{d}t)\mathrm{d}\lambda$ has been used. From Eqs. (15), (19) and (20) it is straightforward to obtain the expression for the

AC conductivity. In particular, the DC conductivity is just $\sigma_{\mathrm{DC}} = \sigma(\omega = 0)$:

$$\sigma_{\mathrm{DC}} = \frac{e}{\Omega} \int_0^{\infty} \mathrm{Tr} \left[\hat{\rho}_{eq} \int_0^{1/kT} \dot{r}(-\mathrm{i}\hbar\lambda) \dot{r}(\tau) \, \mathrm{d}\lambda \right]_0 \mathrm{d}\tau \, . \tag{21}$$

3.2. *Greenwood–Peierls formula for the* DC *conductivity*

Now, we turn to the Greenwood–Peierls' formula.

If we consider a system of electrons of charge e, and the electric field E is slowly switched on in the far distant past, the perturbation $V(t)$ in Eq. (1) can be written as

$$\hat{V}(t) = -eE\hat{r}\mathrm{e}^{\eta t} \, , \tag{22}$$

where η is a vanishingly small positive quantity.[2] Then, from Eq. (5), and after integrating over t', the coefficients $a_{\alpha\beta}$ become

$$a_{\alpha\beta} = -\frac{e}{\mathrm{i}\hbar} E \langle \beta | \hat{r} | \alpha \rangle \frac{\mathrm{e}^{(\eta - \mathrm{i}\omega_{\alpha\beta})t}}{\eta - \mathrm{i}\omega_{\alpha\beta}} \, , \tag{23}$$

where we have introduced the notation $\omega_{\alpha\beta} \equiv (\varepsilon_\alpha - \varepsilon_\beta)/\hbar$.

If the total current density J is written as $(e/\Omega)\mathrm{d}/\mathrm{d}t\langle r(t)\rangle$, from Eqs. (9) and (23), we can compute the time derivative of the mean value $\langle \hat{B}(t) \rangle$, i.e., taking $\hat{B}$ proportional to $\hat{r}$ we are now interested in $(\mathrm{d}/\mathrm{d}t)\langle \hat{B}(t) \rangle$. Since $(\mathrm{d}/\mathrm{d}t)\langle \hat{B}_{eq} \rangle = 0$ we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \hat{B}(t) \rangle = \frac{e}{\mathrm{i}\hbar} E \cdot \frac{\mathrm{d}}{\mathrm{d}t} \left[\sum_{\alpha\beta} p_\alpha^{eq} \left[\langle \beta | \hat{B} | \alpha \rangle \langle \alpha | \hat{r} | \beta \rangle \frac{\mathrm{e}^{\eta t}}{\eta + \mathrm{i}\omega_{\alpha\beta}} \right] \right.$$
$$\left. - \sum_{\alpha\beta} p_\alpha^{eq} \left[\langle \alpha | \hat{B} | \beta \rangle \langle \beta | \hat{r} | \alpha \rangle \frac{\mathrm{e}^{\eta t}}{\eta - \mathrm{i}\omega_{\alpha\beta}} \right] \right] . \tag{24}$$

If we swap the summation indices of the second term and take the time derivative we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \hat{B}(t) \rangle = \frac{e}{\mathrm{i}\hbar} E \sum_{\beta\alpha} (p_\alpha^{eq} - p_\beta^{eq}) \langle \beta | \hat{B} | \alpha \rangle \langle \alpha | \hat{r} | \beta \rangle \frac{\eta \mathrm{e}^{\eta t}}{\eta + \mathrm{i}\omega_{\alpha\beta}} \, . \tag{25}$$

Hence, in Greenwood–Peierls' framework, to obtain the total current density we should consider – in linear response theory – the observable $\hat{B}$ as

$$\hat{B} = \frac{e}{\Omega} \hat{r} \, . \tag{26}$$

The steady–state current of a system due to a constant electric field can be assumed to be equal to that flowing at $t = 0$ in our case, then from Eqs. (26) and (25)

$$J = \frac{e^2}{\mathrm{i}\hbar\Omega} E \sum_{\alpha\beta} (p_\alpha^{eq} - p_\beta^{eq}) \langle \beta | \hat{r} | \alpha \rangle \langle \alpha | \hat{r} | \beta \rangle \frac{\eta}{\eta + \mathrm{i}\omega_{\alpha\beta}} \, . \tag{27}$$

[2] It should be pointed out that since E cannot have any implicit time dependence the Greenwood–Peierls formula can be applied *only* in the DC limit.

Now, we can rewrite Eq. (27) using that α and β are dummy indices, i.e., putting $J = \frac{1}{2}(J + J)$ and interchanging α and β, that is,

$$J = \frac{e^2}{2i\hbar\Omega} E \left[\sum_{\alpha\beta} (p_\alpha^{eq} - p_\beta^{eq}) \langle \beta | \hat{r} | \alpha \rangle \langle \alpha | \hat{r} | \beta \rangle \frac{\eta}{\eta + i\omega_{\alpha\beta}} \right.$$
$$\left. + \sum_{\beta\alpha} (p_\beta^{eq} - p_\alpha^{eq}) \langle \alpha | \hat{r} | \beta \rangle \langle \beta | \hat{r} | \alpha \rangle \frac{\eta}{\eta - i\omega_{\alpha\beta}} \right], \tag{28}$$

which is equivalent to

$$J = \frac{e^2}{\hbar\Omega} E \left[\sum_{\beta\alpha} \frac{(p_\alpha^{eq} - p_\beta^{eq})}{\omega_{\alpha\beta}} \langle \beta | \hat{r} | \alpha \rangle \langle \alpha | \hat{r} | \beta \rangle \omega_{\alpha\beta}^2 \, \mathrm{Im}[[\omega_{\alpha\beta} + i\eta]^{-1}] \right] \tag{29}$$

where $\mathrm{Im}[[\omega_{\alpha\beta} + i\eta]^{-1}]$ is the imaginary part of $[\omega_{\alpha\beta} + i\eta]^{-1}$. If we take the limit $\eta \to 0$ the only terms that do not vanish are those for which $\omega_{\alpha\beta} \to 0$ [this can be seen from the singular behavior of the term $\eta/(\eta + i\omega_{\alpha\beta})$ in Eq. (27)]. Consequently, in this limit we can replace

$$\frac{(p_\alpha^{eq} - p_\beta^{eq})}{\hbar\omega_{\alpha\beta}} = \frac{df}{d\varepsilon}\Big|_{\varepsilon = \varepsilon_\alpha} \tag{30}$$

here $f(\varepsilon)$ is the electron probability distribution. [3]

If we assume $\hat{H}_0$ to be a *free particle* Hamiltonian, then

$$[\hat{H}_0, \hat{r}] = -\frac{i\hbar}{m} \hat{p}, \tag{31}$$

where $\hat{p}$ is the momentum operator and m is the mass of the electrons. We note that

$$\hbar\omega_{\alpha\beta} \langle \alpha | \hat{r} | \beta \rangle = \langle \alpha | \hat{H}_0 \hat{r} | \beta \rangle - \langle \alpha | \hat{r} \hat{H}_0 | \beta \rangle = \langle \alpha | [\hat{H}_0, \hat{r}] | \beta \rangle \tag{32}$$

and then, we can rewrite Eq. (29) as

$$J = \frac{e^2}{m^2\Omega} E \left[\sum_{\beta\alpha} \langle \alpha | \hat{p} | \beta \rangle \langle \beta | \hat{p} | \alpha \rangle \, \mathrm{Im}[[\omega_{\alpha\beta} + i\eta]^{-1}] \frac{df}{d\varepsilon}\Big|_{\varepsilon = \varepsilon_\alpha} \right], \quad \eta \to 0 \tag{33}$$

which is just the Greenwood–Peierls formula [4] for the total current density $J = E\sigma$. Note that the scattering of *free* electrons is taken into account through the term $\mathrm{Im}[[\omega_{\alpha\beta} + i\eta]^{-1}]$ in (33), i.e., proportional to the Green function of one electron in the presence of the scattering potential.

[3] As usual at low temperatures, Eq. (30) might be approximated by a delta function at the Fermi energy.

[4] Using the fact that $\eta \to 0$, this formula can also be written in the compact form: $\sigma = (-e^2\hbar/\pi m^2\Omega)\mathrm{Tr} \int G^i(\mathscr{E}) \hat{p} G^i(\mathscr{E}) \hat{p} (df/d\mathscr{E}) \, d\mathscr{E}$, in terms of the Green function $G(\mathscr{E}) = [\mathscr{E} - H_e]^{-1}$, where $G^i(\mathscr{E})$ is its imaginary part and H_e is assumed to be the electron Hamiltonian in presence of the scattering potential (see Ref. [12]).

3.3. Remarks

While Kubo's formula gives the general AC conductivity of a given system, Greenwood–Peierls' formula applies only in the DC limit. From the comparison between the derivation of the two formulas we have seen that while Kubo's conductivity is written for any equilibrium n-body Hamiltonian $\hat{H}_0$ (including everything in the absence of the external field: the kinetic energy, the potential energy of the electrons and of the lattice atoms, the interaction between electrons and phonons, etc.), the derivation of Greenwood–Peierls formula implied the strong assumption of a *free-particle* Hamiltonian (see Eq. (31)). There is an apparent discrepancy in the definition of the current since in Greenwood–Peierls formula (33) a *mean* current $J \propto (\mathrm{d}/\mathrm{d}t)\langle\hat{r}\rangle$ is used as opposed to the use of $\langle\dot{r}\rangle$ in Kubo. However, since in Greenwood–Peierls $[\hat{H}_0, \hat{r}] = -(\mathrm{i}\hbar/m)\hat{p}$, then by virtue of Ehrenfest's theorem [6] $(\mathrm{d}/\mathrm{d}t)/\langle\hat{r}\rangle = \langle(-1/\mathrm{i}\hbar)[\hat{H}_0, \hat{r}]\rangle = \langle\dot{r}\rangle$.

In this way, we have shown that the equivalence between the Greenwood–Peierls and the Kubo DC conductivity is only true in the semi-classical limit of free electrons. As a matter of fact this is why the Greenwood–Peierls formula can be shown to reproduce, considering a diagrammatic *ladder* perturbation theory, the Boltzmann transport result. [5] On the other hand, using the semiclassical Boltzmann approach it is possible to show that the Boltzmann result for the DC conductivity can be written as in the *classical limit* of Kubo's formula. [6]

4. General conclusions

Here we summarize the main results of this paper:

(1) Kubo's fluctuation–dissipation theorem has been proved without using Liouville–Neumann perturbation theory. Our derivation is based on the fact that the first-order corrections to an open system, with respect to the external fields, comes from the first-order corrections to the quantum state of the system; where *the occupancies* of the perturbed states are assumed to remain the same as those for the corresponding states in thermal equilibrium (canonical ensemble). This fact cannot be realized from the standard Liouville–Neumann phase space evolution. Using our approach we remark that the crucial *stochastization* assumption is that the small perturbation $\hat{V}(t)$ leaves unchanged the thermal statistical weights of the perturbed eigenvectors (see Eqs. (6) and (7)). In this way, Kubo's after-effect function $\phi_{BA}(t)$ has been revisited in terms of a first-order time-dependent perturbation in the Schrödinger picture, and the assumption of the canonical ensemble occupancies.

[5] This *ladder approximation* can, for example be seen in Eq. (8.5.4) in Taylor's book [12].

[6] Solving the time-dependent Boltzmann equation, up to a linear approximation in the external field, it is possible to show that the electric current density can be expressed in terms of the velocity correlation function, as in the classical limit of Kubo's formula (see exercise no. 19 Ref. [13, p. 413]).

(2) Using our approach the Greenwood–Peierls DC conductivity has been explicitly shown to be a particular case of Kubo's linear response theory. However, Greenwood–Peierls DC conductivity is only a semiclassical approximation for free electrons.

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