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On van Kampen's Objections Against Linear Response Theory

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A discussion is given of the derivation of the Kubo–Green formulas. A reformulation of the derivation is presented, which leads to an exact result, involving field-dependent transport coefficients. Kubo's result is obtained as the first-order term in a resolvent expansion. For the general Liouville operator case, in accord with van Kampen's objections, it cannot be argued that the other terms are negligible. However, for a large class of systems, this can be justified. This is shown for systems where dissipation is due to weak interactions, amenable to the Van Hove limit, and having sufficiently short relaxation times.

KEY WORDS: Kubo–Green formulas; linear response; master equation; resolvent; electrical conductivity.

1. THE LINEARIZATION PROBLEM

Linear response theory, as formulated several decades ago by Kubo,(1) Green,(2) and others, provides very general expressions for transport coefficients in terms of correlation functions, response functions, or relaxation functions. A survey of Kubo's results was given previously.(3) The derivation of Kubo's basic result is so simple that it can be stated in a few lines.

Consider a system subject to an external field $F(t)$. Its Hamiltonian can be expresed in the form

$$H_F = H - AF(t) \tag{1.1}$$

Here H is the system Hamiltonian, being in general of the many-body type, i.e., expressible as an ordered power series of creation and annihilation

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operators and n-body interaction matrix elements; $-AF(t)$ is the external field coupling operator, with A being a system operator and the force $F(t)$ being a c-number. For example, in an electric field, A and F are vectors, $AF \rightarrow \mathbf{A} \cdot \mathbf{F}$, with $\mathbf{A} = \sum_i (\mathbf{r}_i - \mathbf{r}_{i,\text{eq}})$ and $\mathbf{F} = q\mathbf{E}$, q being the charge of the particles at positions $\mathbf{r}_i$ while $\mathbf{r}_{i,\text{eq}}$ are the positions of the particles prior to switching on the field. The von Neumann equation for the density operator in a system with (1.1) reads

$$\partial\rho/\partial t + (i/\hbar)[H, \rho] = (i/\hbar)\, u(t)\, F(t)[A, \rho] \tag{1.2}$$

where it is assumed that the field is "switched on" at $t = 0$ as expressed by the unit step function $u(t)$. With the Liouville superoperator $\mathscr{L}K = (1/\hbar)[H, K]$, Eq. (1.2) also reads

$$\partial\rho/\partial t + i\mathscr{L}\rho = (i/\hbar)\, u(t)\, F(t)[A, \rho] \tag{1.3}$$

Its solution is expressible by the Volterra integral equation

$$\rho(t) = \rho_{\text{eq}} + (i/\hbar) \int_0^t e^{-i\mathscr{L}(t-t')}\, F(t')[A, \rho(t')]\, dt' \tag{1.4}$$

For the response of an operator B due to the field switched on at $t = 0$, we then find

$$\begin{aligned} \langle \Delta B(t) \rangle &= \mathrm{Tr}[\rho(t) B] - \mathrm{Tr}(\rho_{\text{eq}} B) \\ &= (i/\hbar)\, \mathrm{Tr} \left\{ \int_0^t dt'\, B e^{-i\mathscr{L}(t-t')}\, F(t')[A, \dot{\rho}(t')] \right\} \end{aligned} \tag{1.5}$$

The assumption of linear response theory is now that on the right-hand side $\rho(t')$ can be replaced by ρ_{eq}, the density operator prevailing in equilibrium, prior to the switching on of the field. Equation (1.5) then expresses a *linear* response. With minor manipulation using the property of cyclic permutivity of the trace, one now obtains

$$\langle \Delta B(t) \rangle = (1/\hbar i)\, \mathrm{Tr} \left\{ \int_0^t d\tau\, [A, B(t-\tau)]\, \rho_{\text{eq}} F(\tau) \right\} \tag{1.6}$$

where $B(t)$ is the Heisenberg operator $e^{i\mathscr{L}t} B = e^{iHt/\hbar} B e^{-iHt/\hbar}$. Letting $b(s)$ and $f(s)$ be Laplace transforms of $\langle \Delta B(t) \rangle$ and $F(t)$, respectively, we can write $b(s) = \chi_{BA}(s)\, f(s)$, where $\chi(s)$ is the generalized susceptibility. In the frequency domain we find, with $s = i\omega + 0$,

$$\chi_{BA}(i\omega) = (1/\hbar i) \int_0^\infty dt\, e^{-i\omega t} \langle [A, B(t)] \rangle_{\text{eq}} \tag{1.7}$$

$\langle \cdot \rangle_{eq}$ being the equilibrium average. One can also obtain the "Kubo form" or the "correlation form" (see ref. 3, Section 3). One then finds with a little algebra, and setting $\beta = 1/kT$,

$$\chi_{BA}(i\omega) = \int_0^\infty dt\, e^{-i\omega t} \int_0^\beta d\beta' \, \langle \dot{A}(-i\hbar\beta')\, B(t)\rangle_{eq} \tag{1.8}$$

A more symmetrical result is obtained if one considers the response of a current flux $\dot{B}$. Writing $J_B \equiv \dot{B}$ and $J_A \equiv \dot{A}$, one then finds for the generalized conductivity

$$L_{BA}(i\omega) = \int_0^\infty dt\, e^{-i\omega t} \int_0^\beta d\beta' \, \langle J_A(-i\hbar\beta')\, J_B(t)\rangle_{eq} \tag{1.9}$$

which is the standard Kubo–Green formula. For "classical frequencies" $\hbar\omega \ll kT$, this reduces to

$$L_{BA}(i\omega) = \beta \int_0^\infty dt\, e^{-i\omega t} \langle J_A e^{i\mathscr{L}t} J_B\rangle_{eq} \tag{1.10}$$

Note that operators without argument, such as J_A, are Schrödinger operators.

The simplicity of this derivation is at the same time the cause of its beauty and of its circumspectness. How can so general a result be obtained with so little physics, no molecular dynamics, etc.? Indeed, it cannot. Criticism against this derivation was first voiced by van Kampen.[4] Further criticism was added by Van Vliet.[3] The culprit apparently is the linearization assumption, between Eqs. (1.5) and (1.6). Such a linearization simulates randomization (van Kampen) and thereby simulates dissipation. But nowhere is the dynamics commensurate with dissipation introduced (Van Vliet). Basic to the problem is that no time scales (transition or collision duration times τ_t, relaxation times between collisions τ_r, hydrodynamic times τ_h) emerge in the treatment (see Fig. 1). Therefore, in

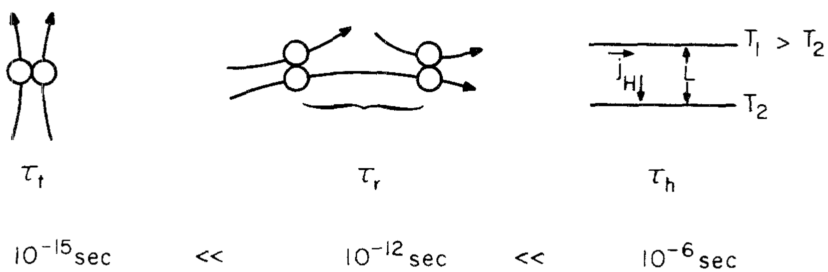

Fig. 1. The different regimes in time constants.

principle the linearization must work *over all macroscopic time*, say 1 sec. Van Kampen clearly shows that this is an impossibility, limiting the electric field to $E \leqslant 10^{-18}$ V/cm! See also his example with the "pin-ball machine"—or, in more scientific language, the Galton board.[4]

The question therefore is posed: in what sense is linear response theory correct? The problem was discussed by Cohen at a 1981 statistical mechanics meeting.[5] It was there shown that, with appropriate dynamics, Kubo's result can be validated for a dilute gas. Subsequently, we generalized Cohen's result for many-body quantum systems, with Hamiltonian $H = H^0 + \lambda V$, where λV represents dissipation due to weak interactions. This is the subject of this paper. It will be shown that in the thermodynamic limit plus the Van Hove limit the linearization of linear response theory can be justified. Both in Cohen's case and in the general case of quantum systems considered here, it is clear that extensive physical arguments must supplement the deceivingly simple derivation of Eqs. (1.1)–(1.10). First, however, the derivation is reformulated in a form appropriate for later discussion, in Section 2.

2. AN EXACT RESULT

Let us write the von Neumann equation as

$$\partial \rho / \partial t + i\mathscr{L}_F(t)\, \rho(t) = 0 \tag{2.1}$$

where now $\mathscr{L}_F(t)$ is the Liouville operator pertaining to the full Hamiltonian (1.1), i.e.,

$$\mathscr{L}_F(t) K = (1/\hbar)[H - AF(t), K] = \mathscr{L}K - (1/\hbar)\, F(t)[A, K] \tag{2.2}$$

The formal solution of (2.1) is with the field being switched on again at $t = 0$,

$$\rho(t) = \exp\left[-i \int_0^t \mathscr{L}_F(t')\, dt' \right] \rho_{\text{eq}}, \qquad t \geqslant 0 \tag{2.3}$$

For the current $J_B = \dot{B}$ associated with the flow of an observable $\mathscr{B}$ represented by the operator B, this then yields

$$\langle J_B(t) \rangle = \text{Tr} \left(\dot{B} \left\{ \exp\left[-i \int_0^t \mathscr{L}_F(t')\, dt' \right] \right\} \rho_{\text{eq}} \right) \tag{2.4}$$

We now need an appropriate form for the propagator $W(t) \equiv \exp[-i \int_0^t \mathscr{L}_F(t')\, dt']$ with $\mathscr{L}_F$ a time-dependent superoperator acting in Liouville space.[6] This can be done similarly as for the evolution operator $U(t)$ in ordinary quantum mechanics when the Hamiltonian involves a time-dependent perturbation.[6] Thus, consider the differential equation

$$\frac{dW(t)}{dt} = -i\mathscr{L}_F(t)\, W(t) = -[i\mathscr{L} + \mathscr{M}(t)]\, W(t) \tag{2.5}$$

where $\mathscr{L}_F(t) = \mathscr{L} - i\mathscr{M}(t)$ with [see (2.2)]

$$\mathscr{M}(t)\, K = (1/\hbar i)\, F(t)[A, K] \tag{2.6}$$

Now let $W^0(t) \equiv \exp(-i\mathscr{L}t)$ or $dW^0/dt = -i\mathscr{L}W^0$. Let further

$$W_{\mathrm{I}}(t) = W^{0\dagger}(t)\, W(t) \tag{2.7}$$

$$\mathscr{M}_{\mathrm{I}}(t) = W^{0\dagger}(t)\, \mathscr{M}(t)\, W^0(t) \tag{2.8}$$

We then obtain from (2.5), (2.7), and (2.8),

$$\begin{aligned} dW_{\mathrm{I}}(t)\, dt &= i\mathscr{L}W^{0\dagger}(t)\, W(t) - W^{0\dagger}(t)[i\mathscr{L} + \mathscr{M}(t)]\, W(t) \\ &= -W^{0\dagger}(t)\, \mathscr{M}(t)\, W(t) \\ &= -W^{0\dagger}(t)\, \mathscr{M}(t)\, W^0(t)\, W_{\mathrm{I}}(t) \\ &= -\mathscr{M}_{\mathrm{I}}(t)\, W_{\mathrm{I}}(t) \end{aligned} \tag{2.9}$$

with solution

$$W_{\mathrm{I}}(t) = 1 - \int_0^t d\tau\, \mathscr{M}_{\mathrm{I}}(\tau)\, W_{\mathrm{I}}(\tau) \tag{2.10}$$

This can be further iterated, so we obtain

$$W_{\mathrm{I}}(t) = 1 + \sum_{n=1}^{\infty} (-1)^n\, W_{\mathrm{I}}^{(n)}(t) \tag{2.11}$$

where we have the time-ordered integrals

$$W_{\mathrm{I}}^{(n)}(t) = \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1\, \mathscr{M}_{\mathrm{I}}(\tau_n) \cdots \mathscr{M}_{\mathrm{I}}(\tau_1) \tag{2.12}$$

Finally, with the inversions of (2.7) and (2.8),

$$W(t) = W^0(t)\, W_{\mathrm{I}}(t) \tag{2.13}$$

$$\mathscr{M}(t) = W^0(t)\, \mathscr{M}_{\mathrm{I}}(t)\, W^{0\dagger}(t) \tag{2.14}$$

Equations (2.10)–(2.14) now yield the Volterra integral equation equivalent to (2.5)

$$W(t) = e^{-i\mathscr{L}t} - \int_0^t d\tau\, e^{-i\mathscr{L}(t-\tau)} \mathscr{M}(\tau)\, W(\tau) \tag{2.15}$$

and also

$$W(t) = e^{-i\mathscr{L}t} + \sum_{n=1}^{\infty} (-1)^n\, W^{(n)}(t) \tag{2.16}$$

where

$$\begin{aligned} W^{(n)}(t) = \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \\ \times e^{-i\mathscr{L}(t-\tau_n)} \mathscr{M}(\tau_n)\, e^{-i\mathscr{L}(\tau_n - \tau_{n-1})} \mathscr{M}(\tau_{n-1}) \cdots \\ \times e^{-i\mathscr{L}(\tau_2 - \tau_1)} \mathscr{M}(\tau_1)\, e^{-i\mathscr{L}\tau_1} \end{aligned} \tag{2.17}$$

For present purposes, we need (2.15). The result (2.4) becomes

$$\langle J_B(t) \rangle = \mathrm{Tr}[\dot{B} e^{-i\mathscr{L}t} \rho_{\mathrm{eq}}] - \int_0^t d\tau\, \mathrm{Tr}[\dot{B} e^{-i\mathscr{L}(t-\tau)} \mathscr{M}(\tau)\, W(\tau) \rho_{\mathrm{eq}}] \tag{2.18}$$

For ρ_{eq}, take the canonical ensemble as in Kubo's theory, $\rho_{\mathrm{eq}} = e^{-\beta H}/\mathscr{Z}$. Since $e^{-i\mathscr{L}t} \rho_{\mathrm{eq}} = \rho_{\mathrm{eq}}$ and $\langle J_B \rangle_{\mathrm{eq}} = 0$, the first term in (2.18) disappears. With the definition (2.6) for $\mathscr{M}(\tau)$ the above becomes

$$\begin{aligned} \langle J_B(t) \rangle &= (1/\hbar i) \int_0^t d\tau\, \mathrm{Tr} \left\{ \dot{B}\, e^{-i\mathscr{L}(t-\tau)} F(\tau) [W(\tau)\, \rho_{\mathrm{eq}}, A] \right\} \\ &= (1/\hbar i) \int_0^t d\tau\, \mathrm{Tr} \left\{ \left[\exp\left\{ -i \int_0^\tau \mathscr{L}_F(\tau')\, d\tau' \right\} \rho_{\mathrm{eq}}, A \right] e^{i\mathscr{L}(t-\tau)} J_B F(\tau) \right\} \end{aligned} \tag{2.19}$$

Here we used Lemma 4 of ref. 7. The above result is exact. However, it is not of the form $\int_0^t d\tau\, \phi_{\dot{B}A}(t-\tau)\, F(\tau)$; therefore, there is *no general nonlinear sinusoidal response* $L_{BA}(i\omega)$. Note that if on the right-hand side $\mathscr{L}_F$ is replaced by $\mathscr{L}$, Eq. (2.19) reduces correctly to the linear response result (1.6).

A simpler exact result occurs if consideration is restricted to the dc conductivity, $\omega \to 0$. Thus, let in (2.2) $F(t) = F$ be constant. For (2.4) one now finds

$$\langle J_B(t) \rangle = \mathrm{Tr}[\dot{B} e^{-i\mathscr{L}_F t} \rho_{\mathrm{eq}}] = \mathrm{Tr}[\rho_{\mathrm{eq}} e^{i\mathscr{L}_F t} \dot{B}] = \langle e^{i\mathscr{L}_F t} J_B \rangle_{\mathrm{eq}} \tag{2.20}$$

Here a result analogous to Lemma 4 of ref. 7 was employed

$$\begin{aligned}\mathrm{Tr}[Ce^{-i\mathscr{L}_F t}D] &= \mathrm{Tr}[Ce^{-iH_F t/\hbar}De^{iH_F t/\hbar}] \\ &= \mathrm{Tr}[De^{iH_F t/\hbar}Ce^{-iH_F t/\hbar}] = \mathrm{Tr}[De^{i\mathscr{L}_F t}C]\end{aligned} \tag{2.21}$$

Next, consider the resolvent of $e^{i\mathscr{L}_F t}$, defined as the Cauchy principal value if $s \to 0$. One has the identity

$$\frac{1}{s - i\mathscr{L} - \mathscr{M}} = \frac{1}{s - i\mathscr{L}} + \frac{1}{s - i\mathscr{L}}\mathscr{M}\frac{1}{s - i\mathscr{L} - \mathscr{M}} \tag{2.22}$$

or by inverse Laplace transform

$$e^{i\mathscr{L}_F t} = e^{i\mathscr{L} t} + \int_0^t d\tau\, e^{i\mathscr{L}(t-\tau)}\mathscr{M}e^{i\mathscr{L}_F \tau} \tag{2.23}$$

corresponding to the complex conjugate of (2.15). It can also be iterated similar to (2.17). Substitution of (2.23) into (2.20) yields

$$\langle J_B(t)\rangle = \langle e^{i\mathscr{L} t}J_B\rangle_{\mathrm{eq}} + \int_0^t d\tau\, \langle e^{i\mathscr{L}(t-\tau)}\mathscr{M}e^{i\mathscr{L}_F \tau}J_B\rangle_{\mathrm{eq}} \tag{2.24}$$

The first term is again zero. For the second term, using (2.6), we have

$$\langle J_B(t)\rangle = (F/\hbar i)\int_0^t d\tau\, \langle e^{i\mathscr{L}(t-\tau)}[A, e^{i\mathscr{L}_F}J_B]\rangle_{\mathrm{eq}} \tag{2.25}$$

Furthermore,

$$\begin{aligned}\mathrm{Tr}\{\rho_{\mathrm{eq}}e^{i\mathscr{L}(t-\tau)}[A, e^{i\mathscr{L}_F\tau}J_B]\} &= \mathrm{Tr}\{[A, e^{i\mathscr{L}_F\tau}J_B]\, e^{-i\mathscr{L}(t-\tau)}\rho_{\mathrm{eq}}\} \\ &= \mathrm{Tr}\{[A, e^{i\mathscr{L}_F\tau}J_B]\, e^{-\beta H}\}/\mathscr{Z} \\ &= \mathrm{Tr}\{[e^{-\beta H}, A]\, e^{i\mathscr{L}_F\tau}J_B\}/\mathscr{Z}\end{aligned} \tag{2.26}$$

Now, by Kubo's identity [ref. 3, Eq. (3.21)]

$$[e^{-\beta H}, A] = \hbar i\int_0^\beta d\beta'\, e^{-\beta H}J_A(-i\hbar\beta') \tag{2.27}$$

where $\beta = 1/kT$. This and (2.26) in (2.25) yields

$$\langle J_B(t)\rangle = F\int_0^t d\tau\int_0^\beta d\beta'\, \langle J_A(-i\hbar\beta')e^{i\mathscr{L}_F\tau}J_B\rangle_{\mathrm{eq}} \tag{2.28}$$

For $\hbar\omega \ll kT$, the argument of J_A can be taken to be zero. Letting further $t \to \infty$, we find for the dc conductivity

$$L_{BA} = \beta \lim_{t\to\infty}\lim_{\mathrm{th}}\int_0^t d\tau\, \langle J_A e^{i\mathscr{L}_F\tau}J_B\rangle_{\mathrm{eq}} \tag{2.29}$$

where we added the thermodynamic limit N, $\Omega \to \infty$ with finite particle density. The exact result (2.29) replaces the linear response result (1.10). For the electrical conductivity, the current density $\mathbf{J} = q \sum \mathbf{v}_i/\Omega = q\dot{\mathbf{A}}/\Omega$, while $\mathbf{F} = q\mathbf{E}$. If μ, ν refer to Cartesian coordinates, then

$$\sigma_{\mu\nu} = \beta \lim_{t \to \infty} \lim_{\text{th}} \Omega \int_0^t d\tau \, \langle J_\nu e^{i\mathscr{L}_F \tau} J_\mu \rangle_{\text{eq}} \tag{2.30}$$

3. WEAK INTERACTIONS AND THE VAN HOVE LIMIT

As noted in Section 1, the reduction of (2.29) to (1.10) cannot be justified when nothing about the dynamics of the system is specified. Also, the existence of the integral (1.10) cannot be proven unless decay of the correlation function $\langle J_A e^{i\mathscr{L}t} J_B \rangle_{\text{eq}}$ is established.[3] Therefore, appropriate tenets of the system must be introduced. While no necessary conditions for the validity of Kubo's results are known, we indicate here that sufficient conditions involve a large class of systems in which dissipation is due to weak interactions; i.e., further to (1.1), we write

$$H_F = H - AF(t) = H^0 + \lambda V - AF(t) \tag{3.1}$$

Here λV is the randominizing agent which causes transitions $W_{\gamma\gamma'}$ among the states $|\gamma\rangle$ of H^0, which part describes the motion of interest. Here $|\gamma\rangle$ may be a quantum mechanical many-body state or a classical state defined, e.g., in four-vector space.[8] While the dichotomy of the Hamiltonian H is microscopically rather arbitrary, the macroscopic description of physical systems usually delineates the two parts in a natural fashion. For instance, in a solid, H^0 is made up of the electron gas and phonon gas energies, while λV describes electron–phonon interaction. Generally H^0 is the largest Hamiltonian that can be diagonalized; λV contains no diagonal part (part which commutes with H^0) and causes dissipation in a description based on the subdynamics of H^0. This has been extensively discussed in ref. 3.

We consider systems for which the interactions are sufficiently weak. The total propagator is given in (2.16) and (2.17). Since the operators $\mathscr{M} \cdots \mathscr{M}$ involve repeated commutators, we will for simplicity consider the correspondence limit for the case of electrical conduction, $F(t) = qE_z(t)$, $A = \sum_i (z_i - z_{i,\text{eq}})$. Then, from (2.6), denoting by $\{\ ,\ \}$ the Poisson bracket,

$$\mathscr{M}(t) K \approx qE_z(t) \left\{ \sum_i (z_i - z_{i,\text{eq}}), K \right\} = \frac{qE_z(t)}{m} \sum_i \frac{\partial K}{\partial v_{i,z}} \tag{3.2}$$

For the total propagator we now have

$$\exp\left[-i\int_0^t \mathscr{L}_F(t')\,dt'\right]$$
$$= [\exp(-i\mathscr{L}t] - \left(\frac{q}{m}\right)\int_0^t d\tau_1\,\{\exp[-i\mathscr{L}(t-\tau_1)]\}\,E_z(\tau_1)$$
$$\times \sum_i \frac{\partial}{\partial v_{iz}} \exp(-i\mathscr{L}\tau_1)$$
$$+\left(\frac{q}{m}\right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1\,\{\exp[-i\mathscr{L}(t-\tau_2)]\}\,E_z(\tau_2)$$
$$\times \sum_i \frac{\partial}{\partial v_{iz}} \{\exp[-i\mathscr{L}(\tau_2-\tau_1)]\}\,E_z(\tau_1)$$
$$\times \sum_i \frac{\partial}{\partial v_{iz}} \exp(-i\mathscr{L}\tau_1) - \cdots \tag{3.3}$$

Next, in the propagators without field, $\exp(-i\mathscr{L}t)$, we carry through the Van Hove limit $\lambda \to 0$, $t \to \infty$, $\lambda^2 t = \text{const}$. This can be done with a "two-resolvent method" applied to the expression

$$[\exp(-i\mathscr{L}t)]K = \exp[-i(H^0+\lambda V)t]K\exp[i(H^0+\lambda V)t] \tag{3.4}$$

(see ref. 3) or by using projection operators[9] $\mathscr{P}K = K_{\mathrm{d}}$ and $(1-\mathscr{P})K = K_{\mathrm{nd}}$ to split the differential equation

$$dK/dt = -i\mathscr{L}K = (1/\hbar i)[H^0 + \lambda V, K] \tag{3.5}$$

into parts which are diagonal and nondiagonal in the representation of H^0 (see ref. 7). The parts $K_{\mathrm{d}}^{\mathrm{R}}$ and $K_{\mathrm{nd}}^{\mathrm{R}}$, with superscript R denoting the reduced operators after the Van Hove limit, are later reunited. Very elaborate calculations yield the result

$$K^{\mathrm{R}}(t) = \lim_{\lambda,t}\lim_{\mathrm{th}}[\exp(-i\mathscr{L}t)]K = \{\exp[-(\Lambda_{\mathrm{d}} + i\mathscr{L}^0)t]\}K \tag{3.6}$$

where $\lim_{\lambda,t}$ denotes the Van Hove limit; $\mathscr{L}^0$ is the interaction Liouvillian, $\mathscr{L}^0 K = (1/\hbar)[H^0, K]$, and Λ_{d} is the master operator in diagonal Liouville space [first introduced in ref. 3, Eq. (6.4)],

$$\Lambda_{\mathrm{d}}K = \sum_{\gamma\gamma''} |\gamma\rangle\langle\gamma|[W_{\gamma\gamma''}\langle\gamma|K|\gamma\rangle - W_{\gamma''\gamma}\langle\gamma''|K|\gamma''\rangle] \tag{3.7}$$

where $W_{\gamma\gamma''} = W_{\gamma''\gamma}$ is given by Fermi's golden rule

$$W_{\gamma\gamma''} = (2\pi\lambda^2/\hbar)|\langle\gamma| V|\gamma''\rangle|^2\, \delta(\varepsilon_\gamma - \varepsilon_{\gamma''}) \tag{3.8}$$

The Van Hove limit drastically alters the behavior of the Heisenberg operators and of the correlation functions, since $\Lambda_{\rm d}$ has positive-semidefinite eigenvalues.[10] Integrals like (1.10), which in Kubo's theory have only *formal* validity, now converge and exist, as amply discussed in ref. 3.

We now enter the result (3.6) in all terms $\exp(-i\mathscr{L}t)$ of Eq. (3.3) and resum the series. We then obtain

$$\begin{aligned}\lim_{\lambda,t}\lim_{\rm th} \exp&\left[-i\int_0^t \mathscr{L}_F(t')\,dt'\right]\\ &= \exp\left[-(\Lambda_{\rm d} + i\mathscr{L}^0)t - \frac{q}{m}\int_0^t E_z(t')\,dt' \sum_i \frac{\partial}{\partial v_{iz}}\right]\end{aligned} \tag{3.9}$$

Next we examine the result pertaining to (2.19). The propagator (3.9) is to act on $\rho_{\rm eq} = [\exp(-\beta H^0)]/\mathscr{Z}$, where H^0 contains a part $(1/2)\sum_i mv_{iz}^2$. Thus, $\partial/\partial v_{iz} \to mv_{iz}/kT$. Let the relaxation time τ_r^{-1} be the smallest non-zero eigenvalue of $\Lambda_{\rm d}/n$, where n is the number of electrons. Then the field term in (3.9) is negligible if

$$\frac{1}{\tau_r} \gg \frac{qE_z\langle v_z\rangle}{kT} \tag{3.10}$$

Or, if $\lambda = \langle v_z\rangle\tau_r \approx \langle v\rangle\tau_r$ is the mean free path,

$$E_z \ll kT/q\lambda \tag{3.11}$$

Let $\lambda = 1000$ Å, $T = 300$ K. Then this requires $E_z \ll 2.5\times10^3$ V/cm. This estimate is certainty different than van Kampen's[1] $E \ll 10^{-18}$ V/cm! Thus, for realistic electric fields the replacement of $\exp(-i\mathscr{L}t)$ for the full propagator is hereby justified.

To finish the result (2.19) in the Van Hove limit, we need $\rho_{\rm eq} = [\exp(-\beta H^0)]/\mathscr{Z}$ in the subdynamics condidered; then,

$$\{\exp[-(\Lambda_{\rm d} + i\mathscr{L}^0)\tau]\}\,\rho_{\rm eq} = \rho_{\rm eq} \tag{3.12}$$

This is seen by series expansion: $\mathscr{L}^0 \exp(-\beta H^0) = 0$; also, $\rho_{\rm eq}$ is an eigenvector of $\Lambda_{\rm d}$ with eigenvalue zero:

$$\Lambda_{\rm d}\rho_{\rm eq} = \sum_{\gamma\gamma''} |\gamma\rangle\langle\gamma|\, W_{\gamma\gamma''}[\exp(-\xi_\gamma) - \exp(-\xi_{\gamma''})]/\mathscr{Z} = 0 \tag{3.13}$$

by virtue of the delta function in (3.8). We now use Kubo's lemma (2.27) with $H \to H^0$ and add the superscript R for the operators after the Van Hove limit. Then (2.19) yields the result

$$\langle J_B(t)\rangle = \int_0^t d\tau \int_0^\beta d\beta' \, \langle J^{\mathrm{I}}{}_A(-i\hbar\beta')\{\exp[(-\Lambda_{\mathrm{d}} + i\mathscr{L}^0)(t-\tau)]\} \, J_B^{\mathrm{R}} F(\tau)\rangle_{\mathrm{eq}} \tag{3.14}$$

Here $J_A^{\mathrm{I}}(-i\hbar\beta')$ is the interaction operator

$$J_A^{\mathrm{I}}(-i\hbar\beta') = [\exp(\hbar\beta'\mathscr{L}^0)] \, J_A^{\mathrm{R}} = \exp(\beta' H^0) J_A^{\mathrm{R}} \exp(-\beta' H^0) \tag{3.15}$$

We also have in (3.4) the reduced operator

$$J_B^{\mathrm{R}}(t) = \{\exp[(-\Lambda_{\mathrm{d}} + i\mathscr{L}^0)t]\} J_B^{\mathrm{R}} \tag{3.16}$$

Letting $j_B(s)$ and $f(s)$ be the Laplace transforms of $\langle J_B(t)\rangle$ and $F(t)$, respectively, then with $j_B(s) = L_{BA}(s) f(s)$ and $s = i\omega + 0$, we find for the sinusoidal response

$$L_{BA}(i\omega) = \int_0^t e^{-i\omega t} \int_0^\beta d\beta' \, \langle J_A^{\mathrm{I}}(-i\hbar\beta') J_B^{\mathrm{R}}(t)\rangle_{\mathrm{eq}} \tag{3.17}$$

We also note that J_A^{R} and J_B^{R} are more than the Schrödinger operators $\dot{A}$ and $\dot{B}$; we have $J_A^{\mathrm{R}} = -\Lambda_{\mathrm{d}} A + \dot{A}$ (see ref. 7) and similarly for J_B^{R}. In (3.17) the time integral converges and can be carried out,

$$L_{BA}(i\omega) = \int_0^\beta d\beta' \left\langle J_A^{\mathrm{I}}(-i\hbar\beta') \frac{1}{\Lambda_{\mathrm{d}} - i\mathscr{L}^0 + i\omega} J_B^{\mathrm{R}} \right\rangle_{\mathrm{eq}} \tag{3.18}$$

Equations (3.17) and (3.18) are the proper Kubo forms for systems with weak interactions, with the linear response approximation now being justified, provided the limitations (3.10) or (3.11) are observed.

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