Linear Response Theory & Kubo's Formula for Electronic Transport

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Main References

D. Spehner, *Contributions à la théorie du transport électronique, dissipatif dans les solides apériodiques*, Thèse, 13 mars 2000, Toulouse.

J. Bellissard, *Coherent and dissipative transport in aperiodic solids*, in *Dynamics of Dissipation*, pp. 413-486, Lecture Notes in Physics, 597, Springer (2002). P. Garbaczewski, R. Olkiewicz (Eds.).

Content

1. Linear Response Theory: Heuristic Background
2. Transport Cœfficients
3. Kubo's Formula

Warning

This lecture gives a heuristic discussion of problems posed by the linear response theory in view of a more rigorous study. It does not intend to give mathematically rigorous results.

I - Linear Response Theory: Heuristic Background

Linear Response

Experiments show that if a *force* $\vec{F}$ is imposed to a system, its response is a *current* $\vec{j}$ vanishing as the force vanishes. Thus for $\vec{F}$ small

$$\vec{j} = L \cdot \vec{F} + O(\vec{F}^2),$$

Here L is a matrix of *transport cœfficients*.

Examples:

1. FOURIER's law: a temperature gradient produces a heat current $\vec{j}_{heat} = -\lambda \vec{\nabla} T$.
2. OHM's law: a potential gradient (electric field) produces an electric current $\vec{j}_{el} = -\sigma \vec{\nabla} V$.
3. FICK's law: a density gradient produce a flow of matter $\vec{j}_{matter} = -\kappa \vec{\nabla} \rho$.

-*What is the domain of validity ?*
-*What happens for quantum systems ?*

A No-Go Theorem: Bloch's oscillations

If $H = H^*$, the *one-electron* Hamiltonian, is *bounded* and if $\vec{R} = (R_1, \cdots, R_d)$ is the *position* operator (self-adjoint, commuting coordinates), the *current* is

$$\vec{J} = const. \frac{\imath}{\hbar}[H, \vec{R}] \,,$$

Adding a force $\vec{F}$ at time $t = 0$ leads to a new evolution with Hamiltonian $H_F = H - \vec{F} \cdot \vec{R}$. The 0-frequency component of the current is

$$\vec{j} = \lim_{t \to \infty} \int_0^t \frac{ds}{t} \quad e^{\imath s H_F/\hbar} \;\; \vec{J} \;\; e^{-\imath s H_F/\hbar} \,,$$

Simple algebra shows that (since $\|H\| < \infty$)

$$\vec{F} \cdot \vec{j} = const. \lim_{t \to \infty} \frac{H(t) - H}{t} = 0 \,,$$

WHY ?

This is called *Bloch's Oscillations*

Dissipation

Dissipation is the *loss of information* experienced by the system observed as the time goes on

SECOND PRINCIPLE OF THERMODYNAMICS
Clausius-Boltzman entropy

The sources of dissipation can take various aspects

1. External noise random in time
2. Exchange with a thermal bath (reservoir with infinite energy)
3. Collisions/interactions with other particles
4. Loss of energy at infinity (infinite volumes)
5. Chaotic motion: sensitivity to initial conditions *Kolmogorov-Sinai entropy*
6. Quantum measurement (wave function collapse)
7. Quantum Chaos: the Hamiltonian behaves like a random matrix. *Voiculescu entropy* .

Length, Time & Energy Scales

1. Length scales:
   - *Scattering length:* range of interactions between colliding particles.
   - *Mean free path:* minimum distance between collisions
   - *Mesoscopic scale:* minimum size for the system to reach a local thermodynamical equilibrium.
   - *Sample size*
2. Times scales:
   - *Scattering time*
   - *Collision time:* time between two consecutive collisions
   - *Relaxation time:* time for a mesoscopic size to relax to equilibrium
   - *Mesurement time*
   - Other times: Heisenbeg times $\hbar/\Delta E$, $\cdots$
3. Energy scales

Exchanges of Limits

1. *Infinite volume* limit & *low dissipation* limit:
   - Usually

     $$\textit{mean free path} \quad \ll \quad \textit{sample size}$$

     (i) infinite volume limit (ii) low dissipation limit.
   - In nanoscopic systems linear response may fail ! The *resistivity* of a molecule is meaningless !
2. *Zero external force* limit & *large time measurement* limit:
   - in solids

     $$\frac{\hbar}{eV} \approx 10^{-12} - 10^{-15}\, s. \quad \ll \quad \textit{measurement time}$$

     (i) infinite measurement time limit
     (ii) low external field.
   - In *pico-femtosecond* laser experiments, failures of linear response theory are observed.

II - Transport Cœfficients

Local Equilibrium Approximation

- **Length Scales:**

$$\ell \ll \delta L \ll L$$

ℓ is a typical *microscopic* length scale
L the typical *macroscopic* length scale.
Then δL is called *mesoscopic*.

- **Time Scales:**

$$\tau_{rel} \ll \delta t \ll t$$

τ_{rel} is a typical *microscopic* time scale
t the typical *macroscopic* time scale.
Then δt is called *mesoscopic*.

- The system is partitionned into *mesoscopic cells*
  the time is partitionned into *mesoscopic intervals*.

- Mesoscopic cells are *completely open* systems
  After a time $O(\delta t)$ they return to *equilibrium*.

- Let H be the Hamiltonian of the part of the subsystem contained in the mesoscopic cell located at $\vec{x}$ at time t.
- Let $\hat{X}_1 = H, \hat{X}_2 \cdots, \hat{X}_K$ be a complete family of first integral, namely observables commuting with the Hamiltonian.
- Let $\mathcal{Q}(\vec{x}, t)$ be the set of indices labeling a common eigenbasis of the $\hat{X}_\alpha$'s: it is the set of *microstates* of the system contained in the mesoscopic cell.
- If $\mathbb{P}_{(\vec{x},t)}(q)$ denotes the Gibbs probability of the microstate $q \in \mathcal{Q}(\vec{x}, t)$, its *Boltzman entropy* is given by

$$S(\mathbb{P}) = -k_B \sum_{q \in \mathcal{Q}(\vec{x},t)} \mathbb{P}_{(\vec{x},t)}(q) \ln \mathbb{P}_{(\vec{x},t)}(q)$$

- The *maximum entropy principle* gives *Lagrange multipliers* $T(\vec{x}, t), F_2(\vec{x}, t), \cdots, F_K(\vec{x}, t)$ called *conjugate variables*. (In the following $F_1 = 1$)

- The Gibbs state for the mesoscopic cell centered at $\vec{x} \in \mathbb{R}^d$ at time t is:

$$\mathbb{P}_{(\vec{x},t)}(q) = \frac{1}{\mathcal{Z}(\vec{x},t)} e^{-\frac{\sum_{\alpha=1}^{K} F_\alpha(\vec{x},t)\,\hat{X}_\alpha(q)}{k_B T(\vec{x},t)}}$$

- The average values of the first integrals are

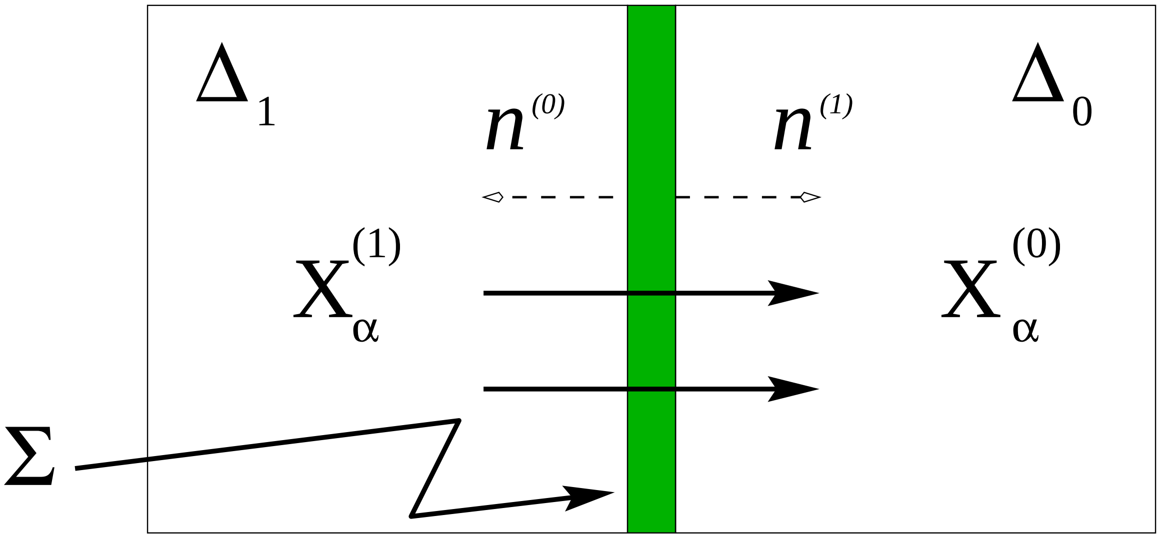
$$\delta X_\alpha(\vec{x},t) = \sum_{q \in \mathcal{Q}(\vec{x},t)} \mathbb{P}_{(\vec{x},t)}(q)\, \hat{X}_\alpha(q)\,.$$

- The *volume* of the cell $\delta V(\vec{x},t) = \delta V$ is mesoscopic and chosen constant in space and time.
- Then $\delta X_\alpha(\vec{x},t) = O(\delta V)$ and the *local density* of X_α is

$$\rho_\alpha(\vec{x},t) = \frac{\delta X_\alpha(\vec{x},t)}{\delta V}\,.$$

- Under an infinitesimal change of equilibrium the entropy changes as $TdS = \sum_\alpha F_\alpha d\delta X_\alpha$

Fluxes & Currents



- Transfer of X_α from cell $\Delta^{(1)}$ to cell $\Delta^{(0)}$ across area $\delta\Sigma$ during time δt gives a variation in time

$$\delta X_\alpha(\vec{x},t) \;=\; -\vec{j}_\alpha(\vec{x},t)\cdot\vec{n}^{(1)}\delta\Sigma\delta t\,.$$

  where $\vec{n}^{(1)}$ is the normal to area oriented from $\Delta^{(1)}$ to $\Delta^{(0)}$.

- $\vec{j}_\alpha(\vec{x},t)$ is the *local current* associated with X_α. It is *mesoscopic* rather than *microscopic*.

- Since X_α is conserved under evolution the balance leads to the *continuity equation*

$$\frac{\partial \rho_\alpha}{\partial t}(\vec{x},t) + \vec{\nabla} \cdot \vec{j}_\alpha(\vec{x},t) \;=\; 0\,.$$

- The *entropy density* is $s \;=\; \frac{\delta S}{\delta V}$
The entropy variation is then given by

$$\frac{\partial s}{\partial t} \;=\; \sum_{\alpha=1}^{K} \frac{F_\alpha}{T}\,\frac{\partial \rho_\alpha}{\partial t}\,.$$

- The *current entropy* is define through

$$\vec{j}_s(\vec{x},t) \;=\; \sum_{\alpha=1}^{K} \frac{F_\alpha}{T}\;\vec{j}_\alpha(\vec{x},t)\,.$$

- The *entropy production rate* is then

$$\frac{ds}{dt} \;=\; \frac{\partial s}{\partial t} + \vec{\nabla} \cdot \vec{j}_s \;=\; \sum_{\alpha=1}^{K} \vec{\nabla}\left(\frac{F_\alpha}{T}\right)\;\vec{j}_\alpha(\vec{x},t)\,.$$

and is *positive* thanks to the 2nd Principle.

Linear Response

- A variation of the F_α/T's produces currents. In the local equilibrium approximation

$$\vec{j}_\alpha = \sum_{\beta=1}^{K} L_{\alpha,\beta} \vec{\nabla}\left(\frac{F_\beta}{T}\right) + O\left\{\left|\vec{\nabla}\left(\frac{F_\beta}{T}\right)\right|^2\right\}$$

  – The $L_{\alpha,\beta}$'s are $d \times d$ matrices called *Onsager cœfficients*.

  – The gradient of F_α/T is an *affinity*. It plays a role similar to *forces*.

- By 2nd Principle, the positivity of entropy production rate implies

$$\mathbb{L} = ((L_{\alpha,\beta}))_{\alpha,\beta=1}^{K} \quad \Rightarrow \quad \mathbb{L} + \mathbb{L}^t \geq 0$$

- **Reciprocity Relations:** if, under time reversal symmetry, $X_\alpha \xrightarrow{TR} \varepsilon_\alpha X_\alpha$ then

$$L_{\beta,\alpha}(\textit{parameters}) = \varepsilon_\alpha \, \varepsilon_\beta \, L^t_{\alpha,\beta}(\textit{TR-parameters})\,.$$

Dissipative & Nondissipative Response

- **Dissipation = Loss of Information**
  Dissipation contributes to entropy production.
  Hence
  $$\mathbb{L}^{(diss)} = \frac{1}{2}\left(\mathbb{L} + \mathbb{L}^{t}\right)$$

- The *nondissipative* part
  $$\mathbb{L}^{(nondis)} = \frac{1}{2}\left(\mathbb{L} - \mathbb{L}^{t}\right)$$

  contains quantities exhibiting *quantization* at very low temperature !
  - The *Hall conductivity* is nondissipative. It is quantized a $T = 0$.
  - Quantization of currents in superconductors.

- **Warning:** In *mesoscopic* systems, the quantization of conductance, thermal conductance, mechanical response, is due to the lack of dissipation. The system is too small for the local equilibrium approximation to hold.

III - Kubo's Formula

Mesoscopic Quantum Evolution

- *Observable algebra* $\mathcal{A} = \mathcal{A}_S \otimes \mathcal{A}_E$
  (S = system, E = environment).
- *Quantum evolution* $\eta_t \in \mathrm{Aut}(\mathcal{A})$,
  $t \in \mathbb{R} \mapsto \eta_t(B) \in \mathcal{A}$ continuous $\forall B \in \mathcal{A}$.
- *Initial state* $\rho \otimes \rho_E$
- *System evolution*

$$\rho(\Phi_t(A)) \;=\; \rho_t(A) \;=\; \rho \otimes \rho_E\left(\eta_t(A \otimes \mathbf{1})\right)$$

  $\Phi_t : \mathcal{A}_S \mapsto \mathcal{A}_S$ is *completely positive*,
  $\Phi_t(\mathbf{1}) = \mathbf{1}$ and $t \mapsto \Phi_t(A) \in \mathcal{A}_S$ is continuous.
- *Markov approximation*: for δt mesoscopic

$$\Phi_{t+\delta t} \;\approx\; \Phi_t \circ \Phi_{\delta t} \;\approx\; \Phi_{\delta t} \circ \Phi_t$$

  Then

$$\frac{\delta \Phi_t}{\delta t} \;=\; \mathfrak{L} \circ \Phi_t \;=\; \Phi_t \circ \mathfrak{L}$$

  $\mathfrak{L}$ is the *Linbladian*.
- *Dual evolution* $\Phi_t^\dagger(\rho) = \rho \circ \Phi_t$ giving rise to $\mathfrak{L}^\dagger$.

Theorem 1 (Linblad '76) *If $\mathcal{A}_S = \mathcal{B}(\mathcal{H})$ and if Φ_t is pointwise norm continuous, there is a bounded selfadjoint operator H on $\mathcal{H}$ and a countable family of operators L_i such that*

$$\mathfrak{L}(A) \;=\; \imath[H, A] + \sum_i \left(L_i^\dagger A L_i - \frac{1}{2}\{L_i^\dagger L_i, A\} \right)$$

The first term of $\mathfrak{L}$ is the *coherent part* and corresponds to a usual Hamiltonian evolution.
The second one, denoted by $\mathfrak{D}(A)$ is the *dissipative* part and produces damping.

- *Stationary* states correspond to solutions of $\mathfrak{L}^\dagger \rho = 0$.
- *Equilibrium* states are stationary states with maximum entropy.
  They are equivalent to *KMS* states with respect to the *thermal dynamics* which is generated by

$$H_{th} \;=\; H + \sum_{\alpha=2}^{K} F_\alpha \hat{X}_\alpha$$

Derivation of Greene-Kubo Formulæ

- In many cases there is a *position operator* acting on the Hilbert space of states and given by a commuting family $\vec{R} = (R_1, \cdots, R_d)$ of selfadjoint operators. They describe the position of particles in the system S.
- $\vec{R}$ generates a d-parameter group of automorphisms $\vec{k} \in \mathbb{R}^d \mapsto e^{\imath\vec{k}\cdot\vec{R}} A e^{-\imath\vec{k}\cdot\vec{R}}$ of the C^*-algebra $\mathcal{A}_S$. Thus $\vec{\nabla} = \imath[\vec{R}, \ \cdot\ ]$ defines a $*$-derivation of $\mathcal{A}_S$.
- The *mesoscopic velocity* of the particles is given by

$$\vec{V} \ = \ \mathfrak{L}(\vec{R}) \ = \ \vec{\nabla} H + \mathfrak{D}(\vec{R})$$

  The first part corresponds to the *coherent velocity* the other to the *dissipative one*.
- The current associated with $\hat{X}_\alpha$ is given by

$$\vec{J}_\alpha \ = \ \frac{1}{2}\{\vec{V}, \hat{X}_\alpha\} \ = \ \vec{J}_\alpha^{\,(coh)} + \vec{J}_\alpha^{\,(diss)}$$

- At time $t = 0$, S is at equilibrium

$$\Rightarrow \rho_S = \rho_{eq.} \qquad\qquad \mathfrak{L}^\dagger \rho_{eq.} = 0$$

- At $t > 0$, *forces* are switched on

$$\mathcal{E} = (\vec{\mathcal{E}}_1, \cdots, \vec{\mathcal{E}}_K) \quad \text{with} \quad \vec{\mathcal{E}}_\alpha = \vec{\nabla}(F_\alpha / T)$$

so that

$$\mathfrak{L}_{\mathcal{E}} = \mathfrak{L} + \sum_{\alpha, j} \mathcal{E}_\alpha^j \mathfrak{L}_\alpha^j + O(\mathcal{E}^2)$$

- Hence the current becomes

$$J_\alpha^{\mathcal{E},i} = J_\alpha^i + \sum_{\alpha', j} \mathcal{E}_{\alpha'}^j \{\mathfrak{L}_{\alpha'}^j (R^i), \hat{X}_\alpha\} + O(\mathcal{E}^2)$$

- Then, if the forces are constant in time

$$\begin{aligned}
\vec{j}_\alpha &= \lim_{t \uparrow \infty} \int_0^t \frac{ds}{t} \rho_{eq.} \left(e^{s \mathfrak{L}_{\mathcal{E}}} \vec{J}_\alpha^{\mathcal{E}} \right) \\
&= \lim_{\epsilon \downarrow 0} \int_0^\infty \epsilon dt \; e^{-t\epsilon} \rho_{eq.} \left(e^{t \mathfrak{L}_{\mathcal{E}}} \vec{J}_\alpha^{\mathcal{E}} \right) \\
&= \lim_{\epsilon \downarrow 0} \rho_{eq.} \left(\frac{\epsilon}{\epsilon - \mathfrak{L}_{\mathcal{E}}} \vec{J}_\alpha^{\mathcal{E}} \right)
\end{aligned}$$

- Since $\mathfrak{L}^\dagger \rho_{eq.} = 0$, $\rho_{eq.} \left(\frac{\epsilon}{\epsilon - \mathfrak{L}} \vec{J}_\alpha \right) = 0$

- Thus

$$\begin{aligned}\vec{j}_\alpha &= \lim_{\epsilon\downarrow 0}\rho_{eq.}\left(\frac{\epsilon}{\epsilon-\mathfrak{L}_{\mathcal{E}}}\vec{J}^{\,\mathcal{E}}_\alpha - \frac{\epsilon}{\epsilon-\mathfrak{L}}\vec{J}_\alpha\right)\\ &= \lim_{\epsilon\downarrow 0}\rho_{eq.}\left(\frac{\epsilon}{\epsilon-\mathfrak{L}}\sum_{\alpha'}\vec{\mathcal{E}}_{\alpha'}\cdot\vec{\mathfrak{L}}_{\alpha'}\frac{1}{\epsilon-\mathfrak{L}_{\mathcal{E}}}\ \vec{J}_\alpha\right)\\ &\quad+\lim_{\epsilon\downarrow 0}\rho_{eq.}\left(\frac{\epsilon}{\epsilon-\mathfrak{L}}\sum_{\alpha'}\mathcal{E}^j_{\alpha'}\cdot\{\mathfrak{L}^j_{\alpha'}(\vec{R}),\hat{X}_\alpha\}\right)\\ &\quad+O(\mathcal{E}^2)\end{aligned}$$

- Since $\rho_{eq.}\circ\mathfrak{L}=0$ this gives

$$\begin{aligned}j^i_\alpha &= -\sum_{\alpha',j}\mathcal{E}^j_{\alpha'}\ \ \rho_{eq.}\left(\mathfrak{L}^j_{\alpha'}\ \frac{1}{\mathfrak{L}}\ J^i_\alpha\right)\\ &\quad+\rho_{eq.}\left(\{\mathfrak{L}^j_{\alpha'}(R^i),\hat{X}_\alpha\}\right)\\ &\quad+O(\mathcal{E}^2)\end{aligned}$$

- Hence the *Onsager cœfficients* are

$$\boxed{L^{i,j}_{\alpha,\alpha'} = -\rho_{eq.}\left(\mathfrak{L}^j_{\alpha'}\ \frac{1}{\mathfrak{L}}\ J^i_\alpha + \{\mathfrak{L}^j_{\alpha'}(R^i),\hat{X}_\alpha\}\right)}$$

Validity of Greene-Kubo Formulæ

The previous derivation is formal. Various conditions must be assumed.

- The explicit expressions for $\mathfrak{L}$ and the $\vec{\mathfrak{L}}_{\alpha'}$'s are *model dependent*.
- It is necessary to prove that $\mathfrak{L}_{\mathcal{E}}(\vec{R}) \in \mathcal{A}_S$.
- The *inverse* of $\mathfrak{L}$ is not *a priori* well defined.

However, the dissipative part $\mathfrak{D}$ is usually responsible for the existence of the inverse. This is because

$$\mathrm{Spec}(\imath[H, \cdot]) \subset \imath\mathbb{R}$$

while $\mathfrak{D}$ gives a *non zero real part* to eigenvalues.
In the *Relaxation Time Approximation*,

$$\mathfrak{D}(A) = A/\tau \quad \Rightarrow \quad \mathrm{Spec}\left(\imath[H, \cdot] + \frac{\mathbf{1}}{\tau}\right) \subset \imath\mathbb{R} + \frac{1}{\tau}$$

where τ is the *relaxation time*.

IV - Relaxation Time Approximation

Conclusion

1. Linear response theory requires taking *dissipation* into account. Various limits take care of time or length scales.
   These limits usually do not commute !
2. Dissipation is described through the *local equilibrium approximation* (LEA), leading to entropy creation by constant return to local equilibrium.
3. Thanks to the LEA, the currents becomes smooth functions of the *affinities* leading to the *transport* or *Onsager* cœfficients.
4. A quantum treatment of transport cœfficients must be provided for electrons in a solid.
   The *Master equation* describes the dynamics within the LEA.
5. The Master Equation leads to the Greene-Kubo formula for Onsager cœfficients.