Linear Response Theory
& Kubo’s Formula
for Electronic Transport

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Main References


Content

1. Linear Response Theory: Heuristic Background
2. Transport Coefficients
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 coefficients.

Examples:

1. **Fourier**'s law: a temperature gradient produces a heat current $\vec{j}_{\text{heat}} = -\lambda \vec{\nabla}T$.

2. **Ohm**'s law: a potential gradient (electric field) produces an electric current $\vec{j}_{\text{el}} = -\sigma \vec{\nabla}V$.

3. **Fick**'s law: a density gradient produce a flow of matter $\vec{j}_{\text{matter}} = -\kappa \vec{\nabla}\rho$.

- 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

\[
\vec{J} = \text{const.} \frac{i}{\hbar} [H, \vec{R}],
\]

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

\[
\vec{j} = \lim_{t \to \infty} \int_0^t \frac{ds}{t} e^{isH_F/\hbar} \vec{J} e^{-isH_F/\hbar},
\]

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

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

**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 $\hbar/\Delta E$, ⋯

3. Energy scales
Exchanges of Limits

1. *Infinite volume* limit & *low dissipation* limit:
   - Usually
     \[ \text{mean free path} \ll \text{sample size} \]
     (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
     \[ \frac{\hbar}{eV} \approx 10^{-12} - 10^{-15} \text{s.} \ll \text{measurement time} \]
     (i) infinite measurement time limit
     (ii) low external field.
   - In *pico-femtosecond* laser experiments, failures of linear response theory are observed.
II - Transport Coefficients
Local Equilibrium Approximation

• **Length Scales:**

\[ \ell \ll \delta L \ll L \]

\( \ell \) is a typical *microscopic* length scale
\( L \) the typical *macroscopic* length scale.
Then \( \delta L \) is called *mesoscopic*.

• **Time Scales:**

\[ \tau_{rel} \ll \delta t \ll t \]

\( \tau_{rel} \) is a typical *microscopic* time scale
\( t \) the typical *macroscopic* time scale.
Then \( \delta t \) 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 $\hat{X}_1 = H, \hat{X}_2, \ldots, \hat{X}_K$ be a complete family of first integral, namely observables commuting with the Hamiltonian.

• Let $Q(\vec{x}, t)$ 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 $P(\vec{x}, t)(q)$ denotes the Gibbs probability of the microstate $q \in Q(\vec{x}, t)$, its Boltzmann entropy is given by

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

• The maximum entropy principle gives Lagrange multipliers $T(\vec{x}, t), F_2(\vec{x}, t), \ldots, F_K(\vec{x}, t)$ 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:

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

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 \( X_\alpha \) 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

\[
TdS = \sum_\alpha F_\alpha d\delta X_\alpha
\]
• Transfer of $X_\alpha$ from cell $\Delta^{(1)}$ to cell $\Delta^{(0)}$ across area $\delta \Sigma$ during time $\delta t$ 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 $X_\alpha$. It is mesoscopic rather than microscopic.
• Since $X_\alpha$ is conserved under evolution the balance leads to the *continuity equation*

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

• The *entropy density* is $s = \frac{\delta S}{\delta V}$

The entropy variation is then given by

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

• The *current entropy* is define through

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

• The *entropy production rate* is then

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

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

- A variation of the $F_\alpha/T$'s produces currents. In the local equilibrium approximation

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

- The $L_{\alpha,\beta}$'s are $d \times d$ matrices called Onsager coefficients.
- The gradient of $F_\alpha/T$ is an affinity. It plays a role similar to forces.

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

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

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

$$L_{\beta,\alpha}(\text{parameters}) = \varepsilon_\alpha \varepsilon_\beta L_{\alpha,\beta}^t (\text{TR-parameters}).$$
Dissipative & Nondissipative Response

• **Dissipation = Loss of Information**
  
  Dissipation contributes to entropy production. Hence
  
  \[
  L^{(diss)} = \frac{1}{2} (L + L^t)
  \]

  - The **nondissipative** part

  \[
  L^{(nondis)} = \frac{1}{2} (L - L^t)
  \]

  contains quantities exhibiting *quantization* at very low temperature!

  - The *Hall conductivity* is nondissipative. It is quantized at \( T = 0 \).
  
  - 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** \( \mathcal{A} = \mathcal{A}_S \otimes \mathcal{A}_E \)
  \((S = \text{system}, E = \text{environment}).\)

- **Quantum evolution** \( \eta_t \in \text{Aut}(\mathcal{A}), \)
  \( t \in \mathbb{R} \mapsto \eta_t(B) \in \mathcal{A} \) continuous \( \forall B \in \mathcal{A}. \)

- **Initial state** \( \rho \otimes \rho_E \)

- **System evolution**
  \[ \rho(\Phi_t(A)) = \rho_t(A) = \rho \otimes \rho_E(\eta_t(A \otimes 1)) \]
  \( \Phi_t : \mathcal{A}_S \mapsto \mathcal{A}_S \) is completely positive,
  \( \Phi_t(1) = 1 \) and \( t \mapsto \Phi_t(A) \in \mathcal{A}_S \) is continuous.

- **Markov approximation**: for \( \delta t \) 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 $A_S = \mathcal{B}(\mathcal{H})$ and if $\Phi_t$ is pointwise norm continuous, there is a bounded selfadjoint operator $H$ on $\mathcal{H}$ and a countable family of operators $L_i$ such that

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

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

- **Stationary** states correspond to solutions of $\mathcal{L}^\dagger \rho = 0$.

- **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 Formulae

• 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 \( \vec{k} \in \mathbb{R}^d \mapsto e^{i \vec{k} \cdot \vec{R}} A e^{-i \vec{k} \cdot \vec{R}} \) of the \( C^* \)-algebra \( \mathcal{A}_S \). Thus \( \vec{\nabla} = i[\vec{R}, \cdot] \) 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

$$\Rightarrow \rho S = \rho_{eq.} \quad \mathfrak{L}^\dagger \rho_{eq.} = 0$$

• 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

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

• Hence the current becomes

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

• Then, if the forces are constant in time

$$\vec{j}_\alpha = \lim_{t \uparrow \infty} \int_0^t ds \frac{\rho_{eq.}}{t} \left( e^{s\mathfrak{L}_\mathcal{E}} \vec{j}_\alpha^\mathcal{E} \right)$$

$$= \lim_{\epsilon \downarrow 0} \int_0^\infty \epsilon dt \ e^{-t\epsilon} \rho_{eq.} \left( e^{t\mathfrak{L}_\mathcal{E}} \vec{j}_\alpha^\mathcal{E} \right)$$

$$= \lim_{\epsilon \downarrow 0} \rho_{eq.} \left( \frac{\epsilon}{\epsilon - \mathfrak{L}_\mathcal{E}} \vec{j}_\alpha^\mathcal{E} \right)$$

• Since $\mathfrak{L}^\dagger \rho_{eq.} = 0$, $\rho_{eq.} \left( \frac{\epsilon}{\epsilon - \mathfrak{L}_\mathcal{E}} \vec{j}_\alpha^\mathcal{E} \right) = 0$
Thus
\[
\mathbf{j}_\alpha = \lim_{\epsilon \downarrow 0} \rho_{eq.} \frac{\epsilon}{\epsilon - \mathcal{L}_\epsilon} \mathbf{j}_\alpha^{\mathcal{E}} - \frac{\epsilon}{\epsilon - \mathcal{L}_\epsilon} \mathbf{j}_\alpha
\]
\[
= \lim_{\epsilon \downarrow 0} \rho_{eq.} \left( \frac{\epsilon}{\epsilon - \mathcal{L}_\epsilon} \sum_{\alpha'} \mathcal{E}_{\alpha'} \cdot \nabla_{\alpha'} \mathbf{j}_\alpha \right)
\]
\[
+ \lim_{\epsilon \downarrow 0} \rho_{eq.} \left( \frac{\epsilon}{\epsilon - \mathcal{L}_\epsilon} \sum_{\alpha'} \mathcal{E}_{\alpha'} \cdot \left\{ \mathcal{L}_{\alpha'}(\mathbf{R}_i), \dot{X}_\alpha \right\} \right)
\]
\[
+ O(\mathcal{E}^2)
\]

Since \( \rho_{eq.} \circ \mathcal{L} = 0 \) this gives
\[
\mathbf{j}_\alpha^i = - \sum_{\alpha',j} \mathcal{E}_{\alpha'}^j \rho_{eq.} \left( \mathcal{L}_{\alpha'}^j \frac{1}{\mathcal{L}_\epsilon} \mathbf{j}_\alpha^i \right)
\]
\[
+ \rho_{eq.} \left( \left\{ \mathcal{L}_{\alpha'}^j(\mathbf{R}_i^i), \dot{X}_\alpha \right\} \right)
\]
\[
+ O(\mathcal{E}^2)
\]

Hence the \textit{Onsager coefficients} are
\[
L_{\alpha,\alpha'}^{i,j} = - \rho_{eq.} \left( \mathcal{L}_{\alpha'}^j \frac{1}{\mathcal{L}_\epsilon} \mathbf{j}_\alpha^i + \left\{ \mathcal{L}_{\alpha'}^j(\mathbf{R}_i^i), \dot{X}_\alpha \right\} \right)
\]
Validity of Greene-Kubo Formulæ

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

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

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

\[
\text{Spec}(\iota[H, \cdot]) \subset \iota\mathbb{R}
\]

while \( \mathfrak{D} \) gives a non zero real part to eigenvalues.

In the Relaxation Time Approximation,

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

where \( \tau \) is the relaxation time.
IV - Relaxation Time Approximation
Conclusion

1. Linear response theory requires taking \textit{dissipation} into account. Various limits take care of time or length scales. These limits usually do not commute!

2. Dissipation is described through the \textit{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 \textit{affinities} leading to the \textit{transport} or \textit{Onsager} coefficients.

4. A quantum treatment of transport coefficients must be provided for electrons in a solid. The \textit{Master equation} describes the dynamics within the LEA.

5. The Master Equation leads to the Greene-Kubo formula for Onsager coefficients.