Introduction to Linear Response Theory
Liouville's Theorem

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Supervision

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1 Abstract

This paper aims to develop a basic formalism of Linear Response Theory and Liouville's Theorem, as well as their quantum analogs for future research projects that aim to solve particular open and closed quantum systems. The section on Linear Response Theory does not include its application in energy absorption and prepared state relaxation, which will be developed later.

2 Introduction to Linear Response Theory

Linear response theory is a powerful calculation tool used in classical and quantum systems, describing a system's evolution towards or away from equilibrium under certain perturbative conditions. Using its formalism, we aim to decipher how systems react to external (driving) forces. Usually, these forces include pressure, magnetic fields, and electric fields. Real quantities that can be observed under this theory are called response functions. We will study the theory by examining a weakly perturbed non-equilibrium system and show that for small changes in the state, the equilibrium fluctuations serve as a good indicator for non-equilibrium responses.

3 Weakly Perturbed System

We will examine a state given by the Hamiltonian H_0 and see how it interacts with an external time-dependent stimulus $V(t)$. In this case, the system is moving away from equilibrium via the external stimuli by absorbing energy. Obviously, there is a weak coupling between the system and the external agent, and we assume that the external agent interacts with our equilibrium system through an internal variable A. This makes our Hamiltonian take the following form:

$$H = H_0 - f(t)A. \tag{1}$$

In the above equation, we symbolize the time dependence of the external agent using $f(t)$. An illustration of the complete system is given below.

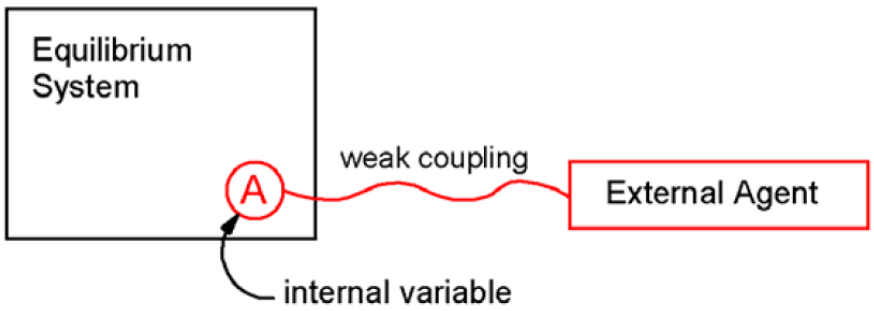

Figure 1: Equilibrium system coupled with external agent

We describe the system's behavior through an ensemble setup where the ensemble is initially at thermal equilibrium by assuming that each item in the ensemble interacts equally with the external agent and ensemble averaging. In this state, the internal variable A can be characterized by an equilibrium ensemble average $\langle A \rangle$. The external agent is then applied; we note this time as t_0, moving the system away from equilibrium. The new ensemble is called the non-equilibrium ensemble average $\overline{A(t)}$ where $\langle A \rangle \neq \overline{A(t)}$ as shown in the diagram below:

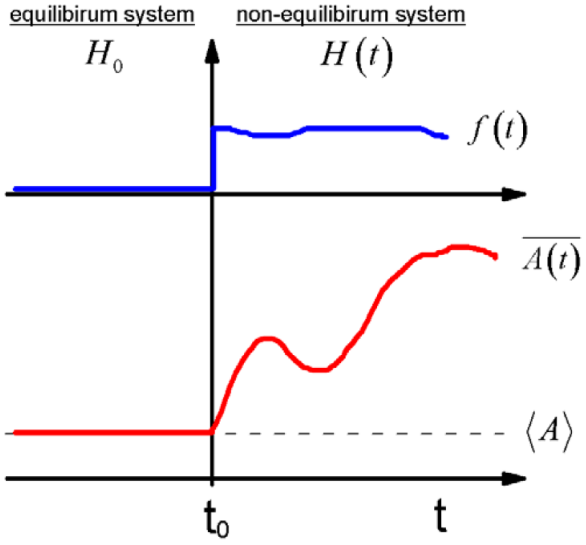

Figure 2: Disequilibrium due to interaction with external agent

We can now perform a power expansion of $f(t)$ in order to illustrate $\overline{A(t)}$ since it is a weak interaction.

$$\overline{A(t)} = (terms\, f^{(0)}) + (terms\, f^{(1)}) + ... \tag{2}$$

$$\overline{A(t)} = \langle A \rangle + \int dt_0 R(t, t_0) f(t_0) + ... \tag{3}$$

In this expression, the external agent begins acting on the system at t_0, and we begin our observations of the system at t. The leading term in the expansion is independent of f, meaning it must be $\langle A \rangle$. The next term in equation 3 represents the deviation from the equilibrium position through the linear dependence on the external agent. The linear response function $R(t, t_0)$ is the quantity that contains the microscopic information describing how the system responds to the applied stimulus. We integrate the response function to depict that the non-equilibrium behavior corresponds to the whole history of the application of the external agent and not just the exact time we are measuring. We now analyze the various properties of the response function to express it quantitatively.

4 Properties of the Response Function

4.1 Causality

This idea states that a system can not respond to the stimulus before it has been applied. Hence, $R(t, t_0) = 0$ for $t < t_0$ and the time-dependent change in

A is:

$$\delta\overline{A(t)} = \overline{A(t)} - \langle A \rangle = \int_{-\infty}^{t} dt_0 R(t, t_0) f(t_0) \tag{4}$$

The negative infinity in the integration's lower limit represents that the system is initially at equilibrium, and the upper limit is that we observe the system. We can also reflect the causality principle by introducing a step function in the integral such that:

$$\Theta(t - t_0) = \{ \begin{array}{ll} 0 & \text{if}\,(t < t_0) \\ 1 & \text{if}\,(t \geq t_0) \end{array} \} \tag{5}$$

4.2 Stationarity

Just like our discussion of the correlation function, the time dependence of the system only depends on the time interval between the application of the stimulus as the observation. Hence we can write $R(t, t_0) = R(t - t_0)$ and

$$\delta\overline{A(t)} = \int_{-\infty}^{t} dt_0 R(t - t_0) f(t_0). \tag{6}$$

The above expression confirms that the observed response of the system to the agent is a convolution of the physical response with the time development of the applied force. Rather than measuring in absolute time intervals, we define a time interval τ which is equal to $t - t_0$ so we can rewrite our equation as:

$$\delta\overline{A(t)} = \int_{0}^{\infty} d\tau R(\tau) f(t - \tau). \tag{7}$$

4.3 Impulse Response

Since we have a perturbation in terms of the delta function:

$$f(t) = \lambda\delta(t - t_0), \tag{8}$$

we can obtain:

$$\delta\overline{A(t)} = \lambda R(t - t_0). \tag{9}$$

Hence, R describes how the system evolves when a sudden perturbation is applied, this is usually called the impulse response function, and an illustration is shown below.

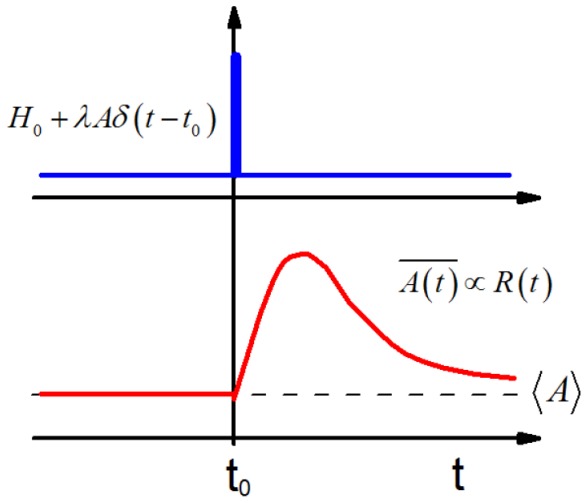

Figure 3: Equilibrium system undergoing an impulse perturbation

5 Frequency-Domain Representation

Let us also observe the behavior of the non-equilibrium system in the frequency domain as a spectral response function (susceptibility). We Fourier transform both sides of equation 7 to get:

$$\delta\overline{A(\omega)} = \int_{-\infty}^{\infty} dt[\int_{0}^{\infty} d\tau R(\tau) f(t-\tau)] e^{i\omega t}. \tag{10}$$

We now insert $1 = e^{-i\omega t} e^{+i\omega t}$ into the right hand side to get:

$$\delta\overline{A(\omega)} = \int_{-\infty}^{\infty} dt \int_{0}^{\infty} d\tau R(\tau) f(t-\tau) e^{i\omega(t-\tau)} e^{i\omega\tau}. \tag{11}$$

$$\delta\overline{A(\omega)} = \underline{\int_{-\infty}^{\infty} dt' e^{i\omega t'} f(t')} \underline{\int_{0}^{\infty} d\tau R(\tau) e^{i\omega t}}. \tag{12}$$

Hence we can write $\delta\overline{A(\omega)} = \tilde{f}(\omega)\chi(\omega)$. Note that in equation 12, we have switched variables by setting $t' = t - \tau$. $\tilde{f}(\omega)$ represents the complex part of the frequency domain representation of the driving force, which is retrieved after doing the Fourier transform on $f(t')$. The second term, i.e., $\chi(\omega)$ is the susceptibility which is the Fourier transform of the impulse response function. This is a frequency domain representation of the linear response function. We can switch between time and frequency domains to show that a convolution of the force and response in time leads to the product of the force and response in frequency. This is known as the convolution theorem, which states:

$$A(t) \bigotimes B(t) \equiv \int_{-\infty}^{\infty} d\tau A(t-\tau)B(\tau) = \int_{-\infty}^{\infty} d\tau A(\tau)B(t-\tau) = \mathscr{F}^{-1}[\tilde{A}(\omega)\tilde{B}(\omega)], \tag{13}$$

where $\tilde{A}(\omega) = \mathscr{F}[A(t)]$ and $\mathscr{F}, \mathscr{F}^{-1}$ is the Fourier and inverse Fourier transform respectively. It is important to be mindful of the fact that although $R(\tau)$ is a real function depicting an observable, $\chi(\omega)$ is complex:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega), \tag{14}$$

as we have defined $\chi(\omega)$ as:

$$\chi(\omega) = \int_0^{\infty} d\tau R(\tau) e^{i\omega\tau}. \tag{15}$$

We then have:

$$\chi' = \int_0^{\infty} d\tau R(\tau) cos(\omega\tau) = Re[\mathscr{F}(R(\tau))] \tag{16}$$

and

$$\chi'' = \int_0^{\infty} d\tau R(\tau) sin(\omega\tau) = Im[\mathscr{F}(R(\tau))], \tag{17}$$

where χ' and χ'' are even and odd frequency functions. Hence we can say:

$$\chi'(\omega) = \chi'(-\omega), \tag{18}$$

$$\chi''(\omega) = -\chi''(-\omega), \tag{19}$$

such that:

$$\chi(-\omega) = \chi^*(\omega). \tag{20}$$

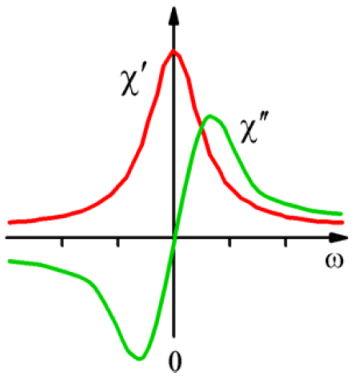

Figure 4: Graphical Representation of χ' and χ''

6 Kramers-Krönig Relations

We can see that χ' and χ'' are not truly independent of one another, given that they are sine and cosine transforms of the same function. We use Kramers-Krönig Relationships to equate the two:

$$\chi'(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega' - \omega} d\omega', \tag{21}$$

$$\chi''(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\chi'(\omega')}{\omega' - \omega} d\omega'. \tag{22}$$

The following equations can be acquired by substituting the inverse sine transform of equation 18 into equation 17:

$$\chi'(\omega) = \frac{1}{\pi} \int_{0}^{\infty} dt cos(\omega t) \int_{-\infty}^{\infty} \chi''(\omega') sin(\omega' t) d\omega', \tag{23}$$

$$\chi'(\omega) = \frac{1}{\pi} \lim_{L \to \infty} \int_{-\infty}^{\infty} d\omega' \chi''(\omega') \int_{0}^{L} cos(\omega t) sin(\omega' t) dt. \tag{24}$$

Using the identity: $cos(ax)sin(bx) = \frac{1}{2} sin(a+b)x + \frac{1}{2} sin(b-a)x$, we can rewrite the above equation as:

$$\chi'(\omega) = \frac{1}{\pi} \lim_{L \to \infty} P \int_{-\infty}^{\infty} d\omega' \chi''(\omega) \frac{1}{2} [\frac{-cos(\omega' + \omega)L + 1}{\omega' + \omega} - \frac{cos(\omega' - \omega)L + 1}{\omega' - \omega}]. \tag{25}$$

The rapid oscillations of the cosine terms make us expect they will vanish when taking the limit $L \to \infty$. This is the same as averaging over a monochromatic field. On the other hand, we can also average over a single oscillation: $L = 2\pi(\omega' - \omega)$ to acquire equation 21. All of this is only possible when we adhere to the concept of causality explained earlier, Kramers-Krönig relationships are bounded by the lower limit of $t_{initial} = 0$ on the first integral evaluated above.

7 Quantum Linear Response Functions

Having developed a classical understanding of the Linear Response Theory, we turn to its quantum counterpart. To develop a quantum description of the linear response function, we observe that the response of a system to an applied external agent can be solved in the interaction picture where our time-dependent Hamiltonian is:

$$H(t) = H_0 - f(t)\hat{A} = H_0 + V(t). \tag{26}$$

Here H_0 is the material Hamiltonian for the equilibrium system, and the external stimulus acts on the system through $\hat{A}$. $\hat{A}$ is an operator in the system

states with a time-dependency of $f(t)$. We treat this as a perturbation problem by asserting that $V(t)$ is small. Our goal is to describe the non-equilibrium response of $\overline{A(t)}$, which we will obtain by doing an ensemble average of the expectation value of $\hat{A}$. In the interaction picture, the pure state can be represented as:

$$\langle A(t)\rangle = \langle \Psi_I(t)|\, A_I(t)\, |\Psi_I(t)\rangle \tag{27}$$

$$\langle A(t)\rangle = \langle \Psi_0|\, U_I^\dagger(t) A_I U_I(t)\, |\Psi_0\rangle\,. \tag{28}$$

Let's also rewrite equation 26 in the interaction picture:

$$V_I(t) = U_0^\dagger(t) V(t) U_0(t), \tag{29}$$

$$V_I(t) = -f(t) A_I(t). \tag{30}$$

In order to calculate the ensemble average after applying the external stimulus, we observe that the non-equilibrium state of the system can be described by $|\Psi_I(t)\rangle$ which is related to the initial equilibrium state $|\Psi_0\rangle$, as seen in equation 27 and 28. Hence the non-equilibrium expectation value can be acquired by an equilibrium averaging over the expectation value of $U_I^\dagger A_I U_I$:

$$\overline{A(t)} = \sum_n p_n \,\langle n|\, U_I^\dagger A_I U_I\, |n\rangle\,, \tag{31}$$

where $|n\rangle$ are just the eigenstates of H_0. In our calculations, we will just work with the first-order solutions to $U_I(t)$:

$$U_I(t, t_0) = 1 + \frac{i}{\hbar}\int_{t_0}^{t} dt' f(t') A_I(t'). \tag{32}$$

We now plug in the value of the unitary time operator into $A(t)$ and integrate it over the entire temporal history of the system once the external agent starts to interact with the equilibrium system.

$$A(t) = U_I^\dagger A_I U_I \tag{33}$$

$$A(t) = \{1 + \frac{i}{\hbar}\int_{t_0}^{t} dt' f(t') A_I(t')\} A_I(t) \{1 - \frac{i}{\hbar}\int_{t_0}^{t} dt' f(t') A_I(t')\} \tag{34}$$

Note that the f is the dependence of the external agent. It commutes with A and is not involved with the unperturbed Hamiltonian H. Since we are dealing with a linear theory, we retain the linear terms of $f(t')$.

$$A(t) \cong A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt' f(t') \{A_I(t) A_I(t') - A_I(t') A_I(t)\}, \tag{35}$$

$$A(t) = A_I(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt' f(t')[A_I(t), A_I(t')]. \tag{36}$$

We set t_0 equal to inf as our system is initially in equilibrium. We also switch variables to the time interval $\tau = t - t'$ and utilize $A_I(t) = U_0^\dagger A U_0(t)$ to obtain:

$$A(t) = A_I(t) + \frac{i}{\hbar}\int_{0}^{\infty} d\tau f(t-\tau)[A_I(\tau), A_I(0)]. \tag{37}$$

This allows us to calculate the expectation value of A by using the ensemble averaging method. Assuming the external stimulus applies force equally to all the particles in the ensemble, we get:

$$\overline{A(t)} = \langle A \rangle + \frac{i}{\hbar}\int_{0}^{\infty} d\tau f(t-\tau) \left\langle [A_I(\tau), A_I(0)] \right\rangle . \tag{38}$$

Note that the first term does not include any f term, which means it comes from the ensemble average of the equilibrium for the value of A. This naturally leads us to believe that $\langle A \rangle$ is time-independent in our calculations:

$$\langle A(t) \rangle = \sum_n p_n \langle n | A_I | n \rangle = \langle A \rangle . \tag{39}$$

The second term is just an ensemble averaging done over the commutator in $A_I(t)$:

$$\langle [A_I(\tau), A_I(0)] \rangle = \sum_n p_n \langle n | [A_I(\tau), A_I(0)] | n \rangle . \tag{40}$$

Now we compare equation 38 with the expression of the linear response function to find the quantum linear response function:

$$R(\tau) = -\frac{i}{\hbar}\Theta(\tau) \left\langle [A_I(\tau), A_I(0)] \right\rangle . \tag{41}$$

Note that the step function has been added to ensure the causality property. The crucial idea here is that the time development of the system with the applied external potential is dictated by the dynamics of the equilibrium system (which was also our initial goal to show). The entire dependence in the response function is under H_0. Therefore, the linear response function is the sum of two correlation functions with the order of operators interchanged. This is the imaginary part of the correlation function depicted by $C''(\tau)$.

$$R(\tau) = -\frac{i}{\hbar}\Theta(\tau)\{\langle A_I(\tau)A_I(0)\rangle - \langle A_I(0)A_I(\tau)\rangle\}, \tag{42}$$

$$R(\tau) = -\frac{i}{\hbar}\Theta(\tau)(C_{AA}(\tau) - C^*_{AA}(\tau)) \tag{43}$$

,

$$R(\tau) = \frac{2}{\hbar}\Theta(\tau)C''(\tau). \tag{44}$$

As expected, the linear response function is real. If we express the correlation function in the eigenstate description, we get the following:

$$C(t) = \sum_{n,m} p_n |A_{mn}|^2 e^{-i\omega_{mn}t}, \tag{45}$$

which then becomes:

$$R(\tau) = \frac{2}{\hbar}\Theta(\tau)\sum_{n,m} p_n |A_{mn}|^2 sin(\omega_{mn}t). \tag{46}$$

Note that $R(\tau)$ can always be expanded in sines because it is an odd function of time. This means that the impulse response must have a value of 0 at $t = t_0$ and move away from 0 at the point where the external potential is applied.

8 Liouville Equations

The Liouville theorem uses equations to describe the time evolution of the phase space distribution function. It is a fundamental equation commonly used in statistical mechanics with a wide range of applications in quantum mechanics. Consider a Hamiltonian system with canonical coordinates q_i and conjugate momenta p_i, where $i = 1, ..., n$. Then the phase space distribution $\rho(p, q)$ determines the probability of the system being found in the infinitesimal phase space volume $d^n q\, d^n p$. The Liouville Equation dictates the evolution of $\rho(p, q; t)$ in time t:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{n}(\frac{\partial\rho}{\partial q_i}\dot{q_i} + \frac{\partial\rho}{\partial p_i}\dot{p_i}) = 0. \tag{47}$$

The Hamiltonian of the system determines the time derivatives of q and p. The above equation shows the conservation of density in phase space. Liouville theorem states that the distribution function is constant along any trajectory in phase space. The proof of Liouville's theorem uses the n-dimensional divergence theorem. The proof is contingent on the fact that the evolution of ρ obeys an n-dimensional version of the continuity equation:

$$\frac{\partial\rho}{\partial t} + \sum_{i=1}^{n}(\frac{\partial(\rho\dot{q_i})}{\partial q_i} + \frac{\partial(\rho\dot{p_i})}{\partial p_i}) = 0. \tag{48}$$

This means that the tuplet $(\rho, \rho\dot{q_i}, \rho\dot{p_i})$ is a conserved current. The only difference between the above equation and the Liouville equation is the terms where H is the Hamiltonian and the Hamiltonian's equations, and the conservation of the Hamiltonian along the flow, have been used. This is illustrated in the equation below:

$$\rho \sum_{i=1}^{n} (\frac{\partial \dot{q_i}}{\partial q_i} + \frac{\partial \dot{p_i}}{\partial p_i}) = \rho \sum_{i=1}^{n} (\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i}) = 0. \tag{49}$$

Viewing the motion through phase space as a 'fluid flow' of system points, the theorem that the convective derivative of the density is zero follows from the continuity equation by noting that the 'velocity field' $(\dot{p}, \dot{q})$ has zero divergence. Similarly, since a conserved current exists, there is implied symmetry via Noether's theorem. This symmetry is invariant under time, and the symmetry's generator is the Hamiltonian of the system.

9 Quantum Liouville Equation

For our research, we are interested in the quantum mechanical formulation of the Liouville equation. In quantum mechanics, the Liouville theorem describes the time evolution of a mixed quantum state. Canonical quantization yields a quantum analog of the theorem, utilizing the Von Neumann equation. To do so, we describe a Hamiltonian using classical mechanics. The classical variables are then replaced by their analogous quantum operators, and commutators replace Poisson brackets. In our case, we get:

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho], \tag{50}$$

where ρ is now the density matrix for the mixed state. When this equation is applied to the expectation value of the observable in question, the new equation is given by Ehrenfest's theorem and takes the form:

$$\frac{d}{dt} \langle A \rangle = \frac{1}{i\hbar} \langle [A, H] \rangle . \tag{51}$$

where A is our observable. The difference is sign follows from the assumption that the operator is stationary while the state is dependent on time.