Quantum Reciprocity Conjecture for the Non-Equilibrium Steady State

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A consideration of the lack of history dependence in the non-equilibrium steady state of a quantum system leads us to conjecture that in such a system, there is a set of quantum mechanical observables whose retarded response functions are insensitive to the arrow of time, and which consequently satisfy a quantum analog of the Onsager reciprocity relations. Systems which satisfy this conjecture can be described by an effective Free energy functional. We demonstrate that the conjecture holds in a resonant level model of a multi-lead quantum dot.

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Although the fundamental principles of thermal equilibrium were established by Boltzmann more than a century ago, their generalization to the non-equilibrium steady state has proved elusive. The non-equilibrium steady state is thought to be defined by a set of characteristic variables such as the current, the thermal and chemical potential gradient and as such, it is expected to be independent of the history of how it was prepared. This has led to the notion that general principles should govern the instantaneous properties of the steady state. One recurring idea is that a generalized free energy functional might apply to the non-equilibrium steady state. This was first speculated by Rayleigh in the late 19th century. Variants on Rayleigh’s approach were later used his reciprocity relations to support this conjecture, but the idea has remained controversial to the present day.

Non-equilibrium steady state behavior plays an important role in electronic transport theory, and becomes particularly important in driven nano devices, such as a d.c. biased quantum dot. Variant on Rayleigh’s approach would be invaluable in this new context, and might provide an important first step along the road to Boltzmann’s approach the non-equilibrium steady state.

Recent work on non-equilibrium hydrodynamics has shown how Onsager’s reciprocity relations can be generalized to the non-equilibrium steady state. This motivates us to re-examine Onsager’s reciprocity relations in the context of non-equilibrium quantum physics. By considering the history independence of the non-equilibrium steady state, we are led to conjecture that Onsager’s reciprocity theorem continues within a limited class of quantum variables, in the non-equilibrium steady state. Within this restricted class of variables, the concept of a Free energy can be used to describe the steady state of non-equilibrium quantum systems.

The lack of history dependence of the equilibrium steady state means that the work done on the system by coupling various internal degrees of freedom $A_i$ ($i = 1, n$) to corresponding external “forces” $\lambda_i(t)$, does not depend on the path $P$ over which the $(\lambda_i)$ are adiabatically incremented to their final value. If we increment $\lambda_j(t)$ at two different times $t_2$ and $t_1 > t_2$, we may do it two ways, illustrated in Fig. (1).

![Fig. 1. Two variations in the path $P$ where the increments in $\lambda_j$ at times $t_2$ and $t_1 > t_2$ are interchanged.](image)

In the first variation $\lambda_j(t_1) \rightarrow \lambda_i(t_1) + \delta \lambda_i$ and $\lambda_j(t_2) \rightarrow \lambda_j(t_2) + \delta \lambda_j$, whereas in the second the variations are reversed $\delta \lambda_j \leftrightarrow \delta \lambda_j$. The second-order change in the work done along both paths must be equal, i.e

$$\delta^2 W = \delta \lambda_i \delta \lambda_j \left( \frac{\delta \langle A_i(t_1) \rangle}{\delta \lambda_j(t_2)} \right) = \delta \lambda_i \delta \lambda_j \left( \frac{\delta \langle A_j(t_1) \rangle}{\delta \lambda_i(t_2)} \right)$$

(1)

from which if follows that

$$\frac{\delta \langle A_i(t_1) \rangle}{\delta \lambda_i(t_2)} - \frac{\delta \langle A_i(t_1) \rangle}{\delta \lambda_j(t_2)} = 0.$$  

(2)

We can relate these functional derivatives to the corresponding response functions,

$$\frac{\delta \langle A_i(t) \rangle}{\delta \lambda_i(t')} = -i \langle [A_j(t), A_i(t')] \rangle \theta(t - t')$$

(3)

from which it follows that

$$-i \langle [A_j(1), A_i(2)] \rangle \theta(1 - 2) = -i \langle [A_i(1), A_j(2)] \rangle \theta(1 - 2).$$

(4)

These are the quantum generalization of Onsager’s reciprocity relations. The relations are understood to hold only in the long-time limit corresponding to a slow adiabatic variation of the source terms. Onsager identified relations with the microscopic reversibility of the equations of motion and the absence of any “arrow of time”
in thermal equilibrium. This derivation shows how reciprocity is directly related to a lack of history dependence. Since our proof makes no reference to thermal equilibrium, it offers the intriguing prospect of an extension to the non-equilibrium steady state.

To extend the discussion away from thermal equilibrium, we consider a tiny system $S$ which may be a quantum dot, a quantum wire, or other small system that is coupled to two very large baths of electrons ("leads") at different chemical potentials $\mu_L$ and $\mu_R$ where $\mu_L > \mu_R$. The entire coupled system is completely isolated from the outside world.

![Diagram](image)

FIG. 2. The non-equilibrium steady state is obtained by adiabatically connecting system $S$ to two heat baths at chemical potentials $\mu_{L,R}$.

If we connect $S$ to the leads at time $t = 0$, then after an equilibration time $\tau_1$, the system will arrive at a steady state where a current flows from the left to the right-hand lead. This state persists for a long time, $\tau_2(L)$ until a substantial fraction of the additional electrons on the left lead have flowed into the right lead. The time $\tau_2(L)$ will diverge rapidly as $L \to \infty$, which permits us to define the steady state value of some variable $A$ as

$$\langle A \rangle = \lim_{L \to \infty} \langle A(t) \rangle$$

with the understanding that $\tau_2(L) >> t >> \tau_1$.

Suppose the steady state is arrived by adiabatically turning on an interaction $H_I = ghI$ between the leads, and by coupling source terms $\lambda_j$ to various quantities $A_j$ which are localized within $S$. Since the combined system is closed, when we adiabatically change these variables the amount of work done in reaching the steady state is simply the change in the total energy of the system

$$W_{NE} = \int \langle h_I(t) \rangle dg(t) + \langle A_i(t) \rangle d\lambda_i.$$ 

If the work done $W_{NE}$ is independent of the path by which $g$ and the $\lambda_j$ reach their final values, then we can use the previous proof to show that the corresponding variables satisfy a quantum reciprocity relation. The converse will also hold true. This motivates the "Quantum Reciprocity Conjecture":

In the non-equilibrium steady state, the set of quantum mechanical observables contains a non-trivial subset $P$ of "protected" quantum observables $P = \{a_1, a_2, \ldots, a_n\}$ whose correlation functions in the steady state are insensitive to the arrow of time, and which consequently satisfy a quantum mechanical analog of the Onsager reciprocity relations

$$\langle[a(1), b(2)]\rangle = \langle[b(1), a(2)]\rangle, \quad (a, b \in P).$$

Of course we do not expect the reciprocity relation to extend to all variables, as it does in thermal equilibrium, because this would mean that the arrow of time is completely invisible.

Consider the retarded and advanced Green functions between protected variables,

$$G_{ab}^{(R,A)} = \mp i ([a(1), b(2)]) \theta_{\pm}(t_2 - t_1) \quad (5)$$

where $\theta_{\pm}(t) = \theta(\pm t)$. Since $a$ and $b$ are hermitian, these are real functions ($G_{ab}^{(R,A)}(t) = [G_{ab}^{(R,A)}(t)]^*$). The conjectured Onsager relations mean that in the steady state, they also satisfy

$$G_{ab}^{R}(t_2 - t_1) = G_{ab}^{A}(t_1 - t_2),$$
$$G_{ab}^{(R,A)}(t_2 - t_1) = G_{ba}^{(R,A)}(t_2 - t_1), \quad (6)$$

where the order of the subscripts and time variables is important. If we write $G^{R}(t_1 - t_2) = [G^{R}(t_1 - t_2)]^*$ in the first relation, and then Fourier transform, we obtain the more familiar result

$$G_{ab}^{A}(\omega) = G_{ab}^{R}(\omega)^*$$

which means that the retarded and advanced Green functions of protected variables share the same spectral decomposition

$$G_{ab}^{(R,A)}(\omega) = \int \frac{dE}{\pi} \frac{1}{\omega - E \pm i\delta} A_{ab}(E).$$

where $A_{ab}(E) = \pm i \text{Im}[G_{ab}^{(R,A)}(E)]$.

Provided that the set of protected quantum variables includes the interaction $H_I = ghI$, then we can define an effective Free energy from the virtual work done $W_{NE}$ in reaching the steady state. Suppose we evaluate $W_{NE}$ along the two paths shown in Fig. 3. Since $W_{NE}$ is the same along both paths, for small $\Delta \lambda$ we have

$$A(g_1, \lambda) \Delta \lambda + \int_{g_1}^{g_2} \frac{dg'}{g'} H_I(g', \lambda + \Delta \lambda) dg' = A(g_2, \lambda) \Delta \lambda + \int_{g_1}^{g_2} \frac{dg'}{g'} H_I(g', \lambda) dg', \quad (7)$$

so that

$$\Delta A = A(g_2, \lambda) - A(g_1, \lambda) = \frac{\partial}{\partial \lambda} \Delta F \quad (8)$$

where

$$\Delta F = \int_{g_1}^{g_2} \frac{dg'}{g'} H_I(g', \lambda). \quad (9)$$

Thus if reciprocity holds, the change in the variables $\{A_j\}$ associated with a change in the coupling constant $g$ can be evaluated as derivatives of a single Free energy variable $\Delta F$.

We now illustrate the correctness of this conjecture in a simple non-interacting model. We consider a single...
resonant level in a quantum dot carrying a D.C. current between two or more leads according, where the Hamiltonian \( H = H_0 + H_I \) and

\[
H_0 = \sum_{\alpha, k \sigma} \epsilon(k) c_{\alpha, k \sigma}^\dagger c_{\alpha, k \sigma} + \sum_{\sigma} \epsilon_{d \sigma} d_\sigma^\dagger d_\sigma,
\]

\[
H_I = J \sum_{\alpha, k} \left[ \gamma_{\alpha} c_{\alpha, k}^\dagger d_\sigma + H.C. \right].
\]

Here \( \alpha = 1, N \) labels the leads, each one characterized by a distinct chemical potential \( \mu_{\alpha} \), \( \epsilon_{d \sigma} = \epsilon_d - \sigma B \) is the energy of the localized state in the dot in a magnetic field \( B \), \( J \) is the overall coupling constant and \( \gamma_{\alpha} \) is a parameter which sets the relative strength of hybridization with the \( \alpha \) lead. This is an exactly solvable problem, and has well known results found by the Keldysh method.

As a first step, by comparing the retarded and advanced correlation functions, we are able to explicitly confirm the interaction, together with the dot magnetization \( M \) and occupancy \( n_d \), form a set of protected variables \( \{ H_I, M, n_d \} \) which satisfy reciprocity and for which a Free energy functional can be defined.

For example, for the relation

\[
\langle [H_I(t_1), n(t_2)] \rangle = \langle [n(t_1), H_I(t_2)] \rangle,
\]

we compare the retarded and advanced Green functions:

\[
G_{H_I, n}^R(\omega) = \text{Tr} \sum_{\alpha} J_{\gamma_{\alpha}} \int \frac{d\epsilon}{2\pi} \left[ G_{d \sigma d \sigma}^R(\epsilon) (i\tau_1) G_{c_{\alpha} d \sigma}^R(\epsilon + \omega) + G_{c_{\alpha} c_{\alpha} d \sigma}^R(\epsilon) (i\tau_1) G_{d \sigma d \sigma}^R(\epsilon + \omega) \right]
\]

and

\[
G_{H_I, n}^A(\omega) = \text{Tr} \sum_{\alpha} J_{\gamma_{\alpha}} \int \frac{d\epsilon}{2\pi} \left[ G_{c_{\alpha} d \sigma}^A(\epsilon + \omega) (i\tau_1) G_{d \sigma d \sigma}^A(\epsilon) + G_{d \sigma d \sigma}^A(\epsilon) (i\tau_1) G_{c_{\alpha} c_{\alpha} d \sigma}^A(\epsilon) \right].
\]

where the \( G_{ab} \) refer to the Larkin-Ovchinikov matrix Greens functions between electron fields \( a \) and \( b \) and the trace is over Keldysh indices. By writing these expressions out explicitly, we are able to explicitly confirm that they are related by complex conjugation, \( G_{H_I, n}^R(\omega) = [G_{H_I, n}^L(\omega)]^\dagger \), from which reciprocity between \( n_d \) and \( H_I \) holds. A similar method enables us to check that

\[
\langle [H_I(t_1), M(t_2)] \rangle = \langle [M(t_1), H_I(t_2)] \rangle.
\]

The correlation function between \( M \) and \( n_d \) identically vanishes, trivially satisfying reciprocity.

We now confirm that an effective Free energy correctly determines the occupancies and magnetization. The expectation value of the interaction energy determined by the equal time Keldysh Green functions between the conduction and dot electron, given by

\[
\langle H_I \rangle = J \sum_{\alpha, \sigma} \gamma_{\alpha} \int \frac{d\omega}{4\pi i} \left[ G_{d \sigma c_{\alpha}^\dagger}(\omega) + G_{c_{\alpha} d \sigma}^K(\omega) \right]
\]

After integrating over the coupling constant we obtain

\[
\Delta F_{\text{eff}} = \int_0^J \frac{dJ'}{J'} \langle H_I \rangle
\]

\[
= \sum_{\alpha, \sigma} 2 \gamma_{\alpha}^2 \Re \left[ -2\pi T \log \Gamma \left( \frac{1}{2} + \frac{\epsilon_{d \sigma} + \mu_{\alpha}}{2\pi i T} \right) \right] + 2\pi T \log \Gamma \left( \frac{1}{2} + \frac{\epsilon_{d \sigma} - \mu_{\alpha}}{2\pi i T} \right) + \Delta \log \left( \frac{D}{2\pi T} \right).
\]

where \( \Delta = \sum_{\alpha} \pi \rho(J_{\gamma_{\alpha}}^2) \). The expectation value of local state occupancy \( n_d \) and magnetization \( M \) are then

\[
\langle n_d \rangle = \frac{\partial \Delta F_{\text{eff}}}{\partial \epsilon_d} + c_1,
\]

\[
\langle M \rangle = -\frac{\partial \Delta F_{\text{eff}}}{\partial B} + c_2,
\]

where the constant terms gives the limiting value of the occupancy and magnetization when \( J \to 0 \). We can fix these constants by using the condition that \( \langle n_d \rangle \to 1 \) and \( \langle M \rangle \to 0 \) as \( \Delta \to \infty \), which gives

\[
\langle n_d \rangle = 1 + \sum_{\alpha, \sigma} \frac{\gamma_{\alpha}^2}{\pi} \Im \left[ \psi \left( \frac{1}{2} + \frac{\epsilon_{d \sigma} + \mu_{\alpha} + i\Delta}{2\pi i T} \right) \right],
\]

\[
\langle M \rangle = \sum_{\alpha, \sigma} \frac{\gamma_{\alpha}^2}{\pi} \Im \left[ \psi \left( \frac{1}{2} + \frac{\epsilon_{d \sigma} + \sigma B - \mu_{\alpha} + i\Delta}{2\pi i T} \right) \right].
\]

The distribution function of \( n_d \) as a function of \( \epsilon_d \).

\( \mu_1 = 1, \mu_2 = -1, \lambda_1 = 0.75, \lambda_2 = 0.25, \Delta = 0.01, \) and \( T = 0.001. \)

Both results can be independently confirmed by direct calculation from the Keldysh Green functions. It is remarkable that the derivative of a single Free energy functional reproduces the results of two separate Keldysh calculations, even though a D.C. current is flowing through...
the dot. It is interesting to see that even at the zero coupling limit, the occupancy and magnetization of the “dot” a non-thermalized form, and depends on the ratios between hybridization $\gamma_\alpha$. The non-thermal function $\nu_\alpha(\epsilon_\alpha)$ is reminiscent of the occupancy observed in quantum wire experiments. Here the parameters $\lambda_i$ play the similar role of distances between the measured point and leads in the experiment.

It is instructive to examine the the magnetization in the two-lead case which for zero temperature is

$$\chi(B, \Delta) = \frac{2\Delta(B^2 + \Delta^2 + V^2)}{\pi((B - V)^2 + \Delta^2)((B + V)^2 + \Delta^2)} \quad (17)$$

whilst for $\Delta \to 0$,

$$\chi(B, T) = \frac{1}{4T} \left[ \sech^2 \left( \frac{B + V}{2T} \right) + \sech^2 \left( \frac{B - V}{2T} \right) \right] \quad (18)$$

In both limits, the bias voltage dramatically reduces the susceptibility and at a finite voltage the $T = 0$ magnetic susceptibility in the limit of $J \to 0$ is always zero. Non thermal magnetizations of this kind have recently obtained in the zero order magnetic susceptibility calculation for quantum dot. Can we extend the set of “protected” variables to include other quantities of interest, such as the current or the spin current? The answer appears to be “no”. When we directly compare the retarded and advanced correlators involving any operator that involves the lead electrons, other than $H_1$, we find that they are not complex conjugates. This means that we cannot change the ratio of the couplings $\gamma_\alpha$ as we turn on the interaction, for to do this would be to introduce new variables which do not satisfy the Onsager reciprocity relation with $h_1$.

The validity of our conjecture in more complex systems is an open issue. We can not prove that reciprocity is stable against the presence of interactions within the dot, but we have circumstantial support for this idea. The above methods can be used in the large $N$ limit of the infinite $U$ Anderson model to examine how the mean-field equations evolve away from equilibrium. We have also compared the local susceptibility in the non-equilibrium Kondo problem obtained using the reciprocity conjecture with that obtained using Majorana techniques. An interesting recurring feature of these calculations, is the appearance of non-thermal distribution functions in the limit that the coupling with the leads is taken to zero. In interacting systems, these limiting distribution functions will need need to be computed self-consistently from the limiting form of the Dyson equation, before the change in Free energy can be computed.

In conclusion, we have examined the idea that the principle of virtual work can be extended to the non-equilibrium steady state of quantum systems. This has led us to conjecture the existence of a class of steady state variables which satisfy the quantum generalization of Onsager’s reciprocity relation out of equilibrium. If this conjecture holds, then the notion of a free energy can be extended to the quantum non-equilibrium steady state, permitting the expectation values of steady state variables to be computed as derivatives of a free energy functional. This idea works for the simplest possible example, and leaves open the possibility that it will apply to more complex and interesting interacting situations.

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1. Lord Rayleigh, Proc. Math. Soc London 4, 357, [363], (1873); Theory of Sound (London, MacMillan Co, 1st Ed 1877), Vol 1, p 78 (2d ed 1878), Vol 1, p 102.
2. L. Onsager, Physical Review 37, 405(1931)
3. L. Onsager, Physical Review 38, 2265(1931).
4. S. Hershfield, Phys. Rev. Lett 70, 2134, (1993).
5. T. Christen, Phys. Rev. B 55, 7606, (1997).
6. B. Derrida, J. L. Lebowitz and E. R. Speer, Phys. Rev. Lett. 87, 1506001 (2001).
7. M. A. Kastner, Rev. Mod. Phys. 64, 849 (1992); R. C. Ashoori, Nature 379, 413 (1996); L. P. Kouwenhoven and C. Marcus, Physics World 11, 35 (June 1998).
8. J.A. McLennan, Phys. Rev. A 10, 1272 (1974).
9. J.W. Dufty and J.M. Rubí, Phys. Rev. A 36, 222 (1987).
10. A. Kaminski, Yu. V. Nazarov, and L. I. Glazman, Phys. Rev. B 62, 8154(2000).
11. P. Coleman, C. Hooley and O. Parcollet, Phys. Rev. Lett. 86 4088 (2001).
12. H. Pothier et al., Phys. Rev. Lett. 79, 3490 (1997);
13. N. Wingreen A-P Jauho and Y. Meir, Phys. Rev. B 48, 8488(1993).
14. Larkin, A. I., and Yu.N. Ovchinnikov, 1975, Zh. Eksp. Teor. Fiz. 68, 1915 (Sov. Phys.-JETP 41, 960 (1975)).
15. For a review of Keldysh method, see J. Rammer and H. Smith, Rev. Mod. Phys., 58, 323(1986).
16. A. Kaminski and L. Glazman, private communication (2001).
17. O. Parcollet and C. Hooley, to be published cond-mat/0204273.
18. A. Rosch, J. Passke, J. Kroha and P. Wölfle, cond-mat/0202404 (2002).
19. W. Mao et al, to be published (2002).
20. The results of P. Coleman and W. Mao, cond-mat/0203001. I did not take this fact into account and will be revised in a future posting.