Maximum-entropy theory of steady-state quantum transport

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We develop a theoretical framework for describing steady-state quantum transport phenomena, based on the general maximum-entropy principle of nonequilibrium statistical mechanics. The general form of the many-body density matrix is derived, which contains the invariant part of the current operator that guarantees the nonequilibrium and steady-state character of the ensemble. Several examples of the theory are given, demonstrating the relationship of the present treatment to the widely used scattering-state occupation schemes at the level of the self-consistent single-particle approximation. The latter schemes are shown not to maximize the entropy, except in certain limits.

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During the last few years many *ab initio* calculations have addressed the electronic structure of systems with nonzero electrical current.[1–3] We will refer to these as the occupation scheme approaches (OS) since in practice one occupies the right- and left-going scattering states up to two different electrochemical potentials, μ^R and μ^L, respectively. The essential idea of the OS comes from Landauer's treatment of coherent transport in terms of the transmission matrix of the conductor.[4] Later, Caroli *et al.*[5] and independently Feuchtwang[6] developed a formal theory of tunneling based on the technique of Keldysh nonequilibrium Green's functions[7] which could be extended to address coherent transport as well. Recently it has been shown[8] that these two approaches are indeed equivalent at the level of a single-particle approximation in the spirit of Kohn-Sham density-functional theory. However, the latter approximation is very hard to justify. It is not clear what effective potential one should use; the use of the local density approximation is a mere hope rather than a secure approximation. We also believe that a certain difficulty might lie in the formal search for steady-state nonequilibrium Green's functions using a unitary (Hamiltonian-driven) evolution for $t\rightarrow\infty$ from an undisturbed system. For example, when we adiabatically turn on an external field, the Keldysh technique predicts no change in temperature, in contradiction with statistical thermodynamics. We therefore believe that any alternative point of view is of great utility here.

We build such an alternative theory using the generalized maximum-entropy principle as established by Jaynes.[9] Similar ideas were heavily exploited in the development of the projector techniques for nonequilibrium statistical mechanics by Mori,[10,11] yet detailed application to concrete problems is not widespread. Of the few papers, let us mention those of Ng[12] and Heinonen and Johnson,[13] who consider current-carrying ensembles, similar to ours. However, in these papers, the essential steady-state character of the ensemble is not considered. This results in certain problems when dealing with the matrix elements of current operator which are not present in our work. Our theory treats the stationarity of the nonequilibrium density matrix (DM) that involves constraint on an operator (the current operator in our case) which does not commute with the Hamiltonian. At the same time, the theory can be straightforwardly implemented for practical calculations as is demonstrated in the second half of our paper. Our formalism does not depend on the complexity of the system, i.e., without restriction to noninteracting particles or simple band-structure models.

The statistical DM, which represents an ensemble with known or controlled averages of given operators $\langle A_i\rangle = \mathrm{Tr}[\rho\hat{A}_i]$, is obtained by maximizing the information entropy $S[\hat{\rho}]=-\mathrm{Tr}[\hat{\rho}\log(\hat{\rho})]$, subject to constraints on the traces of the above-mentioned operators.[9] In the case of quantum transport, experiments suggest that for a given temperature, composition and total current we obtain a well-defined thermodynamic state (or, in the case of N-shaped *I-V* curves, a small number of states differing by applied bias voltage). The maximum-entropy principle, together with these physical constraints, simply represent the search in the phase space (Hilbert space) for the most likely density matrix.

Firstly, the total energy is conserved. This constraint is associated with the Lagrange multiplier β, corresponding to inverse temperature for equilibrium or near-equilibrium systems. Conservation of the total energy is not in contradiction with the dissipative character of the transport. The dissipation is realized through the increase in the energy flow behind the nanocontact (constriction). Similarly, the number of electrons is conserved and on an average is given by the total positive charge in the background, i.e., atomic nuclei. Therefore, a constraint on the number of particles is used with the usual symbol μ for the related Lagrange multiplier. The total current I should be the next thermodynamical parameter of the theory. On the contrary, the vast majority of present approaches to quantum transport use the applied bias ΔV instead. However, ΔV is not convenient for it is defined uniquely only between two ideal reservoirs, each being in equilibrium. These could never be a part of a practical calculation. In contrast, the current flowing through the system is represented by a simple operator and is well-defined even in the strongly nonequilibrium regime. We use the symbol A for the Lagrange multiplier accompanying the current constraint, and we later show that A is universally related to ΔV.

Finally we impose the steady-state condition $[\hat{\rho},\hat{H}]=0$. For this to have a nontrivial solution, the system must be infinite along the direction of the current. Otherwise, the only

steady state would correspond to zero current. This is equally present in the Keldysh formalism, where one has to first consider the limit of infinite size, and only afterwards can the time evolution of the response to the turned-on transfer Hamiltonian go to infinity. We note that this condition is a nontrivial one here. In previous work, it has been either satisfied automatically (equilibrium systems, nonequilibrium but translationally invariant systems) or not considered at all. To implement the steady-state constraint, we write the steady-state condition in any complete set of states $\langle E,\alpha|[\hat{\rho},\hat{H}]|E',\alpha'\rangle=0$, for all E,E',α, and α'. This particular notation stresses the fact that we work with a continuum of eigenstates of $\hat{H}$, normalized to a delta function of energy.[16] The index α runs over the discrete set of degenerate states at energy E. Each of these equations must be now guaranteed, with a separate Lagrange multiplier $\lambda_{\alpha,\alpha'}(E,E')$ and the expression in the functional to be maximized can be manipulated into

$$\int dE dE' \sum_{\alpha,\alpha'} \lambda_{\alpha',\alpha}(E',E)\langle E,\alpha|[\hat{\rho},\hat{H}]|E',\alpha'\rangle = \mathrm{Tr}[\hat{\lambda}\ [\hat{\rho},\hat{H}]] = \mathrm{Tr}[\hat{\rho}\ \hat{L}], \tag{1}$$

where we have introduced $\hat{L}=[\hat{H},\hat{\lambda}]$. This form is suitable for the variation with respect to the DM.

Collecting all the above terms we obtain the variational condition

$$\delta\{-\langle\log(\hat{\rho})\rangle+(\Omega+1)\langle\hat{1}\rangle-\beta\langle\hat{H}\rangle+\beta\mu\langle\hat{N}\rangle+\beta A\langle\hat{I}\rangle-\beta\langle\hat{L}\rangle\}=0. \tag{2}$$

The term $(\Omega+1)\langle\hat{1}\rangle$ guarantees the normalization of the DM. We also note that we have deliberately introduced the parameter β in the definition of all the other multipliers so that the limit $\beta\to\infty$ can be conveniently studied. As a result of variation we obtain the stationary nonequilibrium DM $\hat{\rho}=\exp\{\Omega-\beta\hat{K}\}$, where $\hat{K}=\hat{H}-\mu\hat{N}-A\hat{I}+\hat{L}$. The practicality of this expression relies on the knowledge of the $\hat{L}$ operator. We obtain its form from the solution of $[\hat{\rho},\hat{H}]=0$, as an equation for $\hat{L}$. Expanding the DM in terms of $\hat{K}$, we see that this is equivalent to $[-A\hat{I}+\hat{L},\hat{H}]=0$. If we cast the last expression in the representation of the eigenstates of $\hat{H}$, it is seen that the role of $\hat{L}$ is to remove the off-diagonal elements of the current operator. We shall show below that $\hat{L}$ should be of the form

$$L_{\alpha,\alpha'}(E,E')=I_{\alpha,\alpha'}(E,E')(A-\tilde{A}\delta(E-E')), \tag{3}$$

where $\tilde{A}$ is a finite constant, related to A as $\tilde{A}=\pi\epsilon A$, with $\epsilon\sim 1/l$ an infinitely small energy inversely proportional to the length of the system. The result is a finite number, since by inspection of Eq. (3) we deduce that $A\sim l$ due to $I\sim 1$.

To prove Eq. (3) we set $\hat{Y}=-A[\hat{I},\hat{H}]$ and write in the basis of $\{|E,\alpha\rangle\}$ the equation for $\hat{L}$ as:

$$iY_{\alpha,\alpha'}(E,E')+iL_{\alpha,\alpha'}(E,E')(E'-E)=0, \tag{4}$$

for $E\neq E'$, we have

$$L_{\alpha,\alpha'}(E,E')=\frac{iY_{\alpha,\alpha'}(E,E')}{i(E-E')}=AI_{\alpha,\alpha'}(E,E'). \tag{5}$$

Since $Y(E,E')$ is a result of a commutator, it is also proportional to $E-E'$. However, we need $L_{\alpha,\alpha'}(E,E')$ to be zero for $E=E'$ to keep the current at its given value and to satisfy the fact that $\hat{L}$ is also the result of a commutator with $\hat{H}$. This is uniquely achieved by

$$L_{\alpha,\alpha'}(E,E')=I_{\alpha,\alpha'}(E,E')(A-A\lim_{\epsilon\to 0^+}\epsilon\pi\delta_\epsilon(E-E')), \tag{6}$$

where

$$\delta_\epsilon(E-E')=\frac{1}{\pi}\frac{\epsilon}{(E-E')^2+\epsilon^2}, \tag{7}$$

which manifestly satisfies both conditions, since for $E=E'$, $\pi\epsilon\delta_\epsilon=1$. This is the stated result (3). Equation (6) can now be written in basis-independent form as

$$\hat{L}=A(\hat{I}-\hat{I}^0),\quad \hat{I}^0=\lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}\hat{I}(t)dt, \tag{8}$$

where the operator $\hat{I}^0$ has the form of *the invariant part of the current operator* with respect to the time evolution, introduced by Kubo in the linear response theory,[11] where the time dependence of the operator $\hat{I}(t)$ is determined by the Hamiltonian $\hat{H}$. If we insert the solution Eq. (8) for the $\hat{L}$ in the stationary DM obtained from Eq. (2), we obtain the final result for the statistical density matrix

$$\rho=\exp\{\Omega-\beta(\hat{H}-\mu\hat{N}-A\hat{I}^0)\}. \tag{9}$$

This is the general form, valid even for a fully interacting system. It is an interesting observation, that a sole requirement of the constraint on the time average of current operator is equivalent to the strong stationarity of the DM and the constraint on the current operator. We note that if $\hat{H}$ contains the electron-electron interaction, that interaction enters the invariant current operator in Eq. (8), so that interaction terms appear in the nonequilibrium DM in a rather nontrivial way.

We will now deduce the meaning of the parameter A. We consider two steady-state systems 1 and 2, with nonzero currents (see Fig. 1) described by their respective DM's $\hat{\rho}_{1(2)}$. The current is maintained with the parameters $A_{1(2)}$, but we can equally well imagine that there are ideal reservoirs at far left and far right to which we apply bias $\Delta V_{1(2)}$, so that A and ΔV is in correspondence. If we were to describe a single compound system, comprising weakly coupled systems 1 and 2, with only the total current being known, the DM would have had the form $\rho_{1+2}=\exp\{\beta[H_1+H_2-\mu(N_1+N_2)-A(I_1^0+I_2^0)]\}$. On the other hand, if we weakly couple the originally disconnected system 1 and 2,

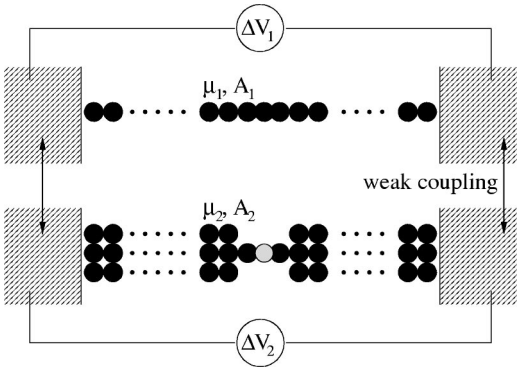

FIG. 1. Compound system 1+2 (see text) and related quantities.

we have $\hat{\rho}_{1,2}=\hat{\rho}_1\hat{\rho}_2$. Clearly, the averages with respect to ρ_{1+2} and $\rho_{1,2}$ will be the same if $\beta_1=\beta_2,\mu_1=\mu_2$, and $A_1=A_2$, i.e., no change of total current, as well as of I_1 and I_2, is introduced by coupling. Exactly This happens when the applied biases $\Delta V_{1(2)}$ are identical, so we conclude that ΔV should be an universal function of A,μ, and β. The universality comes from the fact that systems 1 and 2 are arbitrary. The 'ΔV-meter' could be represented by a Landauer's concept of infinitely large reservoirs adiabatically connected through one-dimensional (1D) conducting channel.[14] We leave detailed analysis of this situation for a future paper and here infer the $A-\Delta V$ relation from specific results in the following, giving $\Delta V=2\tilde{A}$, for small $\tilde{A}$. This is a very general thermodynamical statement and removes the detailed considerations of near-equilibrium in reservoirs from the actual transport problem of interest in the nanocontact.

We will now demonstrate several features of the general theory developed above, at the level of a self-consistent single-particle approximation. In the single-particle approximation, it is sufficient to know the single-particle density matrix for evaluation of any quantity, in our case the current and the electron density. These are well-defined for infinite system, unlike the total energy or total number of particles. Since we deal with a system that is genuinely infinite, i.e., there is a potential drop when comparing the right and left asymptotic regions, with uniform current flowing, we need to resort to Matsubara Green's function techniques to obtain the density matrix unambiguously. The result is

$$n(x,x')=\int dE\sum_{\alpha}\ \frac{\chi_{E,\alpha}(x)\chi^{*}_{E,\alpha}(x')}{e^{\beta(E-\tilde{A}I_{\alpha}(E)-\mu)}+1}, \qquad (10)$$

a Fermi-like distribution with the effective dispersion $\tilde{E}(k)=E-\tilde{A}I_{\alpha}(E)$. The $\chi_{E,\alpha}(x)$ diagonalize the effective Hamiltonian $\hat{K}$. $I_{\alpha}(E)=\pm|t(E)|(\kappa/k)^{1/2}$ are the eigenvalues of the invariant current operator, which in the basis of right- and left-going energy normalized scattering states has the form

$$2\pi\mathbf{I}^{0}(E)=\begin{bmatrix} t^{*}t\dfrac{\kappa}{k} & -r^{*}\tilde{t}\sqrt{\dfrac{k}{\kappa}} \\ -r\tilde{t}^{*}\sqrt{\dfrac{k}{\kappa}} & -\tilde{t}^{*}\tilde{t}\dfrac{k}{\kappa} \end{bmatrix}. \qquad (11)$$

The states $\chi_{E,\alpha}(x)$ are unitary transformation of the scattering states given by the eigenvectors of the matrix $\mathbf{I}^{0}(E)$ at each energy level E. t,r and $\tilde{t},\tilde{r}$ are the usual forward and backward transmission and reflection coefficients respectively, and finally $k=\sqrt{2E}$ and $\kappa=\sqrt{2(E+\Delta\phi)}$ with $\Delta\phi$ being the drop in electrostatic potential energy. Crucially, the scattering states appear here just as a convenient complete set of eigenstates of the Hamiltonian and it is the states $\chi_{E,\alpha}$ which are actually being occupied according to Fermi-like occupancies in Eq. (10). In the limiting case of $|r(E)|\to 0$, we obtain the original right- and left- going scattering states, in agreement with the occupation scheme. On the other hand, for $|t(E)|\to 0$ we get nearly their symmetric and antisymmetric combinations. We discuss the physical significance of these in later paragraphs.

Next we give our motivation for the identification of $\tilde{A}$ as the applied bias through $\Delta V=2\tilde{A}$. We look at the expectation value of the current operator in a 1D perfect wire. In the small $\tilde{A}$ limit, we have

$$I=2\sum_{\alpha=0,1}\int_{0}^{\infty}\frac{dE/2\pi}{e^{\beta(E-\tilde{A}I_{\alpha}(E)-\mu)}+1}(-1)^{\alpha}|t(E)|\sqrt{\frac{\kappa}{k}}$$

$$=\frac{2e}{h}2\tilde{A}|t(E_F)|^2. \qquad (12)$$

Since it is an experimentally well-established fact that the conductivity of a 1D channel is $2e^2/h$,[15] we can directly identify $2\tilde{A}$ with the bias applied between two equilibrium reservoirs. Due to the general arguments above we know that this relation is universal (for small $\tilde{A}$), so it needs to have the same form for any system. Equation (12) is in complete agreement with Landauer's formula[4] even though it comes from rather different considerations.

In the following we will be concerned with the self-consistent determination of the drop in electrostatic potential $\Delta\phi$, and a detailed discussion of the difference between $\Delta\phi$ and the applied bias ΔV. Specifically, let us suppose that our system consists of two identical D-dimensional jellium-like leads. Subtracting the conditions for local charge neutrality in the right and left asymptotic regions lead to the equation ($\beta\to\infty$):

$$\int_{0}^{\mu}\frac{dE}{2\pi}[n(x\to-\infty)-n(x\to\infty)]=\int_{-\Delta\phi}^{0}\frac{d\mathbf{k}^{D}}{(2\pi)^{D}}. \qquad (13)$$

This means that the charge appearing below the potential drop, on the right, must be exactly compensated by the charge transfered to the left by means of the occupancies in Eq. (10). We can analytically evaluate the left-hand side for small $\tilde{A}$, obtaining

$$\Delta\phi=2\tilde{A}|t|^2|r|^2=\Delta V|t|^2|r|^2, \qquad (14)$$

independent of dimensionality D. Through this we can relate the 4-point conductance $G_{4P}=I/\Delta\phi$ to the 2-point conductance $G=I/\Delta V$. We immediately see, that the former gives a surprising result $G_{4P}=(2e^2/h)(1/|r|^2)$, approaching the

quantum of conductance for $|t|\to 0$. This counterintuitive result can be understood in terms of the occupation of nearly antisymmetric admixtures of right- and left-going scattering states, present in $\chi_{E,+}(x)$. While this comes out of our formalism, we can expect that these combinations *in the limit of a weakly connected system* will be destroyed by a finite lifetime of the single-particle states, arising from any weak scattering by phonons or other electrons. If we model this fact by canceling the off-diagonal terms in the invariant current matrix Eq. (11), the resulting 2-point conductance turns out to be $\tilde{G}=(2e^2/h)|t|^4$ and the 4-point conductance $\tilde{G}_{4P}=(2e^2/h)(|t|^2/|r|^2)$, while the relation in Eq. (14) remains unchanged. $\tilde{G}_{4P}$ obtained without the off-diagonal terms is in complete agreement with the seminal work of Büttiker *et al.*,[4] while the two-point formula makes the conductance smaller by factor $|t|^2$. We would also like to stress that the off-diagonal elements may be expected to play a role for situations when $|t|\sim 1$, leading to higher conductances than those obtained from the Landauer formula.

In order to elaborate the relation between the maximum-entropy theory and OS, we observe that even though we work with only one parameter related to the number of particles, μ, from Eq. (10) we see that we can define two auxiliary Fermi energies $\mu_\pm$, up to which the states $\alpha=\pm$ are occupied from $\mu_\pm-\tilde{A}I_\pm(\mu_\pm)=\mu$ (see Fig. 2). In the linear response regime we get $\Delta\mu=\mu_+-\mu_-=2\tilde{A}|t|$ which together with Eq. (14) results in $\Delta\phi=\Delta\mu|t||r|^2$. Similarly, without the off-diagonal elements we have $\Delta\mu=2\tilde{A}|t|^2$ and $\Delta\phi=\Delta\mu|r|^2$. The latter relations demonstrate most clearly the difference between the maximum entropy and OS. Firstly, when ignoring the off-diagonals, the applied bias ΔV in the OS is heuristically identified with $\Delta\mu$ while in our treatment the thermodynamical arguments given in the first part of this paper suggest $2\tilde{A}=\Delta\mu/|t|^2$. Second, it is admixtures of right- and left-going states that are occupied according to μ^R and μ^L, not the states themselves. We believe that particularly for $|t|\sim 1$ this effect can be verified experimentally based on the differences between conductances coming from these two approaches. This comparison between OS and maximum entropy shows that only for $|t|\sim 1$ does the usual OS of scattering states approximately maximize the information entropy.

In conclusion, we have shown how the maximum-entropy formalism can be applied for nonequilibrium steady currents. We have derived the statistical density matrix introducing the $\hat{L}$-operator that guarantees the steady-state character of the statistical ensemble and identified its resolution with Kubo's invariant part of the current operator. A Lagrange multiplier $2\tilde{A}$, conjugate to the current operator, represents the applied bias. Even though the treatment of the fully interacting system within this scheme seems rather arduous, the possibility of describing the nonequilibrium steady state through the maximum principle opens up new ways forward. One prospect is a theory in the spirit of the density-functional theory that could permit the use of a rigorous single-particle approach to nonequilibrium calculations. In the second part of the paper we have demonstrated the theory on simple examples, discussing in detail the character of the density matrix within the single-particle approximation. We have shown that for systems with no reflection probability our theory gives results identical to the usual occupation scheme. This agreement slowly breaks down as the transmission is decreased and the relevant states become coherent combinations of right- and left- going states. We have derived a simple formula for the electrostatic potential drop and discussed its relation to the applied bias within the context of our theory.

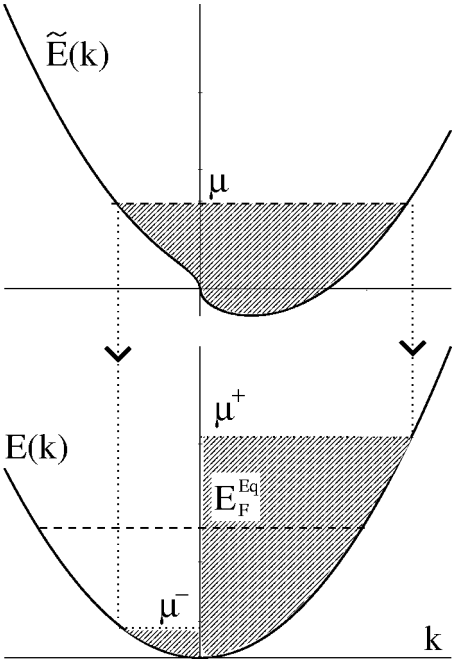

FIG. 2. The effective ($\tilde{E}(k)$) and the true energy ($E(k)$) dispersion relations with the corresponding Fermi energies μ,μ_+, and μ_-.

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