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Maximum-entropy theory of steady-state quantum transport

P. Bokes[*] and R. W. Godby

Department of Physics, University of York,

Heslington, York YO10 5DD, United Kingdom

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Abstract

We develop a new theoretical framework for describing steady-state quantum transport phenomena, based on the general maximum-entropy principle of non-equilibrium 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 non-equilibrium 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-states occupation schemes at the level of the self-consistent single-particle approximation.

During the last few years many *ab-initio* calculations have addressed the electronic structure of systems with nonzero electrical current [1, 2, 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 come 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 non-equilibrium 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 (LDA) 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 non-equilibrium Green's functions using a unitary (Hamiltonian-driven) evolution for $t \to \infty$ 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 generalised maximum-entropy principle as established by Jaynes [9]. Similar ideas were heavily exploited in the development of the projector techniques for non-equilibrium 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 is not considered. This results in differences between the predictions of OS and maximum-entropy methods, in the linear-response regime, that are not present in our work. We give a coherent formalism that does not depend on the complexity of the system, i.e. without restriction to non-interacting particles or simple band-structure models.

The statistical density matrix (DM), which represents an ensemble with known or controlled averages of given operators $\langle A_i \rangle = \text{Tr}[\rho \hat{A}_i]$, is obtained by maximising the information entropy $S[\hat{\rho}] = -\text{Tr}[\hat{\rho} \log(\hat{\rho})]$, subject to constraints on the traces of the above-mentioned operators [9]. In the case of quantum transport, experiments suggest that for a given temper-

ature, 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).

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. Similarly, the number of electrons is conserved and on 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 should never be a part of a practical calculation, to say nothing of the strongly non-local character of this quantity. In contrast, the current flowing through the system is represented by a simple operator and is well-defined even in the strongly non-equilibrium 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 $\left[\hat{\rho}, \hat{H}\right] = 0$. 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 consider the limit of infinite size first, and only afterwards can the time-evolution of the response to the turned-on transfer Hamiltonian go to infinity. To implement the steady-state constraint we write the steady-state condition in any complete set of states $\langle E, \alpha | \left[\hat{\rho}, \hat{H}\right] | E', \alpha' \rangle = 0$ for all E, E', α, α'. This particular notation stresses the fact that we work with a continuum of eigenstates of $\hat{H}$, normalised 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 maximised can be manipulated into

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

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

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

The term $(\Omega + 1)\langle \hat{1} \rangle$ guarantees the normalisation 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 non-equilibrium 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 $\left[\hat{\rho}, \hat{H} \right] = 0$, as an equation for $\hat{L}$. Expanding the DM in terms of $\hat{K}$, we see that this is equivalent to $\left[-A\hat{I} + \hat{L}, \hat{H} \right] = 0$. 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

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

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 (3) we set $\hat{Y} = -A \left[\hat{I}, \hat{H} \right]$ 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

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

Because $Y(E, E')$ 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 result of a commutator with $\hat{H}$. This is uniquely achieved by

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

where

$$\delta_\epsilon(E - E') = \frac{1}{\pi} \frac{\epsilon}{(E - E')^2 + \epsilon^2}, \tag{7}$$
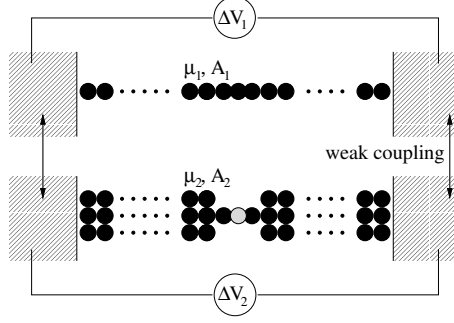
FIG. 1: Compound system 1+2 (see text) and related quantities.

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

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

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 R. 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 for the $\hat{L}$ in the stationary DM obtained from Eq. (2) the solution Eq. (8), 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 will now deduce the meaning of the parameter A. Consider we have 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 far left and far right there are ideal reservoirs 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 $\rho_{1+2} = \exp\left\{\beta\left(H_1 + H_2 - \mu(N_1 + N_2) - A(I_1^0 + I_2^0)\right)\right\}$. On the other hand, if we weakly couple the originally disconnected 1 and 2, 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 a 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 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 nano-contact.

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, 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

$$n(x, x') = \int \frac{dE}{2\pi} \sum_\alpha \frac{\chi_{E,\alpha}(x)\chi_{E,\alpha}^*(x')}{e^{\beta(E - \tilde{A}I_\alpha(E) - \mu)} + 1}, \tag{10}$$

where the $\chi_{E,\alpha}(x)$ diagonalise the effective Hamiltonian $\hat{K}$. $I_\alpha(E) = \pm|t(E)|\sqrt{\frac{\kappa}{k}}$ are the eigenvalues of the invariant current operator, which in the basis of right- and left- going energy normalised scattering states has the form

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

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

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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

$$
\begin{aligned}
I &= 2 \sum_{\alpha=0,1} \int_0^\infty \frac{dE/2\pi}{e^{\beta(E-\tilde{A}I_\alpha(E)-\mu)}+1} (-1)^\alpha |t(E)| \sqrt{\frac{\kappa}{k}} \\
&= \frac{2e}{h} 2\tilde{A} |t(E_F)|^2.
\end{aligned}
\tag{12}
$$

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. Eq. (12) is in complete agreement with Landauer's formula [4] even though it comes from rather different considerations.

Our next example concerns the behaviour of 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. Local neutrality requires ($\beta \to \infty$):

$$
\int_0^\mu \frac{dE}{2\pi} [n(x \to -\infty) - n(x \to \infty)] = \int_{-\Delta\phi}^0 \frac{d\mathbf{k}^D}{(2\pi)^D}.
\tag{13}
$$

The meaning of this is 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 $\tilde{A}$ and $|t|$, obtaining

$$
\Delta\phi = 2\tilde{A}|t|^2 = \Delta V |t|^2,
\tag{14}
$$

independent of dimensionality D. This shows that the electrostatic potential drop is in close correspondence with the non-equilibrium term in the effective Fermi distribution Eq. (10), $\Delta\phi \approx \sum_\alpha \tilde{A}I_\alpha(E)$. This is to be compared with the OS, where a similar correspondence ($\Delta\phi = \mu^R - \mu^L$) is assumed to be correct. There, however, the ΔV and $\Delta\phi$ are taken to be the same.

In our final example of specular tunneling between 2D leads we elaborate the significance of the character of the single-particle states χ_E for $|t| \to 0$ and the role of the off-diagonal

elements in Eq. (11). The current per unit length of the interface d obtained from Eq. (10) is $I/d = \frac{2\tilde{A}|t(\mu)|^2}{\pi^2}\sqrt{2\mu} + O(\tilde{A}^3)$. Therefore the conductance between reservoirs per unit length is $G/d = I/\Delta V/d = \frac{1}{\lambda_F}\frac{2e^2}{h}|t|^2$, where λ_F is the Fermi wavelength. At the same time, the drop in the electrostatic potential over the barrier is $\Delta\phi = 2\tilde{A}|t|^2$ so that the four-point conductance for potential drop measured between the 2D leads is $G_{4P}/l = I/\Delta\phi/l = \frac{1}{\lambda_F}\frac{2e^2}{h}$, independent of $|t|$. This is due to the occupation of nearly anti-symmetric admixtures of right- and left-going scattering states. While this comes out of our formalism, we can expect that these combinations for the weakly connected system will be destroyed by a finite lifetime of the single-particle states, arising from whatever 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 4-point conductance turns out to be $\tilde{G}_{4P} = \frac{1}{\lambda_F}\frac{2e^2}{h}|t|^2$. The relation in Eq. (14) remains unchanged. $\tilde{G}_{4P}$ obtained without the off-diagonal terms is in agreement with the quasi-classical result (see e.g. [15]). The substantial difference between $\Delta\phi$ and ΔV as given by (14) can be understood in terms of the distant ideal reservoirs defining the ΔV. For small $|t|$, the whole drop ΔV must actually occur in those distant regions, which we assumed had no effect on the distribution. The fact that $\Delta\phi \to 0$ for $|t| \to 0$ is a natural consequence of our formulation, although extremely small values of $|t|$ would require very long times for relaxation to the steady state.

In conclusion, we have shown how the maximum-entropy formalism can be applied for non-equilibrium steady states. 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. 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, as the relevant states became a coherent combinations of right- and left- going states. We have derived a simple dimensionality-dependent formula for the electrostatic potential drop and discussed its relation to the applied bias within the context of our theory.

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* Electronic address: pb20@york.ac.uk

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