



Quantum transport through molecular assemblies

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Received 22 June 2009; Accepted 22 April 2010

Abstract

We utilize the $T=0$ transport theory for resistivity R ($\propto G^{-1}$ where G is the conductance), for molecular assemblies connected to metallic leads. Following the early work of Rousseau et al., which gave G^{-1} as a force-force correlation function $R = \langle \vec{F} \vec{F} \rangle$, McCaskill and March introduced a denominator we shall denote by $1 - b$, where b takes account of bound states. Though for molecular assemblies, explicit calculation of both $\langle FF \rangle$ and b present difficulties for potential scattering theory we have adapted different models put forward in the literature to extract b and show that is highly oscillatory. In the case of the Brouwer model of electron pumping, when coulomb blockade is not operative, one-electron theory, such as the treatment of McCaskil and March is appropriate. Transcending that however, we suspect that proximity to a metal-insulator transition is a reason why conductances are often over estimated by orders of magnitude in current treatments of molecular electronics set-ups.

Keywords: Transport Theory; Molecular Crystals; Resistivity

PACS: 72.10.Bg; 64.70.kt; 61.72Hh

1. Introduction

Impurity scattering in metal systems, such as copper with a dilute concentration of zinc atoms, was treated quantitatively in the early work of Huang [1], who gave the resistivity R , in the linear concentration regime in terms of the phase shifts, $\delta_l(E_F)$ at the Fermi energy E_F , caused by the scattering of incident plane waves from the impurity potential created by a single Zn atom.

Independently, and much later, Rousseau et al. [2] gave a theory designed originally to treat pure liquid metals, in which the resistivity R (referred to below as RSM, which should be used at $T=0$ as electrons in metals like Na and K have almost completely degenerate electrons at their freezing points) was expressed as a force-force correlation function, namely

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$$R = \langle \vec{F} \vec{F} \rangle, \quad (1)$$

where explicitly, apart from a known multiplying constant

$$R = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial V(\mathbf{r}_1)}{\partial d_1} \frac{\partial V(\mathbf{r}_2)}{\partial d_1} \frac{\partial \gamma(\mathbf{r}_1, \mathbf{r}_2, E)^2}{\partial E} |E_F \quad (2)$$

where $\gamma(\mathbf{r}_1, \mathbf{r}_2, E)$ is the Dirac density matrix generated by the one-body scattering potential $V(\mathbf{r})$ entering the correlation function denoted $\langle \vec{F} \vec{F} \rangle$. One of us [3] subsequently showed that eqn. (2) reduced exactly to Huang's formula in terms of phase shifts at the Fermi level E_F when the multi centre liquid metal formula (2) was reduced by taking $V(\mathbf{r})$ to be scattering off a single impurity, as treated by Huang. So while eqn. (2) gives back the lowest-order liquid metal resistivity theory [4] when γ is replaced by the free-electron density matrix, it is plainly a strong-scattering theory when $\gamma(\mathbf{r}_1, \mathbf{r}_2, E)$ is generated by the one-body potential $V(\mathbf{r})$.

Nevertheless, the direct application of formula (2) to molecular assemblies connected to metallic leads represents a considerable computational effort, and we shall therefore appeal here, to gain insight, to a number of rather simple analytical models already in the literature.

However, before doing so, it is important to stress at this point that the RSM formula (2) has been transcended in the later study of McCaskill and March[5] to read:

$$R = \frac{\langle \vec{F} \vec{F} \rangle}{1-b} \quad (3)$$

where a further correlation function b appears, which is interpreted in ref. [5] to arise from bound-state effects. Thus, for the present study of molecular electronics we shall write the conductance G in the form of R^{-1} given by eqn. (3):

$$G = \frac{1-b}{\langle \vec{F} \vec{F} \rangle} \quad (4)$$

The outline of the present article is the as follows. In section 2, we shall appeal to the work of Brouwer [6] who was concerned with a set-up designed to simulate electron pumping. Brouwer's work is important in that he proposed a generalization of Landauer's formula [7], involving now derivatives of the same scattering matrix entering Landauer's treatment. We propose then in section 2 a specific form of the correlation function b entering eqn. (4) from Brouwer's modelling of electron pumping. By way of comparison, we consider in section 3 two different models, from both of which we can again extract a form of the factor b in eqn. (4). Section 4 constitutes a summary plus proposals for future directions which should be fruitful, involving experimental studies as well as theory.

2. Brouwer's model related to eqn. (4) for conductance G

Brouwer has considered a parametric electron pump through an open system, by means of scattering theory. As mentioned above, his main achievement is a formula for the pumped current in terms of the same scattering matrix entering Landauer's formula [7]. As

Brouwer [6] stresses, like there sult in ref. [7]. The pumping current contains quantal corrections to the contribution to the current. In relation to eqn. (4), which is a focal point of the represent study, we proceed below to extract b as intimately quantal, from the example worked out by Brouwer describing a simple pump in a one-dimensional wire. In this model, the wire contains a tunnel barrier at $x = 0$ and for the regime $0 < x < L$ a region where the electrostatic potential can be varied. By computing the scattering matrix and using his formula (8), Brouwer [6] finds the current I in his eqn. (10). From the second term in this equation, which he interprets as due to quantum interference, we extract a formula for the factor b entering the conductance G in eqn. (4). The result is:

$$b = \frac{1}{2kL} \{ \sin 2kL - \pi \sin^2 kL \} \quad (5)$$

The denominator of (4), as noted in ref. [7], is related to $2\pi k$, where k^2 in turn determines the incident energy E . The one-dimensional density of states is, in fact $(2\pi k)^{-1}$. The numerator $(1 - b)$ in the conductance G in eqn. (4) is plotted against kL using eqn. (5) in Fig. 1a. This numerator is zero at $kL = 0$, rising rapidly and thereafter exhibiting damped oscillatory behavior towards the large kL limit of unity.

We believe, already, that there is interest as to whether such damped oscillatory behavior is to be found in real molecular assemblies connected (say) to Al leads. Finite one-dimensional chains of atoms, with variable chain length, would seem to offer a promising starting point, but at the time of writing we know of no experiment which reflects directly features shown in Fig.1a. Thus, from the Brouwer model, we shall turn in section 3 to two further models; both of which, in contrast to Brouwer, take the Landauer formula [7], cast now into multichannel form, as the basis for the model conductance calculations.

3. Two further models, worked out using Landauer's transmission probability formula

Datta and Tian[15] use the Friedel sum rule to treat symmetric molecular conductors between two metallic pads. They got an expression for the resistance in terms of the number of conducting channels connecting the molecule to the metallic pads. In contrast to Brouwer[6], they use Landauer formula $(G = \frac{e^2}{\pi\hbar} T(E_F))$ [7] as starting point. Comparing now with eqn. (4) we can extract both the force-force correlations:

$$\langle \vec{F} \vec{F} \rangle = \frac{\hbar}{e^2} \text{ and } G = \frac{e^2}{h} (1 - b) \quad (6)$$

where $b = \cos(\pi N_d)$ (see eqn.(3) of ref. [15] and N_d is related to the difference between the number of electrons occupying the even and odd eigenvalues). The evolution of $1-b$ as a function of N_d (the length of the device region) is plotted in Fig. 1b. The metal-insulator transition ($b=1$) is again in evidence. The results share features in common with Brouwer's approach (oscillatory behavior) but also marked differences (lack of damping; this is also a feature of the next model in contrast to Brouwer's model).

If now we analyze the model treated by Gelin, Li and Koosv [16] based also on the Landauer formula applied to a one-dimensional tight binding model with onsite energy E_0 and nearest-neighbor hopping constant V , we can extract the conductance G proportional

to $\frac{e^2}{\pi^2 \hbar} (1 - \cos^2(\theta))$ where $\cos(\theta) = \frac{E - E_F}{2V}$. Thus the correlation b is given by $b = \cos^2(\theta)$ which extends between 0 and 1 (note that in the previous model $1-b$ was limited between 0 and 2). This is a typical Landauer result with no-damping; the latter is present in Brouwer's model where b goes from -1 to 1 in an oscillatory (damped) manner (see Fig.1a).

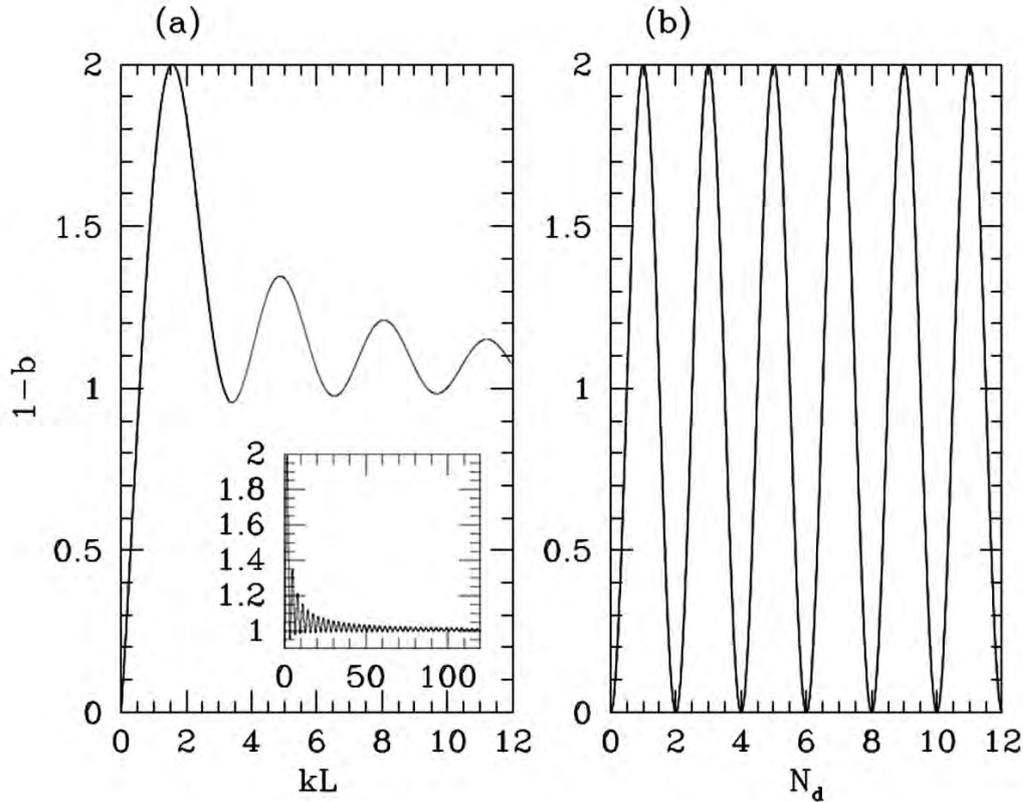


Fig. 1: (a) Extracted from the Brouwer model of one-dimensional pump [6] we plot of conductance G in eqn. (4) is plotted against kL using eqn.(5) of the main text. In set shows how the damped oscillation tends to the unity limit from above. (b) The evolution of $(1 - b)$ as a function of N_d from the Datta and Tian model of asymmetric molecule between leads [15] (N_d is related to the difference between the number of electrons occupying the even and odd eigenvalues).

4. Discussion, summary and proposed future directions

The McCaskill-March form of conductance G at $T = 0$ given in eqn. (4) has been a focal point of the present study. But calculations of the numerator $(1 - b)$ from first-principles remain major computational tasks. Therefore, $1-b$ has been extracted from models in sections 2 and 3. As physical parameters are varied, pronounced oscillatory behavior of the numerator in eqn. (4) is the common feature among the three model utilized here for $= 0$ conductance.

Experimental evidence at room temperature on molecular assemblies connected to leads shows conductance quantization (see also recent studies by Ruitenbeck group [8]). Therefore, it seems clear that, from Fig.1 of the present study, these models can only reflect

experimental behaviors in the low temperature regime. However, we note next the so-called Sharvin(S) limit giving GS as:

$$G_S = \frac{2e^2}{h} (k_F a_{min})^2 / 4 \quad (7)$$

where k_F is the Fermi wave number and a_{min} the effective minimal contact radius(see also ref.[9]) These workers show the conductance in units of $2e^2/h$ from calculations using free-electron and tight-binding models, versus $(k_F a_{min})^2$. Their results appear to show oscillatory behavior around a corrected Sharvin conductance [10], which encourages us to believe that eqn. (4) is again relevant at low temperatures. The actual conductance is always expected to lie below the Sharvin value, and this is what the authors of ref. [9] find in their theoretical studies. Corrections to the Sharvin treatment are discussed in, for example ref. [11].

Brouwer's treatment takes as starting point a result from ref. [12]. For an electron pump, he establishes the way the pumping current I is determined by the parametric derivatives of the scattering matrix S .

One point that emerges immediately from the I-V relationship of Brouwer is that the current is not quantized, unlike the case of electron pumps that operate in the regime of Coulomb blockade [13]. Note also that when Aleiner and Andreev[14] earlier considered adiabatic class of pumping in almost open dots, still highly relevant to the McCaskill-March inverse-transport theory, one involving the Kubo current-current correlation function and the other the force-force correlation function introduced in eqns. (1) and (2). The difference between Aleiner and Andreev and the later study of Brouwer is the question of quantization. Brouwer notes that he is dealing with a system well coupled to the leads, and he argues that then, to a first approximation one can use a model of non-interacting electrons, as in the study of McCaskill and March. The Coulomb blockade being lifted is an essential requirement for the current I not to be quantized, as in the Brouwer treatment.

Acknowledgement

One of us (N.H.M) wishes to acknowledge that his contribution to this study was made during a stay at DIPC, SanSebastián. He wishes to thank Prof. P.M. Etxenike and A. Rubio for generous hospitality. A.R. acknowledges support by the European Community Network of Excellence Nanoquanta (NMP4-CT-2004-500198) and SANES project (NMP4-CT-2006-017310), Basque Country University, Spanish MEC and the 2005 Bessel research award of the Humboldt Foundation.

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