

## Quantum Collision Current in Electronic Circuits

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Dedicated to Professor Michele Parrinello on the occasion of his 60th birthday.

Novel effects and phenomena that are not found at macroscopic length scales characterize the behavior of matter at the nanoscale. Electronic transport is a prominent example. When the spatial dimensions of a device are of the order of the electron wavelength, special features appear such as quantized conductance and ballistic transport. These phenomena are at the basis of molecular electronics and have been widely discussed in the literature.<sup>[1,2]</sup> Here, we shall focus on a different and not as well-known quantum feature of electronic circuits. When a circuit of length  $L$  is described within classical or semiclassical approximations, the power needed for the circulation of a dc current  $I$  is given by  $W = \mathcal{E}LI$  in terms of the applied dc electromotive force  $\mathcal{E}$ . We will argue below that a larger power  $W > \mathcal{E}LI$  is required to circulate a current  $I$  in a quantum device. The reason for the inequality is that, in addition to the power needed to circulate the current  $I$ , some dc power is also needed to maintain a stationary charge distribution in the circuit. This is a genuine quantum effect. In circuits governed by the laws of classical physics, some power is needed to displace charges in the initial transient, but no dc power is required to maintain a stationary charge distribution when a dc current is flowing.

To deal quantum mechanically with an electronic circuit, we consider a system of carriers (electrons) subjected to an applied electromotive force and coupled to a thermal reservoir held at constant temperature  $T$ . Dissipative effects, that is, inelastic scattering with the phonon modes of the reservoir, are necessary to maintain steady state and to prevent the electrons from accelerating indefinitely under the applied electromotive force. Under weak coupling conditions and if the timescale of inelastic scattering is much shorter than the current relaxation time, the reduced dynamics of the electrons is well approximated by a master Equation (1).<sup>[3,4]</sup>

$$\frac{d\bar{S}}{dt} = -i[H(t), \bar{S}(t)] + C[\bar{S}(t)] \quad (1)$$

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Here,  $\bar{S}$  is the electron reduced density operator, the Hamiltonian  $H(t)$  includes the applied electromotive force, the electron kinetic energy, the external potential due to the nuclei, and the electron–electron interaction. The superoperator  $C[\bar{S}(t)]$  describes inelastic scattering with the bath. The dynamics in Equation (1) is *Markovian*, that is, there are no memory effects because the superoperator  $C$  describes completed scattering processes via Fermi's golden rule, which identifies the allowed electronic transitions in a scattering process with phonons of a given frequency. The selection rules are a consequence of time-averaging implicit in the golden rule: on a timescale that is long compared to typical inverse level spacings, all energetically forbidden transitions are oscillating and average to zero. Consequently, the master dynamics in Equation (1) describes properties that are averaged or *coarse-grained* in time, a feature that we indicate with a bar on top of the reduced density operator  $\bar{S}$ . We will show below that coarse-graining in time has important implications on the current. Indeed, the very concept of a dc current is only meaningful as an average over the bath fluctuations. We also note that experiments always measure averages over some typical timescale determined by the interaction of the measurement apparatus with the system.

We adopt the velocity gauge in which the applied dc electromotive force  $\mathcal{E}$  is represented by a vector potential  $A(t)$  depending linearly on time:  $A(t) = -c\mathcal{E}t$ . This choice of gauge is convenient because it allows us to work with a closed circuit, that is, a ring or a periodically repeated structure, whereas the commonly used position gauge, in which  $\mathcal{E}$  is represented by a scalar potential  $\phi(r) = -\mathcal{E}r$ , would require us to work with an *open* structure that can exchange carriers with a battery. The Hamiltonian  $H(t)$  is given by Equation (2):

$$H(t) = \sum_n \left[ \frac{1}{2} \left( p_n - \frac{A(t)}{c} \right)^2 + V_{\text{ext}}(r_n) \right] + \frac{1}{2} \sum_{n \neq m} \frac{1}{|r_n - r_m|} \quad (2)$$

in the velocity gauge.

Here, we use atomic units in which  $e = m = \hbar = 1$  and the sums are over the electron coordinates and momenta. The electromotive force in the velocity gauge is induced by a magnetic flux, which traverses the surface terminated by the circuit loop.

Under steady-state conditions, the applied electromotive force is balanced by the dissipative effect of the bath, and  $d\bar{S}/dt = 0$  in Equation (1). When  $C[\bar{S}(t)]$  is properly defined, the corresponding dc current density  $j(r)$  has zero divergence as required by the continuity equation, guaranteeing local charge conservation.<sup>[5]</sup> The total dc current flowing in the direction of the applied electromotive force is obtained by integrating the current density over the cross-sectional area  $\mathcal{A}$  of the circuit, Equation (3).

$$I = \int_{\mathcal{A}} d\mathcal{A} \cdot j(r) \quad (3)$$

By virtue of the continuity equation,  $I$  is constant along the circuit. As discussed in a recent paper,<sup>[5]</sup> there are two contributions to  $j(r)$ , that is,  $j(r) = j_H(r) + j_C(r)$ . The first contribution, which we call the Hamiltonian current  $j_H(r)$ , describes the charge flow originating from the Hamiltonian evolution in Equation (1): this current has the standard definition  $j_H(r) = \text{Tr}\{\hat{S}\hat{j}(r)\}$  in terms of the current density operator in Equation (4).

$$\hat{j}(r) = \frac{1}{2} \sum_n [\hat{p}_n \delta(r - \hat{r}_n) + \delta(r - \hat{r}_n) \hat{p}_n] \quad (4)$$

Hats are used here to distinguish operators from  $c$  numbers.

The second contribution, which we call the collision (or dissipative) current  $j_C(r)$ , describes the charge flow originating from the collision superoperator in Equation (1). The collision current is a quantum mechanical effect associated with coarse-graining in time within the Markov approximation. This current contribution is absent in the Markovian dynamics of a classical particle system coupled to a bath, such as, for example, a system of charged particles undergoing Brownian motion. That is because classical collisions change the instantaneous momentum distribution but not the instantaneous spatial distribution of the particles. A change in the momentum distribution at time  $t$  can only affect the current distribution at later times  $t' > t$ . By contrast, quantum mechanical collisions change both the momentum and the spatial distribution of the particles, and a current flow must be associated with any instantaneous change in the charge density distribution to account for local charge conservation. The explicit expression for  $j_C(r)$  is reported in ref. [5]. At steady state  $j(r)$  is divergence-free, but  $j_H(r)$  and  $j_C(r)$ , separately, are not.

The power injected in a circuit is equal to the change in the energy of the electrons per unit time, that is, under weak coupling conditions, Equation (5).

$$W = \frac{d}{dt} \text{Tr}\{\hat{S}(t)H(t)\} \quad (5)$$

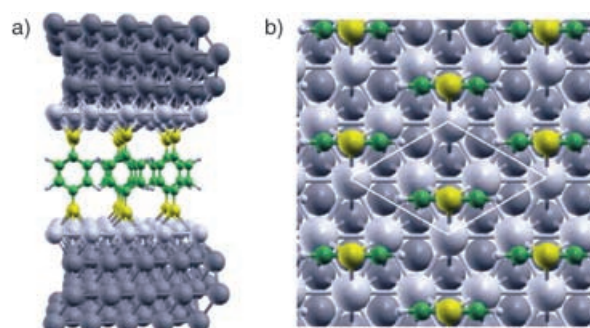
Using Equation (2), we obtain at steady state Equation (6).

$$\begin{aligned} W &= \text{Tr}\left\{\hat{S}(t) \frac{dH(t)}{dt}\right\} = \mathcal{E} \cdot \int_{\Omega} dr j_H(r) \\ &= \mathcal{E} \cdot \int_{\Omega} dr (j(r) - j_C(r)) \\ &= \mathcal{E} LI - \mathcal{E} \cdot \int_{\Omega} dr j_C(r) \end{aligned} \quad (6)$$

Here,  $\Omega = \mathcal{A}L$  is the total volume of the circuit and we took into account that  $j(r)$  is divergence-free. Typically,  $\int_{\Omega} dr j_C(r)$  is opposed to the applied electromotive force  $\mathcal{E}$ : thus,  $W > \mathcal{E}LI$ . When an electromotive force is applied to a circuit, the induced charge distribution is microscopically inhomogeneous. For instance, under a steady current flow electronic charge accumulates on the upstream side of the atoms and/or other mi-

croscopic obstacles whereas charge depletes from their downstream side. Inelastic collisions with the bath oppose this process and act to restore local equilibrium. The ensuing instantaneous charge density change originates a collision current, which is opposed on average to the Hamiltonian current. Ultimately, the quantum collision current translates into an additional resistance of an electronic circuit. This is an effect different from Landauer's so-called *residual resistivity dipole*<sup>[6–8]</sup> although both effects, the quantum collision current and the residual resistivity dipole, originate from the same microscopic inhomogeneity of a sample under current flow. The resistivity dipole is due to *elastic* scattering processes between the carriers and the microscopic inhomogeneities, whereas the quantum collision current is due to *inelastic* scattering processes between the carriers and the phonons of a heat bath in a microscopically inhomogeneous medium. As pointed out by Landauer,<sup>[6,7]</sup> the upstream charge piles up and the downstream charge deficit creates a dipolar field and, correspondingly, a potential energy drops across each obstacle leading to the residual resistivity of the sample. In our master equation formulation [Eq. (1)], this effect is fully included in the Hamiltonian evolution. When inelastic collisions are also taken into account, the *quantum collision current* discussed herein is a further source of resistance.

In the following, we report calculations on a molecular electronic device to illustrate further the above concepts. Our circuit consists of a self-assembled monolayer of benzene dithiolate (BDT) molecules in contact with two gold electrodes according to the geometrical setup in Figure 1. Periodic bound-



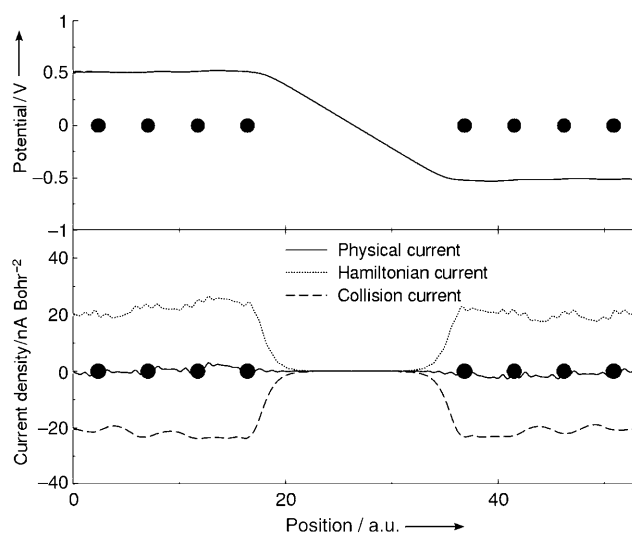
**Figure 1.** a) Lateral view of the BDT monolayer between two Au(111) surfaces. A total of eight layers are included in the unit cell of the simulation. The dark atoms in the slabs indicate the region where dissipation is applied. b) Top view of the BDT monolayer on Au(111): the box indicates the unit cell used in the simulation.

itary conditions are adopted to achieve a closed loop. Here, we briefly mention only a few key computational aspects of these calculations, which will be reported in detail elsewhere.<sup>[9]</sup> The calculations are based on an effective single-particle form of Equation (1), obtained by converting Equation (1) into an equation for noninteracting Kohn–Sham electrons within time-dependent current density functional theory.<sup>[10,11]</sup> We adopt the adiabatic generalized gradient approximation (GGA) for ex-

change and correlation and use the PBE<sup>[12]</sup> form of the GGA functional. We use norm-conserving pseudo-potentials<sup>[13]</sup> to model the effect of the atomic nuclei plus frozen core electrons on the valence electrons and expand the wavefunctions of the latter in plane waves. Numerically, we deal with a discrete set of electronic states calculated at a finite set of k-points in the Brillouin zone of the periodic supercell. With the present choice of k-points, the average level spacing at the Fermi energy is around 0.1 eV. As usual in band structure calculations of metallic systems, the discrete distribution of electronic levels is broadened by convoluting it with a Fermi–Dirac distribution (with  $k_B T = 0.6$  eV in the present calculation). Given the very small size of our supercell compared to the electronic mean free path for inelastic phonon scattering, which in gold at room temperature is of a few hundred Å, we use a very crude model for the bath. In particular, we neglect inelastic scattering processes in the molecular junction inside the non-shaded region in Figure 1, since electrons traverse this region ballistically to a very good approximation. Inelastic processes needed to thermalize the electrons are confined to the shaded region in Figure 1. To achieve thermalization in such a small space, we adopt an artificially large coupling between the electrons and the bath, similar to what is usually done in nonequilibrium molecular dynamics simulations of classical systems. We also hold the bath at an unphysically large temperature corresponding to the adopted broadening of the energy levels. In spite of these very crude approximations dictated by numerical limitations, the calculation reproduces well a number of the physical features of a real molecular device.

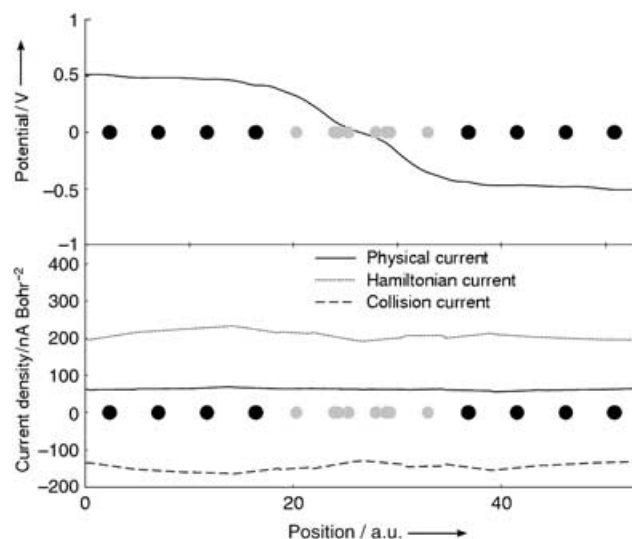
First, we consider a system in which the BDT molecules are removed, but the distance between the two gold electrodes is the same as in Figure 1. Dissipation is still present and limited to the shaded regions. When an electromotive force of 1 eV along the (111) direction is applied to this circuit, the dc current is zero in all practical respects, because the transmission coefficient of the empty space region that separates the two electrodes is essentially zero. The main effect of the applied electromotive force is to charge the two electrodes oppositely, which behave like a condenser, so that the electrostatic potential inside each metallic electrode is completely screened, as shown in Figure 2.

Even though the dc current density  $j(r)$  is zero everywhere (as required by continuity), small Hamiltonian and collision contributions opposed to each other are present (Figure 2). This is a consequence of the fact that the collision term in Equation (1) uses the system in equilibrium *in absence* of an applied electric field as the reference. Therefore inelastic collisions with the phonons tend to discharge the condenser and work against the quantum collision current needed to keep the condenser charged, an effect that would be present even at zero temperature due to spontaneous emission processes. Because of the presence of a small collision current the steady state of the condenser is very close, but not equal, to the true equilibrium state of a charged condenser, which is dissipationless. This small dissipative effect would disappear if we used the equilibrium state of the condenser *in presence* of the applied electric field as reference in the collision term.<sup>[9]</sup>



**Figure 2.** Top panel: sum of the externally applied potential and the induced potential at steady state. The externally applied potential is visualized in the position gauge (see text). Bottom panel: Hamiltonian current  $j_H(r)$ , quantum collision current  $j_C(r)$  and physical current  $j(r) = j_H(r) + j_C(r)$ . The electromotive force is applied along the (111) direction, which is shown in the plot. All quantities are averaged over planes perpendicular to the (111) direction. The black dots indicate gold atomic planes. The small fluctuations of the physical current  $j(r)$  are due to numerical inaccuracies.

Next, we consider the electrodes with the BDT molecules in place. The calculated steady-state potential and currents corresponding to an applied electromotive force of 1 eV are reported in Figure 3. In this case, the steady state is a true current-carrying state (independently of the reference state used in the collision term). It is interesting to compare the potential in



**Figure 3.** Top panel: sum of the externally applied potential and the induced potential at steady state. The externally applied potential is visualized in the position gauge (see text). Bottom panel: Hamiltonian current  $j_H(r)$ , quantum collision current  $j_C(r)$  and physical current  $j(r) = j_H(r) + j_C(r)$ . The electromotive force is applied along the (111) direction, which is shown in the plot. All quantities are averaged over planes perpendicular to the (111) direction. The black dots indicate gold atomic planes. The gray dots indicate BDT atoms.

Figure 3 with that in Figure 2. When no molecules are present, the potential is constant inside the electrodes, indicating perfect screening, and drops linearly in the vacuum region between the electrodes, as expected from elementary electrostatics. In presence of the molecules, the potential shows a small linear drop inside the electrodes, as expected from Ohm's law for a wire of finite resistance when a current circulates. However, most of the potential drop is due to the contact resistance and correctly occurs across the molecular junction. This drop is not purely linear but shows a well defined shoulder within the aromatic ring of the BDT molecules. This reflects the polarization of the ring under the applied bias. The calculated dc current  $I$  is about 3.1  $\mu\text{A}$  per DBT molecule, a value that compares well with the results of recent experiments.<sup>[14]</sup> Our artificial bath model keeps the distribution of the electrons close to a thermal equilibrium distribution, mimicking real experimental conditions, where the distribution of the electrons injected in a molecular device is close to a thermal equilibrium distribution. Having fixed the strength of the inelastic coupling, the main factor controlling the  $I$ - $V$  characteristics of a molecular device such as the one in Figure 1 is electron transmission through the molecular junction. Interestingly, calculations using an open circuit geometry, which ignore explicit dissipative effects, give a current  $I$  which is rather close to the one that we calculate herein.<sup>[15]</sup> Notice that the quantum collision current, which originates from inelastic scattering in the shaded regions, is nonzero inside the molecular junction, where it contributes to the observable current density  $j(r)$ . At variance with the condenser case, in a current-carrying circuit the collision current represents a real physical effect, whose magnitude depends on the strength of dissipative coupling and on the reference state for dissipation.<sup>[9]</sup>

We would like to conclude with a reference to the Car–Parrinello (CP) method.<sup>[16]</sup> In the CP approach, one deals with electronic and nuclear degrees of freedom focusing on what is arguably the most important effect of the electrons on the nuclei: that of originating an effective potential for the nuclei. The nuclear motion is usually well approximated by classical mechanics. In the CP scheme, the effective potential for the nuclei is generated on the fly by a fictitious dynamics of the electrons, which play only an ancillary role dictated by the adiabatic principle. The relevant timescale in the CP approach is that of nuclear dynamics, and the effective potential on the nuclei due to the much faster electrons results from the average coarse-grained dynamics of the latter. Herein, we are interested in the opposite scenario, that of describing the effect of nuclear motion on the long-time relaxation dynamics of the electrons. Here, it is the real quantum dynamics of the electrons that matters, albeit on a long timescale, and the nuclear motion is treated within the (quantum) harmonic approximation. The relaxation dynamics of the electrons originating a dc current is much slower than the characteristic periods of the nuclear oscillators: on this long timescale it is appropriate to coarse-grain the nuclear motion and focus on the reduced dynamics of the electrons, as done in Equation (1).

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