

AN OPEN-BOUNDARY, TIME-DEPENDENT TECHNIQUE FOR CALCULATING CURRENTS IN NANOWIRES

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Abstract In this paper we briefly review the current state of models for computing electrical conduction in nanoscale devices, highlighting the progress made, but also some limitations still present. We then summarise our recent novel theory that allows the simultaneous evolution of the electronic and ionic degrees of freedom to be modelled within the Ehrenfest approximation in the presence of open boundaries. We describe our practical implementation using tight binding and use this theory to investigate steady-state conduction through an atomic scale device. We then use the model to investigate two systems not accessible with other contemporary techniques: the response of a nano-device to a rapidly varying external field, and non-adiabatic molecular dynamics in the presence of a current.

1. Introduction

Advances in experimental techniques mean that it is now possible to measure the current flowing through individual molecules, atomic-scale wires and other systems where carriers have a quantum mechanically coherent history through the sample. When modelling such systems it is conventional to consider the system (or device) to be in contact with two macroscopic reservoirs, with some thermal equilibrium population of carriers deep within them. The connection between the device and the reservoirs is made by some form of tapering lead.

The theory and calculation of conductance for such nanoscale and mesoscopic systems was transformed by two key observations due to Landauer:

- The potential drop across a conductor can be viewed as arising from the self-consistent build-up of carriers, rather than the current arising from the applied electric field [1] (this paper has been reprinted in a more accessible journal [2])
- The conductance of a device can be calculated from the electron transmission through it [3]

A brief overview of these ideas and their development is given in a review [4].

If we have a device with a number of transverse eigenstates, then the conductance (G) can be found using:

$$G = \frac{2e^2}{h} \text{Tr} (tt^\dagger), \quad (1)$$

where t is the transmission matrix for the device. This formula can be derived by taking the zero-frequency limit of the Kubo formula [5], though more generally, it can be derived for systems with interacting (or non-interacting) electrons using the non-equilibrium Keldysh formalism [6]. One important effect on transmission and the calculation of conductance considered is the narrowing of the leads [7, 8] which has a significant effect on the scattering states.

This formalism has been developed and extended in many more directions than can be addressed here. Here we just note one extension that we consider particularly important: it has been generalised to multi-terminal samples [9].

The accurate calculation of the transmission matrix is perhaps the key problem. It can be found in terms of Green's functions and terms coupling the leads to the device [6]:

$$\text{Tr} (tt^\dagger) = \text{Tr} [\Gamma_L G^r \Gamma_R G^a], \quad (2)$$

where $\Gamma_{R(L)}$ is the coupling to the right (left) lead and $G^{r(a)}$ is the retarded (advanced) Green's function for the device.

Various electronic structure techniques have been applied to the calculation of the Green's functions, the transmission coefficients and the current in the system. They include tight binding methods [10–18], some of which have been extended to include the important effects of self-consistency [13, 17–20]. There are now increasing numbers of calculations based on density functional theory (DFT) techniques [21–29] exploiting different basis functions.

Using these formalisms it is possible to calculate some of the effects of the current on the device, notably current-induced forces which can be found from tight binding [30] and DFT [31]. However, any molecular dynamics carried out on the atoms under the influence of these forces is necessarily adiabatic. There have been some initial attempts to model the effect of current-induced heating [32, 33], though these are perturbative in nature. The charging and

deformation of molecules (including formation of defects such as solitons) has been considered to some extent [17, 18]. However, these are all adiabatic solutions, following the Born-Oppenheimer approximation. There are also recent theories which address the fundamental questions of how electronic structure is modified in the presence of a current [34, 35].

There are, however, problems with the present modelling techniques. There is good evidence that charged defects will have important roles in charge transport for conjugated polymers [18, 36] and solid state wires [37, 38], which involve highly non-linear effects due to electron-phonon coupling. These require a method that can handle the electrons and ions on an equal footing. A problem with wider implications is that first principles methods based on *static* DFT are challenged by the well-documented errors that it introduces for excited states. It is still an open question, but it is entirely possible the current carrying states may not be correctly modelled. A technique based on time-dependent density functional theory would have the advantage of standing on solid foundations.

To overcome the limitations of current methods, a different approach is required in which the ions and electrons evolve together in time in a consistent manner. Moving into the time domain allows us to exploit the benefits of time-dependent DFT for describing excited states and transient effects, and to introduce non-adiabatic terms which make possible modelling of heating of the ions as a result of the current flow.

There are a number of possible approaches to modelling non-adiabatic effects of widely varying complexity [39–41]. Here we consider the simplest in which the ions move along unique classical trajectories on which the atomic forces are determined by the Hellmann-Feynman [31] forces (the Ehrenfest, or mean field, approximation). That is, we neglect all quantum contributions to ionic motion.

The Ehrenfest method for closed systems has a long history, but we have extended it to open systems to allow an electric current to flow [42]. Below we describe a time-dependent formalism that is suitable for tight binding models implemented using density matrices. We have focused on tight binding because it is the simplest quantum mechanical model of electron motion that can deliver quantitative results [43]. We favour density matrices over wave functions and Green's functions because they provide a very compact description of the state of all the electrons [44, 45], and have proven very useful in the static description of materials in the context of linear scaling methods [46]. However, it is important to note that they have one particular limitation, namely that those parts of the density matrix treated explicitly must have a finite range if they are to be used in practical calculations. This is elaborated on below.

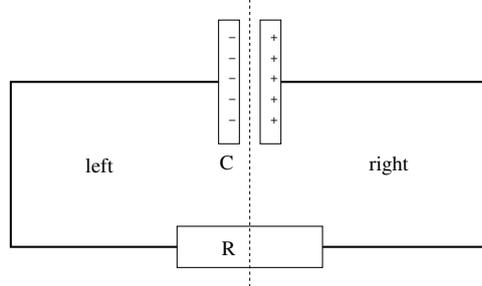


Figure 1. This circuit is the paradigm used to and build a model to describe the creation of an electric current. The capacitor represents the non-equilibrium source of charge, and the resistor the device through which we wish to drive the current.

2. Physical Model

The paradigmatic system that we use to construct a model of current flow is shown in Fig. 1. It consists of a capacitor in series with a resistor, forming a complete circuit. For times $t < 0$, an external potential is applied to the left-hand side of the circuit so that there is an excess of electrons on this side and a deficit on the right-hand side. Most of the net charge will appear on the capacitor so as to minimise the total energy. Formally, this applied external potential arises from a chemical potential for the electrons that differs on the left and right of the system. This can be shown simply by minimising the total energy subject to the constraint that there are more electrons on the left than on the right.

At time $t = 0$, the external potential is removed and the charge is now free to move, and in the process will attempt to remove the imbalance in the charge. This leads to a current flow through the resistor, which in turn produces a potential drop across it. Let us define Ψ_0 to be the many-body wave function for time $t \leq 0$ and let the many-body Hamiltonian for $t \geq 0$ be $\hat{\mathbf{H}}$. The wave function for $t \geq 0$ ($\Psi(t)$) is then given by $\Psi(t) = \exp(\hat{\mathbf{H}}t/i\hbar)\Psi_0$, provided $\hat{\mathbf{H}}$ does not depend on time. Note that this Hamiltonian includes both ionic and electronic degrees of freedom, and so is able to describe the full response of the ions to the electronic current.

In the absence of dissipation we will obtain oscillatory solutions whose frequency spectrum is governed by the energy spectrum of the Hamiltonian. However, if $RC \gg t \gg \hbar/W$ (where W is the range of eigenvalues of $\hat{\mathbf{H}}$ contributing to Ψ_0), there will be a quasi-steady-state. It is this time range in which we are interested.

We now make the following important observation which allows us to perform practical calculations. In the quasi-steady-state regime, the potential in the wires does not vary strongly, and most of the potential drop therefore oc-

curs across the resistor. This allows us to focus on the resistor alone, and to treat the capacitor and most of the wire as an external charge source or sink, which can be modelled by open boundary conditions. This is very similar in spirit to the Landauer approach in which only the transmission coefficient for the *device* needs to be evaluated.

The above formalism cannot be implemented directly because of the huge computational cost associated with such a many-body problem. The first simplifying step is to reduce the many-body electron problem to a single particle one. Provided we are willing to treat the ions in a mean field approach, which we are in this case, then we are free to describe the electrons using time-dependent density functional theory [47]. The key equations that we need are:

$$\begin{aligned}
 n(\vec{r}, t) &= \sum_n f_n |\psi_n(\vec{r}, t)|^2 \\
 \hat{H}_{ks} \psi_n(\vec{r}, t) &= i\hbar \frac{\partial}{\partial t} \psi_n(\vec{r}, t) \\
 \hat{H}_{ks} &= \hat{T} + \hat{V}_{eI} + \hat{V}_{Ha}[n] + \hat{V}_{xc}[n] \\
 M_I \frac{d^2 \vec{R}_I}{dt^2} &= -\vec{\nabla}_I V_{II} - \int d\vec{r} n(\vec{r}, t) \vec{\nabla}_I V_{eI}
 \end{aligned} \tag{3}$$

Here, $n(\vec{r}, t)$ is the charge density, f_n is the orbital occupancy, $\psi_n(\vec{r}, t)$ is an eigenfunction of the Kohn-Sham hamiltonian \hat{H}_{ks} , \hat{T} is the kinetic energy operator, \hat{V}_{eI} is the electron-ion interaction, \hat{V}_{Ha} is the Hartree (electrostatic) interaction, \hat{V}_{xc} is the exchange and correlation potential, \hat{V}_{II} is the ion-ion repulsion, M_I is the mass of ion I and \vec{R}_I is its position. Note that \hat{V}_{xc} is nonlocal in time. It is certainly possible to work directly with these equations (once suitable approximations for \hat{V}_{xc} have been made). However, we prefer to work with the single particle density matrix $\rho(\vec{r}, \vec{r}')$, where

$$\rho(\vec{r}, \vec{r}') = \sum_n \psi_n(\vec{r}) f_n \psi_n^*(\vec{r}'). \tag{4}$$

It is straightforward to write down the equation of motion for the density matrices using Eqs (3) and (4) and to recast the equation of motion for the ions:

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}_{ks}, \hat{\rho}] \tag{5}$$

$$M_I \frac{d^2 \vec{R}_I}{dt^2} = -\vec{\nabla}_I V_{II} - Tr\{\hat{\rho} \vec{\nabla}_I \hat{H}_{ks}\} \tag{6}$$

where we have moved to operator notation.

Continuing in the spirit of reducing complexity to increase computational efficiency, we approximate DFT by tight binding. Further, if we use orthogonal tight binding we can replace operators in our previous equations with matrices.

We will thus continue to use the operator notation with the new understanding that the operators will be represented by tight binding matrices.

As we indicated earlier on, we would like to concentrate our calculations only on the device and treat the environment in an implicit manner. To do this we separate the system into the device and the environment, which means we must divide Eq. (5) into components corresponding to device (designated by the subscript D), environment (designated by the subscript E) and the coupling between the two. We also introduce a damping term for the environment which makes it behave as a nearly equilibrium bath of electrons. This produces the following equations:

$$\begin{aligned}
i\hbar \frac{\partial \hat{\rho}_D}{\partial t} &= [\hat{H}_D, \hat{\rho}_D] + (\hat{H}_{DE} \hat{\rho}_{ED} - \hat{\rho}_{DE} \hat{H}_{ED}) \\
i\hbar \frac{\partial \hat{\rho}_{DE}}{\partial t} &= \hat{H}_D \hat{\rho}_{DE} - \hat{\rho}_D \hat{H}_{DE} + \hat{H}_{DE} \hat{\rho}_E - \hat{\rho}_{DE} \hat{H}_E \\
i\hbar \frac{\partial \hat{\rho}_E}{\partial t} &= [\hat{H}_E, \hat{\rho}_E] + (\hat{H}_{ED} \hat{\rho}_{DE} - \hat{\rho}_{ED} \hat{H}_{DE}) \\
&\quad - 2i\hbar \Gamma (\hat{\rho}_E - \hat{\rho}_{ref}).
\end{aligned} \tag{7}$$

There is a closed form solution for the density matrix for the environment. If we assume that \hat{H}_E is independent of time and define the driver terms \hat{G}_E and $\hat{G}_E^{(0)}$ by $i\hbar \hat{G}_E = (\hat{H}_{ED} \hat{\rho}_{DE} - \hat{\rho}_{ED} \hat{H}_{DE})$ and $0 = [\hat{H}_E, \hat{\rho}_E(0)] + i\hbar \hat{G}_E^{(0)} - 2i\hbar \Gamma (\hat{\rho}_E(0) - \hat{\rho}_{ref})$, we find the following solution for Eq. (7) for the environment:

$$\hat{\rho}_E(t) = \hat{\rho}_E(0) + \int_0^t dx \hat{O}(x) \left(\hat{G}_E(t-x) - \hat{G}_E^{(0)} \right) \hat{O}^\dagger(x) \tag{8}$$

where $\hat{O}(t) = e^{-\Gamma t} e^{\hat{H}_E t / i\hbar}$. For the parts of the density matrix belonging to the device and its coupling to the environment we treat the time evolution explicitly.

As a testbed for this formalism we now develop a very simple model system. It consists of two semi-infinite leads attached to a device. The lead on the left is at a different potential from that on the right. Each lead is represented by a linear chain of atoms with one orbital per atom. There are therefore two parameters that characterise the Hamiltonian for each lead: the on-site energy (a) and hopping integral between the nearest neighbour sites (b). We take b to be the same on the left and on the right. The bias is applied through the difference in onsite energies on the two sides: $a_L - a_R$.

The non-locality in time of Eq. (8) adds considerably to the cost of performing a calculation. However, from Fig. 2 we see that the evolution operator decays rapidly with time. We could thus approximate this by a function that goes strictly to zero outside some cut-off time. This is consistent with keeping

the damping term in Eq. (7). If the evolution operator is truncated in time, it becomes truncated in space as well. This corresponds to the fact that a wave packet can travel only a limited distance in a finite time.

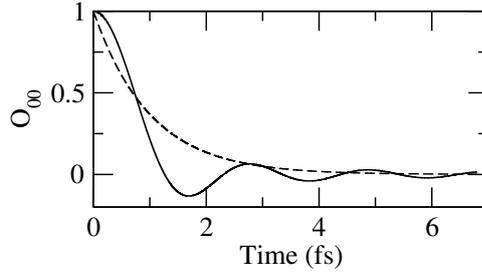


Figure 2. The solid line is the variation with time of the matrix element of the time evolution operator corresponding to the first atom in the environment. There is no damping ($\Gamma = 0$). The decay corresponds to the propagation of a wavepacket down the wire. The dashed line is the exponential damping factor with $\Gamma = 1.0 \text{ fs}^{-1}$.

The final quantities that we need to define in order to completely characterise the environment are the initial and reference density matrices ($\hat{\rho}_E(0)$ and $\hat{\rho}_{ref}$), both of which we take to be equal to the density matrix for the infinite wire (with the device present) in its ground state in the absence of a bias.

To complete our model system we need to introduce a device. The simplest device consists of only one atom. If we give this atom a high on-site energy it behaves as a barrier to current flow. The one-dimensional potential profile for this system is given in Fig. 3.

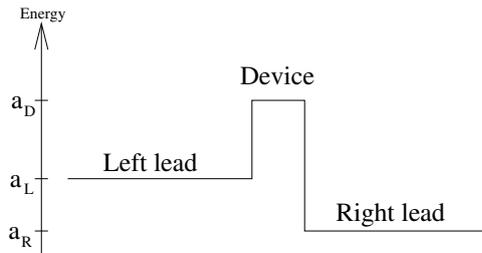


Figure 3. The energy profile for the model system. The energy axis on the left shows the positions of the onsite energies in the left lead (a_L), the right lead (a_R) and the device (a_D).

3. Results

As a check on the method described here, we can compute the conductivity of this system using the Landauer method. For this we need the transmission coefficient which can be found straightforwardly from Schrödinger's equation.

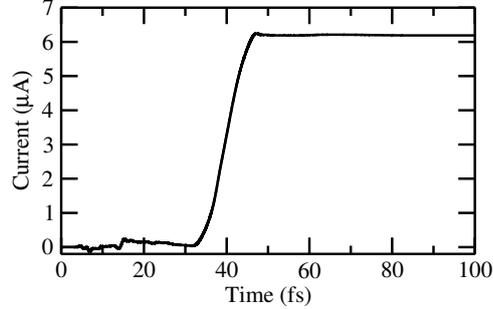


Figure 4. The variation of current into the device as a function of time. Note that it reaches a stable steady state. For the first 30 fs no bias was applied. The bias of -0.1V was then turned on over a period of 10 fs.

In our tight binding formalism, the wave function on the left-hand side has the form $\psi_n = e^{ikn} + Re^{-ikn}$, where ψ_n is the wave function evaluated at site n . On the right it has the form $\psi_n = Te^{iqn}$. Applying Schrödinger's equation ($\sum_j H_{ij}\psi_j = \varepsilon\psi_i$) to the left and right leads and the device gives $T = 2 \sin(k) / (\sin(q) + \sin(k) + i(a_R + a_L - 2a_D)/2b)$ where a_L and a_R are the on-site matrix elements on the left and right respectively, and a_D is that for the device atom. For the special case of a half filled band and infinitesimal bias we get the following conductivity

$$g = \frac{2e^2}{h} \left(1 + \left[\frac{a_D - a_L}{2b} \right]^2 \right)^{-1}. \quad (9)$$

If we have a bias of 0.1V, and the hopping and barrier height are both 1eV, we get a current of about $6.2\mu\text{A}$.

The time dependence of the current is shown in Fig. 4. We see that our time dependent scheme leads to stable steady currents.

One class of phenomena that our time-dependent formalism allows us to study is transient effects in the presence of rapidly changing external potentials. In Fig. 5 we show the effect of applying a voltage to the device atom, rather like the gate voltage in a field-effect transistor. The current responds smoothly and is reduced when the voltage is applied.

The transient effects seen in the current are proportional to the first derivative of the gate voltage. This is easy to understand by considering a hydrodynamic analogy. If you had some kind of large piston at the base of a canal full of water, then the rising gate voltage would correspond to the piston moving upwards from the base of the canal. This will displace water, with the amount being displaced per second being proportional to the rate at which the piston rises. Locally the displaced water will look like a current.

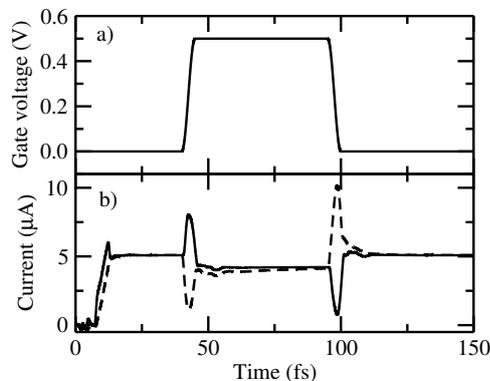


Figure 5. The current into (solid line) and out of (dashed line) the device while a gate-like voltage is applied. The voltage is turned on at 40 fs, over 5 fs, held for 50 fs, and then turned off, again over 5 fs. (a) Voltage applied. (b) Current.

To investigate heating effects, once a steady-state current has been achieved we perform molecular dynamics on the device atom. The position of the atom is allowed to evolve according to Eq. (6). To monitor the heating we follow the evolution of the kinetic energy of the device atom with time. In Fig. 6 we show the effects of two different applied biases. Fig. 6(a) shows that with a bias of $-0.1V$, we have cooling, while Fig. 6(b) shows that a bias of $-1.0V$ gives gradual heating of the system. These heating results will be discussed in more detail in future work.

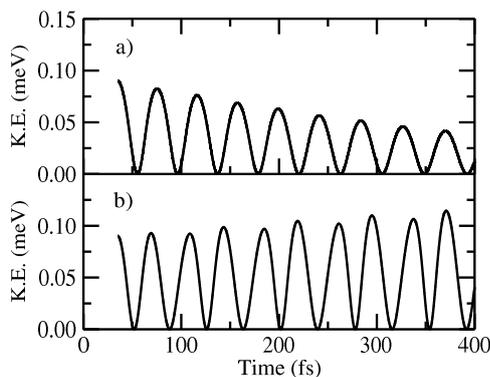


Figure 6. Plots showing kinetic energy of single atom device over time with bias (a) $-0.1V$ (b) $-1.0V$. Molecular dynamics was started after a steady-state current was achieved, at 60 fs.

In conclusion, we have presented a time-dependent technique which allows evolution of electronic and ionic degrees of freedom for an open system. It offers a number of possible improvements over static methods. These include

the ability to study transient behaviour and non-adiabatic processes, as well as possibly providing a framework for an improved density functional description of current carrying electrons. We have implemented the method using tight binding, and demonstrated transient behaviour, and both heating and cooling for a one dimensional metallic wire.

Acknowledgments

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