First principle theory of correlated transport through nano-junctions

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We report the inclusion of electron-electron correlation in the calculation of transport properties within an ab initio scheme. A key step is the reformulation of Landauer’s approach in terms of an effective transmittance for the interacting electron system. We apply this framework to analyze the effect of short range interactions on Pt atomic wires and discuss the coherent and incoherent correction to the mean-field approach.

One of the most pressing problems in nanotechnology is the need for recasting all the know-how about mesoscopic transport physics into the fully quantum mechanical limit appropriate for atomic scale phenomena. In the case of electronic and transport properties of atomic and molecular conductors, we must address at the microscopic level both the chemical complexity of the conductor and the complexity of the interactions between the different components of an extended open system.

The combination of Green’s function methods with a Density Functional Theory (DFT) description of electronic states has become a standard approach to study charge transport at the nanoscale. However, care must be taken in comparing the computed transport characteristics to experiments. Indeed, some important features — such as electron correlations, dissipation, decoherence and temperature effects — are at the moment partly or fully neglected. These deficiencies become more and more crucial when the dimensions of at least one part of the system reach a confinement situation where for instance electron-electron (e-e) interactions may become dominant. Recent observations of Kondo effect and Coulomb blockade in molecules connected to external electrodes, and in nanotubes with magnetic impurities or size confinement, indicate that correlations do play an important role in the mechanism of charge transport in nano-devices. Whereas many efforts have been directed to study other aspects of the transport problem, a standard approach to include correlation effects does not yet exist. One may expect that some of the difficulties in the interpretation of transport experiments on simple atomic chains and individual molecules could be ascribed to the neglect or mistreatment of correlations.

In this Letter we develop a new method for the ab initio computation of quantum transport in the strong correlation regime, and then apply it to specifically address the effect of e-e interactions on electronic transport through atomic-scale conductors. Following closely Meir and Wingreen, we derive a Landauer-like expression for the current through a correlated conductor between uncorrelated leads. Short range e-e interactions in the conductor are described through the Three-Body Scattering (3BS) formalism. The method is implemented through use of “maximally-localized” Wannier functions (MLWF). A particularly well-adapted system for gauging the relevance of e-e correlations is a late-transition-metal break-junction: in such a configuration, e-e effects are negligible in the bulk but, as a consequence of dimensionality, may acquire relevance in the junction region. We apply our method to simulate a model Platinum break-junction of varying length. Our findings show a large suppression of the transmittance that we ascribe to the inclusion of e-e elastic decoherence in the simulation. Moreover, the strong conductance reduction, also for small wire lengths, suggests that correlation cannot be neglected when studying transport properties of systems with localized electrons.

The system is modelled as three different regions, the left (L) and right (R) electrodes and a central conductor (C). We express our operators in a localized basis set which allows us to write the Hamiltonian and the Green’s functions of the whole system as 3 × 3 block matrices defined on the basis in the L, R, and C regions [H_{xy}, G_{xy}(\omega)\text{ where } x, y = L, C, R].

The Hamiltonian reads:

\[ H = \sum_{l} H_{lL} c_{l}^\dagger c_{lL} + \sum_{l'} H_{l'l'} c_{l'}^\dagger c_{l'} + \sum_{i \in C} \left[ H_{li} c_{i}^\dagger d_{i} + h.c. \right] , \] (1)

where \( c_{l} \) and \( c_{l}^\dagger \) (\( d_{i} \) and \( d_{i}^\dagger \)) are the one-electron annihilation and creation operators in the leads (conductor). In the above expression, the first term describes the L and R leads, \( H_{int} \) the conductor, the last term the coupling of the conductor with the L and R leads. We stress that the leads and the coupling Hamiltonian are non-interacting and all the e-e interaction is restricted to the conductor.

From the continuity equation for the steady-state current in the system and using the Keldysh non-equilibrium Green’s function formalism, the following expression
for the current \( I \) is derived:

\[
I = \frac{2ei}{\hbar} \int d\omega \text{Tr} \left\{ \left[ \Sigma^r_C - \Sigma^a_R \right] A_C + \left[ \Gamma_L - \Gamma_R \right] G_C^\omega \right\} . \tag{2}
\]

Here \( A_C = i[G_C^{\omega} - G_C^{a\omega}] \) is the spectral function and \( G_C^{r,a,\omega,>} \) are the (retarded, advanced, lesser, greater) Green’s functions in the conductor. The interaction between conductor and leads is described through the lead self-energies (SE’s), defined as \( \Sigma^{r,a},(\omega) = H_{C,x} G^{r,a,\omega,>}_x H_{x,C} \), where \( x=L,R \). Finally, the \( \Gamma_{L,R} \) terms in Eq. (2) are defined as twice the imaginary part of the retarded lead-SE’s, i.e. \( \Gamma_{L,R} = i \int \frac{d\omega}{\pi} \). Note also that \( \Sigma^{L,R}_{r,a} = i f_{L,R} \Gamma_{L,R} \) and \( \Sigma^{L,R}_{r,a} = -i(1 - f_{L,R}) \Gamma_{L,R} \), where \( f_L \) and \( f_R \) are the Fermi occupation functions for the left and right leads.

While in the non-interacting case the above expression brings to the usual Landauer formula \[15\], in the presence of interaction between electrons this is no longer true and further assumptions are needed. We here adopt the ansatz proposed by Ng \[21\] which relates \( \Sigma^<_{C} (\Sigma^>_{C}) \) to \( \Sigma^r_{C} \), thus defining the statistics of energy levels, in the general out-of-equilibrium interacting case. The starting point is the assumption \[22\]:

\[
\Sigma^<_{C}(\omega) = \Sigma^<_C(\omega) \Lambda(\omega), \tag{3}
\]

where \( \Sigma^<_{C} = \Sigma^<_{L} + \Sigma^<_{R} \) refer to the non-interacting case and include only the coupling with the leads, while the full \( \Sigma^<_{C} \) also include \textit{e-e} interactions. \( \Lambda(\omega) \), which is called \( A \) in other formulations \[22\], is determined by the identity \( \Sigma^<_{C} - \Sigma^<_{C} = \Sigma^r_{C} - \Sigma^a_{C} \) leading to:

\[
\Lambda(\omega) = \left[ \Sigma^<_{C}(\omega) - \Sigma^a_{C}(\omega) \right]^{-1} \left[ \Sigma^<_{C}(\omega) - \Sigma^r_{C}(\omega) \right]. \tag{4}
\]

Here the interacting SE’s take the form:

\[
\Sigma^{r,a}_{C}(\omega) = \Sigma^{r,a}_{L}(\omega) + \Sigma^{r,a}_{C}(\omega) + \Sigma^{r,a}_{corr}(\omega) \tag{5}
\]

where \( \Sigma^{r,a}_{corr} \) account for the \textit{e-e} interactions (while \( \Sigma^{r,a}_{C} \) just drop this last term). Relations (4,5) are the key to relate Eq. (2) to a Landauer-like formula. In fact, following Eq. (6) of Ref. \[22\] and using \( G_C^\omega = G_C^r \Sigma^>_{C} G_C^a \), it is possible to derive \( G_C^\omega = iG_C^r [f_L \Gamma_L + f_R \Gamma_R] \Lambda_G^\omega \), and therefore \( G_C^\omega - G_C^a = -iG_C^r [\Gamma_L + \Gamma_R] \Lambda_G^\omega \). These steps lead to the final expression for the current:

\[
I = \frac{e}{\hbar} \int \frac{d\omega}{2\pi} \left[ f_L - f_R \right] \text{Tr} \left\{ \Gamma_L G_C^\omega \Gamma_R A_G^\omega \right\}. \tag{6}
\]

We remark that the \textit{e-e} correlation plays a twofold role: it renormalizes the Green’s functions, which should now be calculated for the interacting system, and also modifies the expression for the current, introducing the corrective factor \( \Lambda(\omega) \). The quantity traced in Eq. (6), even if not a true transmittance across the scattering region due to the breakdown of Landauer’s theory, still plays the same role as regards transport. For this reason we refer to it as an effective transmittance and compare it to the transmittance of the non-interacting case. In particular, since the imaginary part of the \textit{e-e} self-energy exactly vanishes at the Fermi energy (\( E_F \)), the correction \( \Lambda(\omega = E_F) \) becomes the identity operator and the effective transmittance computed at \( E_F \) is proportional to the conductance at zero temperature, provided that the SE’s are calculated for the interacting system.

An accurate evaluation of the effective transmittance needs to be based on: (i) a good description of the non-interacting system, and (ii) the calculation of the \textit{e-e} correlated SE to include many-body effects arising from the interaction in the conductor. The first problem is solved by exploiting a recent methodology for the \textit{ab initio} calculation of the transmittance in the coherent transport regime \[8\]. The ground state of the mean-field system is described within the Local Density Approximation to DFT, using norm-conserving pseudopotentials and a plane-wave basis set \[23\]. The geometry of the L-C-R nano-junction are as in Ref. \[1\]. To obtain a consistent description of the system in a real-space localized basis set, the MLWF’s are computed both for the leads and for the conductor \[24\]. The details of this transformation and its application to electronic transport are described elsewhere \[8, 18\]. We remark that the basis change from Bloch eigenvectors to MLWF’s preserves orthonormality and completeness in the original Hilbert subspace, thereby avoiding typical problems arising very often for other localized basis functions. The same features allow us to use a minimal basis set for computing transport properties, while employing the system independent plane-wave basis set for the DFT calculation.

To discuss the inclusion of \textit{e-e} correlations we first need to define the interaction hamiltonian in Eq. (1). We focus on the short range \textit{e-e} interaction for two main reasons. On one hand, this regime is characterized by strong deviations from the non-interacting behavior, for instance in terms of quasiparticle lifetimes (which include elastic decoherence in the transport formalism). On the other hand, it allows us to adopt an Anderson-like form \[25\] of the interaction which is suitable for the localization in the conductor region only, as required by our approach.

In this work the \textit{e-e} self-energy \( \Sigma^{corr} \) is computed using a non-perturbative approach based on an effective Anderson hamiltonian, whose \( U \) Coulomb integrals could be either calculated \textit{ab initio} \[26\] or used as adjustable input parameters. It is solved by means of a configuration interaction scheme with up to three bodies (3BS) added to the non-interacting Fermi sea: two (one) electron(s) and one (two) hole(s) for conduction (valence) states. This method has been successfully applied to describe photoemission experiments on strongly correlated systems \[17\]. The 3BS self-energy is formally given \[17\] as a sum over projectors onto atomic states (those with non-negligible \( U \) integrals) and thus can be properly localized in the
conductor.

We now come to the model system: a Pt atomic wire of varying length, where the correlation is switched-on only on a finite number $N_C$ of atoms. It is worth noting that late 5$d$ transition-metal atomic wires have been demonstrated in break-junction experiments \cite{27}. Moreover, in the case of Pt, correlation effects are expected to strongly increase their importance in passing from the bulk leads to the confined wire as an effect of the reduced dimensionality. Therefore, our model system, while neglecting the full complexity of the wire-lead interfaces, retains the basic geometric construct of a correlated wire between uncorrelated leads in a Pt break-junction. Hence, it can be considered suitable to emphasize the effects of correlation and decoherence in nano-junctions, whereas the effects of dimensionality at the junctions (3D instead of 1D leads) is already known \cite{27}.

The setup is described in Fig. 1(a). For region C we consider a supercell containing 11 atoms with an interatomic separation of 3.0 Å, reasonable for experiments under stretching (such as break-junctions \cite{27}). The same geometry is adopted for the leads, which are modelled as semi-infinite wires treated at the single-particle level. Since the $sd$-bands of the Pt chain [Fig. 1(b)] form an isolated subset \cite{18}, we can extract a manifold of MLWF’s which span the same subspace. As an example, a particular wave function well localized within two bond-lengths is shown in the inset of Fig. 1(c). This MLWF subspace allows us to reproduce with good accuracy states more than 2 eV above the Fermi energy, enough to describe transport properties in this system where $p$-orbitals are expected to play a negligible role. Figure 1(c) shows the computed transmittance for the non-interacting Pt chain, which counts, for each energy, the number of channels (bands) available for charge transport, leading to a zero temperature conductance of 3$G_0$ ($G_0 = 2e^2/h$).

In Fig. 2(a,b) we report the spectral function projected on the interacting region and the effective transmittance for a chain with three correlated atoms ($U = 2.0$ eV). The many-body spectral function shows a splitting of the $d$-bands and a slight upward energy shift, which is consistent with our short range interaction picture based on the physics of the Anderson Hamiltonian. The transmittance is strongly suppressed by the inclusion of correlation [Fig. 2(b)], which is particularly effective in the hole region \cite{28}. This can be understood considering that on-site correlation arises from the strongly localized Pt $d$-orbitals, that are largely occupied and produce major features below $E_F$.

The introduction of $e-e$ interactions leads to quasi-particles characterized by energy and lifetime (finite broadening of their spectral features) formally accounted for by the hermitian ($H$) and the antihermitian ($A$) parts of the SE operator. Note that in more common correlation treatments, such as LDA+U, the SE in hermitian and lifetimes are consequently neglected. Although these components must obey analytic constraints \cite{17}, we analyze them separately to highlight their very effect on transport. First of all we divide the SE operator in $H$ and $A$ contributions, $\Sigma_{corr} = \Sigma_H + \Sigma_A$ where:

$$\Sigma_{H,A}(\omega) = \frac{1}{2} [\Sigma(\omega) \pm \Sigma^\dagger(\omega)] \quad (7)$$

In Fig. 2(c,d) and (e,f) we show our results when using $\Sigma_H$ or $\Sigma_A$, respectively, instead of the full correlation SE from 3BS. By definition $\Sigma_A$ vanishes at $E_F$, thus the only contribution to the zero temperature conductance comes from the $H$ part of $\Sigma$. Moreover, at energies different from $E_F$ the major quenching factor on the transmittance is due to the $A$ part of $\Sigma$, while its effect on the spectral function is just a slight broadening of the main peaks. Note that the decrease of the effective transmittance due to $\Sigma_H$ is related to energy misalignment of channels between the conductor and the leads, while that due to $\Sigma_A$ accounts for $e-e$ scattering. Our results thus indicate that $e-e$ scattering plays a fundamental role in suppressing effective transmittance for systems with strong short range correlation. This effect should be hidden in the low temperature conductance but evident in the $I-V$ characteristics [Eq. 10]: a suggestion for further experimental analysis.

Fig. 3 reports the computed conductance and effective transmittance for variable number of correlated atoms $N_C$. Figure 3(a) shows the effective transmittance curves for various $N_C$ values and demonstrates that the effective transmittance decreases with increasing $N_C$. This behavior is consistent with the presence of a scattering mechanism, according to which one expects a vanishing
In conclusion, we derived a generalized Landauer-like expression for the current [Eq. (3)] and the conductance in the presence of e-e interactions. The formalism is suitable for a fully ab initio implementation that we realized using a basis set of maximally-localized Wannier functions for the Green's functions and the 3BS formalism for the e-e self-energy. We applied the method to a finite Pt wire and found a renormalization of the conductance and a strong quenching of the transmittance as a consequence of the e-e scattering. Our results suggest that the inclusion of electron correlation for systems with strong short-range interactions is essential for an accurate description of current and conductance.

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FIG. 2: (color online). Curves: Spectral function projected on the interacting region (left) and effective transmittance (right) for the case of three correlated atoms in the Pt chain. Shaded areas: mean-field reference results. $E_F$ is set to zero. (a) and (b) show the computational results obtained with the total correlation SE $\Sigma_{\text{corr}} = \Sigma_{\text{3BS}}$. The (c,d) [e,f] plots are obtained using only the hermitian [antihermitian] SE $\Sigma_H$ [$\Sigma_A$].

FIG. 3: (color online). (a) Effective transmittance against energy for variable number of correlated atoms in the chain: $A$ is the reference mean-field bulk transmittance. $N_C=1,3,5,7$ in B,C,D,E. (b) Conductance as function of the number of correlated atoms in the Pt chain. Saturation is observed between $N_C=6$ and 7.

effective transmittance at $\omega \neq E_F$ in the limit of infinitely long correlated wires. Figure 3(b) reveals also a rapid decrease of the conductance at small values of $N_C$. The last result shows firstly that the conductance is renormalized as well as the transmittance, although the imaginary part of the SE vanishes at $E_F$. Second, it suggests that the effect of on-site correlation should be experimentally measurable also for short atomic chains (such as those produced by break-junctions).

In conclusion, we derived a generalized Landauer-like expression for the current [Eq. (3)] and the conductance in the presence of e-e interactions. The formalism is suitable for a fully ab initio implementation that we realized using a basis set of maximally-localized Wannier functions for the Green's functions and the 3BS formalism for the e-e self-energy. We applied the method to a finite Pt wire and found a renormalization of the conductance and a strong quenching of the transmittance as a consequence of the e-e scattering. Our results suggest that the inclusion of electron correlation for systems with strong short-range interactions is essential for an accurate description of current and conductance.

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[28] Note that these results are mainly due to the renormalization of the GF’s in Eq. (6) while the correction term A(ω) plays a minor role. This finding may be caused by the very one-dimensional nature of the considered system and further investigation is needed.