



# Atomistic Simulation of the Electronic Transport in Organic Nanostructures: Electron-Phonon and Electron-Electron Interactions

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**Abstract.** Non-equilibrium Green's functions formalism is used to study the influence of molecular vibrations on the current through a benzodithiolate molecule sandwiched in between Cu contacts. Incoherent tunneling and power dissipation in the molecular junction is analyzed in detail. We develop an efficient scheme for quasiparticle correction to the DFT states based on the GW theory. The method is applied to the investigation of tunneling current through the same molecule. We show that the HOMO-LUMO gap renormalization results in a decrease of tunneling current by up to one order of magnitude. The importance of quasiparticle corrections in conjunction to power dissipation analysis is discussed.

**Keywords:** molecular electronics, quasiparticles, GW, Incoherent tunneling, electron-phonon scattering

## 1. Introduction

The field of molecular electronics has seen a tremendous expansion in recent years, thanks to the realization of ingenious experimental setups and the fundamental achievement of reproducible results and behaviors [1–3]. The challenges for a complete understanding of transport in such systems are still considerable, given the large number of uncontrolled variables still present in experimental realizations, including the critical details of contact morphology. Significant progresses have also been made on the theoretical side, although the agreement with experiments is not satisfactory in all cases. The reasons for the discrepancies can be ascribed to several factors, including both the uncertain experimental conditions as well as inherent limits of the approximations made in order to make the problems tractable. It has been understood that accurate predictions ought to include a fully microscopic de-

scription of the metal-molecule-metal ( $M^3$ ) system and include a proper treatment of non-equilibrium transport conditions, inherent in  $M^3$  transport. Particular attention has been devoted to the evaluation of the electron-phonon interactions in molecular systems [4–6] and the role of Joule heating and thermal dissipation. The problem is tackled within the formalism of NEGF including appropriate electron-phonon self-energies. The electron-phonon coupling is derived from the DFTB Hamiltonian. The power dissipated is calculated from the virtual contact current [7] originated from phonon emission and absorption processes. In this work the model and method developed in Ref. [6] are applied to study incoherent electron-phonon current in a dithiophenyl molecule. However, in performing such kind of calculations we should not forget the underlying approximations of the density functional theory (DFT), usually accepted as the standard in solid-state simulations. In fact there are no fundamental reasons to extend

the results of DFT, valid for the investigation of equilibrium ground-state properties of a  $N$ -particle system, to the study of transport, which is a non-equilibrium condition also involving addition and removal of particles. We develop an approximate GW correction applied to the DFTB method and show its applications to molecular systems sandwiched in-between electrodes to obtain a first-principle correction of the  $e-e$  interaction energy. The influence of quasiparticle corrections is discussed and preliminary results of tunneling across a dithiophenyl are shown.

## 2. Electron-Phonon Interactions—Theory

We are interested in modeling the coherent and incoherent electron transport through a molecular wire bridging two metal contacts. While the electrons cross the system, they interact with the molecular ionic vibrations from which they can be inelastically scattered. The electron-phonon scattering within the leads is not considered. The electronic system is described via a single-particle tight-binding Hamiltonian derived from Density functional theory (DFTB) [8,9]. The method has been recently extended to the non-equilibrium Green's function (NEGF) approach [10]. In order to study the electron-phonon coupling we expand the TB Hamiltonian to first order in the atomic displacements [5,6]. The Hamiltonians of the decoupled mode oscillators are quantized in the usual way, by making use of the standard relationships between the position operator and the Bose field operator. Within the NEGF formalism the relevant quantities are the correlation functions,  $G^<$  and  $G^>$ , representing essentially the electron and hole spectral densities, respectively [11]. The relevant phonon self-energy is evaluated within the first order Born approximation [12,13], expressed as

$$\Sigma_{ph}^{<,>}(\omega) = i \sum_q \gamma_q^2 \int \frac{d\omega'}{2\pi} G^{<,>}(\omega - \omega') D_{0,q}^{<,>}(\omega'), \quad (1)$$

where the  $D_{0,q}^{<,>}$  are the correlation functions related to the vibrational modes, which are assumed Einstein oscillators in thermal equilibrium with a bath. In principle the phonon-bath interactions can be included explicitly by solving an additional kinetic equation, which is relevant when studying heat dissipations. The current is computed using a generalized version of the Landauer formula, valid also for non-equilibrium conditions and

in particular when sources of incoherent scattering are present [6].

## 3. Results

We consider a di-thio-phenyl molecule bridging two Cu contacts, which is known to bind sulfur atoms. In practical realizations Au is preferred because it is inert to oxygen. We have chosen Cu in these particular calculations in order to avoid relativistic corrections, necessary for a proper treatment of Au. However the discussion is quite general and the main conclusions can be applied to Au contacts as well.

The Cu surface atoms have been kept fixed, because of the much larger atomic mass and the 36 modes of vibrations corresponding to the degree of freedom of the 12 molecular atoms are calculated. The tunneling current, including all 36 modes, has been calculated at the voltage of 0.4 V and assuming a temperature of 0 K. We find a total current of  $I_{\text{tot}} = 0.47 \mu\text{A}$ , which can be splitted into a coherent component of  $I_{\text{coh}} = 0.42 \mu\text{A}$  and an incoherent component of  $I_{\text{inc}} = 0.05 \mu\text{A}$ . Such theoretical subdivision are possible by manipulating Eq. (??). The corresponding non-equilibrium transmission as a function of energy are shown in Fig. 1(a). Here we can recognize some steps, which correspond to the activation of one particular vibrational mode. Since calculations are performed at 0 K, only the emission channel is possible. A mode becomes activated beyond

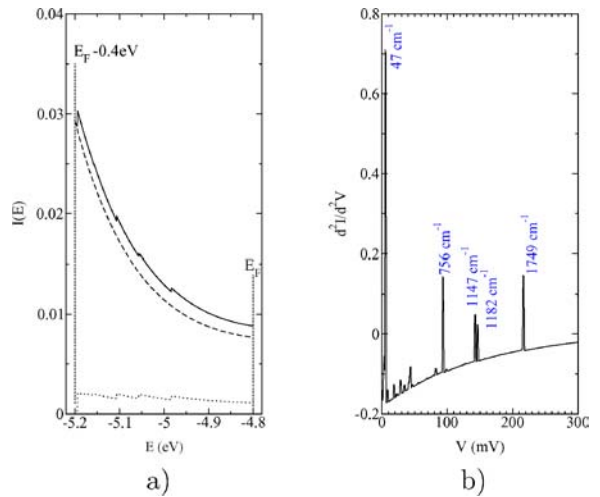


Figure 1. (a) Coherent (dashed), Incoherent (dotted) and total (solid) current densities as a function of injection energy. (b) Second derivative of the current vs. voltage. Peaks corresponds to the activation of a vibrational mode.

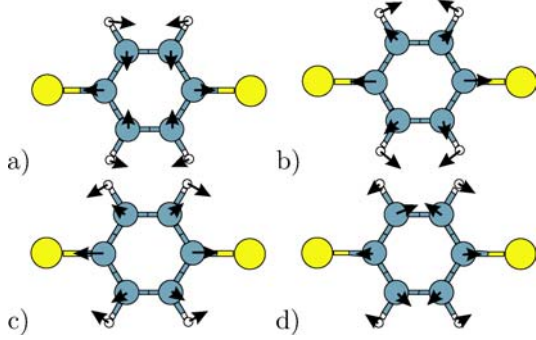


Figure 2. Vibrational mode representation of the most important modes for incoherent electron-phonon scattering: (a)  $756 \text{ cm}^{-1}$ , (b)  $1147 \text{ cm}^{-1}$ , (c)  $1182 \text{ cm}^{-1}$ , (d)  $1754 \text{ cm}^{-1}$ .

an applied bias sufficient to emit a phonon, hence above the phonon energy. At biases below the phonon energy emission is prevented by the exclusion principle, since an electron would emerge at the other contact with an energy below the Fermi sea. The step height is proportional to the electron-phonon scattering strength of the corresponding mode. An interesting quantity to calculate is the second derivative of the I-V characteristics, which can be compared, for instance, to inelastic electron tunneling spectroscopy experiments (IETS). An example of such calculation is shown in Fig. 1(b). The step of Fig. 1(a) maps into the peaks of Fig. 1(b). The energy scale of Fig. 1(b), expressed in eV, corresponds to the phonon frequencies, as in typical IETS experiments. The strongest peaks corresponds essentially to breathing and skewing modes of the benzene cage, as shown in Fig. 2. The low energy mode, giving a large scattering corresponds instead to a rigid twist of the entire molecule around its principal axis. This modes involves essentially a relative hydrogen-Cu oscillation, which is disturbing the electronics of the system. Similar effects have been found also for oscillations of Au-H distances in alkanethiols [6] For this system we have also calculated the total power released, which is computed using the virtual contact current as proposed by Datta [7]. We find a value of 11.5 nW at 0.4 V and 33 nW at 1.0 V of applied bias. This quantity should be compared to the value of 0.16 nW calculated for alkanethiols [6].

#### 4. Quasiparticle Corrections

In the DFT theory Koopman's theorem applies only when the exact exchange functional is used [14]. This

allows to interpret the energy of the highest occupied molecular orbital (HOMO) as the ionization potential. Unlike in the Hartree-Fock (HF) theory, the DFT eigenvalue corresponding to the lowest unoccupied orbital (LUMO) cannot be interpreted as an approximation to the molecular affinity, even if exact exchange is used. However, in transport problems temporary transitions between  $N$  and  $N + 1$  electrons occur. This happens in multistep hopping transport as well as in non-resonant  $M^3$  tunneling, where the unoccupied states are occupied only virtually. The GW method for quasiparticle corrections takes its name from the form of the self-energy [15–17]

$$\Sigma(E) = \frac{i}{2\pi} \int d\omega e^{i\omega_0^+} G_0(E - \omega) W(\omega) \quad (2)$$

where  $G_0$  is the single particle Green's function, which can be built from the DFTB wavefunctions, and  $W = \epsilon^{-1}v$  is the screened Coulomb interaction. The self-energy,  $\Sigma(E)$ , is a non-local and energy-dependent operator accounting for XC effects. GW implicitly takes into account the effect of an extra (test) particle, accounting for the dynamical screening properties of the  $N$ -particle electron gas. The most time consuming step of the GW implementation is the evaluation of the Hartree-Fock exchange energy for each orbital  $i$ . Such calculation involves a Coulomb integral over products of atomic orbital basis functions, which are generally centered on different atomic sites. The key approximation of our implementation is to write the wavefunction products into charge monopoles, as

$$\phi_\mu(r)\phi_\nu(r) \approx \frac{1}{2} S_{\mu\nu} (\|\phi_\mu(r)\|^2 + \|\phi_\nu(r)\|^2), \quad (3)$$

where  $S_{\mu\nu}$  is the overlap matrix, and approximate  $\Sigma_i^x$  as

$$\Sigma_i^x = \sum_j^{occ} \sum_{\mu\nu} q_\mu^{ij} [v]_{\mu\nu} q_\nu^{ij}, \quad (4)$$

where the  $q_\mu^{ij}$  are generalized Mulliken charges [18], and  $v_{\mu\nu}$  are the Coulomb integrals between squared DFTB atomic orbitals. Such an approach provides a very fast, though approximated, GW calculation [18]. Tests show that the approximation is very good when applied to  $\pi$ -conjugated orbitals, however it shows some limits when applied to  $\sigma$  orbitals [18]. Therefore, we can confidently apply our method to the correction

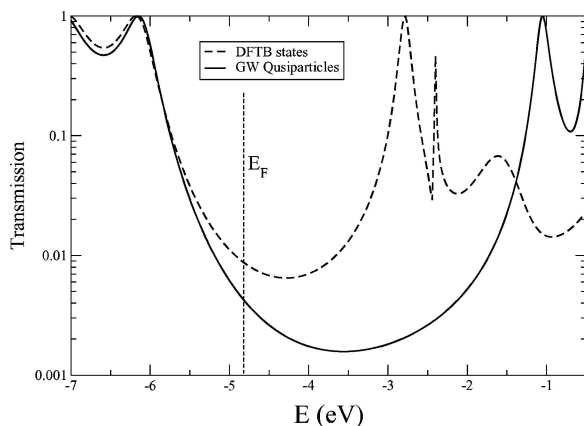


Figure 3. Quasiparticle corrections of a phenyl-di-thiol between Cu contacts. Dashed (solid) line corresponds to DFTB (GW) eigenstate transmission around the HOMO and LUMO resonances.

of the  $\pi - \pi^*$  energy gap of the conjugated dithiobenzene, since we expect that this gives the major correction to non-resonant coherent tunneling transport. We apply the GW correction as briefly outlined above to a simple Cu-dithiobenzene-Cu system. The GW self-energy of Eq. (2) is used to correct the zeroth order GF used in the tunneling calculations. In this particular calculation the contact self-energies are approximated in the wide-band limits, as  $\Sigma = i\pi \|T_{Cu-S}\|^2 \rho(E_F)$  [19], with  $T_{Cu-S}$  representing the Cu-S TB-coupling and  $\rho(E_F)$  the metal density of states at the Fermi level.

This mimics the coupling of the molecule to a bulk-like reservoir, providing the right boundary conditions to allow a current flow. In Fig. 3 we compare the contact to contact tunneling probability using the DFTB states and the GW quasiparticle states. This simple application shows a key result: the quasiparticle states open the energy gap between the HOMO and LUMO resonances decreasing the tunneling current. Such decrease can be of up to one order of magnitude, depending on the position of the metal Fermi Energy. In the case of a Cu contact (whose Fermi energy is indicated as a dashed vertical line in Fig. 3) the decrease is by a factor of about 0.5. We can expect that correction of such kind can go in the direction of giving a closer and deeper understanding of transport in organic molecules as well as giving better agreement with experiments. In particular, we expect that such corrections may be also important in conjunction to the analysis of power dissipation examined in the previous section. Indeed, we expect that the decrease of the coherent current com-

ponent is accompanied by a corresponding decrease of the incoherent component.

## 5. Conclusions

We have shown application of electron-phonon scattering in a benzo-dithiolate between Cu contacts. Our calculations show that four vibrational modes are mainly involved in electron scattering and energy release in the molecule. In particular we calculate a power release of about 30 nW at the applied bias of 1 V and zero temperature. We also show that quasiparticle corrections beyond DFT, can influence the tunneling current, giving a first estimate of such decrease to be at least a factor of 1/2 for a small applied bias.

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