

Summary of the thesis
Inelastic effects in electronic currents at the
nanometer scale

*Effets inélastiques dans les courants électroniques à l'échelle
nanométrique*

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Abstract

This thesis deals with inelastic effects in electronic currents. We developed a time-dependent technique and show that this approach gives rich insight into electron-phonon coupling during transport. We compare our results with a time-independent technique and analyse the validity of our model. Finally, the results of a quantum chemistry calculation are presented in the framework of scanning tunneling microscopy (STM). We study the chemisorption of a tetrathiafulvalene molecule on a gold surface by performing the calculation of the charge transfer, the induced dipole, and the STM images using density functional theory.

Key-words: electronic transport, inelastic effect, non-equilibrium Green's function, tetrathiafulvalene, density functional theory.

1 Time-dependent wave packet propagation

The study of inelastic effects in electronic currents is receiving much attention due to both technological impact (molecular electronics[1][2][3] are an emerging field in nanosciences) and fundamental understanding of physics. From a theoretical point of view, the description of the mutual interaction between atomic vibrations and electrons leads to the development of sophisticated methods which use heavy formalisms for instance based on non-equilibrium Greens functions[4]. I have developed a method to treat electron-phonon coupling to all orders with a time-dependent approach. I show that this simple method is a convenient tool to understand electronic transport in the presence of vibrations. Indeed, wave packet propagation appears to be an intuitive and efficient way of describing phenomena such as inelastic electron tunneling spectroscopy. I present a one-dimensional tight-binding model, and show how transmissions can be calculated with wave packets. Finally, some results are discussed in the context of inelastic electron spectroscopy.

Consider a tight-binding one-dimensional chain, described by a tri-diagonal hamiltonian. Each site has equal on-site energy except for one or more sites, which we term impurity sites. A wave-packet is generated on the left side of the chain, with an initial kinetic energy. It propagates freely until the impurity sites are reached. There, it is reflected and transmitted, due to elastic scattering. If we switch on the electron-phonon coupling in the impurity sites, inelastic effects can occur. This is a time-dependent implementation of the Holstein model[5].

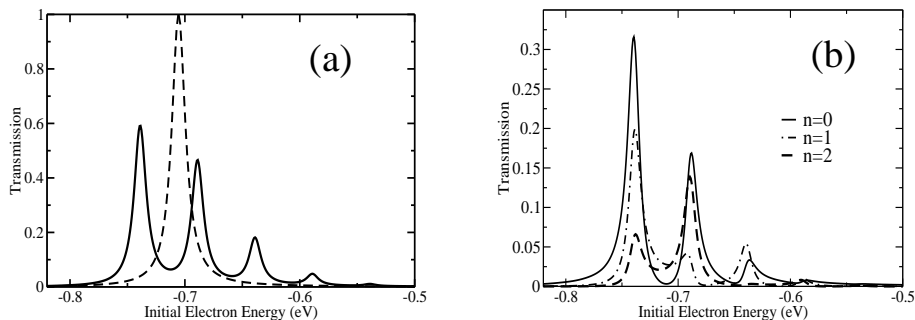


Figure 1: *The electronic transmission versus energy with inelastic electron-vibration coupling (full line) and in its absence (dashed line) are represented in figure a). Are shown in figure b) the different inelastic contributions in the full transmission for the same value of the coupling, n denotes the state of the vibration in the harmonic oscillator approximation*

Transmissions can be calculated using the virtual detectors technique[6]. The weight of the wave-function can be calculated after the impurity sites as a function of time. Using a Fourier transform, we can compute, the probability for an electron to be transmitted as a function of its initial energy. The width of the wave packet is chosen so as to describe the appropriate spectral region of interest where inelastic effects occur. In the presence of vibrations, the shape of the transmission curve is not lorentzian anymore. It shows several peaks, spaced by the energy of the vibration, which are termed phonon sidebands. Furthermore, this technique is capable to analyse the inelastic transmission in a novel way: it is possible to calculate all the inelastic contributions to the total transmission. The wave packets are calculated for each level of vibration, and one can thus, calculate a partial transmission for each of them. We obtain the n -resolved transmission shown in figure 1.

The propagation is performed with the Lanczos algorithm[7], which allows big time steps, rapid convergence, and flexibility in the implementation of the hamiltonian matrix. This last point is extremely important because, as our method permits us to calculate transmissions with an arbitrary number of phonons, we will need to increase the number of phonons until convergence is reached. This time-dependent approach can provide intuitive explanations of the physics involved in inelastic scattering experiments. Moreover, the efficiency of the calculation shows that for single-electron problems, the physics can be understood with simple approaches like ours, wich are nevertheless capable to show the underlying complexity of the systems where vibrations play an important role in conductance properties[8][9].

When measuring inelastic spectra with a scanning tunneling microscope, one expects to see increases of conductance, typically peaks at positive biases, and dips at negative biases in the $\frac{\partial^2 I}{\partial^2 V}$ [8]. A natural explanation for this, in the framework of wave packets calculations is that when a wave packet obtains sufficient energy by means of the bias voltage applied in the tunnel junction, it is allowed to jump from a vibrational state to the next one. This is called an opening of a new conduction channel, which naturally gives rise to an increase of the conductance.

Interestingly enough, dips have been measured at positive biases[9]. This shows that the previous explanation is not universal and might be used with care, depending on the nature of the problem. Actually, in the case of the measures performed by Hahn and co-workers, the molecules are weakly adsorbed on the surface, and it happens that the broadening of the molecular sates is of the same order of magnitude than the typical nuclear vibration. As a consequence, the conductance exhibits a particular form due to the presence of a phonon sideband in the width of the main peak. This gives rise to a dip instead of a peak at positive bias.

Additionally, taking advantage of the fact that our propagation scheme is implemented in a very flexible way, one can include not only several phonons, but several modes of vibration. Actually, even for simple diatomic molecules, one can consider different vibrations leading to interesting features in the conductance, because they can have similar frequency and similar coupling to electrons. If this is the case, it is obvious that one needs to include more than one mode of vibration in the calculation. It is interesting to see that the addition of vibrations lead to significant changes in the form of the transmission function, this is the reason why one should carefully study the relative importance of each mode involved in a particular problem, in order to include them in a calculation. This can be achieved very easily in this time-dependent implementation.

These results have been published in Physical Review B, see reference[10].

2 Time-independent approach

In this second part I have developed a time-independent approach using non-equilibrium Green's functions, also known as Keldysh[11] formalism. The problem under consideration is an non-equilibrium situation because a bias voltage is applied between the two electrodes. A current may then flow in the central region where eventually inelastic phenomena take place. In order to take into account many-body interactions, Green's functions can be used to describe the electronic reservoirs in the electrodes. At first glance, one might think that this approach is more suitable than the above time-dependent because, on the one hand the wave packet propagation is a single particle theory, and on the other hand because the voltage is not explicitly taken into account, in the sense that it does not affect the electronic structure of the central interacting region.

Nevertheless, the technique that we used is perturbative with respect of the electron-phonon coupling. The self-consistent Born approximation (SCBA) has been used to solve the Dyson equation: with an initial Green function, this equation is solved iteratively inserting each newly calculated Green's function as an input until convergence is reached. Very easily, currents and densities of states can be calculated from the converged solution. With this approach, one can for instance examine what is the role of the occupation of the interacting state in the conductance properties. Clearly, this kind of questions were impossible to answer with the wave packet approach given its single particle character. In a spinless calculation, when a single interacting state is half filled, a phonon sideband appears in the projected density of states at high energy, describing the possibility for an electron to

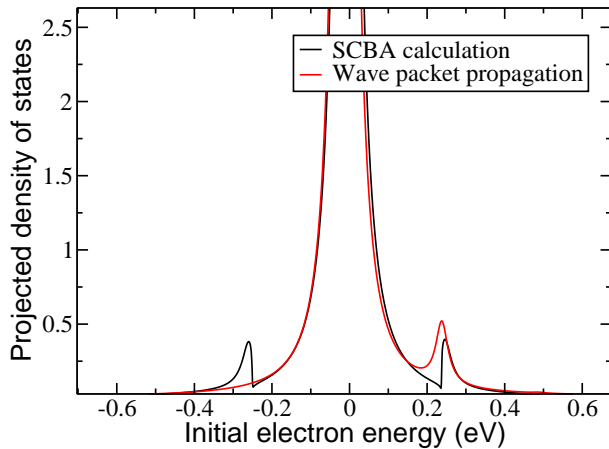


Figure 2: *Density of states projected in the interacting state: comparison between a wave packet propagation and a self-consistent Born approximation calculation for a case where the state is half-filled, all the other parameters being equal.*

travel, say, from the left electrode to the right one. Additionally, a second peak at low energy appears, it accounts for the possibility for an electron to travel in the other sense. One can also notice the effect of the Fermi level of each electrode: the peaks are abruptly cut because the exclusion principle does not permit an electron to go to a state which is already occupied. Of course, this is qualitatively different from what can be seen in the single particle limit where only the high energy sideband exists. This effect, which can also be viewed as a electron-hole pair symmetry, is shown in figure 2.

In this sense, the Green's function approach is reached. However, as previously mentioned, the electron-phonon coupling is accounted like a perturbation in this level of theory. For strong electron-phonon couplings, the SCBA fails to reproduce the position of the sidebands, while the wave packet propagation gives the exact result: the peaks are all equally separated by the phonon or vibration frequency. Furthermore, the so called polaron shift[12], which is the displacement of the main peak, is given exactly with the wave packet technique compared to the SCBA calculation as long as the interacting site is empty in the equilibrium configuration. Of course, as the polaron shift is filling-dependent, the time-dependent approach will fail to give its correct behaviour.

For these reasons, a combined study of a determined interacting system is required with these two approaches. Actually, an approach fails when the other gives good agreement with experiment, and one should not take

for granted that one technique gives the best results unless a clear case is considered. For instance, in the contact regime[13] [14] a single particle approach will systematically fail in giving correct results. In the other hand, it will give an good description in the tunneling regime[8][9].

3 Quantum chemistry simulation

In collaboration with the group of Prof. J. I. Pascual, STM experimentalists (Freie Universität, Berlin, Germany) and in the framework of molecular absorption on metal surfaces, I performed a series of calculations using the VASP code[15], based on density functional theory [16][17]. Using a combination of scanning tunneling microscopy and DFT calculations, we focused on the study of a so-called charge-transfer material, namely the organic complex

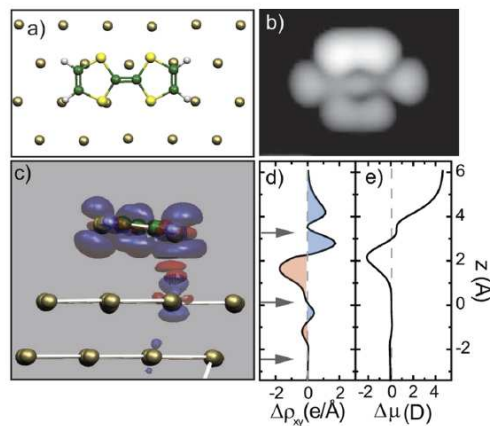


Figure 3: *The calculated geometry is shown from a top view in figure a), figure b) is a calculated STM image with Tersoff-Hamann theory. The figure c) depicts the spatial distribution of the induced charge density, where the blue surface indicates a lack of electrons, and the red an excess. In figure d) the planar average of the induced charge density is represented, and figure e) shows the induced dipole which arises from it.*

tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) on gold.

This molecular complex is known to be a metal[18], characterised by a one-dimensional-like band structure[19] due to a charge transfer from the donor (TTF) to the acceptor (TCNQ). First of all, a calculation to study the properties of the isolated TTF molecule was performed. The induced charge and dipole moment computation showed that these molecules are charged on the surface, and that they repel each other[20]. As shown in figure 3 c), the molecule is slightly tilted because only two sulfur atoms participate to the bond with the surface atoms. As a result, these two sulfur atoms are closer to the underlying gold atoms. In the same figure, the induced charge density is represented, the blue surface indicates a lack of electrons, and the red an excess, confirming the donor nature of the TTF. A negative density is located between the molecule and the surface, while the molecule is positively charged. From this charge separation, an induced dipole arises. The result is shown in figure 3 e). Its large value explains the repulsion between molecules on the surface.

Additionally, to reproduce the STM images measured by Prof. Pascual and co-workers, we calculated images from the results of the quantum chemistry calculation. Actually, in the Tersoff-Hamann approximation[21], the conductance is proportional to the density of states. This approach is simple and intuitive but it has several drawbacks. For instance it is well known that

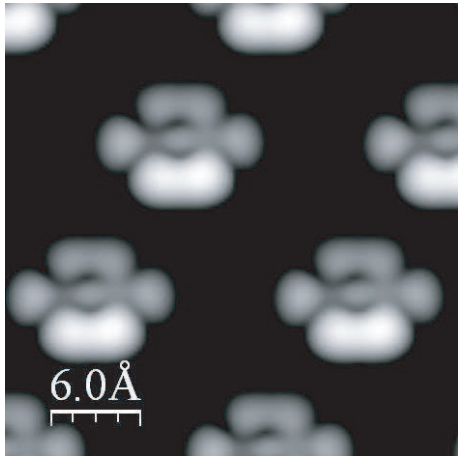


Figure 4: *Calculated constant current STM image with Tersoff-Hamann theory for a negative bias (-0.5V) and a current of 5.2 nA.*

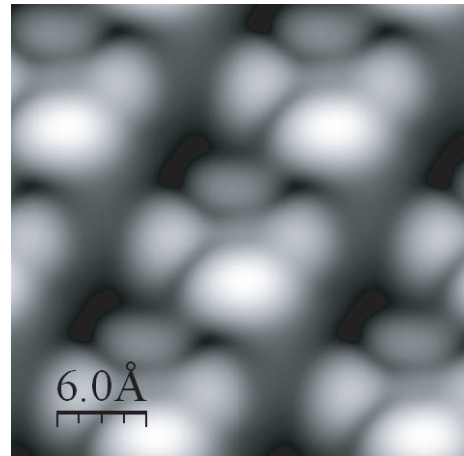


Figure 5: *Calculated constant current STM image with Bardeen's transfer hamiltonian theory for a negative bias (-0.5V) and a current of 5.2 nA.*

the calculated distance between tip and surface is not correctly given[22]. However, when the local density of states is big enough, as in the case of adsorbed molecules, the images are in excellent agreement with measurements.

In this work, a novel method for calculating STM images is presented. Exploiting the outputs of the VASP code, we were able to take the tip explicitly into account in an STM image simulation. This method is based on Bardeen's transfer hamiltonian[23][24]. In the figure 4 the Tersoff-Hamann simulation is presented, the effect of the tilt could be seen and we could identify the orbital contributing to the image as the highest occupied molecular orbital (HOMO), because we calculated the spatial representation of the orbitals of the TTF. In the figure 5, we can see that transitions between low and high values of the conductance occur in a more gradual way, they are not as sharp as in the Tersoff-Hamann simulation, which has a more ideal aspect. This blurring effect, which is of course due to the tip, also gives much more broadening and it turns out that, while in figure 4 the cell was big enough for the molecules to be well separated, in figure 5 we see that the molecules see each other. One of the main drawbacks of the Bardeen approach is this one: the blurred molecules need larger cells, and thus longer calculations.

Conclusion

In the first part of this work we have shown that the time-dependent approach could be a very interesting tool to understand the inelastic phenomena which take place, for instance in a tunnel junction during electron transport. It is a non-perturbative technique which has nevertheless its intrinsic limitations. A single particle approach fails to describe problems where a contact regime is reached. This is the reason why I decided to compare these results with the ones of a non-equilibrium Green's functions calculation. This was done in the second part of my thesis, where it is shown that, because of its perturbative nature, the SCBA fails in his description of highly excited phonons for a given mode. Finally, in the third part, a DFT calculation showed interesting results concerning the distribution of charged molecules which act as dipoles on a metal surface.

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