Alessio Gagliardi, *Theoretical Modeling and Simulation of Electron-Phonon Scattering Processes in Molecular Electronic Devices*. PhD Thesis (in English), Department of Physics, Faculty of Science, University of Paderborn, Germany (2007).

Abstract

The entire field of molecular electronics relies on a very simple concept: a single organic molecule, or a thin layer of organic molecules, are used as a bridge between two metallic contacts. The bias applied induces a current from one contact to the other. The basic idea is that the current is dominated by the chemical properties of the molecule between the contacts and that this electric characteristic can be easily tuned by an external perturbation in order to get a switch. However, despite the intense investigation many issues are still waiting to be fully addressed. One of them is the dissipation induced in the molecule by the coupling between the vibrational modes and the charge carriers. Due to the size of the device this interaction must be described quantum mechanically via an electron-phonon scattering process. The quantitative evaluation of dissipation in molecular electronics is fundamental for the entire field, especially for future introduction of such kind of devices in the electronic industry.

The author of this work and Dr. Alessandro Pecchia of the University of Rome "Tor Vergata" have implemented a code based on non-equilibrium Green's functions formalism to investigate electron-phonon scattering in molecular devices. The first application presented is the evaluation of the dissipation in octane-thiols sandwiched between two gold contacts showing which are the most relevant modes in scattering electrons. The electron-phonon scattering is much more than the study of the "quantum resistance". The inelastically scattered electrons in fact can be directly used as probes to investigate the geometry and the electronic structure of the device. This spectroscopy technique is called inelastic electron tunneling spectroscopy (IETS). Despite the IETS is an old spectroscopy technique, its application in the molecular electronic field is recent and many features need to be fully understood.

The electron-phonon code has been used to investigate the properties of IETS, first simulating directly IETS in octane-thiol systems, later on addressing the problem of selection rules in this spectroscopy technique. It is well known in fact that the selectivity of IETS is rather different from the one of other more conventional techniques, like infrared or Raman. However the lack of a precise knowledge of selection rules in IETS renders a clear assignment of IET spectra difficult.

The definition of selection rules requires two steps. First, the definition of the point group of the system. It is obvious that, also if the molecule in the gas phase shows high symmetry, this will be reduced by the presence of the electrodes and the distortions of the structure. Despite that, the molecule remains the dominant feature of IETS measurements. We can univocally identify the point group of the device just taking the point group of the unperturbed molecule and reducing it to a subgroup due to the effects of the electrodes. The second issue is to define a basis set to which the point group is applied to. It is well known that canonical molecular orbitals are not the best choice due to the strong interference effects between them during transport. However, the current can be decomposed in a sum of independent "channels" obtained diagonalizing directly the operator involved in the transmission and not the Hamiltonian. The choice of this set of channels is not unique, but all of them permit to avoid interference.

These tools have been applied to investigate IETS in a benzenedithiol molecule between model gold contacts. The interpretation of the current in terms of independent channels provides not only information about selection rules, but also in which region electrons are scattered, leading to a deep comprehension of where the dissipation occurs and which chemical substitutions in the device can improve its performances.