Molecular electronics: controlled manipulation, noise and graphene architecture

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Summary

It is fascinating that it is now routinely possible to wire nanoscale entities as small as a single molecule between two metallic leads and measure its charge transport characteristics. It has been three decades ago that the first single-molecule measurement was performed by Reed et al. Since then, many different measurements and analysis techniques have been developed to probe single-molecules. This includes the mechanically controlled break junction (notched-wire and lithographically fabricated) setups, electromigration made junctions and scanning tunnelling microscope based break junctions. In parallel, many theoretical tools have been also developed and refined for describing such transport properties and for obtaining numerical predictions. However, such theoretical tools require a large number of inputs e. g. the shape and atomic structure of the electrodes, binding configurations of the molecule, nature of the chemical bond, orientation and conformation of the molecule, the presence of defects in the leads, the presence of unwanted adsorbates, counter ions and protection groups near the molecule. However, most of the experimental techniques are statistical and do not provide these essential inputs. These inputs together can form a multi-dimensional parameter space which in experiments results in a broad peak in conductance histograms, whose width points towards spontaneous changes of these parameters from one measurement to another. Usually, only the peak value is taken as an estimate of the characteristic conductance of the molecule and compared to the theoretical models which make use of educated guessing for the input parameters. We have worked on three fronts to remove these obstacles, described in the three parts of this thesis.

Benchmark testing system for single molecules

We prepared a benchmark system for measuring the electronic transport of single-molecules, which could provide many of the above mentioned input parameters. To this effect, we modified an ultrahigh vacuum low-temperature scanning tunnelling microscope (STM) by connecting to it a real-time molecular dynamic simulator along with a home-built 3D motion control sensor. To controllably lift off a molecule de-

posited on an atomically flat metallic surface, a certain STM tip trajectory is required. This tip trajectory is not known *a priori* and will depend on the dynamics of different atoms in the molecule and the sequence in which the bonds break. As the tip trajectory is not known, it will not be possible to pre-program a trajectory for the STM tip. For this, we use a 3D motion control system which allows the operator to make an adaptable trajectory as desired. Then to know what tip trajectory has to be taken, we developed a real-time molecular dynamic simulator, which provides a visual feedback showing different dynamics involved during manipulation. This not only helps in deciding the trajectory but also provides information about the molecular conformation and binding as we lift the molecule. To demonstrate the capability of this system we have shown a successful lifting of a chain of gold atoms above the surface, and subsequently placing it back and lifting it again. This controlled manipulation of the chain is confirmed by measuring the conductance parity oscillations. These parity oscillations occur due to a different interference of electron waves when the length of the chain switches between an even and an odd number of atoms in the chain. With our controlled lifting experiment, we could also determine with certainty, the phase of these oscillations, showing that the even number of atoms in the chain leads to higher conductance.

High-bias shot-noise measurement on atomic point contacts and molecules

Earlier, low-bias shot-noise measurements have been widely used for obtaining information about the number of channels involved in electronic transport through single molecules. It has been shown recently, that shot noise can also be used for studying inelastic interactions. These measurements were performed on gold atomic contacts by recording noise up to 100 kHz, which corresponds to a bias range of around 20mV before the $1/f$ noise will start to interfere. For studying the inelastic interactions in molecules where vibration energies can be much higher than for gold, we present here an extension of this system to MHz frequency regime. This is done by introducing cryogenic amplifiers close to the atomic junction, which reduced the input capacitance by nearly two orders of magnitude. Working at higher frequencies has an additional advantage that data acquisition and averaging of the spectra can be much faster. In order to profit from this advantage, the Fourier transform and other spectral manipulations are programmed on an FPGA module, such that the speed of measurement is only limited by data acquisition. The acquisition time scales with the inverse of the lowest frequency in the spectral window. By shifting the spectral window for the Fourier transform from 250 Hz–100 kHz to a window of 122 kHz–100 MHz the measurement time is reduced by a factor 500. With the present speed-up of the system, we can perform Fourier transforms and average 10000 spectra in about 85 ms.

Using this system, a shot-noise measurement on single atom point contacts in non-linear regimes was performed, even up to 800 mV bias. These shot-noise data show highly non-linear behaviour with applied bias, which has no specific trend and is different for each contact. We recorded noise spectra showing a flat dependence on bias or even sometimes a decrease in shot noise. Our work confirmed the white character of the noise by checking its frequency spectra at each bias. Based on this the possibility of other noise sources influencing our measurements can be neglected.

Non equilibrium phonon population and heating can cause V^n (with $n = 2, 3, 4$) character in noise, as predicted by many theoretical works. The non-linearities that we measure do not show such power law characteristics. In fact, many of the non-linear deviations that we record happen at energies much higher than the Debye energy of gold. We have shown that these non-linearities can be explained in the framework of the Landauer formalism as arising due to quantum interference of electronic waves. These interferences occur because of the multiple paths that an electron can take due to elastic scattering on the defects present in the leads close to the point contact. Such quantum interference due to defect scattering gives rise to energy and voltage dependent transmission, which manifests itself as oscillations in differential conductance and non-linear shot noise. This shows that the usual interpretation of linearly increasing shot noise with applied bias or current ($S_I = 2eIF$) is valid only when there are no defects in the leads within the electron phase-coherence length, which could be up to a micron in gold. The results presented here suggest that if the position of defects in the vicinity of the point contact can be controlled, then by exploiting the quantum interference of electronic waves, one could design the transmission as desired and achieve favourable properties in conductance and noise. In a metallic point contact it is not easy to control the position of defects, but in a pre-designed molecular system, a graphene based system or a mesoscopic systems like 2DEG, it might be possible.

Furthermore, we used this state of the art high-bias shot-noise measurement setup to probe a single D_2 molecule between Pt electrodes. We show that at the energies where a vibrational mode or vibron of the molecule exists, a two-level fluctuation (TLF) is excited. Although, the contact shows the usual differential conductance spectra, the TLF is visible in the measured noise. Further, we have demonstrated that an enhanced noise spectroscopy can be done using this TLF, by studying the third derivative of the noise signal (d^3S_I/dV^3). We call this inelastic electron noise spectroscopy-3 (IENS-3). We have shown using several examples how the IENS-3 spectrum can detect inelastic scattering processes more precisely than the usual IETS spectrum. In addition to this, we also report the detection of a step-up or increase in differential conductance in the few of our Pt-D_2-Pt junctions. This increase is in contrast to the conventional picture where for a junction with conduction close to 1 G_0 shows a step-down or decrease in conductance due to back-scattering of electrons. This increase is attributed by Kristensen *et al*. to the coupling of the d-orbital of the Pt junction to its usual s-orbital, under a transverse rotational mode of vibration.

Graphene electrodes

By imaging the complete electrode-molecule junction, a better understanding of the transport measurements through single molecules can be obtained. However, it is rather impossible to image it for three dimensional metallic electrodes. Two-dimensional electrodes like graphene provide an interesting possibility to image the complete electrode-molecule junction. Other than imaging, it also provides access to modify its atomic structure and create electron scattering defects on demand. Moreover, graphene based electrodes have a stable atomic lattice at room temperature which could help in making stable room temperature devices. The electroburning technique is used widely to make graphene nanogaps. However, it does not provide

the control needed for proper characterization of the gap and it also does not allow to scale to multiple electrode circuits. Therefore, more direct cutting methods for making graphene nanogaps, specially the STM tip based cutting are explored here. Cutting using a STM tip can be seen as a controlled localized electro-burning technique. It is understood as an oxidation reaction between the C atoms in the graphene lattice and a layer of water adsorbed under ambient conditions. We have explored the parameter space, which includes tip-sample bias, current set-point and cutting duration or tip speed. Our results show that the cutting technique is more sensitive to the applied bias than to the set-point current. Furthermore, by doing a time domain analysis we found that the top layer graphene on graphite first gets lifted out of the surface and then burns. We have shown that by correctly tuning the parameters one can achieve gap size of around 1.6 nm full width half maximum.