Molecular charge transport : relating orbital structures to the conductance properties

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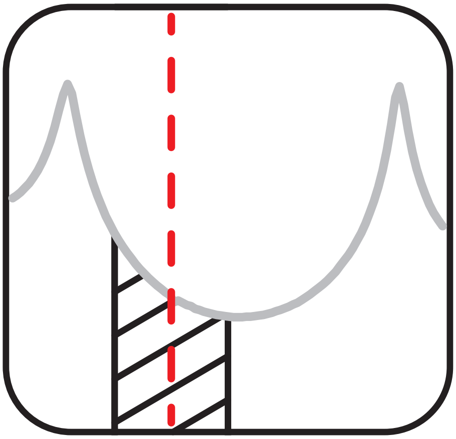
BASIC CONCEPTS



1.1 A BRIEF HISTORICAL VIEW ON MOLECULAR CHARGE TRANSPORT

The field of science that is now called molecular charge transport, emerged with the first measurements on metal-molecule-metal junctions by Mann and Kuhn already back in 1971 [1]. Shortly after a paper by Aviram and Ratner [2], this appealing idea gave a lot of momentum to this field. In their theoretical paper, they did not only predict the rectification properties of their designed molecular junction but also the challenges scientists would encounter trying to connect and characterize molecular junctions: ”A large number of materials and synthesis problems must, clearly, be overcome before such molecular electronics device can be tested in the laboratory.”. To this they added: ” Efforts towards the solution of these problems are presently under way.”, not knowing that it would cost at least twenty years before the first single molecule measurements were claimed [3, 4]. Since then the field of molecular electronics has been an active field developing numerous experiments and techniques. The field also has encountered many ups and downs [5–7]. Nevertheless scientists kept working on the possibilities of contacting molecules developing new methodologies and improving the measurements techniques. By now, the field has gained maturity and the focus is on carefully exploring molecular charge transport.

The promise of molecular electronics in Aviram and Ratner’s seminal paper is, as the name already says, to integrate molecular junctions to replace the ever shrinking integrated circuit components. This has motivated most of the research in the field even though no direct application in integrated circuitry has been found yet. But the truly exciting side of molecular electronics is the fundamental questions it raises. Indeed studying the charge transport in molecular species profits from the versatility of organic chemistry to systematically vary the properties of microscopic conductors contacted by macroscopic leads. The physics of such systems is often referred to as mesoscopic physics. Indeed mesoscopic physics functions as a bridge between the macroscopic world of the bulk materials and the microscopic world of atoms. So we may say that molecular junctions are well suited and versatile tools to study mesoscopic charge transport phenomena. In this chapter we will first introduce some basic concepts about charge transport through nanometer-scale objects and see how molecular junctions fit in this picture. This is followed by a short description of the principal methodologies to connect molecules to electrodes.

1.2 BASIC CONCEPTS

1.2.1 CONDUCTANCE QUANTIZATION

When dealing with conductors on the nanometer scale a few length scales are of great importance, namely: i) L_i, (with $i = x, y, z$) the characteristic dimensions of the conductor in the x, y and z directions (z being in the direction of charge transport). ii) l_e, the elastic scattering length for electrons (or mean free path)i.e. the distance an electron can travel without experiencing an elastic scattering event (walls, dislocations, impurities). iii) l_φ, the phase coherence length i.e. the distance an electron can travel before its phase is randomized. iv) λ_F, the Fermi wavelength, the wavelength of the electrons at the Fermi energy i.e. the electrons responsible for the transport phenomena we describe. The relation between those length scales determine to a great extent the way electrons move through a conductor.

So now, more specifically, if we connect a conductor with dimensions such that $L_{x,y} \ll l_e, l_\varphi$ and $L_{x,y} \sim \lambda_F$ and $l_e, l_\varphi < L_z \gg \lambda_F$, we are in the so called quantum ballistic regime. We can calculate the density of states in such a quantum ballistic conductor by solving the time-independent Schrödinger equation. The solutions to it are the transversal modes propagating in the z-direction. The corresponding energy for these modes is given in equation 1.1 [8]. Solely the modes with an energy crossing the Fermi level do contribute to the conduction.

$$E = \frac{\hbar^2}{2m} \sum_{i=x,y,z} \left(\frac{n_i \pi}{L_i} \right)^2 \tag{1.1}$$

If $L_z \to \infty$ the energy of the electrons are quantized in the x and y direction while continuous in the z direction. Now we know the electron energy, we can express the conductance of the conductor. If the dimensions $L_{x,y}$ for our conductor are small, the resulting energy spacing will be large so we can restrict our discussion to one single mode or conductance channel. We apply a bias of eV_b on the conductor, shifting the chemical potentials μ_L and μ_R of the electrodes (reservoirs) with respect to each other so that: $\mu_L - \mu_R = eV$. We can calculate the density of states, ρ in this single channel (equation 1.2) [8].

$$\rho(E) = \frac{1}{\pi\hbar} \sqrt{\frac{m}{2E}} \tag{1.2}$$

Finally we can express the current by integrating over the density of states, limiting for the right-moving electrons and correcting for the spin degeneracy (equation 1.3) and over $v(E) = \sqrt{2E/m}$ the electron velocity and f_R and f_L the

Fermi-Dirac functions for the right and left electrode respectively (equation 1.4).

$$I = \int_{-\infty}^{\infty} ev(E)\rho(E)(f_L - f_R)dE = \frac{2e^2}{h}V_b \tag{1.3}$$

$$f_{L,R} = \left(1 + \exp\left(\frac{\varepsilon - \mu_{L,R}}{k_B T}\right)\right)^{-1} \tag{1.4}$$

We see here that for an ideal single channel conductor, the conductance G, can be expressed as a function of fundamental constants and it is independent of the length L_z. This fundamental conductance is called the quantum of conductance $G_0 = \frac{2e^2}{h}$. The conductance increases in steps of $\frac{2e^2}{h}$ for an increasing number of channels. The conductance quantization has been first observed in 1988 by van Wees *et al.* in a two dimensional electron gas (2DEG) by tuning the width of the channels with electrostatic gates[9]. The Fermi wavelength in the semiconductor used (GaAs) was in the order of 200 nm, resulting in separation of the modes in the order of meV's and thus requiring low temperatures ($\sim$ 1 K) to resolve the steps. Quantized conductance is also observed in metals, where the Fermi wavelength is about two orders of magnitude smaller ($\lambda_{F,Au} \sim 0.5$ nm) requiring contacts of atomic dimensions to have the conductance quantized[10]. The small dimensions of the atomic contact result in a much larger separation of the modes ($\sim$ eV) as compared to 2DEG's making the observation of quantized conductance possible at room temperature [10].

1.2.2 LANDAUER-BÜTTIKER FORMALISM

The situation above is described in a more generalized way by Landauer and Büttiker by treating the conductor as a scatterer that couples incoming states (I) and outgoing states (O) phase-coherently via a scattering matrix as shown in figure 1.1 and equation 1.5 [11, 12].

$$\begin{pmatrix} O_L \\ O_R \end{pmatrix} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix} \begin{pmatrix} I_L \\ I_R \end{pmatrix} \tag{1.5}$$

The matrices r and t denote the reflection and transmission when the states are coming from the left and r' and t' when the states are coming from the right. Current conservation imposes that $rr^\dagger + tt^\dagger = r'r'^\dagger + t't'^\dagger$. The eigenvalues of $tt^\dagger$ correspond to the transmission probability T_n for all the n eigenchannels of the scatterer. We can now express the conductance as follow:

$$G = G_0 \sum_n T_n \tag{1.6}$$

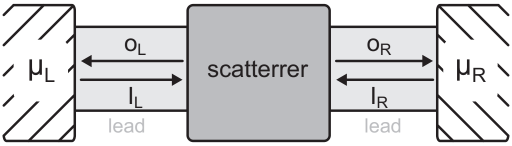


FIGURE 1.1: **Representation of the scattering approach used by Landauer and Büttiker.** μ_L and μ_R are the chemical potentials of the left and right reservoirs respectively. The scatterer is connected to the reservoirs by two fully transparent leads. O_L and O_R represent the outgoing states to the left and right respectively. I_L and I_R represent the ingoing states from the left and right respectively.

In general, we can extend equation 1.6 with an energy dependent transmission for the current through a scatterer (as the channels have independent eigenstates).

$$I = \frac{2e}{h}\int_o^{\infty} T(E)(f_R - f_L)dE \tag{1.7}$$

If we consider conductors involving more electronic orbitals the picture gets more complicated. The Landauer-Büttiker formalism still can be applied together with more involved calculations to find the corresponding T(E) as we will see later on.

1.2.3 A MOLECULE AS A CONDUCTOR

Until now we discussed purely ballistic transport in conductors contacted by transparent leads (reservoirs, leads and conductor made out of the same material). Small organic molecules (nanoscale) tend to fulfill the requirements for ballistic transport at room temperature as their size is still much smaller than the characteristic lengths for electrons (l_e and l_φ). So if we insert organic molecules between the leads what will happen to the transmission characteristics? An important parameter here is the extent to which the molecule interacts with the electrodes, the so-called coupling that we will discuss later on. At one side we have the strong coupling limit where the overlap of the molecular wavefunctions and electrodes wavefunctions is so that we can describe it as a quasi-ballistic conductor i.e. the measured single-molecule conductances will be close to G_0 [13, 14]. At the other side of the spectrum we have the weak coupling limit where the molecule interacts weakly with the leads, in fact in that case the molecule is best described as a quantum dot. In this limit the Landauer approach does not hold anymore, indeed charging effects, like electron-electron interactions take place. In this thesis we consider the strong coupling limit. Molecules also differ from ’traditional’ conductors in the sense that their composition and structure can be engineered by organic chemistry. Additionally in organic molecules the ion-electron interactions are stronger resulting in vibrational influences on the conductance making electronic spectroscopy possible (Inelastic tunneling spectroscopy and point contact spectroscopy [13]).

Organic chemistry tool-box

Organic chemistry offers the possibility to design molecules almost at will and thus engineer the resulting transmission function. Although relating the chemical structure to the conduction properties is still a challenging task, one can rely on empirical organic chemistry rules-of-thumb and on more evolved quantum chemistry calculations. A wide variety of molecules have been engineered. Series of aliphatic carbon chains have been synthesized to study the length dependence of the conduction through ’isolating’ molecular wires (reference [15] for a review of the numerous experiments). Synthetically a bit more involved, series of conjugated molecules of variable length have been synthesized to study the length dependence of molecules with delocalized π-electrons [16–18] (chapter 5). For both groups of experiments on molecules the conduction appeared to be dependent of the length.

Chemists have introduced functionality to molecular conductors. One of the most appealing functionality is the possibility of switching from a low conductance state to a high conductance state by an external stimulus (for a review on molecular switches see reference [19]). Such switchable molecules are highly interesting for both applied and fundamental research. Indeed we can then probe two conducting states in exactly the same conditions. Different stimuli can be used to switch between the two conformations of the molecule. They can be switched by light [20], redox reaction [21], strain [22] or change in the electrochemical potential [23]. To illustrate the possibilities of engineering the conductance of molecule we present here a molecular switch. In figure 1.2 we show the chemical structures of the two conformations of an anthraquinone based switch and the associated change in the transmission function. The ’ON’ state of the molecule is conjugated while in the ’OFF’ state the conjugation is broken, which will lead to quantum interferences that suppress the transmission as can be seen in figure 1.2-B (see chapter 6 for more details). The important message here is that a only a small change in the chemical structure can induce large changes in the transmission function i.e. the conductance of molecule (see equation 1.7).

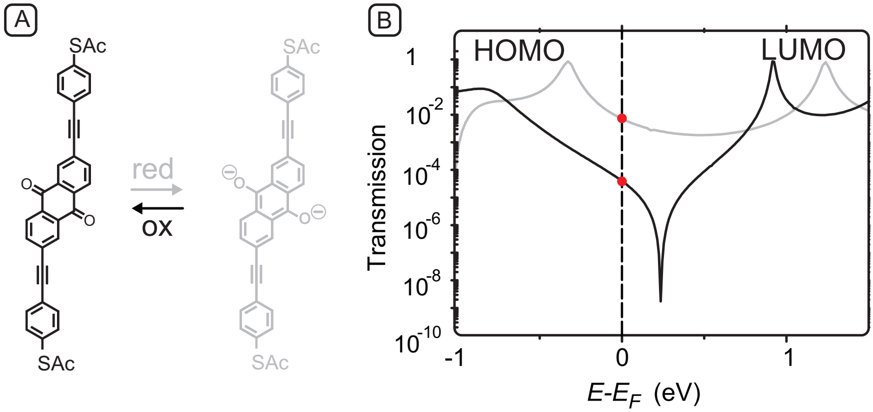


FIGURE 1.2: **Anthraquinone based switch [21]. A** Chemical structure of the two stable configurations of the switch. **B** Corresponding calculated energy-dependent transmission curves. The dots indicate the transmission at the Fermi energy and indicate almost two orders of magnitude difference in conductance (calculations by Troels Markussen).

Connecting the molecules electronically

The molecules need to be connected somehow to the electrodes in order to make charge transport study possible. The most used connection between the organic molecules and the electrodes is the sulfur-gold bond or thiol bond. Indeed a molecule terminated with a sulfur atom binds strongly to the gold electrodes, the bond strength is about 2.1 eV [24]. Besides the most widely used thiol binding a wide range of attachements groups have been used: amines [17], selenols [25], pyridines [26], carboxylic acids [27], isocianides [17] and phosphines [28] or no linking groups at all [13, 14, 29].

We will see that connecting a molecule to metal electrodes results in a dramatic change of its energy landscape. To get an physical intuitive picture of the effect of inserting a molecule in metal-molecule-metal junction, let us have a look at a simple tight-binding model for a virtual molecule. In figure 1.3-A we show the molecule in free space as an interacting chain of hopping sites. In figure 1.3-B we show the molecule connected to electrodes. We can write the corresponding Hamiltonians for the isolated molecule (equation 1.8) resulting

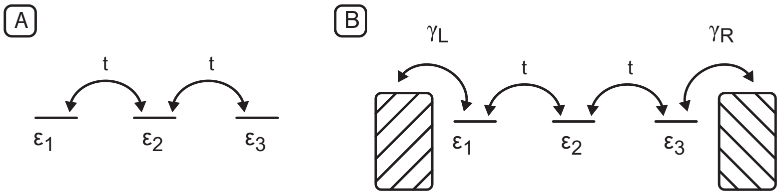


FIGURE 1.3: **Tight-binding representation of a molecule. A** Molecule composed of three site of energy ε and hopping integral t. **B** Same molecule as in A but connected to the electrodes by the coupling γ.

in discrete levels.

$$H_{(mol,isol)} = \begin{pmatrix} \varepsilon_1 & t & & \\ t & \varepsilon_2 & \ddots & \\ & \ddots & \ddots & t \\ & & t & \varepsilon_n \end{pmatrix} \tag{1.8}$$

When the molecule is connected to electrodes as shown in figure 1.3-B (equation 1.9) the levels are broadened.

$$H_{(mol,junction)} = \begin{pmatrix} \varepsilon_1 - \Sigma_L & t & & \\ t & \varepsilon_2 & \ddots & \\ & \ddots & \ddots & t \\ & & t & \varepsilon_n - \Sigma_R \end{pmatrix} \tag{1.9}$$

Here $\Sigma_{L,R}$ represent the self-energy matrices that account for the effect of the electrodes on the molecule. Its anti-Hermitian part is the broadening matrix $\Gamma_{L,R} = i[\Sigma_{L,R} - \Sigma^{\dagger}_{L,R}]$. Now using non-equilibrium Green's function (NEGF) formalism we can calculate the current self-consistently resulting in equation 1.10. The NEGF method is a formalism for solving the many-body Schrödinger equation of a non-equilibrium system coupled to semi-finite electrodes (For a complete description of the NEGF formalism we refer to [30]).

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} [Tr(\Gamma_L G \Gamma_R G^{\dagger})(f_L - f_R)]dE \tag{1.10}$$

With $G(E) = (ES - H - \Sigma_L - \Sigma_R)^{-1}$ being the Green's function and $Tr(\Gamma_L G \Gamma_R G^\dagger)$ being the transmission function $T(E)$ giving the Landauer-Büttiker formula found in equation 1.7. Here the $\Sigma_{L,R}$ matrices, as their name indicate, are responsible for: i) The broadening of the molecular levels as the residence time of the electrons on the level is now finite. ii) The shift of the molecular levels due to charge transfer from the leads to the molecule. In figure 1.4 we show the broadening of a level as it is more and more coupled to a surface i.e. an electrode, illustrating the effect of $\Gamma_{L,R}$.

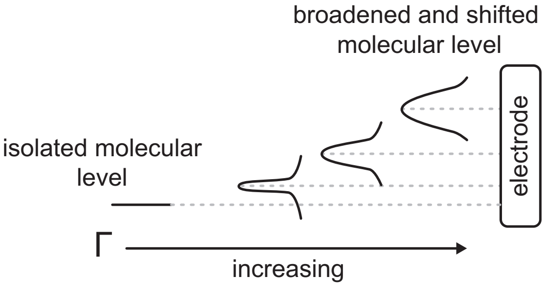


FIGURE 1.4: **Broadening of molecular levels.** Here we schematically show the effect of coupling (to the leads) on a molecular level. On the left we see a discrete level for molecule in free-space and moving to the right we see the level broadening and shifting in energy.

In chapter 4 we use a simplified single level model and we treat the discrete molecular level of a free molecule as a Lorentzian density of state when it connects to a surface [31, 32]):

$$DOS(E) = \frac{1}{2\pi} \frac{\Gamma_L + \Gamma_R}{(E-\varepsilon)^2 + ((\Gamma_L + \Gamma_R)/2)^2} \tag{1.11}$$

With $\Gamma_{L,R}$ still being the coupling between the electrodes (L,R) and the molecule, but not in matrix form anymore. In this simple model the transmission T(E) is 1 at the center of the Lorentzian (resonant tunneling), representing the HOMO or the LUMO depending on the position of the Fermi level, E_F. In the multi-level model presented above and certainly in the more evolved DFT-based calculations both the HOMO and the LUMO are taken into account, the only uncertainty is their relative position to E_F which we will discuss in chapter 6 and appendix C.

Another important ingredient in molecular charge transport, besides the coupling to the leads, is the potential profile over the junction. Indeed this can have a dramatic influence on the current-voltage characteristics. We introduce η a parameter characterizing the voltage profile within the junction. For $\eta = 0.5$ the voltage drop, V_b, over the molecule is symmetric meaning that the chemical potential μ_R is lowered by $eV_b/2$ and μ_L is increased by $eV_b/2$. In the case of $\eta = 1$ or $\eta = 0$ the voltage drop is asymmetric, meaning that the molecular level is following one of the two electrodes. So the chemical potential $\mu_{L,R}$ can be rewritten as $\mu_R = E_F - (1-\eta)eV_b$ and $\mu_L = E_F + \eta eV_b$. Resulting in an expression for the current at $T = 0$K:

$$I = \frac{2e}{\hbar}\int_{-\infty}^{\infty} T(E)(f_L - f_R)dE \tag{1.12}$$

In the experiments we present in this thesis not only the current-voltage (I(V)-curves) characteristics are studied, also the first derivative of those characteristics, the dI/dV are studied to reveal more details on the charge transport through molecules (chapter 5 and 6). In equation 1.13 we express the dI/dV for $T = 0K$ to show the influence of η on the measured dI/dV.

$$\frac{dI}{dV} = \frac{2e^2}{h}(\eta T(E_F + \eta eV) + (1-\eta)(T(E_F - (1-\eta)eV))) \tag{1.13}$$

Here we can see that for a symmetric voltage drop the I(V)-curve is antisymmetric as well as the dI/dV curve whereas for an asymmetric voltage drop and an asymmetric transmission function the resulting curves are asymmetric, this is discussed in further details in chapter 5, 6 and in appendix C.

To summarize, molecules are fascinating systems to study mesoscopic charge transport, their conductance properties can be tuned by organic chemistry. The behaviour of those molecules can be predicted by calculations at different levels of complexity (from a simple single level model to DFT-NEGF calculations). The way molecules couple with the electrodes is determinant for the conductance properties of the formed junction.

1.3 OVERVIEW OF THE MOST COMMON EXPERIMENTAL TECHNIQUES

The principal barrier for the development of molecular electronics since the paper of Aviram and Ratner has long been the technology to connect the molecules to an electronic circuit. A few mile-stones in science have accelerated the development of techniques to contact molecules for charge transport measurements. First, the invention in the 1980's of the scanning tunneling microscope (STM) [33] made the first conductance experiment on a single molecule possible [34]. More generally Binnig and Rohrer opened the way for a whole set of scanning probe techniques that enable the connection to nanometer-scale objects as well as their imaging. Secondly, tremendous advances have been made in the fabrication of nanometer-sized structures by electron beam lithography making molecular electronic based devices possible. Most of the common experimental techniques used nowadays are connected directly or sideways to the two above-mentioned technical advancements. Parallel to the advancement of scanning probe techniques, an other technique was developed by Moreland *et al.* enabling atomic sized contacts with high stability [35]. The mechanically controlled break junction (MCBJ) made the first measurements to a single molecular wire possible [4]. We describe here three types of methodologies to contact molecules and study their charge transport properties, they are representative for a large part of the existing techniques.

We have learned in the short history of molecular charge transport that original mistakes had to do with the lack of information available about the electrode-molecule interface. Indeed voltage-driven switching has been observed while filaments were growing from one electrode to another [6, 36]. Additionally the improper use of electromigrated break-junctions [37, 38] introduced some reasonable doubts on the obtained results (possible presence of metallic clusters in the junction) [39]. So it is of utmost importance to carefully characterize the method for contacting the molecules.

Molecules can be contacted individually (one or a few molecules connected) or as a group usually in the form of a self-assembled monolayer. Most of the measurements are performed in a so-called two-terminal junction, where the molecule is connected to the electrodes at both ends. In a three-terminal junction a third electrode is added, without actually contacting the molecule, to apply an electrical field on the molecule[37]. The third electrode is often referred to as the gate in analogy to transistors. Moreover gating is also obtained in liquid environment in so-called electrochemical gating devices[23, 40]. Experiments on molecular charge transport are often executed at liquid Helium temperatures and high vacuum conditions for an optimal stability [41]. Nevertheless impressive results have also been reported at ambient conditions [42] or even in liquid environment[43], indeed as we have seen above the quantum properties of molecules are still dominant at room temperature due to their small size.

1.3.1 BREAK-JUNCTION EXPERIMENTS

Under the definition ’break-junctions’ we can distinguish three types of junctions: the mechanically controlled break-junction (MCBJ)[10], the electromigrated break-junction [37] that we will discuss in a separated section and the scanning tunneling microscope break-junction (STM-BJ) [44]. The common feature of these techniques is the breaking of a metalic wire into a nanometer-sized junction. The control on the gap size is different for each technique. Here we discuss the MCBJ and the STM-BJ as they allow for a continuous and controlled breaking and making of the junction, in that sense electromigrated junctions are different as the gap can only be formed once.

MCBJs are made of a constricted metallic wire (notched wire or lithographically defined) that is placed on a flexible substrate. The bending of the substrate induces an elongation of the wire at the constriction which eventually breaks. This technique permits a control of the electrode separation on sub-nanometer scale. Moreover, if the breaking is done in high-vacuum, the contacts are atomically clean. The wire can be reformed and broken at will [10, 14, 41, 45].

The same breaking-forming cycles can be obtained with the STM-BJ technique. Unlike for the MCBJ, here we start with two separated electrodes: the conducting substrate and the tip both made of the same metal. By pushing the tip gently in the substrate a wire can be formed and broken again [17, 44, 46, 47]. The STM-BJ does not allow for the same clean conditions and stability but makes it possible to obtain topological information on the substrate.

So the common feature of these two techniques is to be able to repeatedly form and break nanometer-sized junctions. When this is done in the presence of molecules, molecular junctions are formed and broken continuously allowing for a massive, statistically sound, dataset [45, 48]. In figure 1.5 we show the characteristic steps of the measurements on a molecular junction with a break-junction setup. With this technique over 10000 molecular junctions can be measured in one experiment. The molecules can bind to the electrodes in different configurations resulting in different conductance values [49], representing the measured conductances in an histogram shows the variation around the average conductance value.

1.3.2 THREE-TERMINAL ELECTROMIGRATION EXPERIMENTS

Electromigrated break-junctions present the same advantages as the above mentioned MCBJ in terms of contaminations, indeed the wire can be broken in vacuum resulting in atomically clean electrodes. Here the formation of a junction in a metallic wire is due to the direct migration of atoms by momentum transfer from the electrons at high current densities[50]. Hence when the wire

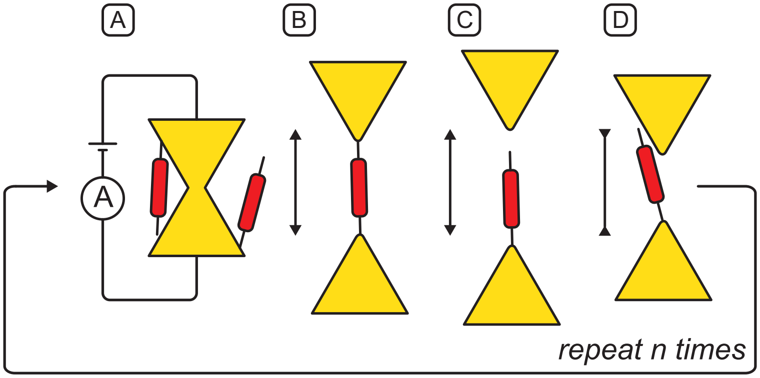


FIGURE 1.5: **Typical break junction experiment performed on a MCBJ or STM-BJ setup.** **A** Both electrodes are still in contact with each other. **B** The molecule bridges the junction. **C** The junction breaks, the contact is lost with molecule. **D** The junction is closing again.

is broken it is not possible to close the junction again as it is done with MCBJ's for example. A careful methodology has been developed to avoid the formation of metallic grains in the junction, which could be confused with molecules in the transport measurements[37]. The main advantage of electromigrated junctions is the possibility to have a gate electrode close to the inserted molecules resulting in an optimal molecule-gate coupling (typically 0.1 [51, 52]). In figure 1.6 we show a schematic view of three-terminal electromigrated junction. Although electromigration break-junctions have a low yield of working devices, they permit the observation of numerous transport phenomena like Kondo effect and Coulomb blockade as it is one of the few techniques making gated measurements possible[51, 53]. Recently Martin *et al.* succeeded in building a promissing MCBJ with a gate electrode [54, 55]. Although in this technique the gate coupling is lower than in electromigrated junctions it combines the robust statistical analysis typical of MCBJ's to a three-terminal junction.

1.3.3 LARGE AREA MOLECULAR JUNCTIONS

A measurement technique with a different philosophy, the large area molecular junction (LAMJ), is described here. These devices are focused on contacting a large area of self-assembled monolayers of molecules (ranging from 10 to 100

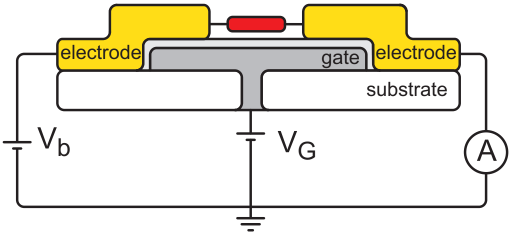


FIGURE 1.6: **Schematic view of an ideal three-terminal electromigrated break-junction.** The gate electrode just below the source and drain electrodes is covered by a thin insulating oxide layer.

μm in diameter) [56, 57]. In LAMJ devices the SAM is sandwiched between the two electrodes, the bottom electrode is used to grow the SAM and the top electrode is evaporated on top of the formed SAM. To prevent damage to the SAM and the formation of metallic filaments during measurements an interstitial layer of conducting polymer (PEDOT:PSS) is used. This fabrication process offers the possibility for up-scaling, indeed wafers with over 20000 junctions have been made with more than 200 junctions connected in series [58].

To wrap up, we discussed three different techniques for studying charge transport in molecular junctions. Important criteria for charge transport measurements are : i) the possibility of harvesting enough data to be able to conduct a statistically sound analysis. ii) the possibility to vary other parameters like the applied voltage bias, a gate voltage or optical probes.

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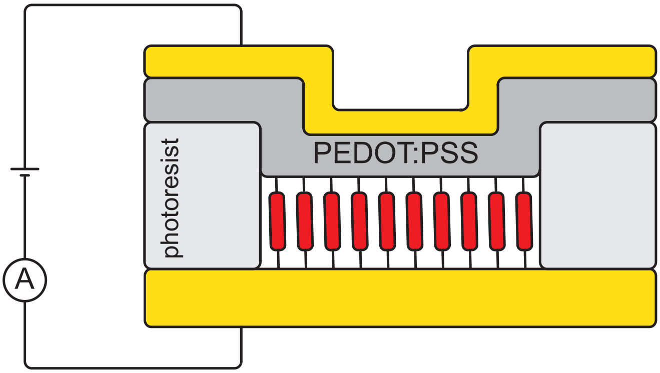

FIGURE 1.7: **Schematic view of a large area molecular junction.** .

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