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Molecular electronics
1.1 A BRIEF HISTORY OF MOLECULAR ELECTRONICS

The field of molecular electronics is derived from the concept of using nature’s smallest possible object as an electronic component. The first experimental paper in this field is usually credited to Kuhn et al., who measured the current through fatty acid monolayers\(^1\). The field itself however, was heralded three years later in 1974 by Aviram and Ratner\(^2\), who discussed transport through a single molecule. Their article suggested that a molecule could act as a rectifier, supported by *ad hoc* calculations. Although stating that solutions to predicted problems, such as contacting the molecule, were underway, it would take until the 1980s for the first tool to probe individual molecules to be developed.

With the creation of the scanning tunneling microscope (STM), it became feasible to experimentally investigate electronic properties of single molecules. In 1995, the first conductance measurement of a single molecule was done by Joachim et al.\(^3\), who used a STM to measure the electrical current through a single Buckminsterfullerene molecule. Interestingly, they found that deforming the molecule by pressing it with the STM tip changed the conductance properties. This was followed up shortly afterwards by Reed et al.\(^4\), who measured the conductance of benzene dithiol in between the electrodes of a mechanically controlled break junction (MCBJ), as developed by van Ruitenbeek et al.\(^5\) (see below). These two initial articles generated a large hype in the field and together with articles such as the reviews published in 2000\(^6\) or the Science Breakthrough of 2001\(^7\) marked the true beginning of the field.

The original dream of molecular electronics was to replace silicon-based technology, as even now, state of the art transistors have a gate width of 50 nm, almost two orders of magnitude larger than single molecules\(^*\). However, with single molecule junctions being notoriously unstable and the current technology heavily invested in the top-down approach of silicon, it is unlikely to be replaced any time soon. Molecules, on the other hand, can also do much more than just boolean logic and can therefore be an extension to silicon-based technology, rather than a complete replacement.

With the extensive library of molecules that organic chemistry provides, the amount of different molecules that can be built is virtually endless. Additionally, even small changes to a molecule, such as changing the bond geometry of a central phenyl ring from para to meta can lead to large changes in its properties\(^8\). In the para configuration, the two electron paths travelling through either side of the phenyl ring have the same path length and interfere constructively. In the meta configuration, these two paths have a different length, and interfere destructively. This quantum interference effect can result in a conductance in that is almost two orders of magnitude lower\(^9\).

Interestingly, the destructive interferences lead to sharp variations in the so-called transmission function, which in turn, can lead to large thermoelectric effects\(^10,11\). This means that molecules can be used to transform a temperature difference into electrical power, as

\(^*\)To paraphrase Richard Feynman: There indeed still is plenty of room at the bottom!
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shown by Reddy et al.\textsuperscript{[12]}. Inspired by earlier experiments by van Ruitenbeck et al.\textsuperscript{[13]}, they measured the thermopower of oligophenyl chains, showing an increase in thermopower with increasing molecule length.

As small changes to a molecule can radically change its electrical properties, molecules that can switch between two states by external stimulus can act as sensors for these external stimuli. Recently, Atesci et al.\textsuperscript{[14]} demonstrated that self-assembled monolayers or SAMs of ruthenium-based molecules showed very large rectification ratios of over 8000 under ambient conditions. Under dry nitrogen, however the rectification disappeared almost completely, to reappear again when water vapor was introduced into the nitrogen atmosphere, indicating a large sensitivity to water.

Other sensitive molecules include diarylethylenes, molecules that switch from a conjugated closed state to a non-conjugated open state upon illumination with light. This switching was first attempted by Dulic et al.\textsuperscript{[15]} using a MCBJ. A sharp conductance decreased was observed upon optical illumination, indicating switching of the molecule. Switching back, however, proved to not be possible. This illustrates the high sensitivity of molecules to their surroundings. Molecules may behave ideally in solution, but lose their functionality once chemically bound to the contacts of a break junction. It would take five years before back-conversion was possible, using molecules with slightly different anchoring groups to decouple the functional backbone from the contacts\textsuperscript{[16]}. In contrast to previous experiments, these new experiments were not done using a MCBJ, but a network of gold nanoparticles, allowing optical probing in addition to the electrical measurements. The observed change in resistance upon switching, however, was much lower (20\%) than using a MCBJ, giving rise to the question of how to increase this ON-OFF ratio.

Molecular electronics is an interesting field, not only due to the applications, but also because it gives a platform to study small-scale physics in a semi-tabletop environment. After its conception in 1974, and the initial hype that followed the first experiments in 2000, the field has now reached maturity, and applications are already commercially available\textsuperscript{[17]}. The inherent quantum nature of molecules due to the small scales involved are interesting in itself, but also provide insight into the relation between form and function on the nanoscale. The next sections will discuss the theory of charge transport on these small scales and the experimental techniques used to probe them.

1.2 Charge transport at the nanoscale

At the macroscopic scale, charge transport behaves as follows: a current $I$ flows through a resistor with conductance $G$ due to an applied voltage $V$ (this is described by Ohm’s law: $I = GV$). Energy is dissipated in the resistor due to inelastic scattering of the electrons with the atoms in the resistor. At the nanoscale, this is no longer the case. For example: electrons flowing through a single gold atom do not necessarily dissipate energy into the atom itself. In this case, it is more accurate to describe the situation as a wave passing through a potential...
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landscape instead.

To see how electrons flow through such a system, consider a thin conducting wire. If the wire is sufficiently thin, the electron wavelength becomes comparable to the thickness of the wire causing it to be confined in the x and y dimensions, but not in the z dimension, defined as along the wire. The electron density of states is then given by

\[ \rho(E) = \frac{1}{\pi \hbar} \sqrt{\frac{m_e}{2E}} , \tag{1.1} \]

where \( m_e \) is the electron mass, \( E \) is its energy and \( \hbar \) is the reduced Plank’s constant. To obtain the electron current, we have to multiply the number of flowing electrons by their velocity \( v \), given by \( v(E) = \sqrt{2E/m_e} \), and integrate over all energies. The net number of flowing electrons is given by the number of electrons flowing from left to right \( f_L(E) \) minus the ones flowing from right to left \( f_R(E) \) times the density of states. Here \( f_{L,R}(E) \) is the Fermi-Dirac distribution \([19,20]\) given by:

\[ f_{L,R}(E) \equiv \frac{1}{1 + \exp\left(\frac{E - \mu_{L,R}}{k_B T}\right)} . \tag{1.2} \]

The electrochemical potentials of the left and the right lead are \( \mu_{L,R} \) respectively. If a bias of \( V \) is applied over the wire, the electrochemical potentials shift such that \( \mu_L - \mu_R = eV \). The net current can then be written as:

\[ I = e \int_{-\infty}^{\infty} v(E) \rho(E) [f_L(E) - f_R(E)] \, dE = \frac{2e^2}{h} V . \tag{1.3} \]

The factor two comes from summing over the two degenerate spin channels. The constant \( 2e^2/h \) is usually called the conductance quantum \( G_0 \), the conductance of one fully transparent transport channel. Interestingly, the conductance does not depend on the length of the wire, in contrast to at the macroscopic scale, where the conductance scales inversely proportional to length. When two of such nanowires are put in series, the conductance remains the same. Furthermore, no energy is dissipated in the wire itself, but rather in the leads connecting to the wire.

If the width of the wire is increased slowly so that additional lateral modes fit inside of it, the conductance increases incrementally with steps of \( G_0 \). This has been first observed experimentally by Bart van Wees et al. in 1988\([21]\) in a two-dimensional electron gas at cryogenic temperatures using electrostatic gates to pinch off the conductance channel. The

\[ \text{This describes all electrons in the left lead attempting to flow to the right, and vice versa, without taking into account the availability of electron states on the other side. A more correct way is actually taking into account the probability of finding an unoccupied state on the other side, resulting in: } f_L(1 - f_R) - f_R(1 - f_L) . \text{ Usually, these expressions are identical, but there are times where they are not, as discussed in Chapter 5.} \]
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same effect can also be observed at room temperature in metal wires being pulled apart to create atomic point-contacts\cite{13}.

The situation from Eq. 1.3 is valid for perfectly transparent systems, and can be generalized for conductors with non-unitary transmission probabilities $\mathcal{T}$. This is called the Landauer\cite{22} formula:

$$G = G_0 \sum_i T_i.$$  

(1.4)

This means that the apparent conductance is given by the sum over the transmission probabilities of all channels. In practice, the sum is usually omitted, and all separate transmission channels are combined in one transmission function ($\mathcal{T} = \sum_i T_i$). Usually, the transmission probability of the electron is not constant but depends on its energy. In this case, Eq. 1.4 is expanded to encompass this dependence:

$$I = G_0 \int_{-\infty}^{\infty} \mathcal{T}(E)(f_L(E) - f_R(E))dE.$$  

(1.5)

It can be seen that if the transmission function is not a constant, the current versus voltage characteristics are nonlinear. This can result in interesting behavior for molecules in electronics, as discussed in the following sections. At low temperatures where $k_B T$ is much smaller than the variation in $\mathcal{T}$ and the electrostatic energy $eV$, the Fermi functions inside the integral approach step-functions. In this case the current can be approximated by omitting the Fermi functions and integrating the transmission function from 0 to $eV$. When $\mathcal{T}$ does not change significantly on the scale of $eV$, it can be approximated by a constant, and Eq. 1.5 reduces to Ohm’s law.

Although this lays the foundation for electron transport at the nanoscale, we haven’t yet discussed transport through molecules themselves, or the shape of their transmission function. This subject will be explained in the next section.

1.3 **Contacting the molecules**

In order to study micro- (or nano-) scopic single molecules, they need to be connected electrically to our macroscopic multimeter. Not only is this a challenging experimental problem, connecting the molecule often changes its properties. Molecular switches for example can lose their ability to switch, as discussed in Chapter 6. Furthermore, the electrical connection can shift the energy levels present in the molecule and seemingly broadens them. This apparent broadening can be explained in an intuitive way, analogous to the apparent broadening of a mode in a Fabry-Pérot interferometer.
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1.3.1 Electron transmission through a molecule

A Fabry-Pérot interferometer consists of two semi-transparent mirrors with a certain distance $x$ between them, forming a cavity. When a monochromatic light ray with wavelength $\lambda$ is incident on this interferometer, it has a certain chance to be transmitted through the first mirror into the cavity. Once inside, it hits the second mirror, having a certain chance to be transmitted by the second mirror out of the cavity (let’s call these left and right transmission probabilities $T_L$ and $T_R$ respectively). Inside the cavity, the light bounces back and forth, interfering with itself, upon each reflection losing amplitude by transmission through the barrier. This self-interference causes the transmission through the cavity to depend on its length. The lower the transmission probabilities of the mirror, the longer the lifetime of the light inside the cavity, allowing it to interfere with itself more. The probability to transmit through the interferometer is given by:

$$T_{\text{Fabry-Pérot}} = \frac{T_LT_R}{1 + R_LR_R - 2\sqrt{R_LR_R} \cos\left(\frac{4\pi x}{\lambda}\right)}, \quad (1.6)$$

where $R_{L,R} = 1 - T_{L,R}$. This is a function periodic in $\lambda$, which makes sense as not only the case where $2\lambda = x$ interferes constructively, also higher resonance modes where $2n\lambda = x$ do so. This function is called a wrapped Cauchy distribution; a sum over Lorentzians, each individual Lorentzian corresponding to one resonance mode.

Now consider a single molecule connected electrically to electrodes on both sides. These connections act as barriers to the environment with a certain transmission probability, much like the mirrors in the Fabry-Pérot interferometer. For a molecule with only one energy level at $E = \epsilon_0$, all other levels in Eq. 1.6 can be ignored, allowing the cosine to be Taylor-expanded around zero. Moreover, the electron energy can be written as a function of the De Broglie wavelength. Using this, Eq. 1.6 can be rewritten to yield:

$$T_M(E) = \frac{4\Gamma_L\Gamma_R}{(E - \epsilon_0)^2 + (\Gamma_R + \Gamma_L)^2}, \quad (1.7)$$

The transmission probabilities are substituted by the molecule/contact coupling $\Gamma$, where $\Gamma_{L,R} = \frac{d\epsilon}{dE} T_{L,R}$ and $\theta = 4\pi x \lambda^{-1}$. Using a more rigorous approach using non-equilibrium Green’s function theory yields the same result. This means that although the molecular level is a delta-function at a well defined energy, the coupling to the environment causes the level to appear broadened. The total transmission through a molecule with multiple levels is then a sum over all individual levels, each with their own coupling and resonance energy.$^4$

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$^4$This is very similar to a Fabry-Pérot interferometer with a cavity filled by a medium with an index of refraction dependent on wavelength $n(\lambda)$ and mirror reflections that also depend on the wavelength ($T(\lambda)$). Or in other words, any real interferometer.
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Fig. 1.1: A schematic of a molecule connected by two leads above the energy diagram. Applying a bias across the electrodes opens up a bias window shown in orange, broadened by temperature. Electrons can flow from the occupied states on the left through the molecule into unoccupied states on the right. The molecular level has a resonance energy of $\epsilon_0$, and the transmission is broadened due to coupling to the leads. It can be intuitively understood from this figure why the current saturates at high applied bias. Applying an even larger bias to the left lead does not significantly increase the current, as the transmission at these energies is low.

Fig. 1.2: Calculated normalized current versus voltage curve for a Lorentzian transmission function with varying $\Gamma$, the temperature is 300 K and $\epsilon_0 = 1$ eV. The current is calculated by computationally solving Eq. 1.5 using the transmission function from Eq. 1.7, assuming that $\Gamma_R = \Gamma_L = \Gamma$. Gamma is varied logarithmically from 1 meV to 300 meV, represented by the different line colors, some of which are shown in the legend. The currents are normalized by dividing each individual curve by $\Gamma$. It can be seen that increasing $\Gamma$ broadens the transmission function and hence smoothenes out the IV-curve. The current at large voltages is equal for each curve, as the transmission function is fully saturated.

Using this transmission function, we can now solve Eq. 1.5 for a molecule connected by two leads, as shown in Fig. 1.1. This figure shows a benzene molecule modelled as a single level connected by leads, causing a broadened transmission function. Applying a bias across the leads opens up a bias window, which is broadened by temperature. Assuming that the temperature is low, the function can be approximated by integrating Eq. 1.7 from $-1/2V$ to $+1/2V$ (assuming the voltage drops symmetrically across the molecule). If $\Gamma_L = \Gamma_R$, the
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result is given by:

\[ I = \frac{G_0 \Gamma}{e} \left[ \arctan \left( \frac{\pm \frac{1}{2} eV - \epsilon_0}{\Gamma} \right) - \arctan \left( \frac{-\frac{1}{2} eV - \epsilon_0}{\Gamma} \right) \right]. \] (1.8)

This means that at high positive or negative voltage \( eV \gg \epsilon_0 \) or \( eV \ll -\epsilon_0 \), the current saturates at a value \( \frac{G_0 \Gamma}{e} \). This happens because the entire channel is saturated, and any other available electrons have energies so far from the resonance that they do not contribute to the current. For nonzero temperatures, the current can be calculated computationally. This is done in Fig. 1.2, where the current is calculated between two leads interconnected by a single level for several molecule/contact couplings.

From the figure it can be seen that there is almost no current at low voltages, until the voltage reaches a threshold of \( 2\epsilon_0 \) where it sharply increases to a saturation value. As \( \Gamma \) increases, the current transitions more smoothly. The currents in the graph are normalized by dividing each current by \( \Gamma \), since the saturation current increases with increasing coupling.

Although the single level model is a good approximation, real molecules have more complex transmission functions that also depend on the contacting method. They are usually calculated using self consistent computational models such as Density Functional Theory (DFT) or Hartree-Fock (HF). An example of such a transmission function can be seen in Fig 1.3.

**Fig. 1.3:** Calculated transmission function of a molecular junction using density functional theory and non-equilibrium Green’s functions. Contrary to a single level approximation, a fully calculated transmission function has many maxima and minima, due to constructive and destructive electron interference within the molecule. This particular transmission function is calculated for a benzenediamine molecule chemically connected to two metal contacts. Adapted from Celis Gil et al.\(^{[23]}\)

Summarizing: molecules as electronic components are interesting not only because of their possible applications, but also due to their fundamentally fascinating properties. Due
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To their small size, molecules show pronounced quantum behavior at room temperature and also allow tuning of their properties, made possible by the large library of organic chemistry. This leaves one problem, however: how can molecules be contacted to our measurement equipment?

1.3.2 Experimental methods

Molecules are small, and therefore do not allow easy access to their properties. Even the recent advances in lithography only allow a resolution down to 7 nm, insufficient for molecules almost an order of magnitude smaller. Contacting the molecules has been a major problem for the field of molecular electronics since its conception. Nowadays, however, a wide range of experimental methods exist to study individual molecules or ensembles of them.

The proverbial work-horse of contacting methods is the mechanically controlled break-junction or MCBJ. A MCBJ uses a bendable substrate to pull apart a notched metallic wire or lithographically confined constriction, controllably breaking it. Since the strain is induced by a push rod on the bottom, the actual strain on the wire is only a fraction of the pushed distance of the rod. This allows control of the electrode separation with sub-nanometer precision.

![Fig. 1.4: Schematic depiction of a mechanically controlled break junction. Two contacts (red) are lithographically fabricated on a bendable substrate, protected by a spacer layer (blue). By pushing against the middle of the substrate while holding the edges, the substrate is bent, separating the red contacts with sub-nanometer precision. When the separation is just right, a molecule exactly fits in between the contacts and IV-traces can be measured.](image)

The MCBJ is commonly used to measure conductance-versus-distance curves. A fixed voltage is set on the electrodes, and the conductance is measured as a function of inter-electrode separation. The junction is then repeatedly formed and broken. When molecules are introduced into the system (either in solution or evaporated in a vacuum), each cycle creates a new junction, as the molecule can bind to the contacts in different orientation. This is repeated in the order of 1000 to 10 000 times, creating a large dataset. When this dataset is represented as a histogram (seen in Fig. 1.5), the signature of the molecule shows up as a peak in the histogram around the conductance of the molecule. Moreover, the current as a function of voltage can be measured at each distance, allowing for the probing of the single
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molecule IV-characteristics\textsuperscript{[24,25]}. This is a tedious task, however, as there are many different junction orientations, all having slightly different transmission functions (if a molecule is present at all!).

A similar approach uses a STM to create a break junction (STM-BJ). The STM-BJ is different from the MCBJ, as the STM-BJ starts separated in contrast to the MCBJ, which starts connected. Pushing the STM tip into the substrate creates a junction that can be broken and reformed at will\textsuperscript{[27]}. Whereas break junction experiments allow for single-molecule measurements, other approaches use many junctions in parallel. One of these approaches is contact-probe atomic force microscopy (CP-AFM) on SAMs\textsuperscript{[14]}, In this technique, an ordered self assembled monolayer is created on top of a substrate, and characterized using a conducting AFM tip. Data from single molecules cannot be obtained in this way, as the AFM tip contacts many molecules simultaneously and hence measures a statistical average. Furthermore, SAMs are very stable and can be measured in ambient conditions for days. CP-AFM on SAMs is ideal for measuring functional molecules, such as switchable rectifiers\textsuperscript{[14]}, as the stability allows repeated measurement, even in high humidity and elevated temperatures.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{histogram}
\caption{Histogram displaying conductance traces (conductance versus junction separation) measured of diazofluorene functionalized buckminsterfullerene, color shows frequency of occurrence. The measurements are done using a MCBJ in air. From the figure it can be seen that a sharp drop in conductance is observed when the junction is broken. However, peaks in the conductance are observed around $2 \times 10^{-5} G_0$, $7 \times 10^{-6} G_0$ and $2 \times 10^{-6} G_0$, indicating the presence of the molecule. If the molecule was not present, only a sharp drop in conductance would be observed. Adapted from Stefani et al.\textsuperscript{[26]}.}
\end{figure}
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1.3.3 Gold nanoparticle networks

In the same vein as CP-AFM on SAMs, statistical averages of molecules can also be investigated by using networks of nanoparticles interconnected by molecular linkers\(^{[28]}\) (see Fig. 1.6). Networks of gold nanoparticles are easy to create using self assembly, and are stable under ambient conditions. Once interlinked by molecules, their conductance at room temperature are an average of the conductance of the interlinking molecules. Interestingly, these electrical measurements can be expanded by optical techniques, as the absorption spectra of the network strongly depends on the interlinking molecule, as we shall see in chapter 6. In this way, molecular functionality such as optical switching can be observed not only by electrical measurements, but also by optical investigation\(^{[16]}\). Moreover, at cryogenic temperatures, the network exhibits Coulomb blockade and electron transport is mediated by (multiple) cotunneling.

Cotunneling is a form of electron transport that is mediated by quantum fluctuations of charge, involving intermediate virtual electron states, yielding a distinct IV-characteristics. In the Coulomb blockade regime, transport through a network linked by molecules is non-trivial, and cotunneling through nanoparticles connected by molecules on both sides will be discussed in chapter 3. Moreover, cotunneling enhances the signature of the interlinking molecule\(^{[29]}\), an intriguing property we tried to utilize to enhance the ON-OFF ratio of molecular switches, discussed in chapter 6. The current theory of multiple cotunneling by Tran et al.\(^{[30]}\) predicts that Coulomb blockaded nanoparticle networks show varying cotunneling length, depending on the temperature and applied bias. In chapter 5 we provide an alternative approach, predicting that the electrical properties are different than previously thought.

The electrical properties of the nanoparticle network do not only depend on the interlinking molecules, but also on the structure of the network itself. The networks are ordered on the scale of a few nanoparticles, but can have cracks and holes in them on the larger scales. We investigate how these imperfections affect the electrical properties in chapter 7.

Networks of nanoparticles provide a viable platform for functional molecular electronics, and inversely, functional molecules provide a method for studying the properties of the networks themselves. Nanoparticle networks interconnected by molecules not only have potential applications, but also show very interesting fundamental properties. This thesis focuses on the transport properties of nanoparticle networks, especially at cryogenic temperatures. The next chapter provides an introduction to this field.
REFERENCES


1. **Molecular electronics**


References


