Flow : a study of electron transport through networks of interconnected nanoparticles

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Summary

The ultimate miniaturization of modern electronics was first discussed by Richard Feynman in 1959. During his lecture titled 'There's plenty of room at the bottom', the future Nobel laureate coined the idea of manipulating single atoms to create the smallest possible electronic components. Now, almost sixty years later, scientists in the field of molecular electronics work on its realization. Although the dream originally was to replace silicon-based technology by one based on single molecules, most scientists now agree that this is beyond our current reach. Single molecules prove to be too unstable to generate fast and consistent signals, something that is crucial for them to be used in our computers.

The greatest challenge that long hindered the development of molecular electronics, is the contacting of the individual molecules. Molecules are very small, typically a few nanometers*, or billionths of a meter. To study the electronic properties of single molecules, you have to connect your macroscopic measurement equipment to the micro- (or nano-) scopic molecule. This is not a trivial problem, and it took around 20 years to solve this problem (outlined in the introduction of chapter 1). Nowadays, a wide variety of methods to connect single, or clusters of molecules exists. One of these is a network of nanoparticles; an ordered structure of small spheres, in my case made of gold. By using the molecules as bridges between the nanoparticles, it is possible to study the molecules by investigating the entire network. Since a network is a hundred to a thousand times larger than the molecules in between the particles, this is much simpler. Moreover, a network like this has a much higher stability than a single molecule, as a network contains countless individual molecules. This is also its largest limitation; a network can not be used to study a single isolated molecule. Nevertheless, networks are an ideal platform to test the functionality of molecules. Functional molecules react to changes in their environment, a reaction which is usually measurable. Among these are light-sensitive switches which can be turned on or off using light, where the off-state has a higher electrical resistance. Other molecules react similarly when encountering a certain chemical compound. In these cases, networks of nanoparticles interlinked by molecules can act as sensors or switches. Moreover, these networks are also intrinsically interesting.

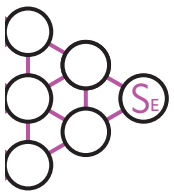
To explain why, let's first consider a single nanoparticle in between two electrodes, rather than an entire network. Electrical current consists of electrons that travel from A to B, which

*A nanometer is an important unit. Us humans usually think in meters (or feet if you want to use a less sensible unit of distance), as most things surrounding us are around a few meters or tenths of meters away from us. Single molecules are usually a few nanometers long, with the distance between the atoms typically being a few tenths of nanometers.

is why I talk about electron transport rather than electrical current[†]. An electrical current through the nanoparticle is facilitated by electrons hopping onto the nanoparticle from one side, and hopping off from the other side. This requires that the electron itself is located on the nanoparticle for a short time. This charges the particle, requiring a bit of energy. Under normal circumstances, like at room temperature and voltages of a few volts, this is not a problem. However, when we cool down the system to a few Kelvin[‡], and we only apply a few millivolts, the behavior changes drastically. Electrons lack the energy to charge the nanoparticle, and the current decreases sharply.

This is called Coulomb blockade, after Charles-Augustin de Coulomb, who described how two charges influence each-other. According to classical mechanics, the behavior inside the Coulomb blockade regime is clear, as conservation of energy forbids any electrons from flowing through the nanoparticle. However, electrons are so small that their behavior is governed by quantum mechanics. Quantum mechanics is not as unforgiving as classical mechanics, and is fine with electrons violating conservation of energy, given that they do not do so for too long. This behavior is described by the Heisenberg uncertainty principle of time and energy, which in this case describes that the shorter the electrons occupy the nanoparticle, the more they can break the law of conservation of energy. Loosely formulated, an electron that wants to travel from left to right through the nanoparticle is allowed to hop onto the nanoparticle, sit there for a while, before it realizes that it's breaking the law and hops back off. Similarly, an electron already residing on the nanoparticle is allowed to hop off, briefly, leaving the nanoparticle charged positively, before realizing this also violates conservation of energy and reluctantly returns to the nanoparticle. However, if these two electrons coincidentally decide to travel at the same time, one from the left onto the nanoparticle, the other to the right off of the nanoparticle, the particle remains uncharged, while we effectively took one electron from the right to the left. Electrical current!

This method of quantum transport is called cotunneling and is explained in more detail in chapters 2 and 3. What is important about this form of transport, is that both electrons need to contribute, otherwise the entire process is canceled. If the chance that one electron will contribute (also called the transmission probability or $\mathcal{T}$) is equal to trowing six with a die (one sixth), then the chance of both electrons contributing is equal to throwing six twice, or one thirty-sixth. In the case of longer chains of nanoparticles, electron transport is facilitated by multiple cotunneling, in which many electrons simultaneously participate in the process of generating an electrical current. Analogously to the previous example, you have to throw a die for every electron individually, and only if you throw six each time, a current arises. The current I therefore scales with the transmission probability $\mathcal{T}$ to a certain power N: $I \propto \mathcal{T}^N$.



[†] In principle, these two are identical. However, there is one small difference: electrons are negatively charged. This means that an electrical current from left to right is caused by electrons traveling in the opposite direction, from right to left

[‡] One Kelvin is one degree above absolute zero, around 273 degrees Celsius below zero.

This has far-reaching consequences. The chance that one single electron hops from one to the next nanoparticle is strongly influenced by the molecule in between the particles. Moreover, if that molecule is a functional molecule, like a switch, this chance can be changed by shining light on the network. If in this case, this changes the probability from one sixth to one half, the current changes not by a factor of three, but by 3^N. For a chain of four nanoparticles ($N = 5$), this difference is a factor of 243, a large difference! You could say that cotunneling increases the sensitivity of the network to the molecules in between the nanoparticles. We try to test this prediction in chapter 6, but learn in chapter 5 that the current theory of multiple cotunneling is not sufficient to describe the current through our networks.

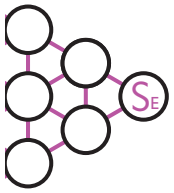
The current theory that describes cotunneling assumes that the probability of an electron hopping from one nanoparticle to the next is independent of the energy of the electron. Normally, this is a good assumption, however, depending on the interlinking molecule, it might not always be correct. If the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) is close to the Fermi energy of the contacts and the nanoparticle (compared to the energy required to charge the nanoparticle), the energy dependence of the transmission probability becomes significant. In chapter 3, we calculate the effect on the current through a single nanoparticle. We approach this problem in two different ways, first for the case that transport through the molecule is resonant. This means that the electron 'flows' through the molecule, during which one orbital or molecular level carries the entire current. In this case, we predict that at high voltages, the current increases as the resonance energy of the molecular level is further away from the Fermi energy of the contacts. This is opposite to the expected result when cotunneling does not play a role. The second approach assumes non-resonant transport through the molecule, which means that the electron hops on to, and off of the molecule rather than 'flowing' through it. In this case, electron transport through the entire molecule-nanoparticle-molecule system is facilitated by multiple cotunneling. If the charging energy of the molecules is larger than that of the nanoparticle, we predict a strong simplification of the behavior of the current. The transmission probability seems independent of the electron energy, and the behavior reduces to the current cotunneling theory by Averin and Nazarov[Ch. 3, ref 16]. This implies that a system with molecules is indistinguishable from one without.

To describe electron transport through entire networks, we not only need to account for cotunneling, but also for multiple cotunneling. The commonly used theory describing multiple cotunneling, however, is but an *ad hoc* expansion of normal cotunneling. It is an approximation that doesn't necessarily always agree with reality. In chapter 5, I describe a new model derived from basic principles which makes more accurate predictions. Moreover, this model is also applicable at high voltages (when the electrostatic energy eV is larger than the charging energy E_C). I fit this model to measured data, but only succeed when I account for disorder in the network. By assuming that the charging energy of every nanoparticle varies slightly from one particle to the next, I am able to model the experimental data. More

importantly, my fits imply no noticeable contribution of (multiple) cotunneling to the current through the network. Electron transport almost completely consists of highly energetic electrons that do not need cotunneling to cross the array. At low voltages and temperatures, a small number of percolating current paths carries all the current through the network. As the voltage increases, more paths contribute to the current, and at large voltages, all possible paths contribute. This is an important conclusion that is in sharp contrast with the current consensus.

This conclusion also has an impact on the prediction from a few paragraphs ago, where we said that networks of nanoparticles have an enhanced sensitivity for the molecules interconnecting them. As cotunneling does not contribute to the current significantly, it remains a question whether this prediction still holds. In chapter 6, I use my new theory to calculate the enhancement in sensitivity. Changing the molecules does not only change the transmission probability, it also changes the permittivity and therefore the charging energy. I predict that a small change in charging energy has a large effect on the current through the network, which means that the network can still enhance the properties of the molecule. To experimentally verify this prediction, we use a molecular switch as a bridge between the particles in the network and try to switch this while measuring the current through the network. Although the molecule does switch in solution, it does not appear to switch after being inserted into the network. Unfortunately, we therefore cannot make any decisive conclusion as to whether we can use nanoparticle networks to enhance the properties of the bridging molecules.

In the last chapter 7, we take a different perspective to look at the flow of electrons through nanoparticle networks. We use a low-energy electron microscope or LEEM to measure the voltage drop across a network with sub-micrometer accuracy. In the LEEM, we fire electrons at the network and slow them down to a near stop before arriving at the network. By applying a voltage across the network, the incoming electrons are locally attracted or repelled, dependent on the local potential. If the electron is repelled, it will end up at the detector and produces a signal. However, if it is attracted, it will reach the network, likely being scattered and not giving a signal at the detector. By tuning the velocity of the incoming electrons and determining at what exact energies they are absorbed, we can deduce the local potential. This does not only give the beautiful pictures in chapter 7, it also provides a lot of information on the electronic structure in the network. We see, for example, that electron are blocked by large gaps in the network, but remain largely unaffected by smaller holes and imperfections. Moreover, we see that they have no problem travelling from the electrodes into the network.



This thesis describes fundamental research on electron transport through networks of nanoparticles. The most important result is that this kind of transport can be described by only first-order contributions, *i.e.* without cotunneling. Disorder is the dominant factor. Despite the absence of higher-order transport, my model predicts that an enhanced sensitivity of the networks to the inserted molecules should still be present.