TRANSPORT AT THE ATOMIC SCALE: ATOMIC AND MOLECULAR CONTACTS

A. Levy Yeyati and J. M. van Ruitenbeek

Departamento de Física Teórica de la Materia Condensada C-V,
and Instituto Universitario de Ciencia de Materiales “Nicolás Cabrera”,
Universidad Autónoma de Madrid, E-28049 Madrid, Spain
and
Kamerlingh Onnes Laboratorium, Universiteit Leiden, Postbus 9504, NL-2300 RA Leiden,
The Netherlands
Photo: width 7.5cm height 11cm
Contents

1. Introduction 5
2. Parity oscillations in atomic chains 6
3. Superconducting quantum point contacts 14
   3.1. The Hamiltonian approach 15
   3.2. Comparison to experimental results 20
4. Environmental effects 23
   4.1. Classical phase diffusion 24
   4.2. Dynamical Coulomb blockade 27
5. Single-molecule junctions 30
6. Concluding remarks 37
References 38
1. Introduction

Atomic and molecular contacts have a special place in the field of nanoscience. From an application point of view they are the playground to investigate the possibilities and limitations of electronics at the very smallest size scale. From a fundamental science point of view they are simple physical systems to test principles of electron transport at the atomic scale. We will mostly address the fundamental issues in this field. Here, an important distinction can be made between atomic and molecular contacts. While simple and reliable experimental techniques are widely available for investigating single-atom contacts for nearly all metals, single-molecule junctions have been more difficult to produce and characterize reliably.

Metallic atomic-sized contacts have proven to provide a rich field of physical phenomena, that we have recently summarized in an extensive review, written together with Nicolás Agraït [1]. It is not our intention to rewrite the review on this topic. Instead, we refer to Ref. [1] for a detailed presentation of the field and mention here only the main results. The major part of this chapter will cover work of the last two years that was not included in our previous review and some aspects of superconducting junctions that did not receive sufficient attention at that time and that are useful for those interested in entering the field.

For contacts between two metal electrodes formed by just a single atom, or just a few atoms, the electron transport can be described in terms of a limited number, \( N \), of conduction channels, each characterized by its own transmission probability \( \tau_i \). The conductance is given by the Landauer expression [2]

\[
G = G_0 \sum_{i=1}^{N} \tau_i,
\]

where \( G_0 = \frac{2e^2}{h} \) is the quantum unit of conductance for spin-degenerate channels. The conductance is easily obtained experimentally, but does not provide much information about the number of channels involved, other than the total sum of their transmission probabilities. Once we have obtained the full set of transmission probabilities \( \tau_i \), also referred to as the mesoscopic PIN code, the junction is fully characterized. Many properties can be predicted quantitatively once the PIN code is known, including the supercurrent [3], dynamical Coulomb...
blockade [4], shot noise [5, 6], and conductance fluctuations [7]. One of the attractive points of this field is that it is actually possible to determine the PIN code experimentally, principally through a measurement of the IV characteristics in the superconducting state, exploiting the information contained in the subgap structure [8, 9]. Thus a detailed quantitative understanding of quantum transport has been obtained. As a central result it has been shown that the number of conductance channels for a single atom is determined by the number of its valence orbitals [9]. The properties of superconducting junctions will be discussed in Sect. 3. The role of the environment has proven to be of importance in analyzing current-voltage relations, and the associated problems will be addressed in Sect. 4.

For molecular contacts the level of sophistication of the experiments is much less. Where atomic contacts of metals are homogenously formed out of a single species of metallic atoms, organic molecules that are sandwiched between metallic leads form an inhomogeneous system with many difficulties associated with the formation and characterization of the interfaces. The attractive point that motivates much of this research is the wide scope of possible organic molecules that can be studied, with functions such as diode characteristics, switching, and memory engineered into the chemical design of the molecule. Although much of the initial optimism in this field has proven premature by the difficulties that surfaced related to the proper characterization an analysis of the observed current-voltage characteristics, more recently important progress has been made. These developments will be briefly summarized in Sect. 5.

One further development that we will address is associated with atomic chains of single metal atoms. Chains of atoms have been demonstrated for Au [10, 11], Pt and Ir [12]. Several groups have predicted that atomic chains for monovalent metals should show oscillations in the conductance with the parity of the number of atoms forming the chain [13–15]. Such oscillations as a function of the length of the chain have been observed, not only for gold as predicted, but also for Pt and Ir, as will be discussed in Sect. 2.

2. Parity oscillations in atomic chains

When a metallic contact is gradually stretched to the point that only a single atom bridges the gap one would expect that further stretching will break the contact at this weakest spot. This is indeed what one observes for most metals, with the noteworthy exception of three metals: Ir, Pt and Au. The linear bond between two atoms in a chain configuration for these metals is so strong that, rather than breaking this bond, new atoms are pulled out of the leads into the chain thus increasing its length. The effect has been observed directly in a high-resolution
transport electron microscope under ultra-high vacuum at room temperature [10]. At low temperatures the chain formation can be inferred from the variation of the conductance as a function of the stretching of the contact [11, 12]. The latter experiments have the advantage that the chains can be held stable over extended periods of time and their properties can be investigated in detail. Further details of the formation of chains of atoms can be found in our review paper [1].

As one of the interesting properties of linear chains of atoms we want to focus in this section on oscillations of the conductance as a function of the length of the chain. As argued above, the last plateau of conductance before rupture is typically due to a single atom contact. The formation of an atomic wire results from further pulling of this one-atom contact, and its length can be estimated from the length of the last conductance plateau [11, 12, 16]. A histogram made of those lengths (filled curves in Fig. 1) shows peaks separated by distances equal to the inter-atomic spacing in the chain. These peaks correspond to the lengths of stretching at which the atomic chain breaks, since at that point the strain to incorporate a new atom is higher than the one needed to break the chain [17]. This implies that the number of atoms in the chain increases by one going from one peak to the next.

For gold, a monovalent metal, both the one-atom contact and the chain have a conductance of about $G_0$ with only small deviations from this value, suggesting that the single conductance channel has a nearly perfect coupling to the banks. However, small changes of conductance during the pulling of the wire can be observed [17, 18] and are suggestive of an odd-even oscillation. Small jumps in the conductance result from changes in the connection between the chain and the banks when new atoms are being pulled into the atomic wire. In order to uncover possible patterns hiding in these changes one can average many plateaus of conductance starting from the moment that a single-atomic contact is formed until the wire is broken. These points can be defined by a criterion, e.g. by the conductance dropping below $1.2 G_0$ and $0.5 G_0$, respectively. In the upper panel of Fig. 1 it can be seen that the thus obtained averaged conductance plateau for gold shows an oscillatory dependence of the conductance with the length of the wire. The amplitude of the oscillation is small and differs slightly between experiments, but the period and phase are quite reproducible. In the averaged curves of the experiment, Fig. 1, the conductance does not quite reach a maximum of $G_0$. This is largely due to the averaging procedure, where for a given length there are contributions from $n$ and $n + 1$-numbered chains and only the relative weight of these varies. In individual traces the maxima come much closer to full transmission. Further suppression of the maximum conductance may result from asymmetries in the connections to the leads. The relatively small amplitude of the oscillations is consistent with the fact that the average conductance is close to unity, implying that the contact between the chain and the banks is nearly
Fig. 1. Averaged plateaus of conductance for chains of atoms of the three metals investigated: Au, Pt, and Ir. Each of the curves are made by the average of individual traces of conductance while pulling atomic contacts or chains. Histograms of the plateau lengths for the three metals obtained from the the same set of data are shown by the filled curves. From Ref. [18].

adiabatic. The rise above $1G_0$ for short lengths in Figs. 1 can be attributed to tunnelling contributions of additional channels.

Similar oscillations of even larger amplitude were observed for the other two metals forming chains of atoms, namely Pt and Ir [18]. These d metals have up to five channels of conductance and therefore the average plateau conductance is expected to show a more complicated behaviour. A one-atom Pt contact has a conductance of about $2G_0$ while for a Pt atomic chain it is slightly smaller, $\sim 1.5G_0$ [19] with variations during the pulling process that can be as large as $0.5G_0$. In the averaged curves one observes oscillations similar to those for Au, which are compared to the peak spacing in the length histogram in Fig. 1. Ir shows a similar behaviour although somewhat less pronounced. The periodicity $p$ of the oscillation in the conductance for the three metals is about twice the inter-peak distance $d$ of their corresponding plateau-length histogram. This behaviour agrees with an alternating odd-even evolution of the conductance with the number of atoms.

In addition to the oscillations for Pt and Ir, the mean conductance of the mea-
measurements in Fig. 1 show an unexpected slope of about 0.3–0.4 $G_0/\text{nm}$. For a ballistic wire the conductance as function of length is expected to be constant, apart from the oscillatory behaviour discussed above.

**Theoretical models:** Even-odd oscillations are already present at the level of simple tight-binding (TB) models. The model considered in Ref. [13] is a linear chain containing $N$ atoms coupled to electrodes described as a Bethe lattice of a given coordination number $Z$. The model Hamiltonian can be decomposed as $\hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_{\text{chain}} + \hat{V}_L + \hat{V}_R$, where $\hat{H}_{L,R}$ correspond to the uncoupled electrodes, $\hat{H}_{\text{chain}} = \sum_{\sigma,i=1}^N v_{\sigma i} \hat{c}_{\sigma i} \hat{c}_{\sigma i+1} + \text{h.c.}$ describes the electron states in the isolated linear chain and $\hat{V}_{L,R} = \sum_{\sigma} t_{L,R} \hat{c}_{\sigma L,R} \hat{c}_{1,N} + \text{h.c}$ correspond to the coupling between the chain and the outermost sites of the left and right electrodes.

Electronic and transport properties within TB models are conveniently analyzed in terms of Green function techniques. For the linear response regime and in the non-interacting case it is sufficient to introduce the retarded and advanced Green operators, formally defined as

$$\hat{G}^{r,a}(\omega) = \lim_{\eta \to 0} \left[ \omega \pm i\eta - \hat{H} \right]^{-1}. \quad (2.1)$$

In terms of the matrix elements of $\hat{G}^{r,a}$ the transmission coefficient through the chain is then given by the following expression

$$\tau(E_F) = 4 \Gamma_L(E_F) \Gamma_R(E_F) \left| G^{r,a}_{1,N}(E_F) \right|^2, \quad (2.2)$$

where $\Gamma_{\alpha}(\omega) = t_{\alpha}^2 \text{Im} g_{\alpha}^{\alpha}(\omega)$ (with $\alpha = L, R$) are the tunneling rates from the chain to the leads. These rates are determined by both the hopping elements $t_{\alpha}$ coupling the chain to the leads and by the density of states on the outermost site of the uncoupled electrodes, determined by $\text{Im} g_{\alpha}$. For the Bethe lattice model we have [20]

$$g_{\alpha}^{r,a}(\omega) = \frac{1}{\sqrt{Z} t_B} \left[ \frac{\omega \pm i\eta}{2 \sqrt{Z} t_B} - \sqrt{\left( \frac{\omega \pm i\eta}{2 \sqrt{Z} t_B} \right)^2 - 1} \right], \quad (2.3)$$

where $t_B$ is the hopping element within the Bethe lattice.

The transmission coefficient and the linear conductance are related by the Landauer formula $G = \frac{2 e^2}{h} \tau(E_F)$. As shown in Ref. [13] the conductance of the chain within this model exhibits an even-odd oscillation when $E_F \simeq 0$. This is essentially an interference phenomenon arising from the commensurability of
Fig. 2. Transmission through a linear chain of $N$ atoms coupled to electrodes represented by Bethe lattices of coordination $Z = 4$. These curves correspond to $v = t_B = t_L = t_R$ (see text for the definition of parameters). The dotted lines correspond to the minimal envelope curve determined by Eq. (2.5).

The Fermi wavelength and the lattice spacing. It is a simple exercise [21] to show that for $E_F = 0$ one has

$$\tau = \frac{4v^2 \Gamma_L \Gamma_R}{(v^2 + \Gamma_L \Gamma_R)^2} \quad \text{for even } N$$

$$\tau = \frac{4 \Gamma_L \Gamma_R}{(\Gamma_L + \Gamma_R)^2} \quad \text{for odd } N. \quad (2.4)$$

This result shows that perfect transmission is robust in the odd case as it only requires left-right symmetry, i.e., $\Gamma_L = \Gamma_R$. In the even case it requires a more stringent condition on the hopping elements (more precisely $v = \sqrt{\Gamma_L \Gamma_R}$) which is not necessarily fulfilled in an actual system. This elementary calculation thus provides a simple model for the appearance of parity oscillations.

When we analyze the transmission as a function of the Fermi energy for fixed $N$ we observe an oscillatory behaviour, as depicted in Fig. 2 for a symmetric case. These oscillations are bound by the maximum value $\tau = 1$ and a minimal envelope curve determined by

$$\tau_{\min}(x) = \frac{4 \Gamma^2 v^2 (1 - x^2)}{(v^2 + \Gamma^2 (1 - 2x^2))^2 + 4 \Gamma^2 v^2 (1 - x^2)}, \quad (2.5)$$

where $\Gamma = \Gamma_{L,R}(0)$ and $x = \omega/2v$. This envelope curve is shown in Fig. 2 as a dotted line.
The even-odd effect has also been reported on the basis of ab-initio calculations for monovalent metals [14,15,22]. The calculations of Sim et al. [15] were based on the Friedel sum rule (FSR) which relates the phase of the transmission amplitude to the charge accumulated within the chain. For a single channel conductor the FSR states that \( \delta Q = 2e\delta(E_F)/\pi \) (the factor 2 is due to spin degeneracy) [23]. For a monovalent metal and assuming local charge neutrality this relation implies that the Fermi energy should lie at the middle of a transmission resonance for odd \( N \), i.e. \( \delta(E_F) = (2n + 1)\pi/2 \), and between two resonances for even \( N \), in agreement with the simple TB calculations shown in Fig. 2. The charge neutrality argument for explaining the observed almost perfect quantization in monovalent one atom contacts was first introduced in Ref. [24].

Ab-initio calculations have also been presented for chains of non-monovalent metals like C, Si and Al [25–29]. These calculations indicate that not only the amplitude but also the actual periodicity can be extremely sensitive to the type of atoms in the chain. For instance, for the case of Al Ref. [28] showed that the conductance exhibits a four-atom period oscillation, which they explained using an effective single band tight-binding model with filling factor 0.25.

In spite of these theoretical efforts, and with the exception of Au, there are not many realistic calculations of the conductance for the actual 5d metals producing stable atomic chains. The simple explanation presented above can account qualitatively for the behaviour in the case of Au, characterized by a full 5d band and a nearly half-filled 6s band. However, for the case of Pt and Ir, in which the contribution of 5d orbitals to the conductance is important there is no reason why this simple picture should be valid.

The behaviour of the conductance for Au, Pt and Ir atomic chains was analyzed in detail in Ref. [30]. They considered model geometries like the one
depicted in Fig. 3 in which the atomic chain is connected to bulk electrodes represented by two semi-infinite fcc perfect crystals grown along the (111) direction. Using a parametrized self-consistent tight-binding model, which basically reproduces the bands around the Fermi energy for the infinite ideal chains, they obtained the evolution of the conductance with the number of atoms in the chain depicted in Fig. 4. This evolution is rather sensitive to the elongation, especially in the case of Pt and Ir (for Au the conductance exhibits small amplitude even-odd oscillations, $\sim 0.04G_0$, which remain basically unaffected upon stretching).

The main features and the differences between Au, Pt and Ir are more clearly understood by analyzing the local density of states and the energy dependent transmissions, shown in Fig. 5 for a $N = 5$ chain of these metals at an intermediate elongation. As has been shown in previous works (e.g., see Refs. [31,32]) Au chains are characterized by a single conducting channel around the Fermi energy with predominant $s$ character. The transmission of this channel lies close to one and exhibits small oscillations as a function of energy resembling the behaviour of the single band TB model discussed above.

In the case of Pt the contribution from the almost filled $5d$ bands becomes
important for the electronic properties at the Fermi energy. There are three conduction channels with significant transmission at $E_F$: one due to the hybridization of $s - p_z$ and $d_{z^2}$ orbitals, and another two almost degenerate with $p_x - d_{xz}$ and $p_y - d_{yz}$ character respectively (here $z$ corresponds to the chain axis). The contribution of the 5$d$ orbitals is even more important in the case of Ir where a fourth channel exhibits a significant transmission.

As discussed in Ref. [30] more insight into these results can be obtained by analyzing the band structure of the infinite chains. The left panel in Fig. 6 shows the bands around the Fermi energy for Pt obtained from ab-initio calculations. Two main features are worth commenting: 1) Symmetry considerations allow to classify the bands according to the projection of the angular momentum along the chain axis, $m$. 2) Close to the Fermi level there is an almost flat filled two-fold degenerate band with $d_{xy}$ and $d_{x^2-y^2}$ ($m = \pm 2$) character. The other partially filled and more dispersing bands have $s - p_z - d_{z^2}$ ($m = 0$) and $p_x - d_{xz}$ or $p_y - d_{yz}$ ($m = \pm 1$) character (see labels in Fig. 6).

The close connection between this band structure and the conduction channels of the chains is realized when analyzing the evolution of the conductance and its channel decomposition for even longer chains than in Fig. 4 ($N > 8$). This is illustrated in the right panel in Fig. 6. As can be observed the decrease of the
Fig. 6. Left panel: band structure of the infinite Pt chain. The bands are classified by the quantum number $m$ corresponding to the projection of the angular momentum on the chain axis. The arrows indicate the crossing of the Fermi level for the $m = 0$ and the $m = \pm 1$ bands. Right panel: channel decomposition for Pt chains as a function of $N$. The legends indicate the symmetry of the associated bands in the infinite chain.

The total conductance of Pt for $N < 7 - 8$ corresponds actually to a long period oscillation in the transmission of the two nearly degenerate channels associated with the $m = \pm 1$ bands. This period can be related to the small Fermi wave vector of these almost filled $d$ bands, as indicated by the arrows in the left panel of Fig. 6. In addition, the upper $m = 0$ band crossing the Fermi level is close to half-filling giving rise to the even-odd oscillatory behaviour observed in the transmission of the channel with predominant $s$ character. The lower $m = 0$ band tends to be completely filled and the corresponding channel is nearly closed for short chains. However, one can appreciate a very long period oscillation in its transmission, rising up to $\sim 0.5G_0$, for $N \sim 13 - 14$.

The general rule that emerges from the above analysis is that the transmission corresponding to each conduction channel oscillates as $\sim \cos^2(k_{F,i}N\alpha)$ where $k_{F,i}$ is the Fermi wave vector of the associated band in the infinite chain. In the case of Pt the total conductance for short chains ($N < 7 - 8$) exhibits an overall decrease with superimposed even-odd oscillations in qualitative agreement with the experimental results of Ref. [18]. For even longer chains (not yet attainable in experiments) these calculations predict an increase of the conductance due to the contribution of conduction channels with $d_{xz, yz}$ character.

3. Superconducting quantum point contacts

Atomic sized conductors have revealed to be unique systems to test predictions on superconducting transport in the strong quantum regime [1]. In order to under-
stand the universal behaviour observed in their superconducting transport properties in terms of the PIN code \( \{ \tau_n \} \) it is important to consider the large difference between energy scales associated with superconductivity and the typical energy scale for the variation of the normal conductance. Thus, for instance, in the case of Al the superconducting gap \( \Delta \) is of the order of 180 \( \mu \)eV, while for observing an appreciable variation in its normal conductance it is necessary to apply a bias voltage much larger than 10 meV. One can then safely assume that normal conduction channels are not affected by the superconducting transition and one is allowed to neglect the energy dependence in the channel transmissions when analyzing superconducting transport. As a consequence, in setting up a theoretical description one can concentrate on the properties of a superconducting quantum point contact (SQPC) with a single channel and with fixed transmission \( \tau \) and describe the experimental results as a collection of independent channels.

3.1. The Hamiltonian approach

In the spirit of tight-binding models discussed in the previous section, the simplest model describing a single channel contact with arbitrary transmission can be written as \( \hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_T \), where \( \hat{H}_{L,R} \) correspond to the left and right electrodes (which in the superconducting case are described by the usual BCS pairing model) that are coupled through \( \hat{H}_T = \sum_\sigma \hat{v}_L \sigma \hat{c}_{R\sigma} e^{i\theta(t)/2} + h.c. \), where \( \theta(t) = 2e/\hbar \int_0^t V(t) dt + \theta_0 \) is the phase difference between the electrodes which is determined by the imposed voltage bias. The normal transmission within this model is given by \( \tau = 4v^2W^2/(W^2 + v^2)^2 \), where \( 1/W\pi \) is the density of states on the normal leads at the Fermi energy [33].

Determining the superconducting transport properties of this model requires the use of some field theoretical techniques. One needs to combine the Nambu formalism appropriate to describe the superconducting state [34] with the Keldysh formalism which allows to deal with a non-equilibrium situation [35]. In the Nambu formalism one introduces spinor field operators \( \hat{\psi}_i \) and \( \hat{\psi}_i^\dagger \) defined as

\[
\hat{\psi}_i = \begin{pmatrix} \hat{c}_{i\uparrow} \\ \hat{c}_{i\downarrow} \end{pmatrix}
\quad \text{and} \quad
\hat{\psi}_i^\dagger = \begin{pmatrix} \hat{c}_{i\uparrow}^\dagger \\ \hat{c}_{i\downarrow} \end{pmatrix},
\]

where the indexes \( i, j \) denote the left and right electrodes.

In terms of these operators the usual retarded and advanced Green functions are given by

\[
G^r_{i,j}(t, t') = -i\theta(t - t') \left< \hat{\psi}_i(t), \hat{\psi}_j^\dagger(t') \right>_+ >
\]

\[
G^a_{i,j}(t, t') = i\theta(t' - t) \left< \hat{\psi}_i(t), \hat{\psi}_j^\dagger(t') \right>_+ >,
\]

(3.2)
A. Levy Yeyati and J. M. van Ruitenbeek

where $[\hat{A}, \hat{B}]_+$ denotes the anticommutator. Notice that these quantities are now $2 \times 2$ matrices in Nambu space. For the calculation of $G^{r,a}$ one needs to solve the corresponding Dyson equation $G^{r,a} = g^{r,a} + g^{r,a} \circ \mathbf{v} \circ G^{r,a}$, relating them to the Green functions of uncoupled electrodes $g^{r,a}$. In this equation the product $\circ$ denotes integration over internal time arguments and summation over intermediate indexes while $\mathbf{v}$ denotes the hopping elements in Nambu space given by

$$\hat{v}_{LR}(t) = v \left( e^{i\theta(t)/2} 0 \\ 0 -e^{-i\theta(t)/2} \right) = (\hat{v}_{RL}(t))^\dagger. \quad (3.3)$$

The local BCS Green functions are given by $\hat{g}_{ij} = \hat{g}_{ij}^* = \delta_{ij} \left( g I + f \sigma_x \right)$, where $g = -\omega/W\sqrt{\Delta^2 - \omega^2} = -\omega/\Delta f$.

The retarded and advanced Green functions are not sufficient for dealing with a general non-equilibrium situation. It is in general necessary to determine in addition the Keldysh Green function defined as

$$G^{+,-}_{i,j}(t, t') = i < \hat{\psi}_{j}^\dagger(t')\hat{\psi}_{i}(t) >, \quad (3.4)$$

which satisfies the equation [35]

$$G^{+,-} = g^{+,-} + G^r \circ \mathbf{v} \circ g^{+,-} + g^{+,-} \circ \mathbf{v} \circ G^a + G^r \circ \mathbf{v} \circ g^{+,-} \circ \mathbf{v} \circ G^a, \quad (3.5)$$

where $g^{+,-}$ corresponds to the uncoupled electrodes and are determined by $\hat{g}_{ij}^{+,-} = \delta_{ij} n(\omega) (\hat{g}_{ii}^a - \hat{g}_{ii}^r)$, $n(\omega)$ being the Fermi distribution.

The various transport properties of the system can be expressed in terms of these quantities. Thus, for instance, the mean current can be written as

$$\langle \hat{I}(t) \rangle = \frac{e}{h} \text{Tr} \left[ \hat{\sigma}_z \left( \hat{v}_{LR}(t) \hat{G}^{+,-}_{RL}(t, t) - \hat{v}_{RL}(t) \hat{G}^{+,-}_{LR}(t, t) \right) \right]. \quad (3.6)$$

Obtaining analytical results in the superconducting case is (even for this simple model) a difficult task. The main difficulty lies in the intrinsic time dependence of the problem when $V \neq 0$. In the stationary case ($V = 0$) the Dyson equations for the retarded and advanced Green functions become $2 \times 2$ algebraic equations which can be readily solved. The main result for this case is the existence of two bound states inside the superconducting gap with energies given by [36]

$$\epsilon_{\pm}(\theta_0) = \pm \Delta \sqrt{1 - \tau \sin^2(\theta_0)/2}. \quad (3.7)$$

These are the so-called Andreev bound states, which result from multiple Andreev reflections (MAR) between the superconducting electrodes [37, 38]. The position of these states depends on the stationary phase difference $\theta_0$ and they
are the current-carrying states. In fact the Josephson current at zero temperature can be directly evaluated as

$$I(\theta_0) = \frac{2e}{\hbar} \frac{d}{d\theta_0} \epsilon(\theta_0),$$ (3.8)

When a constant bias voltage is applied we have $\theta(t) = \omega_J t$, where $\omega_J = 2eV/\hbar$ is the Josephson frequency. For having a more tractable form of the Dyson equations one can perform a double Fourier transformation of the Green functions. Due to the special form of the phase factors in the hopping elements, the dependence on the two frequencies is linked by $G(\omega, \omega') = \sum_n G_{n0}(\omega) \delta(\omega - \omega' + n\omega_J)$. A pictorial representation of the Dyson equations determining the Fourier components $G_{n0}$ is given in Fig. 7. In this figure we draw replicas of the left and right electrodes labeled by an integer number which determines the number of quanta $eV$ which are emitted or absorbed in a given tunneling process. The horizontal lines represent the propagation inside the electrodes as an electron (full lines) or as a hole (dashed lines). The dotted line indicate the coupling between electron and holes due to the anomalous propagator $f$. When a quasiparticle tunnels from left to right as an electron it absorbs an energy quantum $eV$, while when it tunnels as a hole a quantum is emitted. As a result when all processes
up to infinite order in $v$ are considered the replicas from $n = -\infty$ to $n = \infty$ are coupled like in a tight-binding one-dimensional chain with nearest-neighbour hopping. The different components $G_{n0}$ can be expressed as a continued fraction in Nambu space. Thus, for instance

$$
\hat{G}_{r0} = \left[ (\hat{g}_{r0})^{-1} - \hat{v}^+ \hat{G}_{z}^r \hat{v}^- - \hat{v}^- \hat{G}_{z}^{-1} \hat{v}^+ \right]^{-1},
$$

(3.9)

where the quantities $\hat{G}_{\pm n}$ satisfy the recursive equations

$$
\hat{G}_{\pm n}^r = \left[ (\hat{g}_{\pm n}^r)^{-1} - \hat{v}^\pm \hat{G}_{\pm n+1}^r \hat{v}^\mp \right]^{-1} \quad \text{for even } n,
$$

$$
\hat{G}_{\pm n}^r = \left[ (\hat{g}_{\pm n}^r)^{-1} - \hat{v}^\mp \hat{G}_{\pm n+1}^r \hat{v}^\pm \right]^{-1} \quad \text{for odd } n.
$$

In the above expressions $\hat{g}_n^r = \hat{g}^r(\omega + neV)$ and $\hat{v}^\pm = v \left( \hat{\sigma}_z \pm \hat{I} \right) / 2$.

Once the components $G_{n0}$ have been determined one can compute the mean current as

$$
\langle \hat{I}(V,t) \rangle = \sum_m I_m(V) e^{im\omega_Jt}.
$$

The most interesting from the experimental point of view is the dc component $I_0$ which can be written as [33]

$$
I_0 = -\frac{4e}{\hbar} \int d\omega \sum_{n=odd} \text{ReTr} \left[ \hat{\sigma}_z \left( \hat{T}_n \hat{g}_n^a \hat{T}_n \hat{g}_0^a \right) \right],
$$

(3.10)

where $\hat{T}_n = \hat{v}^+ \hat{G}_{n+1}^a + \hat{v}^- \hat{G}_{n-1}^a$. The numerical evaluation of these equations yields the results shown in Fig. 8 for $I_0$ at zero temperature and for a range of values of the transmission $\tau$. As can be observed $I_0(V)$ exhibits a highly non-linear behaviour. The most remarkable feature is the appearance of current steps at $eV = 2\Delta / n$. This is the so-called subgap structure which is more pronounced in the tunnel limit $\tau \rightarrow 0$. Physically the subgap structure appears due to the occurrence of multiple Andreev reflection processes between the superconducting electrodes. Associated with a MAR process of order $n$, a charge $ne$ is transferred coherently with a probability scaling as $\tau^n$ at low transmission. For the occurrence of these processes a minimum bias voltage $eV = 2\Delta / n$ is required, which explains the observed jumps in the current. A rather simple expression can be found for the current for $V \sim 2\Delta / n$ in this low transmission regime [33]:

$$
I_0 \approx \frac{e\pi^2}{\hbar} \tau^n \int_{\Delta-neV}^{-\Delta} d\omega \rho(\omega) \rho(\omega + neV) \Gamma_n(\omega),
$$

(3.11)

where $\Gamma_n(\omega) = \prod_{k=-1}^{n-1} |f(\omega + keV)|^2$ and $\rho(\omega)$ is the BCS density of states. The scaling of the current steps with $\tau^n$ was first confirmed experimentally by van der Post et al. using Nb break junctions [39].
Fig. 8. Zero temperature dc current $I_0$ for a single channel superconducting quantum point contact for values of the transmission ranging from $\tau = 1$ (top) to tunnelling at $\tau \ll 1$ (bottom).

As the transmission is increased the subgap structure becomes progressively more rounded and eventually dissapears for $\tau = 1$. Particularly interesting is the behaviour of the current at low bias voltage when $\tau \to 1$ indicated in Fig. 8. In this region the current exhibits an exponential increase with bias voltage. One can understand this behaviour in terms of the low bias dynamics of the Andreev states [40]. As commented above the zero bias limit is characterized by the presence of Andreev states. Suppose that we have initially the equilibrium situation in which only the lower Andreev state $\epsilon_- (\theta)$ is occupied. When a small bias voltage is applied the state evolves adiabatically according to $\epsilon_- (\omega t)$ as illustrated in Fig. 9. However, close to $\theta = \pi$ the gap between the lower and the upper state gets smaller and a Landau-Zener transition can take place leading to the appearance of a quasiparticle current. The Landau-Zener probability is given by $p = \exp [-\pi \Delta (1 - \tau)/eV]$ and in terms of this probability the mean current is just

$$I_0(V) = \frac{4e\Delta}{\hbar} \exp [-\pi \Delta (1 - \tau)/eV].$$

(3.12)

This simple expression accounts for the behaviour of $I_0$ at low bias and large transmission.
3.2. Comparison to experimental results

The comparison between the theoretical predictions for a single channel SQPC and the experimental results for one atom contacts is particularly instructive. The left top panel of Fig. 10 shows some typical results for Al one-atom contacts together with the set of theoretical curves for $I_0$. As can be observed, the theoretical results for one channel capture the main qualitative behaviour of the experimental IV curves. However, if we compare theoretical and experimental curves having the same normal conductance we see that they look very different. Moreover, we observe that experimental results for contacts with rather similar normal conductance exhibit large differences in their subgap structure.

The reason for this discrepancy, first pointed out in [8] is that i) even for the case of one atom contacts more than a single channel with significant transmission can be contributing to transport and ii) the channel content or PIN code of the three experimental curves can be rather different even when their total conductance is similar. This hypothesis was confirmed by microscopic calculations for Al atomic contacts which predict the contribution of three channels for the one atom geometry [41]. In fact, when the theoretical results for three channels are superposed and their transmissions are varied as fitting parameters one can reach an excellent quantitative agreement with experiments, as shown in the lower panel of Fig.10.
Besides confirming the validity of the microscopic theory of MAR, this fitting procedure provides a powerful tool to determine the set of transmissions $\tau_n$ with high accuracy. Since its introduction in Ref. [8], the technique has been applied to many different materials [9, 42, 43] and to studying different properties of atomic contacts in well controlled conditions [3, 6]. All these studies have confirmed the reliability of the subgap structure analysis. Particularly remarkable are the studies of shot noise in Ref. [6] in which the determination of the PIN code by this technique allowed a direct comparison with the theory without any fitting parameter.

Shot noise is one of the most peculiar features of quantum transport in mesoscopic systems (see the contribution by T. Martin in this volume). It contains information both on the charge of the quasiparticles that are transferred and on their quantum correlations [44]. In the case of superconducting quantum point contacts shot noise studies offer new insight about the MAR mechanism. The
quantity of interest is now the noise spectral density defined as

\[ S(\omega) = \hbar \int dt e^{i\omega t} \left\langle \left[ \delta \hat{I}(t), \delta \hat{I}(0) \right] \right\rangle , \quad (3.13) \]

where \( \delta \hat{I}(t) = \hat{I}(t) - \left\langle \hat{I}(t) \right\rangle \). The noise spectrum can be evaluated using the Keldysh-Nambu Green function techniques discussed above [45, 46]. Although we are not going to discuss this issue in detail let us just point out the more remarkable prediction of the theory, which is the quantization of the effective charge in the tunnel limit. This quantity is defined as \( Q^* = S(0)/2I_0 \). In a normal tunnel junction \( Q^* \) is just the electron charge. However, when the electrodes are superconducting the current in the subgap region is due to MAR processes in which \( n \) quasiparticles are transferred coherently and this is reflected in the fact that \( Q^* \rightarrow ne \), where \( n = [1 + 2\Delta/V] \), when \( \tau \rightarrow 0 \) [45].

The experimental test of these predictions were provided by the work of Cron et al. [6]. Their results for the effective charge are shown in Fig. 11 together with the theoretical calculations. Although these results do not correspond to a very poorly transmitted channel (\( \tau \sim 0.4 \)), one can already observe a tendency to a staircase behaviour as the bias voltage is reduced.
4. Environmental effects

A basic assumption in most theoretical descriptions of transport in atomic-sized conductors is that the nanoscale system can be ideally voltage biased, i.e. it can be connected directly to an ideal voltage source fixing a well defined chemical potential difference between the left and the right leads. The leads are thus assumed to behave as ideal electron reservoirs. An actual experimental situation can certainly deviate from this idealized picture. Our nanoscale device is always embedded in a macroscopic circuit which is determined mainly by the geometry of the metallic leads in the close vicinity of the atomic conductor. The actual situation would be more accurately described as illustrated in Fig. 12 in which the embedding circuit is characterized by a macroscopic impedance $Z(\omega)$. An important ingredient to be taken into account is the effective capacitance $C$ associated with the atomic size conductor itself. Being a nanoscale object this capacitance can be rather small which could result in the appearance of observable charging effects when $e^2/C \gg kT$. In this section we briefly discuss how these environmental effects are manifested in different transport properties.

The theoretical description of these effects requires to analyze the influence on the transport properties of the fluctuations in the phase difference across the atomic conductor induced by the macroscopic impedance. One can distinguish between classical and quantum effects depending on the nature of these fluctuations. Thus, for sufficiently high temperatures, when charging effects are negligible, only thermal fluctuations have to be considered. These fluctuations have
an important effect on the Josephson current, reducing strongly its maximum value from the theoretically predicted result, Eq. (3.8), which explains the almost absence of a supercurrent branch in many experiments. On the other hand, when the charging energy $e^2/C$ is comparable to, or larger than, $kT$ and the series impedance is not negligible compared to $\hbar/e^2$ quantum fluctuations in the phase start to play an important role. This leads a phenomenon called dynamical Coulomb blockade, i.e. a suppression of the current at low bias, which can be observed in normal atomic size conductors when the embedding circuit is designed in order to satisfy the above mentioned conditions.

4.1. Classical phase diffusion

To analyze the influence of thermal fluctuations on the Josephson current in superconducting atomic size contacts one can generalize the so-called resistively and capacitively shunted junction (RCSJ) model, traditionally used in the context of tunnel junctions [47]. The starting point of this approach is to write down a Langevin equation for the phase difference across the contact taking into account the non-sinuosoidal behavior of the current-phase relation at high transmissions. This has been done in Refs. [3] and [48]. In the latter reference the model was generalized to include also the effect a microwave field in order to study the influence of thermal fluctuations on the so-called Shapiro steps.

Within the RCSJ model the parallel combination of the atomic contact with a shunting resistance $R$ and a capacitance $C$ is current polarized by a current source $I_b$. The atomic contact is characterized by its current-phase relation $I(\theta)$. Current conservation then implies

$$I_b = C \frac{dv}{dt} + I(\theta) + \frac{v}{R} + L(t),$$

(4.1)

where $L(t)$ is the Johnson-Nyquist noise produced by dissipation in the resistance. The voltage across the contact and the phase are related by $v = \phi_0 \dot{\theta}$, where $\phi_0 = \hbar/2e$ is the reduced flux quantum. Equation (4.1) is completely analogous to the one describing the motion of a brownian particle in a potential $U(\theta)$, determined by

$$U(\theta) = \phi_0 \theta I_b - \phi_0 \int_0^\theta I(\theta)d\theta.$$

(4.2)

When the capacitance is negligible (overdamped regime) the problem can be translated into the study of the distribution function $\sigma(\theta,t)$ for the phase across the contact, which satisfies a Smoluchowski equation [49]

$$\frac{d\sigma}{dt} = \frac{R}{\phi_0^2} \frac{\partial}{\partial \theta} \left[ - \frac{\partial U}{\partial \theta} + T \frac{\partial \sigma}{\partial \theta} \right].$$

(4.3)
This equation can be written as \( \frac{d\sigma}{dt} + \frac{\partial w}{\partial \theta} = 0 \), where \( w = \frac{R}{\phi_0} \left[ -\frac{\partial U}{\partial \theta} + T \frac{\partial \sigma}{\partial \theta} \right] \).

This quantity can thus be interpreted as a probability current which must be related to \( \sigma \) by \( w = \sigma v/\phi_0 \). From this relation one can obtain the mean voltage \( \langle v \rangle \) across the contact as a function of the biasing current \( I_b \).

Extracting the current-voltage characteristic from the Smoluchowski equation is particularly simple for the case of a constant dc bias. In this case the stationary solution \( \sigma(\theta) \) does not depend on time and \( w \) is just a constant. The equation can then be easily integrated yielding

\[
\sigma(\theta) = \frac{w\phi_0^2}{TR} \left[ f(\theta) \left( \frac{2\pi}{f(\theta) - f(0)} \right) + f(0) \int_0^\theta \frac{d\theta}{f(\theta)} \right], \tag{4.4}
\]

where \( f(\theta) = \exp \left[ -\frac{U(\theta)}{T} \right] \). The normalization condition \( \int_0^{2\pi} d\theta \sigma(\theta) = 1 \) then determines \( w \) and hence \( \langle v \rangle \).

The supercurrent branch in superconducting atomic-sized contacts was analyzed experimentally in Ref. [3] using Al microfabricated break junctions. In order to have good control of the thermal and quantum fluctuations they designed an on-chip dissipative environment with small resistors of known value placed close to the atomic contact, as illustrated in Fig. 13. With the appropriate choice of the environment parameters the current-voltage curve becomes hysteretic, which allows measuring the supercurrent and the quasi-particle branch for the same contact. The advantage is that this permits the determination of the
A typical current-voltage characteristic for this set up is depicted in Fig. 14. The inset in this figure shows a blow up of the supercurrent branch together with the result obtained from the Smoluchowski equation for the corresponding set of parameters. As can be observed the threshold or *switching* current, $I_S$, at which the jump from the supercurrent branch to the quasiparticle current branch takes place lies very close to the maximum in the current-voltage characteristic predicted by the RCSJ model. This value is very sensitive to thermal fluctuations and decreases with increasing temperatures as illustrated by the results shown in Fig. 15. The experimental results for $I_S$ for different sets $\{\tau_n\}$ are in excellent agreement with the theoretical values except for contacts having an almost perfectly transmitted channel (with transmissions between 0.95 and 1.0). In this case it is found that the switching current is less sensitive to thermal fluctuations than predicted by the theoretical model. This discrepancy was attributed in Ref. [3] to the contribution due to Landau Zener transitions between Andreev states, not included in the above description. The development of a unified theory including classical phase diffusion and transitions between Andreev states constitutes one of the open problems in the theory of superconducting quantum point contacts.
Fig. 15. Experimental (open symbols) and theoretical (lines) results for the switching current obtained in Ref. [3]. The results correspond to one atom contacts with different channel content. 

\[ \{ \tau_i \} = \{ 0.21, 0.07, 0.07 \}. \] From the fit a zero-temperature supercurrent of \( I_0 = 8.0 \pm 0.1 \text{ nA} \) is obtained. 

\[ \{ \tau_i \} = \{ 0.52, 0.26, 0.26 \}, \] \( I_0 = 25.3 \pm 0.4 \text{ nA} \). \( \{ \tau_i \} = \{ 0.925, 0.02, 0.02 \} \), 

\( I_0 = 33.4 \pm 0.4 \text{ nA} \). \( \{ \tau_i \} = \{ 0.95, 0.09, 0.09, 0.09 \} \), \( I_0 = 38.8 \pm 0.2 \text{ nA} \). (open squares) \( \{ \tau_i \} = \{ 0.998, 0.09, 0.09, 0.09 \} \), \( I_0 = 44.2 \pm 0.9 \text{ nA} \). The full lines are the predictions of the Smoluchowski equation (4.3) while the dotted lines are the results of a numerical simulation of the circuit equation (4.1) allowing for Landau-Zener transitions between Andreev states. From [3].

4.2. Dynamical Coulomb blockade

Dynamical Coulomb blockade (DCB) in ultra-small tunnel junctions was extensively analyzed in the early 90’s. The basic theory for describing this effect in tunnel junctions is called \( P(E) \)-theory. Within this theory the electromagnetic environment of the junction is described as a set of \( LC \) circuits in the spirit of Caldeira-Legget model for quantum dissipation [50]. One can in principle describe any impedance \( Z(\omega) \) as a continuous distribution of harmonic oscillators which are coupled to the tunnelling electrons. The tunnelling then becomes an inelastic process: the electron can only tunnel if it can excite a mode in the environment. This necessarily reduces the current because there is a reduction in the phase space available for the final electron states. The name of the theory is due to the fact that the current is determined by a certain function \( P(E) \) giving the probability of exciting a mode of energy \( E \).

\( P(E) \)-theory is somewhat equivalent to the Fermi golden rule, i.e. lowest order perturbation theory in the coupling between the leads. This theory is clearly
insufficient for describing the case of an atomic contact of arbitrary transmission. DCB in a normal QPC coupled to a macroscopic impedance was analyzed in Refs. [51, 52]. In Ref. [52] it was shown that there is a close connection between DCB and shot noise in these type of systems. The starting point of their theoretical analysis is again the simple model Hamiltonian of Sect. 3.1 which is modified to include the coupling to the environment. This is done by introducing an additional phase factor $\hat{\Lambda}_e = \exp[i\hat{\theta}]$ in the hopping term, where $\hat{\theta}$ is the phase operator which is a conjugate variable of the charge $\hat{Q}$ between the leads, i.e. $[\hat{\theta}, \hat{Q}] = i\epsilon$. The phase factor $\hat{\Lambda}_e$ then acts as a translation operator which shifts the charge between the leads by one each time an electron tunnels. The modified hopping term then reads

$$H_T = \sum_\sigma v c_L^\dagger \sigma c_R^\sigma \hat{\Lambda}_e + \text{h.c.}$$

The information characterizing the electromagnetic environment is contained in the phase correlation function $J(t) = \langle \hat{\theta}(t)\hat{\theta}(0) \rangle - \langle \hat{\theta}^2 \rangle$, which is related to the total impedance $Z_t(\omega)$ by $J(t) = G_0 \int d\omega \text{Re}Z_t(\omega)(e^{i\omega t} - 1)/\omega$ [53]. Here the total impedance is the parallel combination of $Z(\omega)$ and the contact capacitance, i.e. $Z_t(\omega) = (Z(\omega)^{-1} + i\omega C)^{-1}$.

In Ref [52] the blockade in the current within this model was calculated using Keldysh formalism. However, in the limit of weak coupling with the environment (i.e. $Z \ll \hbar/e^2$) the relation between DCB and noise can be obtained by more conventional methods [54]. To lowest order in $J(t)$ the current blockade is given

$$\langle \delta I \rangle = -\frac{1}{2e^2} \int d\omega J(\omega) \int d\omega' \text{sign}(\omega - \omega') \frac{\partial S_I}{\partial V}(\omega', V), \quad (4.5)$$

where $S_I(\omega, V)$ denotes the current noise spectrum of the QPC.

For a QPC at low frequencies and zero temperature $S_I = 2eG_0 \sum_n \tau_n (1 - \tau_n)(eV - \hbar\omega)\theta(eV - \hbar\omega)$ (see the chapter on noise by T. Martin in this volume) and Eq. (4.5) yields

$$\frac{\delta G}{G} = -G_0 \frac{\sum_n \tau_n (1 - \tau_n)}{\sum_n \tau_n} \int_{eV}^{\infty} d\omega \frac{\text{Re}Z_t(\omega)}{\omega}. \quad (4.6)$$

It should be noted that the correction to the conductance is affected by the same reduction factor that applies for shot noise. In the simple but realistic case for which the impedance is composed by the resistance $R$ of the leads embedding the contact in parallel with the capacitance $C$ of the contact itself, the blockade in the conductance reduces to

$$\frac{\delta G}{G} = -G_0 R \frac{\sum_n \tau_n (1 - \tau_n)}{\sum_n \tau_n} \ln \sqrt{1 + \left(\frac{\hbar\omega R}{eV}\right)^2}, \quad (4.7)$$
where $\omega_R = 1/RC$. At finite temperature the logarithmic singularity in Eq. (4.7) at $V = 0$ becomes progressively rounded. The finite temperature expression of this equation can be found in Ref. [4].

In order to verify these predictions Cron et al. [4] fabricated an atomic contact embedded in an electromagnetic environment essentially equivalent to a pure ohmic resistor of the order of $1 \text{k}\Omega$ defined by e-beam lithography. The material chosen for both the atomic contact and the series resistor was Al, which allowed to extract the channel decomposition or mesoscopic PIN code for the contacts, using the subgap structure analysis in the superconducting state. The environmental Coulomb blockade was then measured in the presence of a 0.2 T magnetic field which brings the sample to the normal state. The results for two contacts with very different transmissions are shown in Fig. 16. The standard $P(E)$-theory is able to account for the results obtained for the contact in the left panel, which has a single weakly transmitted channel. On the other hand, for the contact in the right panel, with a well transmitted channel ($\tau \simeq 0.83$) the ampli-

![Fig. 16. Measured differential conductance curves of two atomic contacts (symbols referred to the left axes, $G_0$ being the conductance quantum), and comparison with the predictions for the dynamic Coulomb blockade (lines, right axes, relative reduction of the conductance). Dashed lines are the predictions for the tunnel case [53] and the full line is the prediction of the theory in [4], (Eq. (4.6)), summing the contributions of the two channels of the contact. The wiggles and asymmetry appearing on the experimental curves are reproducible conductance fluctuations due to interference effects depending on the detailed arrangement of the atoms in the vicinity of the contact. On the left panel, the contact consists of a single weakly transmitting channel, and it is well described by the standard theory of DCB valid for tunnel contacts, as expected. On the right panel, the contact has a well transmitting channel with $\tau = 0.835$. In this case, the relative reduction of conductance is much smaller than for the tunnel case and is in agreement with the predictions of Eq. (4.6).]
tude of the dip at zero bias is markedly reduced with respect to the tunnel limit predictions (dashed line). The experimental results are in good agreement with the predictions of Eq. (4.6) (solid line).

5. Single-molecule junctions

More recently the focus of attention in the field of transport at the atomic scale is moving towards conducting bridges of individual molecules. As early as 1974 Aviram and Ratner [55] proposed that a molecule with donor and acceptor groups separated by a poorly conducting spacer group might act as a diode when connected between metallic electrodes. This and other ideas led to the concept of molecular electronics: the prospect of building electronics out of organic molecular components, that would ideally self-assemble into large integrated circuits. However, the first step would be to contact a single molecule, or at least a single monolayer. Although several initial attempts towards this goal seemed promising it has turned out to be difficult to obtain stable and reproducible results. For self-assembled monolayers of molecules many experimental results have been influenced by defects in the monolayers. Therefore, many attempts more recently focus on contacting single molecules only and some encouraging progress is now being made. For a more complete recent review, see Ref. [56], and the chapter by Dan Ralph in this volume.

Several experimental techniques have been developed that allow measuring single molecules. One approach is using scanning tunnelling microscopes, or conducting-tip atomic force microscopes to find and contact a desired molecule. In order to avoid contacting many molecules in parallel the target molecules are often embedded at defect positions into a monolayer matrix of less conducting alkanethiol molecules [57, 58]. As metal contacts almost exclusively gold has been used, in view of its low-reactive surfaces making it relatively easy to avoid reactions with other molecules. Strong bonds to organic molecules can nevertheless be made through the use of sulfur end-groups (often referred to as the alligator clips). Although a relatively stable junction of the molecules to a gold sample surface can be ensured by allowing a solution of the compounds to react over a period of many hours, the top contact is usually a weak-coupling tunnel junction to the STM or AFM tip. By using thiol alligator clips at both ends and binding a gold cluster to the top of the molecules Lindsay’s group has achieved important progress in reproducibility of the measured conductance [59,60]. Nevertheless, the conductance varies as a result of variations in the metal-molecule bonding. A particularly attractive method for obtaining ensemble averaged values for the conductance of a metal-molecule-metal junction was introduced by Tao and his group [61]. They repeatedly make and break contacts between a gold
sample surface and a gold tip by forcing the STM tip into and out of contact. This is done at room temperature with tip and sample immersed in a solution of the molecules of interest, that have been prepared with the proper thiol end groups. One observes frequently occurring plateaus in the conductance traces recorded during breaking, that were shown to be associated with the molecules. The mean conductance for a molecular bridge configuration can then be obtained from the position of a peak in the histogram of conductance values.

Standard microfabrication approaches are not capable of reproducibly making electrode separations small enough that they can be bridged by a single molecule. Several solutions have been demonstrated that combine microfabrication with other tricks. One method uses electromigration of a microfabricated gold wire on a substrate [62–64]. Prior to the experiment the wire is allowed to interact with the thiol-ended molecules in solution, after which the wire is broken by controllably sending a large current through it. The combination of Joule heating and electron wind force breaks the wire, and it was found that the resulting junction is often bridged by one, or several, of the target molecules. The advantage of this approach is the additional experimental control parameter provided by the gate electrode that can be defined along with the wire. This method has recently been further improved by adding mechanical control over the electrode separation after breaking [65]. The experimental results are discussed in more detail in the chapter by Dan Ralph. Other microfabrication approaches include the low-temperature shadow-evaporation technique introduced by Kubatkin et al. [66] and a combination with electrochemical etching/deposition as described by Kervennic et al. [67, 68].

A significant fraction of the experimental work on single molecule transport was inspired by the paper by Reed et al. [71]. The experiment was performed using a mechanically controllable break junction device [1] working at room temperature, with the junction immersed in a solution of the organic compound of interest. The compound they selected was benzene-1,4-dithiol that has become the workhorse in this field of science. In the experiment the broken gold wire was allowed to interact with molecules for a number of hours so that a self-assembled monolayer covered the surface. Next, the junction was closed and re-opened a number of times and current-voltage (IV) curves were recorded at the position just before contact was lost completely. The IV curves showed some degree of reproducibility with a fairly large energy gap feature of about 2 eV, that was attributed to a metal-molecule-metal junction. The zero-bias conductance was of order $10^9 \Omega$ which is one or two orders of magnitude larger than typically found in model calculations for a benzenedithiol bridging two metal electrodes [72].

Further experiments along these lines have been performed on larger organic molecules in the groups of Bourgoin [73] and Weber [69, 70]. In particular, the latter showed that the symmetry of the molecules is reflected in the symmetry
Fig. 17. Current voltage characteristics, reproducibly recorded for a stable junction in a mechanically controlled break junction (lower) and their numerical derivative $dI/dU$ (upper curve). a) with molecule 1 a spatially symmetric (9,10-Bis((2’-para-mercaptophenyl)-ethinyl)-anthracene) at room temperature, b) with molecule 2 an asymmetric molecule (1,4-Bis((2’-para-mercaptophenyl)-ethinyl)-2-acetyl-amino-5-nitro-benzene) at room temperature, and c) with molecule 2 at $T = 30$ K. From Refs. [69, 70].

of the IV curves, see Fig. 17. Dulić et al. [74] used a photochromic molecule that can be switched from a high-conductance state to a low-conductance state under the influence of visible light and back under near-UV irradiation. The two states had been investigated before in detail in solution. Dulić et al. used a lithographically fabricated break junction device to contact individual molecules of this kind, modified to have thiol-anchoring groups. They observed switching of the conductance of a molecule from the high-conductance state to the low-conductance state, but the reverse step was not obtained. They present evidence that the reverse step is suppressed as a result of the interaction of the UV light with surface plasmons in the gold electrodes.

The early experiments aimed at probing the electronic transport properties of individual organic molecules have shown that it is difficult to identify the number of molecules actually contacted and that the characteristics observed vary widely between experiments. Under such conditions it is not surprising that there is also very little agreement with calculations. This situation forms a strong motivation to study simple systems, that by themselves will not be useful as molecular de-
Fig. 18. Conductance curves and histograms for clean Pt and Pt in a H$_2$ atmosphere. The curves for Pt in the inset and the histogram in the main panel were measured at a bias of 10 mV. The curve for Pt with H$_2$ in the inset was measured at 100 mV, and the histogram was obtained at 140 mV. All data were taken at 4.2 K under cryogenic vacuum. From Ref. [75].

vices, but that may provide a more viable test system to identify the problems in experiment and theory. The simplest molecule is dihydrogen, which has been shown can be contacted between platinum electrodes [75]. The discussion of the hydrogen experiments will occupy most of the remainder of this section.

Smit et al. [75] obtained molecular junctions of a hydrogen molecule between platinum leads using the mechanically controllable break junction technique. The inset to Fig. 18 shows a conductance curve for clean Pt (black) at 4.2 K, before admitting H$_2$ gas into the system. About 10,000 similar curves were used to build the conductance histogram shown in the main panel (black, normalized by the area). After introducing hydrogen gas the conductance curves were observed to change qualitatively as illustrated by the gray curve in the inset. The dramatic change is most clearly brought out by the conductance histogram (gray, hatched). Clean Pt contacts show a typical conductance of $1.5 \pm 0.2 G_0$ for a single-atom contact, as can be inferred from the position and width of the first peak in the Pt conductance histogram. Below $1 G_0$ very few data points are recorded, since Pt contacts tend to show an abrupt jump from the one-atom contact value into the tunnelling regime towards tunnel conductance values well below $0.1 G_0$. In contrast, after admitting hydrogen gas a lot of structure is found in the entire range below $1.5 G_0$, including a pronounced peak in the histogram near $1 G_0$. The research to date on this system has been focussed on the molecular arrangement responsible for this sharp peak. Clearly, many other junction configurations can be at the origin of the large density of data points a lower conductance, but they have not yet been studied in detail.

The interpretation of the peak at $1 G_0$ was obtained from combination of
measurements, including vibration spectroscopy and the analysis of conductance fluctuations, and Density Functional Theory (DFT) calculations. Experimentally, the vibration modes of the molecular structure were investigated by exploiting the principle of point contact spectroscopy for contacts adjusted to sit on a plateau in the conductance near 1 \( G_0 \). The principle of point contact spectroscopy is similar to inelastic tunnelling spectroscopy (IETS), but differs somewhat in a few important details. As for IETS, the differential conductance is measured using a small modulation superimposed on a dc bias that is slowly swept over a wide voltage range. When the bias increases from zero and crosses a voltage corresponding to the energy of a vibration mode in the contact, \( eV = \hbar \omega \), a new channel for electron scattering opens. For an ideal one-channel contact the only option is backscattering since all forward propagating states are occupied. Thus, in contrast to IETS, to first approximation scattering by vibration modes leads to a drop in the conductance.

Figure 19 shows examples for Pt-H\(_2\) and Pt-D\(_2\) junctions at a plateau near 1 \( G_0 \). The conductance is seen to drop by about 1 or 2\%, symmetrically at positive and negative bias, as expected for electron-phonon scattering. The energies are in the range 50–60 meV, well above the Debye energy of \( \sim 20 \) meV for Pt metal. A high energy for a vibration mode implies that a light element is involved, since the frequency is given by \( \omega = \sqrt{\kappa/M} \) with \( \kappa \) an effective spring constant and \( M \) the mass of the vibrating object. The proof that the spectral features are indeed associated with hydrogen vibration modes comes from further
Fig. 20. Distribution of vibration mode energies observed for H$_2$, HD, and D$_2$ between Pt electrodes, with a bin size of 2 meV. The peaks in the distribution for H$_2$ are marked by arrows and their widths by error margins. These positions and widths were scaled by the expected isotope shifts, $\sqrt{2/3}$ for HD and $\sqrt{1/2}$ for D$_2$, from which the arrows and margins in the upper two panels have been obtained. From Ref. [76].

experiments where H$_2$ was substituted by the heavier isotopes D$_2$ and HD. The positions of the peaks in the spectra of $d^2I/dV^2$ vary within some range between measurements on different junctions, which can be attributed to variations in the atomic geometry of the leads to which the molecules bind. Figure 20 shows histograms for the vibration modes observed in a large number of spectra for each of the three isotopes.

Two pronounced peaks are observed in each of the distributions, that scale approximately as the square root of the mass of the molecules, as expected. The two modes can often be observed together, as in the inset to Fig. 19. For D$_2$ an additional mode appears near 90 meV. This mode cannot easily be observed for the other two isotopes, since the lighter HD and H$_2$ mass shifts the mode above 100 meV where the junctions become very unstable. For a given junction with spectra as in Fig. 19 it is often possible to stretch the contact and follow the evolution of the vibration modes. The frequencies for the two lower modes were seen to increase with stretching, while the high mode for D$_2$ is seen to shift downward.
This unambiguously identifies the lower two modes as transverse modes and the higher one as a longitudinal mode for the molecule. This interpretation agrees nearly quantitatively with DFT calculations for a configuration of a Pt-H-H-Pt bridge in between Pt pyramidally shaped leads [76, 77]. The conductance obtained in the DFT calculations [75–77] also reproduces the value of nearly 1 \( G_0 \) for this configuration. The number of conduction channels found in the calculations is one, which agrees with the analysis of conductance fluctuations in the experiment of Refs. [75, 78]. The fact that the conductance is carried by a single channel demonstrates that there is indeed just a single molecule involved.

Several other DFT calculations have been performed, see e.g. Refs. [79, 80], where the agreement is only partial. Although Cuevas et al. [80] find a similar high value for the conductance, the molecular orbitals responsible for the transport are the bonding orbitals, while Refs. [75–77] attribute the transport almost entirely to the antibonding orbitals. This difference implies that the sign of the charge transfer between the molecule and the metal leads differs between the two groups of calculations. Using a slightly different approach Garcia et al. [79] agree with Cuevas et al. on the bonding orbitals as the transport channel, but they obtain a conductance well below 1 \( G_0 \). They propose an alternative atomic arrangement to explain the high conductance for the Pt-H bridge, consisting of a Pt-Pt-bridge with two H atoms bonded to the sides. However, this configuration gives rise to three conductance channels, which is excluded based on the analysis of the conductance fluctuations as discussed above. The rather strong disagreement between various approaches in DFT calculations for this simple molecule show that there is a need for a reliable set of experimental data against which the various methods can be tested. The hydrogen metal-molecule-metal bridge may provide a good starting point since it is the simplest and it can be compared in detail by virtue of the many parameters that have been obtained experimentally.

Conductance histograms recorded using Fe, Co or Ni electrodes in the presence of hydrogen also show a pronounced peak near 1 \( G_0 \) [81], indicating that many transition metals may form similar single-molecule junctions. Also Pd seemed a good candidate, but Csonka et al. [78] did not observe the same suppression of conductance fluctuations as for Pt. There is an additional peak at 0.5 \( G_0 \) in the conductance histogram, and it was argued that hydrogen is incorporated into the bulk of the Pd metal electrodes.

Going beyond the simplest molecule using similar techniques much work is still in progress. Preliminary results have been obtained for CO and for \( \text{C}_2\text{H}_2 \) between Pt electrodes [81, 82].
6. Concluding remarks

In this chapter we have presented an overview of some aspects of electron transport in atomic and molecular contacts. In the case of atomic contacts our fabrication capabilities and theoretical understanding are reaching a level of sophistication which has allowed accurate quantitative agreement between theory and experimental results for several properties. A key ingredient in this analysis is the concept of the mesoscopic PIN code, i.e. the set of transmission eigenvalues which determine all transport properties within the Landauer-Büttiker picture. The results for atomic contacts are consistent with the idea of this set being determined by the valence orbital structure of each element [9].

Superconducting transport has played a central role in these studies, providing a powerful tool to determine the PIN code by the subgap structure analysis. Conversely, atomic contacts have revealed as an almost ideal system to verify the predictions of the microscopic theory of superconducting transport in the coherent MAR regime, which has been developed in the last decade.

As discussed in Sect. 4 some of the observable properties are fundamentally determined by the electromagnetic environment of the nano-junction. The combination of break junctions with lithographic techniques, such as pioneered in Refs. [3, 4], is opening the possibility to study some fundamental rules for circuits at the nanometer scale under well controlled conditions. In spite of this recent progress the influence of environmental effects on the transport properties of atomic size conductors is an issue which still deserves further analysis, specially regarding the superconducting state.

We have also discussed in some detail the question of the length dependence of the conductance through a chain of atoms. Atomic chains constitute an intermediate step between atomic-sized contacts and molecular junctions, and it is rather natural to ask whether the simple one-electron concepts which proved useful to analyze the former are also valid for the latter. The results that we have presented for the conductance oscillations as a function of the number of atoms in the chain seem to indicate that the connection between conduction channels and valence orbital structure remains valid. In the case of the chains the oscillations appear to be associated with the band structure around the Fermi energy of an infinite chain.

Finally we have summarized some developments towards the study of transport across single molecules. Although the level of sophistication in this research is still behind that of the metallic single-atom contacts significant progress has been made. We believe that it is worthwhile to start from simple model molecules and gradually work our way up to the more complicated ones. From the simple molecules we can learn how to analyze the problem and control the level of agreement with model calculations. The simple molecules are also simple in the
sense that they are describable completely in a one-electron picture. Electron-electron interaction effects will gradually show up as we move towards more extended organic molecules, and the models will need to be extended to include these effects. There are many open questions regarding the proper description of non-equilibrium currents, on-site repulsion effects and strong electron-phonon coupling effects. There is already a significant number of theoretical works addressing these issues, but there are not too many experiments that they can be compared with. This poses an immediate challenge to the community of experimental physicists.

We thank our coworkers N. Agraït, J.C. Cuevas, R. Cron, M.H. Devoret, D. Djukic, F. Flores, M. Goffman, M.H. van Hemert, K.W. Jacobsen, P. Joyez, N. Lang, A. Martín-Rodero, Y. Noat, A. Saül, E. Scheer, R.H.M. Smit, K. Thygesen, C. Untiedt, C. Urbina, E. Vecino and L. de la Vega for their contributions to the various works on atomic and molecular contacts which have been discussed in this paper. This work is part of the research program of the "Stichting FOM", and was partially supported by the EU through the DIENOW training network.

References


Transport at the atomic scale: Atomic and molecular contacts


