Single-atom contacts with a scanning tunnelling microscope

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Abstract. The tip of a cryogenic scanning tunnelling microscope is used to controllably contact single atoms adsorbed on metal surfaces. The transition between tunnelling and contact is gradual for silver, while contact to adsorbed gold atoms is abrupt. The single-atom junctions are stable and enable spectroscopic measurements of, e.g., the Abrikosov–Suhl resonance of single Kondo impurities.

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1. Introduction

Facing the ongoing miniaturization of electronic devices, an important issue to be addressed is electron transport through junctions at the atomic scale. A pioneering experiment was performed by measuring the electron flow of an almost two-dimensional electron gas through a constriction

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of a semiconductor heterostructure whose width was continuously varied [1, 2]. Intriguingly, the electrical conductance, \( G = I/V \) (\( I \): current, \( V \): voltage), did not evolve as a continuous function of the constriction width as would be expected from Ohm’s law for macroscopic conductors. Rather, a staircase of conductance values at integer multiples of \( G_0 = 2e^2/h \) (\( e \): electron charge, \( h \): Planck’s constant) was observed and interpreted in terms of conductance quantization in units of \( G_0 \), which is referred to as the quantum of conductance. Quantized conductance of narrow constrictions may be understood in the light of figure 1. A constriction of length \( L \) and width \( W \) gives rise to transverse electron eigenstates, which result from electron scattering at the constriction boundary. Prerequisites for this picture to hold are: (a) the Fermi wavelength, \( \lambda_F \), being of the order of \( W \) and (b) the electron mean free path, \( \ell \), being much larger than \( L \). The transverse antinodes may be identified as transport channels, each of which may contribute to the total conductance of the constriction by up to \( G_0 \). Each time the width of the constriction is increased by \( \lambda_F/2 \), a conduction channel is added and increases the junction conductance by \( G_0 \).

A reduction of the maximum single-channel conductance may occur if electrodes are used to contact the nanoscale conductor. Scattering arises from the extent of matching between electron wavefunctions at the interface between the macroscopic electrodes and the contacted object and let the transmission probability of a conduction channel deviate from 1. For vanishing temperature, the conductance of a so-called quantum point contact may be written as \( G = G_0 \sum_{i,j} |\tau_{i,j}|^2 \), where \( |\tau_{i,j}|^2 \) denotes the transmission probability of an electron incident on contact mode \( i \) and transmitted into mode \( j \) [3]. Using the concept of transport eigenchannels [4], which are a set of non-intermixing transport channels, the total conductance reads \( G = G_0 \sum_i T_i \), where \( T_i \) is the transmission probability of the \( i \)th eigenchannel.

Since the Fermi wavelength for metals, owing to an increased electron density, is usually much smaller than for semiconductors, the width of metallic constrictions must be smaller to observe quantized conductance. Such junctions have been fabricated using a scanning tunnelling microscope [5]–[10] and the mechanically controlled break junction [11, 12]. Gimzewski and Möller [5] reported an experiment in which they moved an iridium tip into contact with a thick...
silver layer adsorbed on Si(111). Simultaneously with this approach, the tunnelling current was recorded, which at a certain tip displacement exhibited a discontinuous change. This change was interpreted as the transition from tunnelling to contact. Similar experiments were performed by monitoring the current during forming and breaking of the contact by tip displacement [6, 7, 9, 10] or by material transfer due to voltage pulses [8]. Combination of atomic force and scanning tunnelling microscopy (STM), as first performed by Dürrig et al [6, 13], led to the picture of conductance through atomic-sized conductors that we have today: integer values of $G_0$ indicate quantized conductance due to laterally confined quantum modes in the conductor while a jump between the different values is caused by abrupt atomic rearrangements [14, 15].

A step forward to more control of the contact has been achieved by combining the imaging capability of STM with the acquisition of current-displacement traces. Along these lines single atoms [16]–[23] and single molecules [24]–[35] were contacted with the tip of the microscope. The advantages of these controlled contacts are obvious. Prior to and after contact the atom or the molecule may be imaged, which allows a characterization of the atomic environment of the contact regime and, to some extent, of the tip structure. This information is valuable for model calculations. Another advantage is the deliberate choice of electrode material, since tip, substrate and contacted object may be combined as desired. We note that upon contact currents of the order of 1–10 µA flow through the atom or the molecule. Similarly high currents have been used to study the influence of the electric field between tip and surface on the energy of Shockley-type surface states [36, 37].

This paper is organized as follows. In section 2, the experimental setup, which is necessary to perform contact measurements with a scanning tunnelling microscope, is introduced. Section 3 compares single-atom contacts on noble metal surfaces (section 3.1) and provides an example for contact spectroscopy of the differential conductance (section 3.2).

2. Experiment

Measurements presented in this paper were performed using a custom-made scanning tunnelling microscope operated at 7 K and in ultra-high vacuum with a base pressure of $10^{-9}$ Pa. Sample surfaces and chemically etched W tips were cleaned by argon ion bombardment and annealing. In vacuo, W tips were gently indented into the substrate until single adsorbed atoms (adatoms) appeared with nearly circular shape in constant-current STM images. As a consequence of this tip preparation we expect the tip apex to be covered with substrate material. Single atoms originating from substrate material were deposited onto the surface by controlled tip–surface contacts as reported in [18]. Deposition of cobalt atoms was performed using an electron beam evaporator and an evaporant of 99.99% purity. Conductance curves were acquired in such a way as to cover tunnelling to contact regimes. To this end, the tip was displaced by 5–6 Å towards the surface and simultaneously the current ranging from the order of 1 nA to the order of 10 µA was recorded. Zero displacement is defined for a given pair of current and voltage at which the feedback loop is opened prior to conductance measurement. The differential conductance ($dI/dV$) was measured by superimposing a sinusoidal voltage onto the sample voltage (root-mean-square amplitude between 1 and 5 mV, frequency of 10 kHz) and by detecting the current response with a lock-in amplifier. The junction current is converted to a voltage by a variable gain transimpedance amplifier. Different gains of the amplifier had to be set to measure the current that varied over four orders of magnitude. The input impedance of the amplifier is 50 Ω at the gain setting, which is relevant for the single-atom contacts. Further, cables that
Figure 2. (a) Conductance curve acquired on a single Ag atom adsorbed on Ag(111). Zero displacement corresponds to a tip–atom distance defined by feedback loop parameters of 0.1 V and 1 μA. Negative displacements denote tip approach towards the adatom. Regimes denoted 1, 2 and 3 are referred to as tunnelling, transition and contact regimes. Displacements $z_t$ and $z_c$ denote the onsets of transition and contact regimes, respectively, with respective conductances $G_t$ and $G_c$. (b) Conductance curve acquired on a single Au adatom on Au(111). Zero displacement corresponds to feedback loop parameters of 0.1 V and 100 nA.

carry tunnelling voltage and current exhibit a resistance of 200 $\Omega$. Consequently, in single-atom contacts with a quantized resistance of $R_0 = G_0^{-1} \approx 12.9$ k$\Omega$, the voltage drop at peripheral resistances is less than 2% of the voltage applied to the junction. Therefore, the associated error, which occurs by calculating the contact conductance via $G = I/V$, is smaller than the precision of the method by which this value is determined from conductance curves (see section 3.1). To further rule out possible systematic errors in presented conductance curves we ensured that (i) the relative gain error of the transimpedance amplifier is less than 1% for each applied gain and (ii) the integral nonlinearity for each gain is less than 0.01%.

3. Results and discussion

3.1. Single-atom contacts on noble metal surfaces

In this paragraph, conductance traces acquired on single adsorbed Ag atoms on Ag(111) (figure 2(a)) and on Au atoms on Au(111) (figure 2(b)) are compared. A single but representative conductance curve of Ag(111)-Ag is used to describe the general evolution of the conductance upon decreasing the tip–atom distance (indicated by decreasing negative tip displacements). In the regime denoted 1, an exponential variation of the conductance with the tip displacement is observed, which is characteristic for the tunnelling regime. Starting from a displacement $z_t$ with related conductance $G_t$, the slope of the conductance curve increases until at $z_c$ the
slope decreases below the value observed in the tunnelling regime. The conductance regime between $z_t$ and $z_c$ is referred to as the transition regime, while the regime with displacements below $z_c$ is referred to as the contact regime. Figure 2(a) shows the definition of the specific displacements ($z_t, z_c$) and conductances ($G_t, G_c$), which is based on the extrapolation of linear fits to the conductance traces in the different regimes. The intersections of these straight lines define ($z_t, G_t$) and ($z_c, G_c$). Comparing the conductance traces taken on adatoms on Ag(111) and Au(111) some remarkable differences are obvious, which concern the transition and contact regimes.

The transition from tunnelling to contact occurs rather gradually for Ag adatoms on Ag(111). In a displacement interval of $\Delta z = z_c - z_t \approx 0.3 \text{ Å}$ the conductance rises from $\approx 0.30 G_0$ to $\approx 0.90 G_0$, giving rise to an average slope of the conductance curve in the transition regime of $\approx 1.9 G_0 \text{ Å}^{-1}$. In contrast, the transition from tunnelling to contact for Au adatoms on Au(111) is abrupt from $G_t \approx 0.13 G_0$ to $G_c \approx 0.98 G_0$. Moreover, the slopes of the conductance curves in the contact regimes are markedly different. While for Ag(111)-Ag the conductance increases with tip–adatom approach by $\approx 0.7 G_0 \text{ Å}^{-1}$, the conductance remains almost constant for Au(111)-Au.

At present, model calculations, which explain the observed differences are not available. We therefore suggest possible reasons and hope to spark theoretical investigations. On flat surfaces (Ag(111) and Cu(111)) discontinuous jumps from the tunnelling to the contact regime were reported, while forming contact to adatoms (Ag on Ag(111) and Cu on Cu(111)) was characterized by a continuous transition between these regimes [18]. Using density functional methods it was argued [18] that in case of the tip–adatom contact the tip–adatom interaction does not surmount the value, which is required for a tip fracture. This may be understood in terms of the tip apex atom being farther away from the surface at the tip–adatom contact than at the tip–surface contact. Moreover, elastic constants of the adatom were shown [18] to be almost twice as large as those found for the flat surfaces. This increase of the adatom bonding was traced to the creation of a surface dipole due to the Smoluchowski effect. Consequently, even when the tip apex atom is very close to the adatom relaxations are small compared to the tip–surface contact. Adhering to this picture of a tip–adatom contact and assuming that the surface dipole for an Au adatom on Au(111) is similar to the dipole of Ag on Ag(111) and Cu on Cu(111) we arrive at the following scenario of tip–adatom contact on Au(111). Upon approaching the tip towards the Au adatom the adhesive forces between tip and adatom induce a jump of the tip apex atom to the adatom. According to figure 2(b) the jump to contact to the Au adatom occurs already at a conductance of $\approx 0.13 G_0$, which is less than half of the corresponding conductance for contact to the Ag adatom ($\approx 0.30 G_0$). Consequently, the contact to the Au adatom is formed at a larger tip–adatom distance, which signals a rather high separation between the adatom and the tip apex atom. This observation is in agreement with the findings reported by Ohnishi et al [38] who imaged a single Au atom chain bridging an Au tip and an Au substrate with a transmission electron microscope. They found that Au atoms in the chain exhibit a mutual distance which may exceed the Au lattice constant by as much as 40%. A jump to contact between two gold electrodes, which were presumably terminated by a single Au atom, has also been reported using other techniques [14, 39, 40].

The second marked difference, which concerns the slope of the conductance curve in the contact regime, is closely related to the relatively large separation of Au atoms in contact. Approaching the tip further towards the Au adatom implies a reduction of the intrachain distances. Before reaching an intrachain distance, which is similar to the Au lattice constant, the
contact conductance stays nearly constant. The plateau-like contact conductance for Au is in agreement with previous experiments performed by the mechanically controlled break junction technique [41]. Cuevas et al [41] suggested the following microscopic origin for the observed behaviour of the conductance in contact. The local density of states of the Au atom bridging the electrodes exhibits a sp$_z$ resonance at the Fermi level and stays there upon elongating or compressing the junction. This pinned resonance at the Fermi level was suggested [41] to be the reason for the almost constant contact conductance. Other materials like Al or Pb do not exhibit pinned resonances and show, respectively, positive and negative slopes of the conductance trace in contact upon elongation of the contact. Krans et al [42] pointed out that the behaviour of the conductance plateaux is characteristic of the specific material used in the experiments.

For the Ag contact (figure 2(a)) an increase of the contact conductance upon further approach of the tip towards the adatom is observed. This is a surprising observation since on the basis of the picture emerging from [41] one would expect quite a similar behaviour for Au. Currently, for Ag no calculations of transport channels are available and thus we tentatively suggest possible reasons for the different conductance curve of a silver junction. Combining the differences listed above we suggest that just after contact the Ag junction consists of two Ag atoms (tip apex atom and adatom), which, in contrast to the Au junction, exhibit a mutual distance very similar to the Ag lattice constant. Approaching then the tip further to the Ag adatom may lead to additional transport channels, which contribute to the total conductance. The additional transport channels may be provided by second-layer tip atoms, which come closer to the surface.

In a previous work, we reported a continuous transition from tunnelling to contact for a single Au adatom on Au(111) [20], which is in contrast to the abrupt transition reported here. Two possible reasons may be responsible for these different observations. Firstly, mechanical vibrations, which were present at the earlier experiments most likely feigned a continuous transition. To test this idea, a sinusoidal modulation, $\delta \sin(2\pi \nu t)$, was added to the tip displacement. Conductance traces on an Au adatom on Au(111) with different amplitudes $\delta$ are displayed in figure 3. As expected, the transition regime between tunnelling and contact broadens and conveys the impression of a gradual transition. Secondly, the transition between

**Figure 3.** Conductance curves acquired on a single Au adatom on Au(111) with modulation $\delta \sin(2\pi \nu t)$ superimposed on the tip displacement. The modulation frequency was set to $\nu = 8$ kHz and the amplitudes, $\delta$, are indicated in each plot.
tunnelling and contact depends on the configuration and the composition of the tip. While the substrate electrode is characterized at the atomic scale, the tip status may be controlled only to some extent. Continuous together with abrupt transition regimes have also been observed by the mechanically controlled break junction technique [43].

3.2. Contact spectroscopy

Apart from the electrical conductance of a single adsorbed atom it is interesting to monitor the evolution of its electronic structure from tunnelling to contact. We address this issue by reviewing results obtained for the Kondo effect of single magnetic impurities [19]. Contact spectroscopy of surface states localized in the attractive potentials of single adatoms [21], of molecular orbitals [29] and of the energy gap of superconductors [44] have also been reported.

Single magnetic adatoms, whose magnetic moment is screened by the conduction electrons of the substrate exhibit the Kondo effect [45, 46]. The spectroscopic signature of the Kondo effect is the Abrikosov–Suhl resonance at the Fermi level, which is induced below a characteristic Kondo temperature, \( T_K \). In [19], we showed that the many-body Kondo ground state may be controllably modified by the proximity of the tip apex atom.

The lower curve in figure 4(a) shows a \( dI/dV \) spectrum of the Abrikosov–Suhl resonance of a Co adatom on Cu(100) acquired at 7 K in the tunnelling regime. The resonance lineshape may be described by a Fano lineshape [45, 46]

\[
\frac{dI}{dV} \propto \frac{(q + \epsilon)^2}{1 + \epsilon^2},
\]

where \( q \) is the asymmetry factor and \( \epsilon = (eV - \epsilon_K)/(k_B T_K) \) with \( \epsilon_K \) the resonance energy and \( k_B \) Boltzmann’s constant. The result of the fit is presented in figure 4(a) as a full line. The best results were obtained in a voltage interval extending from −25 to 15 mV with fit parameters \( T_K = 78 \pm 5 \) K and \( q = 1.2 \pm 0.1 \) [19]. In the tunnelling regime, even at elevated currents the lineshape of the Abrikosov–Suhl resonance was not altered. Upon contact, however, the lineshape changed appreciably (figure 4(a), upper curve). To characterize the changes quantitatively, the spectroscopic signature in contact was fitted by a Fano lineshape in the same voltage interval as used for the fits in the tunnelling regime. As a result, fit parameters of \( T_K = 137 \pm 10 \) K and \( q = 2.1 \pm 0.1 \) were obtained (full line in upper data set of figure 4(a)).

Before explaining these results in terms of a hybridization effect, another possible source of resonance broadening is discussed. At contact, currents of the order of 1 \( \mu \)A are passed through a single atom, which correspond to current densities of the order of \( 10^{13} \) Am\(^{-2}\). Such elevated current densities may give rise to local heating effects, which have been reported for single-atoms, single-molecule and quantum point contacts [26, 32], [47]–[50]. Indeed, effective temperatures of a few hundreds of kelvin in an otherwise cryogenic environment have been proposed for contacted \( C_{60} \) molecules [26]. In the following we show that local heating effects alone do not account for the observed resonance broadening. To this end, the convolution of the Fano lineshape, equation (1), with the thermal broadening function [51]

\[
\chi(V) \propto \left[ \cosh \left( \frac{eV}{2k_B T_{\text{eff}}} \right) \right]^{-2}
\]

(\( T_{\text{eff}} \): effective temperature) was fitted to experimental data. While the Kondo temperature was fixed to the value obtained in the tunnelling regime and the asymmetry factor was fixed to the
Figure 4. (a) Spectroscopy of $dI/dV$ performed on a single Co atom adsorbed on Cu(100) at 7 K. Lower curve: $dI/dV$ spectrum taken in the tunnelling regime with feedback loop parameters of 0.06 V and 100 nA (data multiplied by 50 and shifted vertically by 6 $\mu$S to be at the same scale as the upper curve. Upper curve: $dI/dV$ spectrum taken in the contact regime with feedback loop parameters of 0.06 V and 6 $\mu$A. Full lines represent fits of Fano lineshapes, equation (1), to experimental data (lower curve: $T_K = 78 \pm 5$ K, $q = 1.2 \pm 0.1$, upper curve: $T_K = 137 \pm 10$ K, $q = 2.1 \pm 0.1$). (b) Contact spectrum of $dI/dV$ (circles) fitted by a Fano lineshape with an increased Kondo temperature (full line, as in (a)) and by a thermally broadened Fano lineshape with $T_K = 78$ K, $q = 2.1$ and $T_{\text{eff}} = 60 \pm 10$ K (dashed line).

value obtained in the contact regime, the effective temperature was used as a fit parameter. In figure 4(b) fits to spectroscopic data obtained at contact (same as upper curve in figure 4(a)) are shown. While the full line represents the Fano lineshape discussed above, the dashed line is the best fit obtained with the thermally broadened Fano lineshape. From this fit an effective temperature of $(60 \pm 10)$ K was extracted. It is obvious from figure 4(b) that experimental data are best fitted by a Fano lineshape reflecting an increased Kondo temperature rather than by a thermally broadened Fano lineshape. We therefore conclude that temperature broadening of the resonance and thus local heating effects play a minor role in modifying the Abrikosov–Suhl resonance. Indeed, in the case of electron and hole injection into pure metal, a temperature increase of the order of 1 mK may be estimated for the used currents and voltages assuming that electrons deposit their energy within their inelastic mean free path [52].

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Using the Anderson single-impurity model and density functional calculations, in [19] the broadening of the resonance was traced to, first, a shift of the spin-up d states of the Co adatom toward the Fermi level and, second, to a broadening of the individual Co d states. This result matches the intuitive expectation considering that the d level width is a measure of the hybridization with the conduction electrons of the substrate and the tip. Consequently, the level width is increasing as well as the effective exchange coupling and thus the Kondo temperature. We remark, however, that in general the Kondo temperature does not evolve monotonically with the number of hybridizations. In a recent study of the Kondo effect of a Co atom embedded in Cu clusters of various sizes we showed that the Kondo temperature evolves non-monotonically with the number of coordinating Cu atoms. As a result, the width of the Abrikosov-Suhl resonance depends on the local geometric environment of the magnetic atom and on the specific electronic structure at the magnetic site [53].

4. Conclusion

The scanning tunnelling microscope is a suitable tool to study ballistic electron transport through single atoms and molecules. Imaging the contact area prior to and after the contact experiment enables a clear characterization of the local environment and, to some extent, of the tip. By deliberately choosing tip and substrate, a wide variety of electrode materials may be combined for contacts. Contact spectroscopy provides the opportunity to investigate electronic and vibrational properties of single atoms and molecules in vertical hybridization geometries.

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References

[1] van Wees B J, van Houten H H, Beenakker C W J, Williamson J G, Kouwenhoven L P, van der Marel D and Foxon C T 1988 Phys. Rev. Lett. 60 848
[2] Wharam D A, Thornton T J, Newbury R, Pepper M, Ahmed H, Frost J E F, Hosko D G, Peacock D C, Ritchie D A and Jones G A C 1988 J. Phys. C: Solid State Phys. 21 L209
[3] Landauer R 1970 Phil. Mag. 21 863
[4] Büttiker M 1988 IBM J. Res. Dev. 32 63
[5] Gimzewski J K and Möller R 1987 Phys. Rev. B 36 1284
[6] Dürig U, Züger O and Pohl D W 1990 Phys. Rev. Lett. 65 349
[7] Kuipers L and Frenken J W M 1993 Phys. Rev. Lett. 70 3907
[8] Pascual J I, Méndez J, Gómez-Herrero, Baró A M, García N and Binh V T 1993 Phys. Rev. Lett. 71 1852
[9] Olesen L, Lægsgaard E, Stensgaard I, Besenbacher F, Schiøtz J, Stoltze P, Jacobsen K W and Nørskov J K 1994 Phys. Rev. Lett. 72 2251
[10] Kröger J, Néel N and Limot L 2008 J. Phys.: Condens. Matter 20 223001
[11] Muller C J, van Ruitenbeek J M and de Jongh L J 1992 Phys. Rev. Lett. 69 140
[12] Agraït N, Levy Yeyati A and van Ruitenbeek J M 2003 Phys. Rep. 377 81

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