An experimental set-up to probe the quantum transport through a single atomic/molecular junction at room temperature

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MS received 23 March 2022; revised 13 July 2022; accepted 30 August 2022

Abstract. Understanding the transport characteristics at the atomic limit is the prerequisite for futuristic nanoelectronic applications. Among various experimental procedures, mechanically controllable break junction (MCBJ) is a well-adopted experimental technique to study and control atomic or molecular scale devices. Here, we present the details of developing a piezo-controlled table-top MCBJ set-up, working at ambient conditions, along with the necessary data acquisition technique and analysis of the data. We performed the conductance experiment on a macroscopic gold wire, which exhibits a quantised conductance plateau upon pulling the wire. Conductance peak up to ~ 20$G_0$ ($G_0 = 2e^2/h$ where $e$ is the electronic charge and $h$ is the Planck’s constant) could be resolved at room temperature. A well-known test bed molecule, 4,4′-bipyridine, was introduced between the gold electrodes and the conductance histogram exhibits two distinctive conductance peaks, confirming the formation of a single molecular junction, in line with the previous reports. This demonstrates that our custom-designed MCBJ set-up can measure the quantum transport of a single molecular junction at ambient conditions.

Keywords. Mechanically controllable break junction; quantum transport; gold atomic junction; conductance quantisation; 4,4′-bipyridine.

PACS Nos 73.63.-b; 73.23.Ad; 66.35.+a; 73.63.Rt

1. Introduction

Despite many experimental challenges, electronic transport at the atomic scale has drawn significant attention recently. An atom or molecule suspended between two macroscopic metallic leads offers an atomic-scale laboratory [1]. At this length scale, electronic transport occurs primarily in the ballistic regime governed by the laws of quantum mechanics [2], in contrast to diffusive transport. A comprehensive and quantitative understanding of transport in these systems is addressed in a recent review by Thoss et al. [3]. Many fascinating phenomena arising due to quantum mechanical effects may lead to modern technological implementation like quantised resistors, capacitors [4], switches [5], spin filters [6,7], molecular rectifiers [8,9] and so on. Molecules being complex objects with multiple chemical configurations and vibrational degrees of freedom, understanding electronic transport through a single molecular junction is still an open topic of research [10–15]. However, Evers et al summarise the advances and challenges in single molecular transport by critically studying the theoretical and experimental findings so far [16]. Controlling the transport functionalities of the molecular junction via external gating [17,18] offers a promising strategy for developing high-performance molecular devices such as molecular switches [19], molecular transistors [20,21], thermoelectric devices [22] and single electron logic calculator (SELC) [23].

One immediate question is how to wire a single molecule (with a typical size of ~ 1 nm) to the electrodes. Due to the limited resolution in the existing microfabrication techniques like electron or focussed ion beam lithography, creating a gap size below ~ 10 nm is practically challenging. One way to circumvent this problem is to create a nanometre-sized gap using electromechanical methods with the possibility to fine-tune the gap between the contact electrodes. Many such methods were tried in literature, e.g., scanning tunnelling microscopy break junctions (STMBJs) [11,24,25], crossed wire [26], mechanically controllable break junctions (MCBJs) [10], electromigration...
break junctions (E-BJs) [27,28], nanopores [29,30], liquid metal junctions [29,31,32] etc. to form atomic size contacts. The mechanically controllable break junction [10,33,34] (MCBJ technique is one of the widely used techniques to study the electronic [35–37], mechanical [38,39], thermal [40,41] and spin-dependent [6,42–44] properties of a molecular junction. In the case of the MCBJ technique, a macroscopic metallic wire with a weak spot in the middle is placed on top of a flexible substrate. Three-point bending mechanisms of the MCBJ ensure an increase in strain in the wire during bending, which is concentrated at the notched spot, until the wire breaks. By relaxing the bending and incorporating fine control of the gap separation using a piezoelectric actuator, atomic junctions can be formed and broken repeatedly. Moreover, the piezo can be stopped at a desired configuration to carry out the I–V measurements. A small value of the ‘attenuation factor’ ($\Delta = 6ut/L^2$, where $t$ is the thickness of the substrate, $u$ is the length of the weak spot and $L$ is the length between the counter support of the three-point bending mechanism) defined as the ratio between gap separation and displacement of the piezo, makes it suitable to manipulate the conformation of the junction with a sub-Angstrom resolution [45] and provides excellent mechanical stability. Moreover, controllable breaking and making cycles help us to collect a huge number of independent traces which can give a good statistical description of the junction. By creating a conductance histogram from these traces, one can obtain the most probable conductance values for an atomic or a molecular junction. For a metallic junction, it was shown that the conductance histogram is the fingerprint of the available valence orbitals of the metal. Several metals have been characterised using MCBJ technique and statistically, these exhibit different conductance values for a single atomic contact. Conductance values of gold (Au), silver (Ag), copper (Cu), platinum (Pt), aluminium (Al), iron (Fe), niobium (Nb), lead (Pb) and sodium (Na) are 1.0$G_0$, 1.0$G_0$, 1.0$G_0$, 1.6$G_0$, $\sim 0.8G_0$ (< 1.0$G_0$), 2.1$G_0$, 2.3$G_0$, 1.7$G_0$, 1.0$G_0$, respectively [46–50]. The wave nature of the electron is considered to be responsible for conductance-quantisation as the dimensions of the conductor are comparable to the de Broglie wavelength of the electrons at the Fermi surface and electrons can traverse across the conductor ballistically.

Here, we demonstrate an experimental set-up based on the MCBJ technique comprising relatively low-cost materials instead of a conventional electric motor or highly sensitive mechanical gear, reducing the fabrication cost significantly. Moreover, the preparation and assembly of the sample do not require any advanced techniques such as lithography or clean-room facility. Our experimental set-up is highly stable and capable of probing quantum mechanical phenomena even at room temperature. Before entering into the experimental observations, a brief summary of the quantum transport theory for an atomic conductor is presented. Initial characterisation with gold atomic contact demonstrates the conductance quantisation at an integer multiple of $G_0$, in line with the previous report [46]. Further measurements with 4,4′-bipyridine molecular junction reveal two conductance peaks (9.33±0.29×10^{-4} G_0 and 4.28±0.07×10^{-4} G_0) [51–53] in the conductance histogram which in turn validate the binary conducting switching behaviour of 4,4′-bipyridine molecular junction [36].

2. Conductance in the quantum limit

Before discussing the experimental part, it is convenient to discuss the transport mechanism of atomic-scale junctions theoretically. Conductance through a few atoms to a single atom or molecule is fundamentally different from its macroscopic counterpart and Ohm’s law does not hold at this point. In the case of the atomic or molecular junction, the characteristic length scale is smaller than the mean free path (the distance between two successive elastic collisions with static impurities) and the transport is assumed to be ballistic in nature. Momentum of the electron is considered to be constant in that regime and is only limited to the scattering from the boundaries of the contacts. Most celebrated theoretical formalism till date to describe the conductance of atomistic contact is the Landauer formalism of scattering approach, shown schematically in figure 1 [54]. As per this approach, a transport problem can always be considered as a scattering problem ignoring inelastic interactions. It essentially demonstrates that electrical conductance is intimately related to the transmission probability of the electron.
crossing the system and conductance can be expressed as
\[ G = \frac{2e^2}{h} \sum_{n=1}^{N} \tau_n = G_0 \sum_{n=1}^{N} \tau_n. \] (1)

It is known as the multichannel generalisation of Landauer formula \[55\], where conductance is viewed to be carried by \( N \) independent conductance channels. The transmission probability of each channel is \( \tau_n \) and the conductance of a fully open channel is \( G_0 \) (\( G_0 = \frac{2e^2}{h} \approx 12.9 \, \text{k}\Omega \)), known as 'quantum of conductance'. This is an important contradiction compared to a macroscopic conductor, where it is obvious to expect zero resistance for a perfect conductor. Conductance channels of the atomic contacts are determined by the chemical nature of the atom and the number of active channels corresponds to the number of valence electrons \[46\].

So far, our concern is limited to atomic contacts only. In this subsection, we will shed light on the transport mechanism through a molecular junction. The description of a molecular junction is rather complex compared to the atomic junction due to its multiple chemical conformations and vibrational degrees of freedom. Electronically, a molecule is different from its gaseous phase, when placed in a junction. For simplicity, we shall discuss the coherent transport model, a well-accepted model in the community to describe the current–voltage characteristics of a molecular junction, in which electrons flow elastically through the molecule without exchanging any energy. It is assumed that inelastic interaction takes place only inside the electrodes but not inside the molecule so that the phase information is conserved. In principle, different molecular orbitals can participate in the electron transport simultaneously. Some possible conduction mechanisms include direct tunnelling, Fowler–Nordheim tunnelling, thermionic emission or hopping transport \[56, 57\]. In an experiment, a particular mechanism is identified by studying the shape of the current–voltage characteristics and their temperature dependence. For the sake of simplicity, we schematically represent the model using a single-level resonant tunnelling model in figure 2. Level position is denoted by \( \epsilon_0 \), the separation between the Fermi level and nearest molecular orbital in energy scale. Another key parameter in this model is the scattering rate \( \Gamma_{L,R} \) which essentially demonstrates the strength of the coupling to the metallic leads (\( L, R \)). \( I–V \) characteristics (calculated by considering the Landauer approach) adopt the following form:

\[ I = \frac{2e^2}{h} \int_{-\infty}^{+\infty} dE \ T(E, V) \left[ f(E - eV/2) - f(E + eV/2) \right], \] (2)

where factor 2 comes from the spin symmetry, \( f(E) \) is the Fermi function and \( T(E, V) \) is the energy and bias voltage-dependent transmission coefficient, given by the Breit–Wigner formula,

\[ T(E, V) = \frac{4\Gamma_L \Gamma_R}{(E - \epsilon_0(V))^2 + [\Gamma_L + \Gamma_R]^2}. \] (3)

This simple model explains why, in a highly coupled molecular junction, the conductance may be significant, even though in many cases the central energy of the molecular level is located far from the electrochemical potentials of the leads.

### 3. Design of experimental set-up

To prepare the MCBJ sample, a notch (weak spot) is created at the centre of a macroscopic metallic gold wire (diameter \( \sim 0.1 \, \text{mm} \), Alfa Aesar, 99.998\%) using a surgical blade (Swan Morton) which is controlled by a Z positioner (Holmarc, India) as shown in figure 3c. Metallic wire with the notch at the middle is then fixed on top of a flexible substrate (phosphor bronze of thickness \( \sim 1 \, \text{mm} \)), covered by a Kapton sheet for electrical insulation. An epoxy glue (Stycast 2850 FT with catalyst 9)
is employed at both sides of the notch to rigidly fix the wire (shown in figure 3b) with the substrate. The stycast is advised to be put very close to the junction, preferably within 100 μm for better junction stability. It is then mounted in a home-made three-point bending configuration (schematic: figure 3a and real set-up: figure 3d), where the flexible substrate is fixed at the two ends. Bending the substrate in the middle using a Z positioner leads to a strain in the wire, concentrated primarily at the weak spot. Further increase of the strain leads to the breaking of the wire, forming two freshly exposed atomistic electrodes. Then, the junction can be repeatedly broken and formed using a piezoelectric actuator (Piezomechanik GmbH, Germany (PST 150/2×3/7)), attached to the rod of the z-positioner. The details of the components used are given in table 1.

The circuit diagram shown in figure 3e is used to measure the electrical conductance of a single atomic or molecular junction. To record the conductance vs. electrode separation traces, a triangular waveform is applied to the piezoelectric actuator which essentially translates to a small displacement of atomic electrodes and continues the successive break-make cycle. For conductance measurement, a DC bias from the output channel of a 16-bit DAQ card (PCI 6221, National Instruments) is applied and the current is measured by the input channel of the DAQ card after amplification using a current to voltage preamplifier (SP 983, electronics lab, University of Basel). Data acquisition is performed with the help of a custom-built LABVIEW program. To increase the dynamic range, keeping the amplifier gain constant, a series resistance Rs (50 kΩ in our experiment) is connected [58]. Thus, when the conductance of the junction is higher, current is determined by the series resistance and in the case of extremely low conducting junction (resistance ~ GΩ), contribution of the series resistance is negligible and can be ignored. Conductance of the junction is thus measured by measuring the current and the voltage drop across the junction following the equations:

\[
V_{\text{Bias}} = (V_{Rs} + V_{\text{Junction}});
\]

\[
G_{\text{Junction}} = \frac{I}{V_{\text{Junction}}} = \frac{I}{(V_{\text{Bias}} - V_{Rs})},
\]

where \(V_{\text{Bias}}\) is the applied bias, \(V_{Rs}\) is the voltage drop across the series resistance, \(V_{\text{Junction}}\) is the voltage drop across the junction, and \(G_{\text{Junction}}\) is the conductance of the junction.

**Figure 3.** (a) Schematic representation of the three-point bending configuration of the MCBJ technique, (b) a picture of the MCBJ sample with a notched gold wire where the two black spots are the epoxy (Stycast) that fixes the wire on top of the Kapton foil, (c) the wire ‘notcher’ designed to make the weak spot or notch in the wire by rolling the wire underneath the blade, (d) MCBJ set-up fabricated to achieve the three-point bending mechanism and (e) schematic of electrical circuits, used for DC conductance measurements.
Table 1. Details of the components.

| Materials or components                  | Company (model)                                      |
|------------------------------------------|------------------------------------------------------|
| Data acquisition system                  | National Instruments (PCI-6221 or PCI 4461)          |
| Piezostacks                              | Piezomechanik Gmbh, Germany (PSt 150/2 × 3/7)        |
| Piezocontroller                          | Piezomechanik Gmbh, Germany (SVR 150/1)              |
| Current to voltage preamplifier          | Electronics lab, University of Basel (SP 983)        |
| BNC cables and resistance                | Element 14                                           |
| Z positioner                             | Holmarc Opto-Mechatronics Ltd                        |
| Phosphor bronze substrate                | Local market                                         |
| Kapton foil                              | Local market                                         |
| Stycast epoxy                            | Digi-Key Electronics (2850 FT with catalyst 9)       |
| Scalpel or surgical blade                | Swann Morton (No.-24)                                |
| Aluminium bar                            | Local market                                         |
| Electrode materials (gold)               | Alfa Aesar                                           |
| Silver paint                             | SPI (05.002-AB)                                      |

across the junction, \( I \) is the current through the junction.

By measuring the current and the voltage drop across the junction, one may obtain the conductance of the junction. An important consequence of this series resistance is that voltage drop across the junction is not constant throughout the measurements even though the applied bias is constant.

4. Data analysis tool

In this section, we will briefly explain the most frequently used data analysis tools: 1D conductance histogram and 2D conductance-displacement histogram. In the case of the break junction experiment, conductance of the junction is measured as a function of displacement between two electrodes, starting from bank of atoms to the vacuum tunnelling (i.e. no atom) by a tiny and constant increment of gap size. Such a complete measurement cycle is called a conductance trace and thousands or even more such traces are collected to proceed further statistical analysis. Before entering the next cycle, electrodes are always crashed up to several value of \( G_0 \) which essentially erase the memory from the previous cycle. Statistical analysis of a large number of traces thus ensures the estimation of the most probable values of quantities like conductance, thermopower etc., from many independent events. 1D conductance histogram is constructed from the distribution of the conductance values of a large number of traces. If a conductance plateau is frequently occurred in a certain conductance regime, it will be reflected as a peak in the histogram. By fitting those peaks in the histogram, most probable conductance values of the junction are obtained. In the case of atomic junction, histogram is usually presented in linear scale in contrast to molecular junction where logarithmic binning is efficient since the single molecular conductance is lower than \( 1G_0 \) and can be as low as \(<10^{-6}G_0 \) [59]. The conductance histogram provides only the conductance values, ignoring information related to the displacement which is important to understand the evolution of the atomic or molecular junction during mechanical stretching or squeezing. A two-dimensional conductance-displacement histogram is thus developed to look into the correlation between conductance and displacement statistically. First, a conductance value is assigned for each trace as the origin of the distance axis, i.e. zero distance point. Each point in the traces is then contributed to one of the 2D bins of the histogram, defined by conductance and distance from the starting point. The resulting histogram can then be considered as a stack of many traces, placed on top of each other and is helpful to figure out the most common feature during stretching. MATLAB scripts are used to carry out the statistical analysis.

5. Results and discussion

A representative conductance trace of the gold nano junction at ambient conditions, obtained using our home-made MCBJ set-up, is shown in figure 4a. The curve reflects the evolution of a particular atomic configuration upon stretching, during which conductance decreases in a series of sharp, vertically descending steps, known as conductance plateaux. As the number of atoms is reduced, the number of channels available for conduction also decreases and conductance drops discretely. Transport behaviour at this atomic scale cannot be explained by the Ohm’s law as stated earlier. As the Fermi wavelength of the electron is comparable to the dimension of the constriction, one needs to consider quantum mechanical confinement effect. Conductance of the latest atomic configuration is \( 1.0G_0 \) (equivalent to \(~12.9\ k\Omega\) and it has been argued that this configuration corresponds to the single atom at its narrowest cross-section [46]. When the junction is pulled further, exponential quantum mechanical tunnelling behaviour between two atomic leads is clearly visible and shown...
Figure 4. (a) Characteristics breaking conductance trace of the gold atomic junction. Inset shows the same traces in logarithmic scale to illustrate the quantum mechanical tunnelling behaviour indicated by a black arrow, (b) conductance histogram constructed from 10,000 consecutive breaking traces using 200 bins. Number in the histogram is used to assign those characteristic peaks and (c) two-dimensional conductance–length histogram of the same 10,000 traces, constructed using 50 bins.

As a black arrow in the inset of figure 4a. The conductance histogram of gold nanojunction constructed from 10,000 consecutive breaking traces having 200 number of bins, is shown in figure 4b. Peaks at the conductance values ~ 0.96G₀ (1), 1.75G₀ (2), 2.75G₀ (3), 3.70G₀ (4), 4.46G₀ (5) correspond to the most probable values of conductance occurring from different configurations. Close inspection of the data reveals conductance peaks even up to conductance ~ 20G₀ (see Appendix B). The peak near 1.0G₀ (~ 0.95G₀) indicates the conductance of an single atomic gold junction, the characteristic signature of an s-metal having a single conduction channel [46]. Figure 4c shows the 2D conductance–distance histogram constructed from the same number of traces used in figure 4b. It can be seen that the 1G₀ plateau can be stretched up to ~ 2 Å without much change in conductance. It is important to mention that one can observe the quantum transport behaviour at such a high temperature (~ 300 K). Because of the inelastic electron–phonon scattering, one would expect that there will be a mixing of different quantum channels. However, in the recent shot noise measurement on atomic point contact of gold at 300 K [60], a clear suppression of shot noise is observed near $G = 1.0G₀$, indicating the ballistic transport even at room temperature. It indicates that the inelastic scattering length is much larger than the dimension of the atomic point contact (~ a few Å) at room temperature and at a finite bias of a few tens of millivolt range.

After characterising the set-up with gold atomic junction, we will now discuss the possibility of studying the conductance of a molecular junction between two gold electrodes. Here, our choice is 4,4′-bipyridine (chemical structure is shown in the inset of figure 5a), one of the well-studied molecules in the community [36, 61–65]. For creating molecular junction, the molecule is evaporated on top of the notched metallic wire. Figure 5a shows the typical breaking traces of 4,4′-bipyridine molecular junction in logarithmic scale where molecular plateaus (from $3 \times 10^{-3}G₀$ to $2 \times 10^{-4}G₀$) are observed along with the atomic plateaus at 1.0G₀. To get a meaningful estimate of the conductance value of the molecular junction, 5000 such independent traces are analysed and presented as a logarithmically binned normalised 1D histogram in figure 5b (100 bins per decade). Histogram demonstrates a peak at 1G₀ which corresponds to Au atomic contact, associated with a prominent molecular characteristics ($5 \times 10^{-3}G₀$ to $1 \times 10^{-4}G₀$). The molecular conductance peak can be fitted with two Gaussian peaks ($9.33 \pm 0.29 \times 10^{-4}G₀$ and $4.28 \pm 0.07 \times 10^{-4}G₀$) (shown as white dash-dot line in figure 5b). Conductance values of these two peaks are in good agreement with the values in the previous report [36]. To look into the conductance behaviour during stretching, 2D conductance displacement histogram is generated (employing the same traces as used in 1D histogram) by aligning them at 2.0G₀ and using 50 bins per decade. In the 2D histogram, we observed that the molecular junction can be stretched up to ~ 8 Å and the conductance decreases with stretching. The low conductance peak mainly originates from the configuration when the molecule is completely stretched [36]. To gain detailed insight into the formation of these two different configurations, a conditional histogram shown in figure 6 is considered. The blue area demonstrates the histogram containing all the molecular traces. However, the line plots represent the histograms which are generated by selecting
traces with only high conductance (high-$G$) peak (red) or low conductance (low $G$) peak (black). It is evident that selecting one of the peaks does not completely remove the other peak, rather we observe a small suppression. It can be shown that these two configurations are plateau length-wise anticorrelated, as shown in ref. [66]. Thus, statistical analysis of the experimental data confirms the successful formation of the 4,4′-bipyridine molecular junction using our home-built experimental set-up.

6. Conclusions

In this work, we have demonstrated a simple and robust experimental arrangement based on MCBJ technique without using sophisticated electric motor or high-resolution gear to look into the electronic transport behaviour at the atomic scale. Initial characterisation of our experimental set-up with gold atomic junction shows well-defined conductance plateaus at the integer multiple of $G_0$ ($G_0 = 2e^2/h$) which has been further verified by the statistical analysis of a large number of traces. We have also studied the 4,4′-molecular junction and are happy to conclude that the most probable conductance value of this molecular junction is in excellent agreement with the previous report. Thus, our experimental set-up is good enough to probe the quantum transport behaviour through atomic and molecular junctions. Fabrication of this table-top set-up will be more helpful for motivated high school students and for lab courses at the undergraduate or postgraduate level. Moreover, direct observation of the quantum mechanical phenomena at room temperature and ambient condition will be a fascinating demonstration of quantum mechanics in our daily lives.

Acknowledgements

B Pabi acknowledges the support from DST-Inspire fellowship (Inspire code IF170934) and A N Pal acknowledges the funding from the Department of Science and Technology (Grant No. CRG/2020/004208). The authors acknowledge Amit Ghosh for the technical help.
in designing the experimental set-up at the workshop and characterisation facilities under the TRC project at SNBNCBS. Authors appreciate help from Ayelet Vilan regarding the MATLAB code and Oren Tal for fruitful discussions.

Appendix A: Calibration between the displacement (or electrode separation) and the voltage applied to piezoelement

Experimentally, distance between two electrodes is manipulated by applying a voltage to the piezoelectric actuator. Adopting the procedure from ref. [67], exponential dependence of the current on the vacuum gap is used to make a rough calibration of the gap size. Linear relation between the piezoexpansion that means the voltage at piezo \( V_{\text{piezo}} \) and gap size \( \Delta \) (i.e. electrode separation or displacement) helps to define a simple calibration constant \( c \),

\[
c = \frac{\Delta }{V_{\text{piezo}}}. \tag{A1}
\]

Tunnel current \( I \) between two electrodes which are separated by a distance \( \Delta \) (provided the applied voltage \( V_0 \) is smaller than the work function of the electrodes) can be expressed as [68]

\[
I(V_0) = kV_0e^{-2\Delta \sqrt{2m\phi/\hbar^2}}, \tag{A2}
\]

where \( m \) is the mass of the electron, \( \phi \) is the work function of the electrode, \( k \) is a constant related to the area of the electrode and to the electron density of states at the Fermi level and \( \hbar \) is the reduced Planck constant. Resistance of the tunnel junction is thus,

\[
R = R_0e^{2\Delta \sqrt{2m\phi/\hbar^2}}. \tag{A3}
\]

Combining eqs (A1) and (A3), we can write,

\[
R = R_0e^{2cV_{\text{piezo}}\sqrt{2m\phi/\hbar^2}}. \tag{A4}
\]

Slope \( m \) of the logarithmic resistance with respect to the piezovoltage is thus

\[
m = \frac{\partial (\ln R)}{\partial V_{\text{piezo}}} = \frac{\partial (2cV_{\text{piezo}}\sqrt{2m\phi/\hbar^2})}{\partial V_{\text{piezo}}} = \frac{\sqrt{2m\phi}}{\hbar}2c, \tag{A5}
\]

Calibration constant, \( c = \frac{m \times \hbar}{2\sqrt{2m\phi}}. \tag{A6} \)

This expression is indeed very simple and clean electrodes follow an exponential behaviour (shown in figure 7a) of the current as a function of \( V_{\text{piezo}} \), which would make this a suitable method to calibrate the gap size with voltage applied to the piezoelectric actuator. A histogram of calibration constant (shown in figure 7b) is prepared using slopes, calculated from a large number of conductance traces. Then, most frequent \( c \) value is obtained by Gaussian fitting to this histogram and is used further to calibrate. However, major source of inaccuracy in this method comes from the value of work function used which is very much sensitive to the fine-structure details of the junction [69] and also the local environment [70].

Appendix B: Gold atomic junction at higher conducting configuration

See figure 8.
Figure 8. One-dimensional conductance histogram of the gold atomic junction till conductance value upto $20G_0$, constructed from the same 10,000 traces used in figure 4, using 200 bins. High conductance peaks can be resolved even upto ~ $20G_0$.

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