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THEORETICAL COMPUTATION OF CURRENT AND NOISE

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A.1 MODELING OF THE AU ATOMIC CHAIN

We model the Au atomic chain by using the minimal model described in detail in the supplementary material of [1]. We also adopt in the following the reduced units $\hbar = e = k_B = 1$. In such a model (see A.1), the central atomic chain is described as a single molecular level of energy $\omega_d$ which is coupled to perfect left (L) and right (R) electrodes through the $\Gamma_{L(R)}$ coupling terms. Excitation of a local phonon mode of energy $\omega_0$ with interaction strength $\lambda$ is made possible when the kinetic energy of transferred electrons given by the voltage drop $\mu_L - \mu_R = V$ exceeds the phonon energy $\omega_0$. The total Hamiltonian of the system is then written as in [1]

$$\mathcal{H} = \sum_{X=L,R} \mathcal{H}_X + \omega_d d^\dagger d + \omega_0 a^\dagger a + \mathcal{V}_T + \mathcal{V}_{e-ph}$$ (A.1)

$$\mathcal{V}_T = \sum_{X=L,R} t_{Xa} c_X^\dagger d + \text{H.c}$$ (A.2)

$$\mathcal{V}_{e-ph} = \lambda (a + a^\dagger) d^\dagger d$$ (A.3)

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In order to derive some analytical results for the current and noise in presence of e-ph interactions, we suppose that the coupling to the leads is symmetric ($\Gamma_L = \Gamma_R = \Gamma/2$) and that the energy dependence of the transmission factor $\tau(\omega)$ of the nano-junction can be neglected. The later assumption is equivalent to evaluate the transmission factor at Fermi energy, namely that

$$\tau \approx \frac{\Gamma^2}{\omega_d^2 + \Gamma^2}$$  \hspace{1cm} (A.4)

This condition will have to be relaxed in part IV when trying to fit quantitatively the experimental curves at low transmission.

**A.2 COMPUTING THE MEAN CURRENT AND NOISE IN THE Au ATOMIC CHAIN**

We use the formalism of Avriller et al.[1] in order to compute the mean current and noise characteristics. It is based on a Keldysh Green functions framework which has been generalized in [2] in order to address higher order cumulants of the current operator. The correction to the current and noise upon phonon excitations are then computed at second order of the e-ph coupling strength [1, 3, 4].

In order to provide some microscopic picture of the elementary processes responsible for the correction to the noise induced by e-ph interactions, we will rewrite in a slightly different way the results derived in [1, 3, 4]. We will provide...
some compact expressions for the current and noise characteristics that are valid at finite temperature (for the electrons), in the limit where the energy dependence of the transmission factor $\tau(\omega)$ can be neglected.

### A.2.1 MEAN CURRENT

The correction to the mean current at second order of e-ph interactions is obtained as

$$
\delta I(V) = \frac{1}{2\pi} \left( \frac{\lambda \tau}{\Gamma} \right)^2 \int d\omega \left\{ (1 - 2\tau) \left[ 2f_{L;+}(1 - f_R) + f_L(1 - f_{R;+}) \right] + 2\tau f_L(1 - f_R) - (L \rightarrow R) \right\} \tag{A.5}
$$

where we introduced the notation $f_{X;\pm} = f_X(\omega \pm \omega_0)$ for the Fermi distributions of the $X = L, R$ leads evaluated at energies $\omega \pm \omega_0$.

Eq.(A.6) relates the current to elementary one-electron processes during which an electron is transferred from left to right electrode either elastically or inelastically. At zero temperature, only phonon emission is allowed and one obtains for the current at positive voltages:

$$
\delta I(V) \approx \frac{1}{2\pi} \left( \frac{\lambda \tau}{\Gamma} \right)^2 \left\{ 2(1 - \tau)V + (1 - 2\tau)(V - \omega_0)\theta(V - \omega_0) \right\} \tag{A.6}
$$

The first term on the rhs stands for an elastic correction that might be included into an effective transmission factor (renormalization of $\tau$ by e-ph interactions), whereas the second term is an inelastic correction that is activated when $V > \omega_0$ (the transferred electrons acquire enough kinetic energy to excite the local vibrational mode). Within our approximation, the sign of the correction to the conductance is positive (negative) for $\tau < (>) 1/2$. The crossover at $\tau = 1/2$ has been observed recently experimentally in molecular junctions made of single water molecules contacted to Pt electrode [5].
A.2.2 Noise

A similar although more lengthy expression can be derived for the correction to the noise induced by e-ph interactions

\[
\delta S(V) \approx \frac{1}{2\pi} \left( \frac{\lambda \tau}{\Gamma} \right)^2 \int d\omega \left\{ (1 - 2\tau) A_1 - \tau A_2 + A_3 - 2\tau A_4 \right\} \\
A_1 = \sum_{X=L,R} \left\{ f_X (1 - f_X) + f_{X;+} (1 - f_{X;+}) \right\} \\
A_2 = A_1 \sum_{X=L,R} \left\{ f_{X;+} - f_X \right\} \\
A_3 = \sum_{X=L,R} f_{X;+} (1 - f_X) \\
A_4 = \sum_{X=L,R} X (f_X + f_{X;+}) \sum_{X=L,R} X f_{X;+} (1 - f_X)
\]
In the limit of zero temperature and positive voltages, we obtain a simpler expression
\[
\delta S(V) \approx \frac{1}{2\pi} \left( \frac{\lambda \tau}{\Gamma} \right)^2 \left\{ 2(1-\tau)(1-2\tau)V + \left[ 1-8\tau(1-\tau) \right] (V-\omega_0)\theta(V-\omega_0) \right\} \tag{A.12}
\]
The correction to the noise also exhibits a threshold behavior when the local vibrational mode is excited \((V > \omega_0)\). Given the two critical values of the transmission factor \(\tau_\pm = 1/2(1 \pm 1/\sqrt{2})\), the correction to the noise is positive (super-Poissonian) when the transmission factor is such that \(0 < \tau < \tau_-\) and \(\tau_+ < \tau < 1\). This correction to the noise becomes negative (sub-Poissonian) in the remaining regime \(\tau_- < \tau < \tau_+\), which is a much less intuitive result.

In order to understand the microscopic mechanism responsible for this crossover between positive and negative correction to the noise, we kept track of the terms that dominate in the limit of zero temperature and positive voltages. In equation (A.13), we have split the correction to the noise into the sum of two contributions:
\[
\delta S(V) \approx \delta S_{1e}(V) + \delta S_{2e}(V) \tag{A.13}
\]
The first contribution \(\delta S_{1e}(V)\) is first analyzed and is associated to one-electron processes written as
\[
\begin{align*}
\delta S_{1e}(V) &= \delta S_{1e}^{(el)}(V) + \delta S_{1e}^{(in)}(V) \tag{A.14} \\
\delta S_{1e}^{(el)}(V) &= \frac{1}{2\pi} (1-2\tau) \delta \tau_{el} \int d\omega f_{1e}^{(el)}(\omega;V) \tag{A.15} \\
\delta S_{1e}^{(in)}(V) &= \frac{1}{2\pi} \delta \tau_{in} \int d\omega f_{1e}^{(in)}(\omega;V) \tag{A.16}
\end{align*}
\]
In equation (A.15)-(A.16), the e-ph interaction modifies the elastic transmission factor \(\tilde{\tau} = \tau + \delta \tau_{el}\) and opens a new inelastic channel when \(V > \omega_0\), with a probability given by the inelastic transmission factor \(\delta \tau_{in}\). The activation of e-ph interaction also provides an inelastic contribution to the electronic distribution functions \(f_{1e}^{(el,\text{in})}(\omega;V)\) that appear in the multi-channel version of the standard shot-noise formula [6]. The corresponding expressions for the renormalized transmission factors and electronic distribution functions are provided below
\[
\begin{align*}
\delta \tau_{el} &= 2(1-2\tau) \left( \frac{\lambda \tau}{\Gamma} \right)^2 \tag{A.17} \\
\delta \tau_{in} &= \left( \frac{\lambda \tau}{\Gamma} \right)^2 \tag{A.18} \\
f_{1e}^{(el)}(\omega;V) &= f_L(1-f_R) \tag{A.19} \\
f_{1e}^{(in)}(\omega;V) &= f_{L+}(1-f_R) \tag{A.20}
\end{align*}
\]
It is interesting to notice that the one electron inelastic contribution to shot-noise \( \delta S_{1e}^{(i)}(V) \) is always positive. This contribution was shown to be dominant in the limit \( \tau \to 1 \) and to distort the counting statistics for the transferred electrons into a Poissonian distribution upon activation of phonon emission (rare events) [1].

The second contribution to Eq.(A.13) \( \delta S_{2e}(V) \) cannot be understood in terms of simple one-electron effects. It rather originates from coherent two-electron processes that provide a negative correction to the noise upon phonon excitations. Figure(A.2-(a) and (b)) show a first class of such processes, where the elastic transmission of one electron (from left to right lead) is correlated to an inelastic transmission event assisted by the emission of a phonon. The corresponding two-electron correlation finds its deep origin in Pauli exclusion principle, namely into the fact that the transmitted charges are fermions. For instance, in Fig.A.2-(a), after a first elastic transmission event has occurred, the next coming inelastic transmission event will compete for the same final scattering state. If this final state is fully occupied (which is the case in the limit of perfect transmission), the contribution of such a process will vanish as a result of Pauli blocking. At finite transmission (the final state is partially occupied), the above mentioned Pauli blocking mechanism will still reduce the current fluctuations and thus decrease the noise. Figure(A.2(c)) shows the other class of two-electron events responsible for the negative correction to the noise. It is associated to the case where two electrons are coherently transmitted (bunching of two electrons) with emission and re-absorption of a phonon, thus generating an effective electron-electron interaction.

Similarly to the previous case, we derived compact expressions for \( \delta S_{2e}(V) \)

\[
\delta S_{2e}(V) = \delta S_{2e}^{(el)}(V) + \delta S_{2e}^{(in)}(V) \tag{A.21}
\]

\[
\delta S_{2e}^{(el)}(V) = \frac{1}{2\pi} \frac{\tau}{2} \delta \tau_{el} \int d\omega f_{2e}^{(el)}(\omega; V) \tag{A.22}
\]

\[
\delta S_{2e}^{(in)}(V) = -\frac{1}{2\pi} 2\tau (1 - \tau) \delta \tau_{in} \int d\omega f_{2e}^{(in)}(\omega; V) \tag{A.23}
\]

In equation(A.22)-(A.23), the electronic distribution functions \( f_{2e}^{(el, in)}(\omega; V) \) are modified by phonon mediated two-electron processes and are obtained as

\[
f_{2e}^{(el)}(\omega; V) = \sum_{\alpha = \pm 1} f_L (1 - f_R) f_{L; \alpha}^{a-1} \left( 1 - f_{R; \alpha}^{a+1} \right) \tag{A.24}
\]

\[
f_{2e}^{(in)}(\omega; V) = \sum_{\alpha = \pm 1} \left\{ f_L (1 - f_R) f_{L; \alpha}^{a+1} \left( 1 - f_{R; \alpha}^{a-1} \right) \right. \tag{A.25}
\]

Interestingly, the global contribution of two-electron inelastic processes to shot-
noise $\delta S_{2e}^{(in)}(V)$ is negative and proportional to $-(1-\tau)$, as expected from the general arguments about Pauli blocking. Equation (A.26) enables to perform a mapping between the diagrammatic expansion of the two-electron processes and their contribution to $\delta S_{2e}^{(in)}(V)$. Indeed, the first term in the expression of $f_{2e}^{(in)}(\omega;V)$ provides the class of two-electron processes depicted in figure (A.2(a) and (b)) whereas the second term corresponds to the class of processes depicted in figure (A.2(c)).

### A.3 Theoretical Analysis of Experimental Curves

The fitting of the experimental data at high transmission, i.e. for $G$ close to $1G_0$, is straightforward. It becomes slightly more involved for $G$ well below $1G_0$ because conductance fluctuations give rise to a background of asymmetric bias-dependent conductance. These conductance fluctuations are suppressed at $G = 1G_0$, as has been shown in [7]. We present now some details about the theoretical analysis of the experimental curves. Of particular interest are the samples for which $G < 0.85G_0$, i.e. for which the correction to the noise induced by e-ph interactions is expected to be negative. In this case, the reduced noise $Y = (S(V) - S(0))/S(0)$ versus the reduced voltage $X = (V/2T)\cot(V/2T)$ results from the interplay between conductance fluctuations induced by intrinsic disorder in the experimental setup and the inelastic signal activated when $V > \omega_0$. It is then required to deconvolute the effect of background fluctuations from the inelastic signal in the samples for this region of parameters. In the high transmission regime $G > 0.95G_0$, such an analysis is not needed, because the inelastic signal clearly dominates over the background fluctuations.

The pattern of conductance fluctuations is rich because of the contribution of several (many) scattering centers, and it cannot be described in terms of just a few parameters. In order to capture the main effects we adopt the following procedure. We need to relax the assumption of energy independence of the transmission factor and to complement the description of the nano-junction by superimposing energy dependent fluctuations to the flat density of states (DoS) of the L-lead

$$
\rho_L(\omega) = \rho_0 \left[ 1 + \alpha_D e^{-|\omega|/\omega_c} \cos \left( \frac{2\pi}{\Omega_D} \omega + \phi_D \right) \right] \\
\rho_0 = \frac{1}{\pi W}
$$

Those fluctuations stand for the existence of intrinsic disorder in the experimental setup at the origin of conductance fluctuations. They are characterized by a typical disorder strength $\alpha_D$, a mean period $\Omega_D$, a phase $\phi_D$ and a cutoff $\omega_c$ (fixed so that the fluctuations decay to zero far from the Fermi energy). Within this model, the transmission factor of the junction is still given a the standard Lorentzian-shape
A. Theoretical computation of current and noise

**Figure A.3:** Theoretical fitting of the experimental conductance and noise curve: Two examples A and B of conductance \(G(V)\) and reduced noise \(Y(X)\) measured on Au atomic chains. Common to the \(G(V)\) curves (A)−1 and (B)−1 : Blue points : experimental points for the conductance. Plain black curve : conductance with elastic background fluctuations only (\(\lambda = 0\) and \(\alpha_D \neq 0\)). Plain red curve : conductance (output of the fit) with both elastic fluctuations and inelastic effects induced by e-ph interactions (\(\lambda \neq 0\) and \(\alpha_D \neq 0\)). Common to the reduced noise curves (A)−2 and (B)−2 : Blue points : experimental points for the reduced noise \(Y(X)\). Dashed black curve : fitted reduced noise in the low bias regime (\(V < \omega_0\)), in absence of e-ph interactions and background fluctuations (\(\lambda = 0\) and \(\alpha_D = 0\)). Plain black curve : reduced noise with elastic background fluctuations only (\(\lambda = 0\) and \(\alpha_D \neq 0\)). Plain red curve : reduced noise (output of the fit) with both elastic fluctuations and inelastic effects induced by e-ph interactions. Parameters for the output of the fit (red curves) : Sample (A) : \(\tau = 0.818; \omega_0 = 12.2\) meV; \(\lambda/\Gamma = 0.20; \alpha_D = 12.7\%; \phi_D = 0.85\pi/2; \omega_D = 52.0\) meV. Sample (B) : \(\tau = 0.663; \omega_0 = 8.5\) meV; \(\lambda/\Gamma = 0.37; \alpha_D = 6.0\%; \phi_D = 0.98\pi/2; \omega_D = 50.0\) meV.

But with renormalized dot level position \(\tilde{\omega}_d\) and coupling to the L-lead \(\tilde{\Gamma}_L\)

\[
\tau(\omega) = \frac{4\tilde{\Gamma}_L(\omega)\Gamma_R}{[\omega - \tilde{\omega}_d(\omega)]^2 + [\tilde{\Gamma}_L(\omega) + \Gamma_R]^2} \quad (A.28)
\]

\[
\tilde{\Gamma}_L(\omega) = \Gamma_L\frac{\rho_L(\omega)}{\rho_0} \quad (A.29)
\]

\[
\tilde{\omega}_d(\omega) = \omega_d + \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{d\omega'}{\omega - \omega'} \tilde{\Gamma}_L(\omega') \quad (A.30)
\]
We present on figure A.3 the results obtained for two particular samples (A) and (B), by fitting self-consistently the experimental conductance and reduced noise \( Y(X) \) characteristics.

## A.3.1 Fitting procedure for the conductance curves

We consider the conductance curve of figure (A.3(A)-1), obtained for the sample (A) at temperature 6 K. It is characterized by a zero voltage conductance \( G(V = 0) \approx 0.789 G_0 \). The local vibration mode energy is more difficult to recognize because it is masked by the conductance fluctuations, just as the inelastic shot noise signal. We take it to be given by the first maximum in the second derivative of current with voltage, \( \omega_0 = 12.2 \) meV. We will make use of the minimal model described above, for which the transmission factor is modulated by the position of the molecular level \( \omega_d \) and the energy dependent DoS fluctuations in the L-electrode. For simplicity, we fix the couplings to the contacts to be symmetric \( (\Gamma_L = \Gamma_R = \Gamma/2) \). We are thus left with five parameters in order to fit the experimental data, namely \( \{\omega_d, \alpha_D, \Omega_D, \phi_D, \lambda\} \). Those parameters are neither free to choose nor independent and are imposed by the features of both experimental conductance and noise characteristics.

We first consider the non-interacting model \( (\lambda = 0) \) and fit the behavior of the conductance close to zero voltage by modulating the energy dependence of the transmission factor. We fix the dot level position \( \omega_d \) so that the transmission factor at zero energy \( \tau = \tau(\omega = 0) \) is close to the experimental zero voltage value. We start by choosing an amplitude and period for the oscillations that capture the dominant behavior in the relevant voltage range, \( \Omega_D = 52 \) meV and \( \alpha_D = 9.4\% \). The slope of the conductance curve close to zero voltage then fixes the phase \( \phi_D \) to the value \( \phi_D = 0.65\pi/2 \) (see Black curve of figure (A.3-(A)-1). A similar curve is shown for the sample (B) on figure (A.3-(B)-1).

## A.3.2 Fitting procedure for the noise curves

We consider the noise curve of figure (A.3(A)-2) obtained for the same setting of the junction as in (A)-1. We obtain the zero energy transmission factor \( \tau = 0.818 \) (see the corresponding dashed black curve of figure (A.3(A)-2). When taking into account the energy dependence of the transmission factor \( (\alpha_D = 9.4\% \text{ and } \lambda = 0) \), we then obtain the plain black curve of figure (A.3-(A)-2). We notice that despite the absence of any inelastic effect \( (\lambda = 0) \), the noise is decreased in the voltage region where \( V > \omega_0(X > 12.2) \) compared to the black dashed curve (energy independent transmission factor). We have made conservative estimates of the strength of the DoS fluctuations, which demonstrates clearly that there remains a large difference between the black curve and the experimental blue points of figure (A.3(A)-2),
which we assign to an intrinsic inelastic effect in the noise induced by e-ph interactions.

Finally we quantify the inelastic contribution to the noise by considering the case of non-zero e-ph interaction. The renormalization of the transmission due to the e-ph interactions requires adjusting the value of the molecular level position (maintaining the other parameters fixed) in order to fit the conductance. We obtain the red curve of figure(A.3(A)-2) for a value of the e-ph coupling strength $\lambda/\Gamma = 0.2$ that describes the experimental data well.

A similar curve is shown for the measurement (B) on figure(A.3(B)-2). For this sample, the negative correction to the noise above the threshold is almost entirely due to inelastic effects in the noise induced by e-ph interactions.

**A.3.3 **SELF-CONSISTENCY

The procedure described above for the fitting of conductance and noise characteristics of sample (A) is repeated until self-consistency is achieved, namely all the features due to either conductance fluctuations and inelastic effects are consistent for both $G(V)s$ and $Y(X)s$. The discrepancy between the experimental zero-bias conductance and the fits is a consequence of the limited experimental accuracy (1% in $G(V)$ and $3-4\%$ in $Y(X)$). The final outputs for this fitting procedure are shown on the red curves of figure(A.3(A)-1) and figure(A.3(A)-2) for the following choices of parameters : $\tau = 0.818; \omega_0 = 12.2$ meV; $\lambda/\Gamma = 0.2; \alpha_D = 12.7\%; \phi_D = 0.85\pi/2; \omega_D = 52$ meV.

Similarly the output for the fitting procedure for the other sample (B) are shown by the red curves of figure(A.3(B)-1) and figure(A.3(B)-2) obtained with the following choices of parameters : $\tau = 0.663; \omega_0 = 8.5$ meV; $\lambda/\Gamma = 0.37; \alpha_D = 6\%; \phi_D = 0.98\pi/2; \omega_D = 50$ meV.

To conclude, the analysis of the data for high conductance, close to perfect transmission, is straightforward. For lower transmission, conductance fluctuations mask some of the intrinsic effects and a more involved analysis is required. With the analysis of the measurements (A) and (B) presented in figure(A.3), we show that it is possible to deconvolute the effects of background fluctuations induced by intrinsic disorder from the inelastic signal induced by e-ph interactions. By fitting self-consistently the experimental conductance and noise characteristics, it appears that the inelastic signal, although difficult to see in the conductance curves (masked by the background fluctuations) has a significant contribution (more than 50\% for sample (A) and dominant in the case of sample (B)) to the negative correction to the noise observed above the threshold ($V > \omega_0$).
REFERENCES


THE KONDO EFFECT FOR POINT CONTACTS

B.1 THE KONDO EFFECT

For bulk metals the electrical resistivity at room temperature is dominantly determined by electron-phonon (atomic lattice vibration) interactions. This scattering decreases with the lowering of temperature due to freezing out of phonons. At low temperatures electrons can travel with very little interaction leading to a decrease in the resistance. The resistance value of metals like gold and copper saturates at low temperatures to some value due to interaction of the electrons with lattice imperfections and grain boundaries. The value of the low temperature resistance remains constant on further reduction of the temperature and its value can only be changed by addition or removal of defects in the lattice. This can be seen from the schematic illustration shown in figure (B.1). Apart from this saturation there is a second kind of observation seen in these metals, with the resistance passing through a minimum and increasing upon further reduction of the temperature. This effect was first seen in 1930 in Leiden by de Haas et al. [1] and was explained by Jun Kondo [2] in 1964. The increase in resistance is due to an increase in the effective scattering cross section of magnetic impurities. Magnetic impurities are antiferromagnetically screened by the conduction electrons by forming enveloping electron clouds around them, which leads to an increase in scatterer size. This phenomena is dominant at low temperatures, while at high temperatures electron-phonon interaction dominates which destroys the local magnetic interaction. This is illustrated in figure (B.1).
B.  THE KONDO EFFECT FOR POINT CONTACTS

\[ B.1 \]

\textbf{B.1.1 ANDERSON SINGLE IMPURITY MODEL}

The Anderson single impurity model is the simplest model to describe this many body phenomenon, where localized non-zero spin impurities are antiferromagnetically coupled to a sea of conduction electrons \cite{3, 4}. In the Anderson single impurity model a magnetic impurity is viewed as a localized state with a discrete energy \( \epsilon_d \) occupied by an unpaired electron, and coupled to a spin degenerate electron reservoir, as illustrated in figure (B.2) for a localized state connected between two electron reservoirs. The energy \( \epsilon_d \) lies below the Fermi energy of the electron bath and \( U \) is the Coulomb charging energy for adding a second electron to the localized state. Let us consider the case that \(|\epsilon_d| < U/2\). A finite \( s=1/2 \) spin moment is trapped in the energy state \( \epsilon_d \). The transfer of the electron from \( \epsilon_d \) to either of the leads is classically forbidden without adding energy to the system. However, the uncertainty principle allows the transit of electrons between the leads and the localized state on the time scale \( \tau \sim h/|\epsilon_d| \), where \( h \) is Planck’s

\[ \text{FIGURE B.1: Introduction of the Kondo effect: (a) Bulk metals containing a low concentration of magnetic impurities show an increase in the resistivity with lowering of the temperature. This is due to an increase in the effective scattering size as a result of the formation of an electron screening cloud around the magnetic impurities. (b) At high temperatures, due to a high rate of electron-phonon scattering, the magnetic impurity is not screened and hence the Kondo effect vanishes. (c) At lower temperature the conduction electrons form a screening cloud around the magnetic impurity which leads to an increase in the effective size of the scatterer, giving rise to an increase in the resistance.} \]
constant. This can be written mathematically as:

\[ H_{\text{Anderson}} = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \varepsilon_\sigma d_{\sigma}^\dagger d_\sigma + U n_{d_\uparrow} n_{d_\downarrow} + \sum_{k\sigma} (\nu_{k\sigma} d_{\sigma}^\dagger c_{k\sigma} + \nu^*_{k\sigma} c_{k\sigma}^\dagger d_\sigma), \quad (B.1) \]

where \( c_{k\sigma}^\dagger \) and \( c_{k\sigma} \) in the first term represent creation and annihilation operators for the electrons in the leads with momentum \( k \), spin \( \sigma \) and energy \( \varepsilon_k \). It represents the electrons in the leads. The second term represents the electrons in the localized state \( \varepsilon_d \), i.e. \( d_{\sigma}^\dagger \) and \( d_\sigma \) create and annihilate an electron in the localized state. In the last term \( v \) is the rate of electron transfer from the localized state to the leads. A simplified pictorial representation of the Anderson single impurity model is shown in figure (B.2). For \( U = 0 \) and \( v = 0 \), the Hamiltonian \( H_{\text{Anderson}} = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \varepsilon_\sigma d_{\sigma}^\dagger d_\sigma \). In this case two electrons of opposite spin fill the impurity state \( \epsilon_d \) as shown in figure (B.2a).

For \( U \neq 0 \) and \( v \neq 0 \) the Coulomb interaction leads to a cost in energy \( U \) to transfer a second electron to the discrete energy state \( \varepsilon_d \) due to the electron-electron repulsive interaction, hence \( \varepsilon_d \) can be only singly occupied. The situation turns out to be more complicated in the case when both \( U \neq 0 \) and \( v \neq 0 \). The coupling of the dot, i.e. the localized state, with the leads gives rise to a widening of the discrete energy state to a width \( \Gamma \). This width depends upon the coupling strength \( \nu_k \). As stated above, through the Heisenberg uncertainty principle, electrons from the leads tunnel to \( \epsilon_d \) or tunnel out of \( \epsilon_d \), which is allowed provided the transition time \( \tau \sim \hbar/|\epsilon_d| \) is very short. This virtual process can have two transit paths as shown in figure (B.2c): In the first process an electron from the left lead tunnels to \( \epsilon_d \) giving rise to a virtual double occupancy of the state, and within the time \( \tau \sim \hbar/|\epsilon_d| \) the electron leaves the dot again. This is process 1 in figure (B.2c). In the second process the electron in the localized energy state \( \epsilon_d \) transits out of the dot, leading to the formation of a virtual empty state. Then an electron from the left lead with opposite spin w.r.t. the initial spin state tunnels into the level \( \epsilon_d \). The spin state of the dot changes during this process, giving rise to a spin flip excitation in the dot. This is process 2 in figure (B.2c). These two virtual processes are dominant at low temperatures and give rise to a resonant feature in the conductance at zero bias. At higher temperatures, the virtual condensate state is not able to form due to dominant electron-phonon and electron-electron interactions and hence this feature is smeared out.

Using the Schrieffer-Wolff unitary transformation and considering terms up to second order in \( \nu_k \) only, \( H_{\text{Anderson}} \) can be simplified to the Kondo Hamiltonian \( H_{\text{Kondo}} \) where the interaction takes the form of a net spin-spin interaction [2, 5],

\[ H_{\text{Kondo}} = H_{\text{cond}} + H_{\text{int}} \quad (B.2) \]

where the first term \( H_{\text{cond}} \) defines the conduction electrons and the second term
\textbf{B. The Kondo Effect for Point Contacts}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure-B.2.png}
\caption{Anderson single impurity model: (a) In the absence of Coulomb interaction \((U = 0)\) and in absence of coupling between the dot and reservoir \((\nu = 0)\) the dot can host a pair of electrons of opposite spins. (b) When only Coulomb interaction \((U \neq 0, \nu = 0)\) is switched on, addition of a second electron on the dot costs an additional amount of energy \(U\), which puts the electron on the next available energy state \(\epsilon_d + U\). (c) When both interactions are switched on \((U \neq 0, \nu \neq 0)\) at low temperatures the electrons from the leads form an entangled state with the electron in the dot. Classically, the electron on the dot cannot tunnel to the leads without supplying an external amount of energy. But Heisenberg’s uncertainty principle allows the electron in the dot to tunnel out of the lead provided an electron from the leads tunnels into the dot within the \(\tau \sim h/|\epsilon_d|\) where \(h\) is Planck’s constant. This permits transport of an electron through the dot (either by process 1 or 2) producing an entanglement of the spins in the lead with the local spin. This leads to the Kondo resonance seen as a zero bias anomaly in the conductance.}
\end{figure}

\(H_{\text{int}}\) defines the interaction of the conduction electrons with the localized magnetic moment. This interaction is antiferromagnetic in nature \([3, 5]\) and is given as,

\[
H_{\text{int}} = J s_{\text{cond}} \cdot S
\quad (B.3)
\]

where \(S\) is the spin of the localized state, \(s_{\text{cond}}\) is the local spin density of the conduction electrons and \(J\) represents the spin- spin interaction. This antiferromag-
netic interaction leads to the formation of a singlet state with net total spin 0. This singlet state \( \frac{1}{2} (|↑↓⟩ - |↓↑⟩) \) is formed between the local moment and many electrons from the conduction states of the leads. The conduction electrons collectively form a spin state \(|↑⟩\) that shields the \( S = \frac{1}{2} \) state of the electron in the localized state. The characteristic energy scale of the singlet state is given by the Haldane relation,

\[
k_B T_K = \frac{\sqrt{\Gamma U}}{2} e^{-\pi \epsilon_d (\epsilon_d + U)/\Gamma U},
\]

where \( \Gamma \) is the width of the discrete energy state due to coupling to the leads. \( T_K \) is the Kondo temperature, which sets the scale below which Kondo phenomena become dominant [6]. \( k_B T_K \) is the binding energy for the singlet state, illustrated in figure (B.1). We see that the Kondo temperature \( T_K \) is exponentially dependent upon \( \Gamma \) i.e. on the coupling strength of the lead to the dot. At higher temperatures transitions to higher energy states become possible and the screening of the impurity state is partially broken, leading to a decrease in the resonance at the Fermi energy. For higher temperatures a renormalization group analysis is needed to describe the conductance across the localized level, which can be approximated by [7],

\[
G(T, V = 0) = \frac{G_0}{(1 + (2^{1/s} - 1)(T/T_K)^2)^s} + G_b,
\]

where \( G_b \) is a background conductance due to parallel transmission paths, \( s = 0.22 \) for a spin-\( \frac{1}{2} \) local state, and \( G_0 \) is the peak conductance of the system at \( V = 0V \) with \( G_b \) subtracted. This equation defines the Lorentzian-like decay of the zero bias Kondo resonance with increasing temperature and the width of the Lorentzian at \( G = G(T, 0)/2 \) gives a measure of the Kondo temperature. For very low temperatures the zero bias resonance in conductance approaches a constant and it decreases approximately logarithmically with increase of temperature. This is a property that is generally associated as a hallmark for Kondo systems.

### B.1.2 Kondo-Fano resonance

The Kondo effect for a bulk metal host-impurity system results in an increase in the resistance at low temperatures due to an increase in the effective scattering size. In contrast, in reduced dimensions for transmission through a localized state the Kondo effect leads to forward scattering of the conduction electrons. This is seen as an increase in the conductance at zero bias and in the differential conductance it shows as a Lorentzian peak. However, parallel transmission of conduction electrons is often possible and this gives rise to interference between the Kondo processes and the non-Kondo processes. This produces a so-called Fano resonance, a 's'-like line shape near zero bias. This can be understood from a simple tight binding approach as shown in figure (B.4). The Fano model was originally proposed by
U. Fano et al. [8] to understand the asymmetries in excitation spectra observed in He. The model describes the interaction of one discrete energy level with two or more continua of states. The coupling between the discrete energy state and the continuum give rise to different resonating features. The width and height of the resonance depends upon the coupling parameter.

The general form of the Fano lineshape in conductance can be written as [8–10],

$$G_{ac} = G_{off} + \frac{A(q + \epsilon)^2}{1 + \epsilon^2} \frac{1}{1 + q^2}$$  \hspace{1cm} (B.6)

where $A$ is the amplitude of the Kondo resonance, $\epsilon = \frac{eV - \epsilon_d}{k_B T}$ and $\epsilon_d$ is center of the Kondo many body resonance. A peak is found for $q \sim \infty$, a dip for $q = 0$, and a pure ‘$s$’ shape for $q = -1$ and $q = 1$. Despite the complex line shape of the resonance in the conductance the height of the resonance has a universal logarithmic dependence upon the temperature.

### B.1.3 PEAK SPLITTING AND SIDE PEAKS

The singlet state can be broken using a magnetic field. Application of a magnetic field lifts the degeneracy of the singlet state and splits the local moment in spin up and spin down states proportional to the applied magnetic field. This leads to
a splitting and suppression of the zero bias anomaly in the differential conductance. The expected splitting in the peak is proportional to twice the Zeeman energy for the applied field, \( \Delta E_B = |g|\mu_B B \). Here, \( \mu_B \) is the Bohr magneton and \( |g| \) is the material dependent gyromagnetic constant [11]. Hence, one could expect peaks in the conductance at bias voltages \( eV = \pm \Delta E_B \). The Kondo peak is only expected to be split for fields larger than the Kondo energy due to screening of the \( s = 1/2 \) magnetic impurity by the conduction electrons [12]. Experimental observations by Zumbuhl et al. [13] and Amasha et al. [14] show splitting in the zero bias resonance peak larger than twice the Zeeman energy. The splitting of the peaks decreases with increasing temperature in qualitative agreement with theory proposed by Costi et al., but quantitatively the decrease in the splitting is larger than expected from the theory. This disagreement could be related to the exchange energy due to interaction between the localized spin impurity and other magnetic impurities in the leads, which was not accounted for in the calculations.
Low lying vibrational modes in combination with Kondo scattering is expected to give symmetric satellite peaks to the zero-bias peak. Inelastic electron scattering on vibration modes is a single-electron effect. For low transmission inelastic scattering opens up a new conductance channel at high bias, leading to an increase in the conductance; for high transmission it leads to backscattering above the threshold for vibration excitation. This is seen as a step-up or a step-down in the differential conductance, respectively [15]. A similar effect is possible in a system where electrons tunnel from one lead to other through a localized magnetic state. Studies on inelastic co-tunneling through localized spin states in magnetic ad-atoms, metal complex molecules, stacked molecular complexes, and carbon nanotubes can be found in Refs. [16–19]. It has been predicted that the coupling of the vibrational states with the magnetic state will give rise to resonance like structures at the vibrational energy of the system [20]. The origin of these satellite peaks in a Kondo system is illustrated in figure (B.5).

Electron transport through a localized magnetic system in the presence of inelastic scattering can be viewed as the sum of elastic and inelastic scattering through the Kondo state. The condition for inelastic scattering is that the bias window should be large enough for electrons to interact with the vibronic state. The elastic scattering gives the background conductance of the system without signature at the vibronic energy. The inelastic scattering in absence of spin interaction gives rise to a step in the differential conductance. In a Kondo system the inelastic excited state together with the localized spin states of the magnetic impurity gives the resonance structures. This can be seen in figure (B.5 d), which shows the spectral function $A(\omega)$ of the magnetic impurity state based on calculations by Korytar et al. The resonance peaks in the differential conductance at the vibronic energy is another signature of the Kondo physics.
Figure B.5: Inelastic Kondo features: (a) A zero-bias Kondo resonance results from the coupling of a continuum electron cloud with a localized spin state. (c) The single particle inelastic electron scattering at high bias in absence of any spin interaction of the electrons with the localized spin state. (b) The many-body inelastic spin interaction due to opening of a new inelastic channel at high bias. (d) The projected density states on the localized spin state i.e. the spectral function \( A \equiv \text{r.t.} \) bias voltage. The elastic scattering gives the background conduction without any prominent feature at the inelastic threshold (red dashed curve). In absence of any interaction with localized spin states the inelastic scattering of the electron gives a step feature at \( \hbar \omega \) (green curve). The black curve shows prominent peaks at the inelastic energy \( \pm \hbar \omega \). The spectral function also shows a zero bias anomaly due to scattering through the singlet ground state (taken from [20]).

References


