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Coulomb singularity effects in tunnelling spectroscopy of individual impurities

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Non-equilibrium Coulomb effects in resonant tunnelling through deep impurity states are analyzed. It is shown that Coulomb vertex corrections to the tunnelling transfer amplitude lead to power law singularity in current-voltage characteristics.

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Localized states of individual impurity atoms and interacting impurity clusters can play the key role in tunnelling processes in small size junctions and often determine the behavior of tunnelling characteristics in STM/STS contacts. Now it is evident that in tunnelling junctions of nanometer scale there exists non-equilibrium distribution of tunnelling electrons which changes local density of states and tunnelling conductivity spectra. Some interesting effects, such as resonance structure of tunnelling conductivity inside semiconductor band gap, increased value of observed band gap and non-equilibrium interaction of neighboring impurity atoms have been recently investigated experimentally and theoretically analyzed [1 – 4]. But all these effects are caused by local changes of the initial density of states in the contact area due to interactions of non-equilibrium particles. The modification of tunnelling amplitude by the Coulomb interaction of conduction electrons in metallic tip with non-equilibrium localized charges was ignored. It is shown in the present paper that corrections to the tunnelling vertex caused by the Coulomb potential can also result in nontrivial behavior of tunnelling characteristics and should be taken into account. One encounters with effects similar to the Mahan edge singularities in the problem of X-ray absorption spectra in metals [5]. The effect is well pronounced if tunnelling rate from a deep impurity level to metallic tip γ_t is much larger than relaxation rate γ of non-equilibrium electron distribution at localized state. This condition can be realized experimentally for a deep impurity state in the semiconductor gap. Direct tunnelling from such states to semiconductor continuum states is strongly reduced due to wide barrier formed by surface band bending. Relaxation rate connected with electron-phonon interaction can be estimated to be of the order $10^8 - 10^{10}\,1/\mathrm{s}$ at low temperatures [6]. As to γ_t – it is parameter, which can be varied in STM/STS experiments changing tip-sample separation. Since tip-sample separation is comparable with atomic scale, γ_t often exceeds the relaxation rate for deep impurity states. Typical experimental value of tunnelling current 1 nA corresponds to $\gamma_t \simeq 10^{11} - 10^{12}\,1/\mathrm{s}$ [3]. As it will be shown below for $\gamma_t \gg \gamma$ the impurity level becomes nearly empty when the value of applied bias voltage approaches the impurity energy. So the core hole Coulomb potential is suddenly switched on and the tunnelling amplitude is changed. One might expect in this situation a power-law singularity in current-voltage characteristics near the threshold voltage.

The system semiconductor – impurity state – metallic tip can be described by the Hamiltonian $\hat{H}$:

$$\hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_{\mathrm{imp}} + \hat{H}_T + \hat{H}_{\mathrm{int}} \qquad (1)$$

where:

$$\begin{aligned} \hat{H}_R &= \sum_{k\sigma} (\varepsilon_k - \mu) c^+_{k\sigma} c_{k\sigma}, \\ \hat{H}_L &= \sum_{p\sigma} (\varepsilon_p - \mu - eV) c^+_{p\sigma} c_{p\sigma} \end{aligned} \qquad (2)$$

describes the electron states in the metallic tip and the semiconductor correspondingly, $c^+_{k\sigma}(c_{k\sigma})$ and $c^+_{p\sigma}(c_{p\sigma})$ describe creation (annihilation) of electron in states $(k\sigma)$ and $(p\sigma)$ in each bank of the contact.

$$\hat{H}_{\mathrm{imp}} = \sum_{d\sigma} \varepsilon_d c^+_{d\sigma} c_{d\sigma} + U n_{d\sigma} n_{d-\sigma} \qquad (3)$$

corresponds to a localized impurity state. We consider "one electron neutral impurity" – the impurity level is single occupied at zero applied voltage due to the on-site Coulomb interaction. But in the case of large tunnelling rate to the metallic tip the on-site Coulomb repulsion of localized electrons can be omitted, if we analyze the

behavior of tunnelling current at applied voltage close to the impurity energy ε_d. Because in this situation the impurity state becomes nearly empty above the threshold value of the applied bias. Let us also point out, that the Kondo regime is destroyed on Anderson impurity for the values of applied bias near the threshold [7, 8]. In this case the Kondo-effect is not responsible for any unusual features of the tunnelling characteristics .

Tunnelling transitions from the impurity state to the semiconductor and the metal are described by the part:

$$\hat{H}_T = \sum_{kp} (T_{kd} c^+_{k\sigma} c_{d\sigma} + T_{pd} c^+_{p\sigma} c_{d\sigma}) + \text{h.c.} \qquad (4)$$

And, finally, part H_{int} includes the Coulomb interaction of the core (impurity) hole with conduction electrons in the metal.

$$\hat{H}_{\text{int}} = \sum_{kk'\sigma\sigma'} W_{kk'} c^+_{k\sigma} c_{k'\sigma} (1 - c^+_{d\sigma'} c_{d\sigma'}). \qquad (5)$$

Hamiltonian H_{int} appears as many particle interaction and describes rearrangement of conduction electrons in the potential of the hole, suddenly switched on by tunnelling transition of the impurity electron. Since we are far from the Kondo regime it is sufficient to consider tunnelling current in the lowest order in the tunnelling amplitude T_{kd}. Scattering by the impurity hole Coulomb potential does not change electron spin. Thus in the lowest order in T_{kd} we can consider renormalization of the tunnelling amplitude independently for each spin – the same one for conduction and impurity electrons. It is also reasonable to use for simlicity an averaged value of screened Coulomb interaction describing s – wave scattering of conduction electrons by a deep hole $W_{kk'} = W$.

Edge singularities in the tunnelling current can be analyzed by means of diagram technique for non-equilibrium processes. Using Keldysh functions $G^<$ the tunnelling current can be determined as (we set charge $e = 1$):

$$I(V) = \text{Im}(J(V)), \qquad J(V) = i \sum_{k,\sigma} \int d\omega T_{kd} G^{\sigma <}_{kd} \qquad (6)$$

where we have defined tunnelling "response function" $J(V)$. If the Coulomb interaction is neglected one can obtain the usual expression for this response function in the lowest order in T_{kd}:

$$J^0(V) = i \sum_{k,\sigma} \int d\omega T^2_{kd} (G^{\sigma <}_{kk} G^{\sigma A}_{dd} + G^{\sigma R}_{kk} G^{\sigma <}_{dd}). \qquad (7)$$

Substituting the correspondent expressions for the Keldysh functions [4] and performing integration over k we get:

$$J^0(V) = \gamma_t \int d\omega \left[\frac{n^0_k(\omega)}{\omega + eV - \varepsilon_d + i(\gamma + \gamma_t)} + \right.$$

$$\left. + \frac{n_d(\omega)(-i(\gamma + \gamma_t))}{(\omega + eV - \varepsilon_d)^2 + (\gamma + \gamma_t)^2} \right] \qquad (8)$$

where the tunnelling rate $\gamma_t = T^2_{kd}\nu$, and ν is unperturbed density of states in the metallic tip. Kinetic parameter γ corresponds to relaxation rate of electron distribution at the localized state. In the suggested microscopic picture (Eq.(4)) this relaxation rate is determined by small enough electron tunnelling transitions from the impurity to the semiconductor continuum states $\gamma = T^2_{pd}\nu_p$. (In general γ can include different types of relaxation processes.)

Non-equilibrium impurity filling numbers $n_d(\omega)$ are determined from kinetic equations for the Keldysh functions $G^<$:

$$n_d(\omega) = \frac{\gamma n^0_p(\omega) + \gamma_t n^0_k(\omega)}{\gamma + \gamma_t}. \qquad (9)$$

As it was explained in the introduction for a deep impurity level the relation $\gamma_t \gg \gamma$ is quite possible. Then $n^0_p(\varepsilon_d) = 1$, while $n_d(\varepsilon_d) \ll 1$ and there is really a core hole in the impurity state. Thus for low temperatures one can obtain from Eq.(8):

$$J^0(V) = \gamma_t \ln(|X|) + i \frac{\gamma_t \gamma}{\gamma + \gamma_t} \times$$

$$\times \left[\text{arcctg}\left(\frac{eV - \varepsilon_d}{\gamma + \gamma_t} \right) - \text{arcctg}\left(\frac{-\varepsilon_d}{\gamma + \gamma_t} \right) \right] \qquad (10)$$

where

$$X = (eV - \varepsilon_d + i(\gamma + \gamma_t))/D) \qquad (11)$$

and D is the band width for electrons in metal.

The usual form of the tunnelling current is of course reproduced from Eqs.(6), (8), (10).

Now let us consider renormalization of the tunnelling amplitude and vertex corrections to the tunnelling current caused by the Coulomb interaction between the impurity core hole and electrons in the metal. Many particle picture strongly differs from the single-particle one near the threshold voltage. First order corrections due to the Coulomb interaction (the first graph in Fig.1a) has logarithmic divergency at the threshold voltage $eV = \varepsilon_d$, which is cut off by the finite relaxation and tunnelling rates.

$$J^1(V) = \qquad (12)$$

$$= i \sum_{k,\sigma} \int d\omega T_{kd} (-G^{\sigma <}_{kk} G^{\sigma A}_{dd} T^{1++}_{kd} + G^{\sigma R}_{kk} G^{\sigma <}_{dd} T^{1--}_{kd}).$$

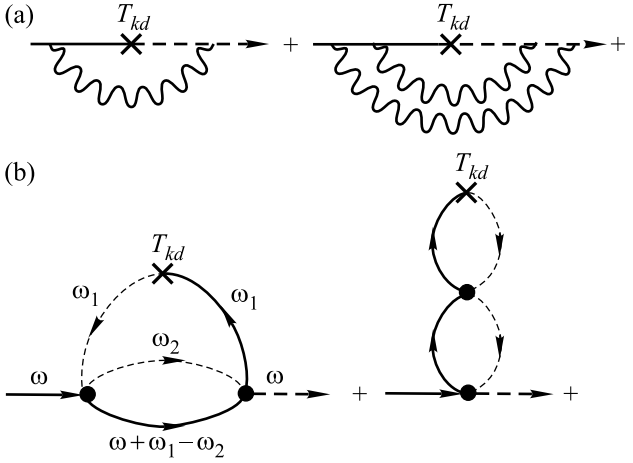

Fig.1. Coulomb corrections to T_{kd}. Solid lines represent G_k and dashed lines – G_d. (a) Ladder approximation, (b) Parquet graphs (Coulomb wavy lines are overdrawn as black circle vertexes)

Tunnelling matrix elements are changed by the Coulomb interaction:

$$T_{kd}^{1--} = \sum_{k,\sigma} \int d\omega T_{kd} W (G_{kk}^{\sigma <} G_{dd}^{\sigma A} + G_{kk}^{\sigma R} G_{dd}^{\sigma <}). \quad (13)$$

If we look at Eqs. (7), (8), it becomes clear, that logarithmic contribution comes from the first combination of the Green functions: $G_{kk}^{\sigma <} G_{dd}^{\sigma A}$. In what follows we retain only logarithmically large parts, assuming that $|\ln((\gamma+\gamma_t))/D)| \gg 1$, so only these combinations of the Green functions are the most important in perturbation series. Then from (13) we obtain that tunnelling amplitude contains logarithmic correction: $T_{kd}^{1--} = -T_{kd} L$, $T_{kd}^{1++} = -T_{kd}^{1--}$, where factor L:

$$L = (W\nu) \ln(X) \quad (14)$$

In high orders of perturbation expansion ladder graphs (Fig.1a) are the simplest "maximally singular" graphs. But this is not the only relevant kind of graphs. If we look at the first graph in Fig.1b, we notice, that a new type of "bubble" appears, which is logarithmically large for small "total" energy $(\omega + \omega_1)$. The important point is that relevant region of integration over ω and ω_1 is region of small ω. It is just this region which gives essential contribution to logarithmic factor L in any other pair of $G_{kk}^{<} G_{dd}^{A(R)}$.

It means that the central bubble also contributes an additional logarithmic factor to the total result. In this situation, which is not new in physics, one should retain in the n-th order of perturbation expansion the most divergent terms proportional to $(W\nu)^n L^{n+1}$. For the first time such method was developed by Dyatlov et al. [9]. It was shown that for a proper treatment of this problem one should write down integral equations for the so-called parquet graphs (Fig.1b), which are constructed by successive substitution the simple Coulomb vertex for the two types of bubbles in perturbation series. These equations represent some extension of the ordinary Bethe-Salpeter equation and describe multiple scattering of conduction electrons by the core hole Coulomb potential in the two "most singular" channels. The integral equations can be solved with logarithmic accuracy, as it was done, for example, by Nozieres [10, 11] for edge singularities in X-ray absorption spectra in metals.

The solution of the "parquet" equations contains nothing new in our problem. So we present the result without getting into technical details. Summing up the most divergent graphs with logarithmic accuracy one can obtain the following singular part of the response function [10]:

$$J(V) = \frac{\gamma_t (1 - \exp(-2L))}{2W\nu}. \quad (15)$$

Then the tunnelling current near the threshold voltage can be expressed as:

$$I(V) = \frac{\gamma_t}{2W\nu} \left[\frac{D^2}{(eV - \varepsilon_d)^2 + (\gamma_t + \gamma)^2} \right]^{W\nu} \sin(2W\nu\phi) \quad (16)$$

where $\phi = \mathrm{arcctg}((eV - \varepsilon_d)/(\gamma + \gamma_t))$. If we consider a deep impurity state in the gap of the semiconductor (below the Fermi level) and positive tip bias voltage, then: $\varepsilon_d < 0, eV < 0$. So, the phase ϕ is a step-like function varying approximatly from 0 to π, when the applied bias crosses the threshold $eV = \varepsilon_d$. Since we retain only the most logarithmically large terms in the tunnelling current, Eq.(16) is valid only if $|eV - \varepsilon_d| \ll D$. In the absence of the Coulomb interaction ($W = 0$) this singular part reduces to the usual first order contribution arising from the first term in Eqs.(7), (8).

In summary, if the tunnelling rate to the metallic tip exceeds the relaxation rate of localized electrons, the Coulomb interaction of the core hole and the conduction electrons in the metal strongly modifies the tunnelling transition amplitude and leads to: i)non-monotonic behavior of current voltage characteristics; ii)power-law singularity of the tunnelling current and conductivity when the value of the applied voltage approaches the impurity level energy; iii) current voltage characteristics can be rather asymmetric, because of different dependence of the phase factor ϕ on the applied bias below and above the threshold value. Power law singular behavior of the tunnelling current is sensitive to the values

of the tunnelling and relaxation rates, as well as to the value of the Coulomb interaction W. So, different exponents in power dependencies of the tunnelling current on the applied voltage can appear with changing tip-sample separation. Some current-voltage characteristics obtained for typical values of parameters are shown in Fig.2.

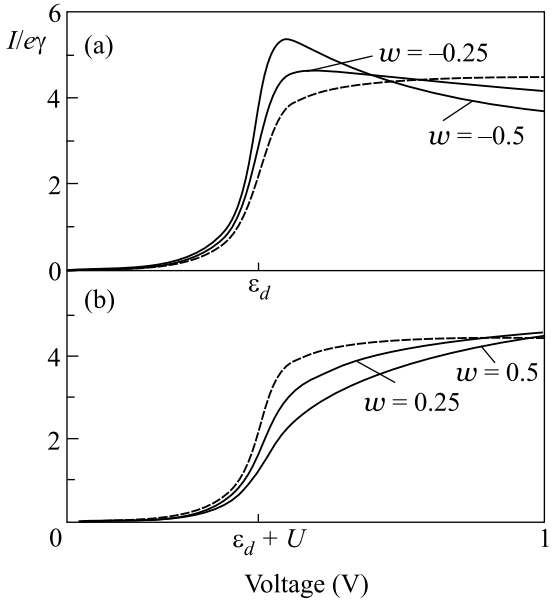

Fig.2. Current-voltage curves for typical values of dimensionless Coulomb and kinetic parameters. Current is measured in dimensionless units $I/e\gamma$. (a) $w = W\nu < 0$, $\varepsilon_d = 0.4$ eV, (b) $w = W\nu > 0$, $\varepsilon_d + U = 0.4$ eV, $\gamma_t/\gamma = 3$, $\varepsilon_d/\gamma = 40$. Dashed lines correspond to $W = 0$. Experimental STM image of Cr impurity on InAs (110) surface is shown in the inset for $V = 0$, $V = 0.5$(V), $V = 1.5$(V) in sequence.

It seems also possible to set up an experiment with negative impurity charge and negative tip voltage close to the value $\varepsilon_d + U$. In this case $W > 0$, and the Coulomb corrections to the tunnelling amplitude result in power-low behavior of the tunnelling current with the opposite sign exponent in Eq.(16). The tunnelling current is suppressed near the threshold, compared to the noninteracting case. This behavior is shown in Fig.2b.

Experimental STM/STS investigations of deep impurity levels on semiconductor surfaces give evidence of the existence of the described effects. Some STM images demonstrate non-monotonic dependence of tunnelling current on applied bias voltage [1]. With increasing of bias voltage impurity atom is "switched on" in STM image – appears as a bright spot. But further increase of the tunnelling bias "extinguishes" the brightness of the impurity atom and it is seen as a dark spot in the STM image (see inset in Fig.2). According to the present model it can be explained by decrease of the tunnelling current caused by the Coulomb vertex corrections to the tunnelling amplitude for some types of impurities.

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