Phonon-assisted and magnetic field induced Kondo tunneling in single molecular devices

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Abstract. We consider the Kondo tunneling induced by multiphonon emission/absorption processes in magnetic molecular complexes with low-energy singlet-triplet spin gap and show that the number of assisting phonons may be changed by varying the Zeeman splitting of excited triplet state. As a result, the structure of multiphonon Kondo resonances may be scanned by means of magnetic field tuning.

Single electron tunneling through molecular bridges in nanodevices is inevitably accompanied by excitation of vibrational modes. Vibration-assisted processes usually manifest themselves in tunneling through nanodevices as phonon satellites, which arise around main resonance peaks (see, e.g., [1] and references therein). However, phonon assistance may *induce* resonance peak due to interplay with magnetic degrees of freedom in transition metal-organic complexes (TMOC). Appearance of Kondo-type zero bias anomaly in tunneling through TMOC was predicted recently [2]. In this paper we consider multiphonon processes in Kondo tunneling in presence of magnetic field. We discuss the fine tuning effect of magnetic field on the Kondo tunneling induced by multiphonon processes in a situation, where the ground state of TMOC with even occupation is a spin singlet. In this case the Kondo resonance in tunneling arises when the phonon emission compensates the gap between one of projections of the excited high-spin and the ground zero spin state of TMOC. Then the Kondo-like effect arises due to singlet/triplet transitions, which can be treated as effective spin-flip processes [3].

Phonon-assisted electron tunneling through TMOC as well as tunneling through other nanoobjects (quantum dots, nanotubes, ets) is described within a framework of Anderson model supplemented with the terms describing vibrational degrees of freedom and their interaction with electron subsystem [1, 2, 4]

$$H = H_d + H_l + H_{tun} + H_{vib} + H_{e-vib} \ . \quad (1)$$

Here H_d stands for the electrons in the $3d$-shell of TMOC. It includes strong Coulomb and exchange interaction, which predetermine the spin quantum numbers of the corresponding electron configuration $3d^n$ (n is even)), H_l contains electrons in the metallic leads playing role of source (s) and drain (d) in the electric circuit, H_{tun} is responsible for electron tunneling between TMOC and leads, H_{vib} describes vibrational degrees of freedom in TMOC, and the interaction between electronic and vibrational subsystems is given by the last term H_{e-vib}. Following the approach developed in [1, 2] we choose the phonon-assisted tunneling as a source of this interaction and represent vibrational subsystem by a single Einstein mode Ω. Then three last terms in (1) are written as

$$H_{vib} + H_{tun} + H_{e-vib} = \hbar\Omega b^\dagger b + \sum_{ak\sigma}\left(te^{-\lambda(b^\dagger - b)}c^\dagger_{ak\sigma}d_\sigma + \text{H.c.}\right). \quad (2)$$

Here the operators b stand for phonons, $c_{ka\sigma}, d_\sigma$ describe electrons in the leads $a = s, d$ and the d-shell of TM ion, respectively, λ is the electron-phonon coupling constant. When deriving (2) we assumed that the coupling is strong enough, so that multiphonon processes are treated exactly by means of the Lang-Firsov canonical transformation (cf. [1]). Another canonical transformation of Schrieffer-Wolff (SW) type [6] excludes H_{tun} from the Hamiltonian (1) and maps it on an effective Hilbert subspace with fixed (even) number of electrons, singlet ground state and low-lying triplet excited state of TMOC. The effective SW-like Hamiltonian is

$$H_{eff} = \frac{1}{2}\Delta\mathbf{S}^2 + hS_z + H_l + \hat{J}_T\mathbf{S}\cdot\mathbf{s} + \hat{J}_R\mathbf{R}\cdot\mathbf{s} + H_{vib} \quad (3)$$

(see [2, 5]). Here H_d [the first two terms in (3)] is represented only by spin degrees of freedom, $\Delta = E_T - E_S$ is the energy of singlet-triplet (S-T) transition, $\mathbf{S}, S_z$ is the spin operator and its z-projection, $h = \mu_B gB$ is the parameter of Zeeman splitting in external magnetic field B. The electron spin operator is given by the conventional expansion $\mathbf{s} = \frac{1}{2}\sum_{kk'}\sum_{\sigma\sigma'} c^\dagger_{k\sigma}\boldsymbol{\tau}_{\sigma\sigma'}c_{k'\sigma'}$ where $\boldsymbol{\tau}$ is the Pauli vector. Unlike the conventional SW Hamiltonian, our Hamiltonian (3) contains one more vector $\mathbf{R}$, which describes three components of S-T transitions [5]. This vector will be specified below. The electron-phonon interaction is now built into the effective exchange constants $\hat{J}_T = t^2e^{-2\lambda(b^\dagger - b)}/\delta E_T$ and $\hat{J}_R = t^2e^{-2\lambda(b^\dagger - b)}/\delta E_S$. Here δE_T, δE_S are the energies of addition of an electron from the leads to the TM ion in a triplet and singlet states, respectively.

The essence of the mechanism of phonon-assisted Kondo cotunneling as it was formulated in Ref. [2], is that the spin excitation energy gap Δ which quenches the conventional Kondo effect in a nanoobject with even occupation, may be compensated by the energy of virtual phonon emission/absorption processes. As a result the zero bias anomaly (ZBA) arises in tunnel conductance in spite of the zero spin ground state of the nanoparticle. This mechanism implies fine tuning $|\hbar\Omega - \Delta| < E_K$, where E_K is the characteristic Kondo energy, which is rather restricttive condition. To make situation more flexible, we address here to the case of strong

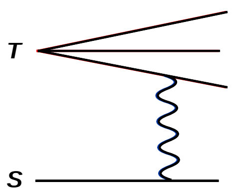

Figure 1. Single phonon connects singlet with spin 1 projection of triplet.

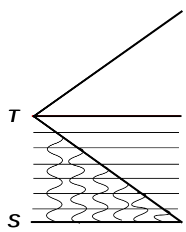

Figure 2. n-phonon processes connect singlet with spin 1 projection of triplet ($n\hbar\Omega < \Delta$).

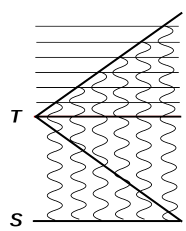

Figure 3. $(n+m)$-phonon processes connect singlet with spin $\bar{1}$ projection of triplet ($(n+1)\hbar\Omega > \Delta$).

electron-phonon interaction and apply magnetic field as an additional tuning instrument. The main ideas are illustrated by Figs. 1-3. The Zeeman term in the Hamiltonian (3) is responsible of splitting of the triplet state $|T_\mu\rangle$ into 3 components with spin projections $\mu = 1, 0, \bar{1}$. If the condition $\Delta - \hbar\Omega - h < E_K$ is satisfied (Fig. 1), then the states $|S\rangle, |T_1\rangle$ form effective vector operator $\mathbf{R}$ with components $R^+ = \sqrt{2}|T_1\rangle\langle S|$, $R^- = \sqrt{2}|S\rangle\langle T_1|$, $R_z = |T_1\rangle\langle T_1| - |S\rangle\langle S|$, which acts effectively as a spin 1/2 operator and enters the SW Hamiltonian (3) (see [3, 5] for further details). The term $\hat{J}_R\mathbf{R}\cdot\mathbf{s}$ is responsible for Kondo-type resonance tunneling in accordance with the mechanism proposed in [2] for zero magnetic field, where all three components of spin $S = 1$ are involved. If the resonance condition is fulfilled for n-phonon processes, $\Delta - h - n\hbar\Omega < E_K$, then the Kondo tunneling is assisted by virtual excitation of n-phonon "cloud" (Fig. 2). If the condition $\Delta + h - (n+m)\hbar\Omega < E_K$ is valid, then the opposite spin projection $|T_{\bar{1}}\rangle$ is involved in Kondo tunneling, and the vector $\mathbf{R}$ has the components $R^+ = \sqrt{2}|S\rangle\langle T_{\bar{1}}|$, $R^- = \sqrt{2}|T_{\bar{1}}\rangle\langle S|$, $R_z = |S\rangle\langle S| - |T_1\rangle\langle T_{\bar{1}}|$.

To find the contribution of phonon-assisted processes in Kondo tunneling, one should calculate the exchange vertex γ_h, which renormalizes the bare vertex $\hat{J}_R$ due to phonon emission/absorption processes and logarithmically divergent parquet insertions. This dressed vertex is shown in Fig. 4. To use the Feynman diagrammatic technique, the spin operators are represented via effective spin-fermion operators [6].

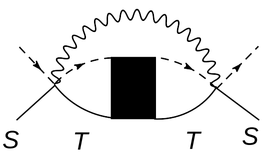

Figure 4. Phonon and parquet corrections to the vertex γ_B. Solid and dashed lines denote spin-fermion and conduction electron propagators, all parquet series are incorporated in the insertion shown by the square box. The multiphonon propagator is shown by the wavy line.

The wavy line corresponds to a single-phonon propagator in the case shown in Fig. 1. Then the straightforward calculation similar to that presented in [2] gives for the corresponding vertex

$$\gamma_h(\Omega) \sim \left[\frac{\rho J_R^2 \log\left(\dfrac{D}{\max[k_BT, h, |\Delta - \hbar\Omega - h|]}\right)}{1 - (\rho J_R)^2 \log^2\left(\dfrac{D}{\max[k_BT, h, |\Delta - \hbar\Omega - h|]}\right)}\right]. \qquad (4)$$

Here T is the temperature, D is the effective width of the electron conduction band and ρ is the density of states on the Fermi level. The tunnel transparency $\mathcal{T}$ is proportional to γ_h^2, and it is seen from (4), that the Kondo peak arises as a ZBA in $\mathcal{T}$, provided $|\Delta - \hbar\Omega - h| \sim E_K \gg B$. If the multiphonon processes are involved in accordance with Fig. 2, then the wavy line in the diagram for γ_h corresponds to the multiphonon propagator [7] weighted with Pekarian distribution, and the vertex function transforms into a sum of phonon satellites

$$\gamma_h = \sum_n e^{-S}\frac{S^n}{n!}\gamma_h(n\Omega). \qquad (5)$$

Here $S = \nu/\hbar\Omega$ is the Huang-Rhys factor and $\nu = \lambda^2/\hbar\Omega$ is the polaron shift. This equation is valid at $kT < \hbar\Omega$ and $\nu > \rho t^2$, otherwise the satellites smear into a single hump around the maximum of Pekarian distribution. Since $\hbar\Omega \gg E_K$, only one phonon replica satisfying the condition $|\Delta - h - n\hbar\Omega| \sim E_K$ survive at *given* magnetic field B . This means that changing B one may "scan" the Pekarian function in a certain interval. In case illustrated in Fig. 3 second system of satellites arises with Kondo peaks satisfying condition $|\Delta + h - (n+m)\hbar\Omega| \sim E_K$.

Since phonon-assisted Kondo tunneling is essentially non-equilibrium process, one should estimate the contribution of decoherence and dephasing effects. Similar problem was discussed in [8, 9] for a situation where the gap Δ is compensated by finite source-drain bias. To evaluate these

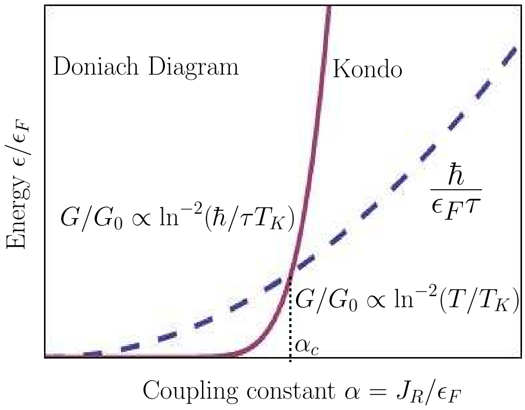

Figure 5. Phase diagram illustrating the competition between Kondo temperature and relaxation damping. Solid line stands for characteristic Kondo energy. Dashed line corresponds to the damping parameter. The phonon-assisted Kondo tunneling is effective for $\alpha > \alpha_c$, where $\alpha_c \sim 10^{-2}$ for TMOC coupled with metallic leads. G/G_0 is ehnancement factor for ZBA in tunnel conductance.

effects, one should calculate the damping of S-T excitation (imaginary part of the corresponding self energy stemming from the vertex part shown in Fig. 4). Performing calculations in analogy with [8], one gets for the lifetime τ the estimate $\hbar/\tau \sim (\rho J_R)^2\Omega$. This damping should be compared with the Kondo energy extracted from (4), $E_K \sim \epsilon_F \exp(-1/\rho J_R)$. The competition between two quantities reminds that between the indirect exchange $I_{in} \sim \rho J_R^2$ and the Kondo energy in the Doniach diagram for Kondo lattices [6]. However, unlike the Doniach dichotomy, in our case E_K dominates in the most part of the phase space because $\hbar/\tau$ contains small parameter $\Omega/D \ll 1$ comparing to I_{in} (see Fig. 5) Thus, the spin-phonon relaxation is not detrimental for the phonon-assisted Kondo effect for realistic model parameters.

To conclude, we have demonstrated that the multiphonon emission/absorption processes may initiate Kondo effect in TMOC with the ground singlet state in a situation where the electron tunneling from metallic reservoir to a 3d orbit of TM is accompanied by polaronic effect in molecular vibration subsystem. The release of vibrational energy compensates the singlet-triplet gap in the spin excitation spectrum. Varying the Zeeman splitting in external magnetic field, one may scan the Pekarian distribution of Kondo-phonon satellites in tunneling conductance. Magnetic field tuning changes drastically the character of phonon-assisted Kondo screening. In zero magnetic field the spin $S = 1$ is underscreened by phonon-assisted Kondo processes [2], whereas the Zeeman splitting results in reduction of effective spin from 1 to 1/2 and hence to complete Kondo screening.

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