The Kondo effect was formulated initially for a spin 1/2 impurity coupled to metallic environment. Later on, various realizations of this effect were studied in more complicated physical systems. Examples are the Kondo effect influenced by crystal field excitations, the multichannel Kondo problem, electron scattering by two-level systems, etc. Usually, the scattering center is represented by its spin (pseudo-spin) degrees of freedom. In this work we consider yet another generalization of the Anderson impurity model, where the impurity possesses both electron and hole branches of single-particle excitations as well as two-particle (excitonic) states. Discrete excitonic states do not show up in a conventional situation of an impurity immersed in a conduction band, even when such an impurity has internal charge degrees of freedom (e.g., rare-earth impurities with two unfilled electron shells). However, long-living excitons can exist when the scattering center is spatially isolated from the conduction electrons, like in semiconductor quantum dots coupled by tunneling to metallic leads or in atoms adsorbed on metallic surfaces. It is well known that the Kondo scattering could results in resonant tunnel current. Recently the Kondo features were observed in the conductance of quantum dots. We demonstrate in this work that the Kondo-type shake-up process leads to an exciton formation in a quantum dot with even number of electrons where the Kondo effect is absent in the ground state, novel midgap excitonic states emerge in the conductance of quantum dots. We demonstrate that the Kondo features were observed in the conductance of quantum dots. We demonstrate in this work that the Kondo-type shake-up process leads to an exciton formation in a quantum dot with even number of electrons where the Kondo effect is absent in the ground state, novel midgap excitonic states emerge in the conductance of quantum dots.
The optical line shape is given by the Kubo-Greenwood formula,
\[ W(h\nu) \simeq \text{Im} \frac{1}{\pi} \langle i | \hat{R}(h\nu) \hat{P} | i \rangle \tag{6} \]
where \( \hat{R}(z) = (z - H)^{-1} \), and \( \langle i | \ldots | i \rangle \) means averaging of initial state over the equilibrium ensemble. Due to Hubbard exclusion mechanism only the states \( |0\rangle \) survive in the brackets of response function \( \langle i | \hat{R} \hat{P} | i \rangle \), and one has to calculate the retarded excitonic Green function
\[ G_{ee}^{R}(z) = -i \int dt e^{izt} \theta(t) \langle [B^\dagger(t)B(0)] \rangle \tag{7} \]
Employing the operator identity \( \hat{R} = \hat{R}_0 + \hat{R}_0 H_t \hat{R} \) for the resolvent \( \hat{R} \) we construct the perturbation series in \( H_t \) where the first term is \( R_{ee}^\rightarrow = \langle e | \hat{R} | e \rangle \) where \( \langle s | \) are the states admixed to the exciton by the tunneling interaction, is obtained. The structure of the system is illustrated in fig.1, and its solution for the excitonic Green function has the form \( R_{ee}^- (\epsilon) = [\epsilon - \Sigma_{0e}(\epsilon)] [D(\epsilon)]^{-1} \). The poles of this function are determined by the equation
\[ D(z) = \text{det} \left| \begin{array}{cc} z - \Sigma_{0e}(z) & -\Sigma_{ee}(z) \\ -\Sigma_{0e}(z) & z - \Sigma_{ee}(z) \end{array} \right| = 0. \tag{8} \]
The self energies are given by
\[ \Sigma_{0e} = \Sigma_{ee}^+ + \Sigma_{vv}^{-}, \]
\[ \sqrt{2} \Sigma_{0e} = \Sigma_{cc}^+ - \Sigma_{cc}^- \tag{9} \]
where
\[ \Sigma_{jj}^\pm = \frac{\sum_k w_j^* w_j f_k}{z - E_j + i\varepsilon_k}, \quad \Sigma_{jj}^- = \frac{\sum_k w_j^* w_j f_k}{z + E_j - i\varepsilon_k} \tag{10} \]
\( f_k \) is the equilibrium distribution function for lead electrons, \( f_k = 1 - f_k \). The tunneling matrix elements \( w_j \) are defined as \( \langle 0 | H_t | kj \rangle \approx \sqrt{2} \langle e | H_t | kv \rangle \approx w_{ve} \), \( \langle 0 | H_t | kv \rangle \approx -\sqrt{2} \langle e | H_t | k\bar{v} \rangle \approx w_{vc}^* \). Then integration gives
\[ \text{Re} \Sigma_{jj}^\pm = \frac{\Gamma_{jj}^\pm \pi}{2\pi} \ln \left( \frac{\sqrt{\epsilon - \Delta_{ve}^2 + (\pi T)^2}}{D^2} \right), \tag{11} \]
where \( \Delta_e = E_e - \epsilon_F, \Delta_v = \epsilon_F - E_v, \Gamma_{jj} = \pi \rho w_e^* w_{ve} \), \( \rho \) is the density of states at the Fermi surface, \( \epsilon_F \) is the Fermi energy and \( D \) is the conduction electron bandwidth. The sign \( \pm \) correspond to \( c,v \), respectively, \( z = \epsilon + is \).

As was mentioned above, the renormalization of the ground state at \( \epsilon = 0 \) is a trivial second-order effect in the case of \( E_e > \epsilon_F, E_v < \epsilon_F \) (even number of electrons in the ground state of the dot). However, novel features appear in the excitation spectrum at \( \epsilon \sim \Delta_e, \Delta_v \). In a process of tunnel relaxation the electron and the hole with finite energy \( \epsilon \) induce Kondo-like peaks at the Fermi level. The physics of "Kondo-excitons" can be illustrated by considering two limiting cases.

(i) Symmetric configuration \( w_e = w_v \equiv w, \Delta_e = \Delta_v \equiv \Delta/2 \). In this case \( \Sigma_{0e} \) vanishes identically, and the secular equation becomes
\[ \epsilon - \Delta - \Sigma_{ee}(\epsilon) = 0. \tag{12} \]
It has a solution at \( \epsilon \sim \Delta = \Delta + \Sigma_{ee}(\Delta) \), corresponding to the normal exciton. Besides, \( \text{Re} \Sigma_{ee}(\epsilon) \) diverges at \( T \to T_K \),
\[ T_K = D \exp(\pi \Delta/2\Gamma) \tag{13} \]
As a result a peak arises in \( \text{Im} G_{ee} \) at \( \epsilon \) around \( \Delta/2 \) which corresponds to maximum of light absorption/emission at this energies. When the particle-hole symmetry is slightly violated \( (\delta \neq 0), \Delta_e = \Delta/2 - \delta, \Delta_v = \Delta/2 + \delta, \delta \ll \Delta/2 \), this midgap peak disappears with increasing \( \delta \) due to cancellation of singular terms with opposite sign in eq. (8). We will see below that this state is also fragile against the lifetime effect.

(ii) Strongly asymmetric configurations, \( \Delta_e \ll \Delta_v, w_e \gg w_v \). This case is closer to the situation in real systems where the electrons are usually less localized than the holes. In the extreme case the level \( E_e \) is below the bottom of the band \( \epsilon_K \) ("Schrieffer-Wolff (SW) limit" [8]), whereas the electron is in resonance with the band electrons. The secular equation \( \Sigma_{ij}(\epsilon) \) may be rewritten as
\[ 2(\epsilon - \Delta) = \Sigma_{ee}^+ + \Sigma_{ee}^- + \frac{|\Sigma_{vv} - \Sigma_{vcc}^2|}{(\epsilon - \Sigma_{cc} - \Sigma_{vv})} \tag{14} \]
To find the resonance solution at \( \epsilon \sim \Delta_e \), we neglect the smooth contributions \( \Sigma_{ij}^+ (\epsilon) \) in comparison with the singular self energies \( \Sigma_{ij}^-(\epsilon) \), and use approximate value of \( \Sigma_{vv}(\Delta_v) \approx -\eta \Delta_v \) in the denominator of the ratio in r.h.s. \( (\eta = (w_v/w_e)^2 \ll 1) \). Then we have
\[ 2(\epsilon - \Delta) \approx \Sigma_{cc}^- + \eta |\Sigma_{vcc}^-|^2 (\Delta_v + \eta \Delta_v)^{-1}. \tag{15} \]
Like eq. (12), this equation has a Kondo-like pole at \( \epsilon = \Delta_v, T = T_K \), where \( T_K = D \exp(-2\pi \Delta_v/\Gamma_{cc}) \) and \( \Gamma_{cc} \approx \Gamma_{ee}(1 - \eta \Delta_e/\Delta_v) \). Repeating the procedure for the resonance at \( \epsilon \sim \Delta_v \), we leave in (13) only the terms \( \Sigma_{ij}^+ \) and find the midgap peak at \( \epsilon = \Delta_v \), with \( T_v = D \exp(-2\pi \Delta_v/|\Gamma_{vv}|), \Gamma_{vv} \approx \Gamma_{vv}(1 - \eta \Delta_v/\Delta_v) \).

Thus, the Kondo-type processes manifest themselves as a shake-up effect with a shake-up energy of \( \Delta_{ve,e} \), i.e., as a final state interaction between the \((e,h)\) pair in the dot and the Fermi continuum in the lead. The
$T$-dependent logarithmic singularity in excitonic self energy is a precursor of "orthogonality catastrophe" in close analogy with the corresponding anomaly in a d-electron self energy in the conventional Anderson model \cite{7}. In the latter case the Kondo peak transforms to undamped Abrikosov-Stulz resonance in a ground state \cite{8}. However, this is not the case for the Kondo exciton because of the finite lifetime $\tau_1$ of the $(e,h)$ pair. The most important contributions to $\tau_1$ are given by the same tunneling processes which are responsible for the very existence of the midgap states. To take them into account one should include the states with $(e,h)$ pairs in the leads in the Green function expansion. These states appear in 4th order of the perturbation theory. In a non-crossing approximation (NCA) they result in renormalization of the self energies \cite{8,10},

$$
\tilde{\Sigma}^+_{jl}(\epsilon) = \frac{\Gamma_{jl}}{\pi} \int_{-D}^{D} \frac{f(\epsilon)d\epsilon}{\epsilon - E_c + \epsilon - B_{jl}^+(\epsilon)},
$$

$$
\tilde{\Sigma}^-_{jl}(\epsilon) = \frac{\Gamma_{jl}}{\pi} \int_{-D}^{D} \frac{f(\epsilon)d\epsilon}{\epsilon + E_c - \epsilon - B_{jl}^-(\epsilon)}. \tag{16}
$$

where $B_{jl}^\pm$ are the integrals similar to (14). In particular,

$$
B_{cc}^+ = \int_{-D}^{D} \frac{f(\epsilon)d\epsilon}{\pi} \left[ \frac{\Gamma_{vv}}{\epsilon - \epsilon' + \epsilon - \epsilon' + \epsilon - \Delta} \right] + \frac{\Gamma_{ee}}{\epsilon' - \epsilon' + \epsilon - \Delta},
$$

$$
B_{vv}^- = \int_{-D}^{D} \frac{f(\epsilon)d\epsilon}{\pi} \left[ \frac{\Gamma_{cc}}{\epsilon' + \epsilon' + \epsilon' - \epsilon + \Delta} \right] + \frac{2\Gamma_{vv}}{\epsilon' + \epsilon' - \epsilon + \Delta}. \tag{17}
$$

In a symmetric case (2) the self energy $B^\pm(\epsilon)$ has imaginary part $\approx 2\Gamma$ at $\epsilon \approx \Delta/2$. Thus, the Kondo processes initiated by one of the partners in the electron-hole pair are killed by the damping of its counterpart due to the same tunneling mechanism. More interesting is the asymmetric configuration described by eq. (14). In this case the singularity of $\tilde{\Sigma}^-_{cc}$ in electron channel at $\epsilon \sim \Delta_v$ survives in a SW limit for a hole $[E_v]$ below the bottom of conduction band, $\text{Im} B_{cc}^+(\epsilon_F) = 0$, whereas the electron lifetime given by $\text{Im} B_{cc}^- \sim \tau_{cc}$ kills the hole peak like in the symmetric case. The electron midgap state survives also when $E_v$ has a finite width, provided $\Gamma_{vv} < \tilde{T}_K$, i.e. $2\pi\Delta_c/\Gamma_{cc} < \ln D/T_{vv}$.

Thus, in the case (ii) the main peak of optical transition at $h\nu = \Delta$ is accompanied by a satellite peak at $h\nu \approx \Delta_v$. The form of this peak is determined by eq. (3), i.e., by

$$
\frac{1}{\pi} \text{Im} G_{ee}(h\nu) = \frac{1}{\pi} \text{Im} \left[ h\nu - \Delta - \tilde{\Sigma}_{cc}^-(h\nu) + i\hbar T_1^{-1} \right]^{-1}. \tag{18}
$$

where $\tilde{\Sigma}_{cc}^-$ is given by the r.h.s. of eq. (14). The lineshape $W(h\nu)$ strongly depends on $T_1/\tilde{T}_K$ and $\tau_1$ \cite{10}.

Two systems where this theory can be applied are suggested below. The first one is an ensemble of semiconductor quantum dots (e.g., the nanosize Si clusters embedded in amorphous SiO$_2$ matrix \cite{8}). Luminescence of confined excitons was observed in these clusters \cite{11}, and the tunneling current through this system exhibits the Coulomb blockade effect \cite{11,11}. In the Coulomb blockade regime the energy $U$ which enters $H_d$, is introduced as $U = E_i^{(n+1)} - E_i^{(n)} + e^2/C_{eff}$, where $E_i^{(n)}$ is the energy level of the $n$-th quantum state of the electron (hole) in the empty well ($n = 1$ in our case), and $C_{eff}$ is an effective capacitance of the barrier layers. Experimental \cite{13} and theoretical \cite{12} estimates of $C_{eff}$ for Si nanoclusters give $U \approx 0.1 \div 0.3$ eV, hence the general condition for realization of the Kondo effect, $\Gamma \ll |E_i|, E_i + U$, is satisfied in these systems. However, the experimental value of $U$ is small compared with $\Delta \sim 1.2 \div 1.3$ eV \cite{11}. Taking into account finite $U$ means inclusion of doubly occupied states $\ket{2c}, \ket{2v}$ in the set $\ket{0,1}$. In close analogy with the conventional Anderson model \cite{8} one expects redistribution of the spectral weight of neutral states $\ket{0} and \ket{1} in favor of the states $\ket{2c}, \ket{2v}$, and increase of $T_K$ with decreasing $U$. However, the inequality $T_K \ll \Delta$ ensures the existence of the midgap states.

Another important condition for the appearance of midgap states is long enough excitonic lifetime $\tau_1 \gg h/T_K$. In addition to tunneling contribution $\Gamma$ discussed above, one should also take into account the electron-hole recombination in the dot resulting in a width $\gamma$ of the excitonic level. This damping gives the contribution to imaginary part $\sim \gamma \Delta \ll \Gamma$ in eqs. (12) and (14) for a Kondo pole. In any case, the experimentally estimated value is $\tau_e \sim 10^{-6}$ s for the singlet exciton \cite{14}. Therefore the Kondo-type processes can survive in these systems if $T_K \gg 10^{-9}$ eV, which is a realistic condition. We therefore believe that our model qualitatively describes those properties of Si nanoclusters which play a crucial role in the formation of Kondo-type states in optical spectra.

The second possible realization is mixed valent rare earth atoms adsorbed on a metallic surface. It is known that the Anderson model can be applied to adatoms with strongly interacting electrons (see \cite{4} for a review). In this case $H_e$ \cite{4} corresponds to covalent bonding between an adsorbed atom and a substrate, $V$ is the corresponding hybridization integral between the electrons in adatom and those in the nearest sites of the metallic surface layer, $U$ is the intra-atomic Coulomb repulsion which prevents charging of the adatom in the process of chemisorption. The model was originally proposed for hydrogen atoms adsorbed on surfaces of transition metals \cite{4}. Later on, the possibility of Kondo-type spin polarization of substrate electrons around adatom spin in the case of $U \gg V^2/D$ was discussed \cite{4}. The most promising candidates from the point of view of excitonic effects are the adatoms with unstable valence, e.g., Sm, whose ground state electronic configuration is $4f^{6}6s^{2}$. The Sm atoms can be adsorbed on surfaces of transition metals (Ni, Co, Cu, Mo). In the process of adsorption, Sm loses its $s$-electrons and exists in two charged
states Sm$^{2+}$ and Sm$^{3+}$ depending on the concentration of Sm ions on the surface. In particular, the isolated ions Sm$^{2+}(4f^6)$ are observed on Mo surface at low submonolayer coverage [17]. The unfilled 4f shell forms a resonant f-state close to the Fermi level of the metal. The excited 5d state forms another level above $\varepsilon_F$. Thus we arrive at a two-level system described by our Hamiltonian $H_d (2)$. Since the ground state term of the configuration $4f^6$ is a singlet $7F_0$, one cannot expect the Kondo coupling for such adatom. However, in the course of virtual transitions between the adatom and the substrate the states $|kv\rangle$ and $|kc\rangle$ arise with excess electron $e_k$ above $\varepsilon_F$ (configuration $4f^5e_k$) and a hole below $\varepsilon_F$ (configuration $4f^55d_{hk}$). According to our calculations, one can excite not only the conventional atomic excited state with energy $\Delta = E(4f^55d) - E(4f^6)$ but also the midgap states with energy close to $\Delta' = E(4f^5e_{F}) - E(4f^6)$ where $e_F$ stands for the electron on the Fermi level of the substrate.

To summarize, this work suggests a generalization of the Anderson impurity model which takes into account excitonic degrees of freedom. The model exhibits Kondo effect in the excited state, despite its absence in the ground state. It is predicted that satellite excitonic peaks of a Kondo origin can be seen in the optical spectra of semiconductor quantum dots or rare earth atoms adsorbed on metal surfaces.

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**Figure Caption**

Fig. 1. Building blocks of the Green function expansion and the secular equation (8). The arrows indicate the tunneling processes which connect different states of this set.