Slave boson theory for transport through magnetic molecules with vibronic states

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We study the electron transport through a magnetic molecular transistor in the Kondo limit using the slave boson technique. We include the electron-phonon coupling and analyze the cases where the spin of the molecule is either $S=1/2$ or $S=1$. We use the Schrieffer-Wolff transformation to write down a low energy Hamiltonian for the system. In the presence of electron-phonon coupling and for $S=1$, the resulting Kondo Hamiltonian has two active channels. At low temperature, these two channels interfere destructively, leading to a zero conductance.

I. INTRODUCTION

The technological advances of the last decades triggered a systematic study of electronic transport in nanoscale systems weakly connected to external electrodes. Confinement of electrons at the nanoscale leads naturally to energy level quantization and charging effects. In small quantum dots, Coulomb blockade becomes a dominant effect, as shown in conductance experiments.[1,2] This effect together with the enhancement of the low-temperature conductance in the valley between Coulomb blockade peaks—a signature of the well known Kondo effect[3,4]—makes evident that electron-electron correlations play a central role in these systems. Since the early experiments in quantum dots,[5,6] the Kondo effect has also been observed in a variety of molecules. The conductance of molecular systems such as C_{60} molecules, Co and Cu complexes connected to metallic leads, or carbon nanotubes shows the signature of Kondo-like behavior.[7–10] In these molecular junctions, the molecule is coupled to the source and drain leads, providing a path for charge transport (Fig. 1). In some cases, a third gate electrode is used to create an external potential that modifies the energy of the molecular orbitals. The use of normal, ferromagnetic, and superconducting electrodes gives rise to a rich behavior and opens new alternatives for the study of the interplay between Kondo screening and electronic correlations in the leads. In addition, transport through highly structured molecules such as the Mn_{12}, a single molecular magnet, has been reported[11] and the Kondo effect has been predicted to occur in this type of systems for both half-integer[12] and integer values of the molecular spin.[13]

Despite of the substantial theoretical and experimental activity devoted to the study of molecular transistors, there are still many open questions. While the theoretical frame for the study of the Kondo effect in semiconducting quantum dots and molecular systems is basically the same, there are some fundamental differences between them. Namely, vibrational modes can play a central role in the single electron transfer through molecules. In fact, molecules distort upon the addition or the removal of electrons, leading to a large electron-phonon interaction. As the Coulomb charging energies in these systems can be considerably reduced by screening due

to the electrodes,[14] electronic and vibrational energies can become of the same order of magnitude generating scenarios where novel effects may emerge.[15–32]

The effect of the coupling between electronic excitations and vibronic states in molecular transistors depends on the symmetry and frequency of the vibrating mode and on the strength of the coupling. Symmetric modes with a Holstein coupling between quantized vibrations and electronic levels may strongly renormalize the molecular parameters reducing charging energies[15] and producing anomalous behavior of the Kondo temperature versus applied gate voltages.[27] Asymmetric modes coupled to the tunnel-barrier parameters, such as the center of mass motion mode, can dynamically open new channels for electron transport.[27] Due to the large variety of magnetic molecules that could be incorporated in molecular circuits with different chemical environments, it is important to characterize and understand the behavior of molecular transistors with different vibronic and electronic structures.

In this work, we discuss the electronic transport through a magnetic molecule with spin $S=1/2$ and $S=1$ in the Kondo limit. We use slave boson techniques and include the electron-phonon interaction with different coupling constants. We show that in the presence of vibrational modes, the low temperature behavior of the $S=1$ case corresponds to a two-channel Kondo problem. In particular, the zero temperature conductance goes to zero.

The paper is organized as follows. In Sec. II, we introduce a model Hamiltonian for the system and use the Schrieffer-Wolff transformation to obtain the low energy Hamiltonian of the molecular system for both $S=1/2$ and $S=1$. In Sec. III, we use slave boson techniques to find the ground state properties of the system in both cases and calculate the conductance. We summarize in Sec. IV.
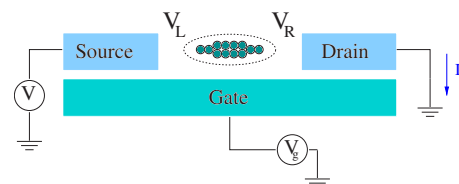

FIG. 1. (Color online) Scheme of a molecular device.

II. MODEL

We first present the case of a spin $S=1/2$ molecule described by the Holstein-Anderson model. The Hamiltonian reads $H=H_0+H_{\text{e-ph}}+H_{\text{hyb}}$, where H_0 describes the molecular degrees of freedom and the electronic excitations of the two leads,

$$H_0 = \sum_\sigma \varepsilon_M d_\sigma^\dagger d_\sigma + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow + \sum_{\alpha,k,\sigma} \varepsilon_k c_{\alpha k\sigma}^\dagger c_{\alpha k\sigma} + \hbar\omega_0 a^\dagger a,$$
(1)

where $d_\sigma^\dagger$ creates an electron in a molecular orbital with energy ε_M, U is the intramolecular Coulomb repulsion, and $c_{\alpha k\sigma}^\dagger$ creates an electron in the k mode of the α lead, where $\alpha=L,R$ stands for the left and right leads, respectively. The last term in Eq. (1) describes the molecular vibronic mode of frequency ω_0. The term $H_{\text{e-ph}}$ in the Hamiltonian describes the Holstein coupling between the electrons in the molecular orbital and the molecular vibrations,

$$H_{\text{e-ph}} = -\lambda(a^\dagger+a)\left(\sum_\sigma d_\sigma^\dagger d_\sigma - 1\right).$$
(2)

Finally, the lead-molecule hybridization term is

$$H_{\text{hyb}} = \frac{1}{\sqrt{N}}\sum_{\alpha,k,\sigma}\hat{V}_\alpha(d_\sigma^\dagger c_{\alpha k\sigma} + c_{\alpha k\sigma}^\dagger d_\sigma)$$

$$= \frac{1}{\sqrt{N}}\sum_{\alpha,k,\sigma} V_\alpha[1+g_\alpha(a^\dagger+a)](d_\sigma^\dagger c_{\alpha k\sigma} + c_{\alpha k\sigma}^\dagger d_\sigma),$$
(3)

where N is the number of band states. For some special relations between the parameters of the Hamiltonian, the model reduces to known and, in some cases, well studied models.

(i) $V_R=V_L$, $\lambda\neq0$, and $g_R=g_L=0$ corresponds to a molecule with a Holstein mode in a symmetric environment.[15,19,24]

(ii) $V_R=V_L$, $\lambda\neq0$ with $g_R=g_L\neq0$ is a generalized Anderson-Holstein model in which vibrations modify the molecular energies and the tunneling barriers.[33]

(iii) $V_R=V_L$, $g_R=-g_L$, and $\lambda=0$ corresponds to a molecule with inversion symmetry and a center of mass motion.[25,27]

(iv) $V_R=V_L$ and $g_R=-g_L$ with $\lambda\neq0$ describes a molecule with no inversion symmetry and a center of mass mode.[25,28]

In the Kondo regime ($-\widetilde{U}<\widetilde{\varepsilon}_M<0$), when the number of electrons in the molecule is well defined, the charge excitations can be integrated out by means of a Schrieffer-Wolff transformation.[34] The resulting Hamiltonian is

$$H = \sum_{k,\alpha}\varepsilon_k\psi_{\alpha k}^\dagger\psi_{\alpha k} + H_K,$$
(4)

with

$$H_K = \sum_{\alpha,\beta=R,L} J_{\alpha\beta}\frac{1}{N}\sum_{k,k'}\boldsymbol{S}\cdot\frac{1}{2}\psi_{\alpha k}^\dagger\boldsymbol{\sigma}\psi_{\beta k'}.$$
(5)

Here, $\psi_{\alpha k}^\dagger=(c_{\alpha k\uparrow}^\dagger, c_{\alpha k\downarrow}^\dagger)$ is a spinor corresponding to the α lead, $\boldsymbol{S}$ is the spin operator associated with the molecular

orbital, and $\boldsymbol{\sigma}$ are the Pauli matrices. The coupling constants are

$$J_{\alpha\alpha} = -2V_\alpha^2\left[\sum_{n=0}^\infty\frac{(\gamma_{0n}+g_\alpha\gamma_{1n})^2}{\widetilde{\varepsilon}_M-\hbar\omega_0 n} + \sum_{n=0}^\infty\frac{(\gamma_{0n}-g_\alpha\gamma_{1n})^2}{-\widetilde{U}-\widetilde{\varepsilon}_M-\hbar\omega_0 n}\right]$$
(6)

and

$$J_{RL} = -2V_LV_R\sum_{n=0}^\infty\frac{(\gamma_{0n}+g_R\gamma_{1n})(\gamma_{0n}+g_L\gamma_{1n})}{\widetilde{\varepsilon}_M-\hbar\omega_0 n}$$

$$-2V_LV_R\sum_{n=0}^\infty\frac{(\gamma_{0n}-g_L\gamma_{1n})(\gamma_{0n}-g_R\gamma_{1n})}{-\widetilde{U}-\widetilde{\varepsilon}_M-\hbar\omega_0 n},$$
(7)

where $\gamma_{0n}=(1/\sqrt{n!})(\lambda/\hbar\omega_0)^n e^{-(\lambda/\hbar\omega_0)^2/2}$, $\gamma_{1n}=\gamma_{0n}[n-(\lambda/\hbar\omega_0)^2]\hbar\omega_0/\lambda$, $\widetilde{\varepsilon}_M=\varepsilon_M+\lambda^2/\hbar\omega_0$, $\widetilde{U}=U-2\lambda^2/\hbar\omega_0$, and $J_{LR}=J_{RL}$. The electron-phonon interaction renormalizes the molecular parameters ε_M and U: the renormalized energy $\widetilde{\varepsilon}_M$ increases with λ, while the intramolecular interaction $\widetilde{U}$ decreases. This naturally leads to an increase of the Kondo temperature, while it reduces the range of gate voltages where the charge state with one electron is stable.[19] For large enough λ, $\widetilde{U}$ becomes negative, which corresponds to an electron-phonon induced attractive interaction. In what follows, we consider the case $\widetilde{U}>0$. In this work, we neglect the potential scattering term generated by the Schrieffer-Wolff transformation.

It is convenient to make a rotation in the $[L,R]$ space to eliminate cross terms. We then define the *even* (e) and *odd* (o) operators,

$$c_{ek\sigma} = uc_{Rk\sigma} + vc_{Lk\sigma},$$

$$c_{ok\sigma} = vc_{Rk\sigma} - uc_{Lk\sigma},$$
(8)

with $u^2=(1+\sqrt{1-F})/2$, $v^2=(1-\sqrt{1-F})/2$, and $F=4J_{RL}^2/[(J_{RR}-J_{LL})^2+4J_{RL}^2]$. In terms of these operators, the Hamiltonian reads

$$H_K = \sum_{\eta=e,o} J_\eta\frac{1}{N}\sum_{k,k'}\boldsymbol{S}\cdot\frac{1}{2}\psi_{\eta k}^\dagger\boldsymbol{\sigma}\psi_{\eta k'},$$
(9)

where

$$J_\eta = \frac{1}{2}[J_{RR}+J_{LL}\pm\sqrt{(J_{RR}-J_{LL})^2+4J_{RL}^2}],$$
(10)

with the $+$ and $-$ signs corresponding to the e channel and o channel, respectively. The Hamiltonian [Eq. (9)] corresponds to a two-channel Kondo model. In our case, the two-channel character is a consequence of the dynamical nature of the hybridization operator and the lack of right-left symmetry: if $g_R=g_L$, then $J_{RL}^2=J_{RR}J_{LL}$ and $J_o=0$. For $g_R\neq g_L$, the system has always two channels coupled to the molecule's spin. However, as in general $J_e>J_o$, the resulting low temperature behavior is dominated by the e channel. In the next section, we discuss this behavior in some detail.

More interesting is the case of an $S=1$ molecule. Such a case can be described by including an additional spin $\mathbf{S}_0 = 1/2$ that couples ferromagnetically to the spin of the electrons in the hybridized molecular orbital described by the first terms in Eq. (1). Then, the Hamiltonian includes a term $-J_H \mathbf{S}_0 \cdot \mathbf{S}$. The total spin of the molecule is either zero or 1 and for large values of the Hund-like coupling J_H, the singlet state can be neglected. Projecting the system onto the total spin $S=1$ state, the Schrieffer-Wolff transformation gives again the Hamiltonian of Eq. (9), where now the molecular spin operator corresponds to $S=1$ and the coupling constants are half the expressions obtained in the previous case with ε_M replaced with $\varepsilon_M - 3J_H/4$.

In the context of semiconducting quantum dots, it has been shown that the zero temperature conductance for an $S=1$ dot coupled with two channels is $G=G_0 \sin^2(\delta_1 - \delta_2)$, where δ_1 and δ_2 are the scattering phase shifts at the Fermi energy for the two channels.[35] Then, we expect molecules with $S=1/2$ and $S=1$ to behave quite differently if phonons open the o channel. Below, we present a slave boson mean-field approach to describe this situation.

Before finishing this section, we would like to emphasize that in our model there is only one hybridized orbital so that the two-channel character arises only from the coupling to the phonons. This is different from the case described in Ref. 35, where the authors considered two different orbitals coupled to the leads. Our model then corresponds to the simplest scenario that allows us to discuss the effect of the electron-phonon coupling. In general, when more than one molecular orbital is coupled to the leads, there would be more than two channels involved, which presumably will lead to a more complex behavior.

III. SLAVE BOSON MEAN FIELD THEORY

For the sake of completeness, we start with a brief discussion of the spin $S=1/2$ case. We review the slave boson mean field theory and calculate the conductance. Although the results for this case are well known, they are presented as a guide to the more interesting case of a spin $S=1$ molecule.

A. $S=1/2$ case

Following standard procedures, we use a fermionic representation for the molecular spin,

$$S_z = \frac{1}{2}(f_\uparrow^\dagger f_\uparrow - f_\downarrow^\dagger f_\downarrow), \quad S^+ = f_\uparrow^\dagger f_\downarrow, \quad S^- = f_\downarrow^\dagger f_\uparrow. \quad (11)$$

In terms of these operator, the Kondo Hamiltonian reads

$$H_K = \frac{1}{N} \sum_{\eta=e,o} J_\eta \sum_{k,k'} \frac{1}{4}(f_\uparrow^\dagger f_\uparrow - f_\downarrow^\dagger f_\downarrow)(c_{\eta k\uparrow}^\dagger c_{\eta k'\uparrow} - c_{\eta k\downarrow}^\dagger c_{\eta k'\downarrow})$$

$$+ \frac{1}{2}(f_\uparrow^\dagger f_\downarrow c_{\eta k\downarrow}^\dagger c_{\eta k'\uparrow} + f_\downarrow^\dagger f_\uparrow c_{\eta k\uparrow}^\dagger c_{\eta k'\downarrow}). \quad (12)$$

In the mean field approach one defines bosonic fields $\lambda_{\eta\sigma} = 1/\sqrt{N} \Sigma_k c_{\eta k\sigma}^\dagger f_\sigma$ and evaluates the physical quantities at the mean field level in these fields. The resulting mean field Hamiltonian can be put as[36]

$$H_K = -\sum_{\eta=e,o} \frac{J_\eta}{\sqrt{N}} \sum_{k,\sigma} \langle \lambda_{\eta-\sigma} \rangle f_\sigma^\dagger c_{\eta k\sigma} + \text{H.c.}, \quad (13)$$

where $\langle \cdots \rangle$ indicates the thermal average. The solution must satisfy the condition $\langle f_\uparrow^\dagger f_\uparrow + f_\downarrow^\dagger f_\downarrow \rangle = 1$ that is imposed by introducing a Lagrange multiplier. The procedure is well justified only when the original model is extended for the spin variable σ to take $\mathcal{N}$ different values with $\mathcal{N} \to \infty$. However, it is well known that the approximation captures essentially the correct low temperature physics even for $\mathcal{N}=2$. In the absence of an external magnetic field, we may take $\langle \lambda_{\eta\uparrow} \rangle = \langle \lambda_{\eta\downarrow} \rangle \equiv \Lambda_\eta$. The self-consistent solutions for the bosonic fields are

$$\Lambda_\eta = -J_\eta \Lambda_\eta \rho \int_{-D}^{D} d\omega f(\omega) \frac{\omega}{\omega^2 + \Gamma^2}, \quad (14)$$

where $f(\omega)$ is the Fermi function, $\rho = 1/2D$ is the lead density of states per spin, and

$$\Gamma \equiv \Gamma_e + \Gamma_o = \pi\rho[(J_e \Lambda_e)^2 + (J_o \Lambda_o)^2]. \quad (15)$$

For $J_e \neq J_o$, these equations do not have a solution with nonzero values for both Λ_e and Λ_o. At zero temperature, we have

$$\Lambda_\eta = \sqrt{\frac{2}{\pi}\frac{D}{J_\eta}} e^{-D/J_\eta}, \quad \Lambda_{-\eta} = 0, \quad (16)$$

where η $(-\eta)$ corresponds to the largest (smaller) Kondo coupling J_η. This solution describes the situation in which one channel completely decouples from the molecular spin. In the renormalization group language, the ratio between the largest and smaller couplings flows to infinity and the Kondo screening is due only to the channel with the largest coupling. Note that for the particular case $J_e = J_o$, the overscreening of the $S=1/2$ spin requires a more elaborate approximation.[37]

In what follows, we assume that $J_e > J_o$. The temperature dependence of the Kondo correlation energy, defined as $E_K = \langle H_K \rangle = -4J_e \Lambda_e^2$, is shown in Fig. 2. At a temperature T_{Ke}, the correlation energy goes to zero in a singular way. This is known to be an artifact of the approximation; T_{Ke} should be interpreted as a crossover temperature between a high temperature regime, where the spin is essentially unscreened, and a low temperature Fermi liquid regime. According to Eq. (14), the Kondo temperature is given by the solution of the following equation:

$$1 = \frac{J_e}{2}\rho \int_{-D}^{D} d\omega \frac{1}{\omega} \tanh\left(\frac{\omega}{2T_{Ke}}\right). \quad (17)$$

The linear conductance through the molecule is calculated using a Landauer approach. At the mean field level described by the Hamiltonian [Eq. (13)], the problem reduces to a single resonant level centered at the Fermi energy. This structure represents the Kondo resonance that leads to resonant tunneling between the source and the drain contacts.

The transmission function is given by $T(\omega) = \Gamma_R G^r \Gamma_L G^a$ with $\Gamma_R = 2u^2 \Gamma_e$ and $\Gamma_L = 2v^2 \Gamma_e$, where G^r and G^a are the retarded and the advanced propagators of the f fermions, respectively. In terms of $T(\omega)$, the conductance is then
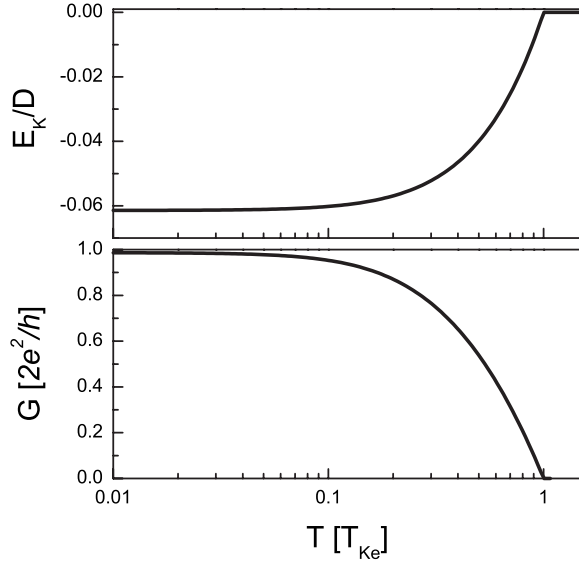
FIG. 2. Temperature dependence of the correlation energy (top) and the conductance (bottom) in the $S=1/2$ case. Parameters: $D=2$, $\rho J=0.22$, and $V_L=V_R$.

$$G = \frac{2e^2}{h} \int d\omega \left[-\frac{\partial f(\omega)}{\partial \omega} \right] T(\omega)$$
$$= \frac{2e^2}{h} \int d\omega \left[-\frac{\partial f(\omega)}{\partial \omega} \right] 4u^2 v^2 \frac{\Gamma_e^2}{\omega^2 + \Gamma_e^2}. \quad (18)$$

The last expression was obtained by using the Green's functions corresponding to a resonant level of width Γ_e. For a system with inversion symmetry, we have $V_L=V_R$ and $4u^2v^2=1$. In this situation, the zero temperature conductance is the quantum unit of conductance $2e^2/h$. As the temperature increases, Γ_e decreases and goes to zero at the Kondo temperature T_{Ke}. The temperature dependence of the conductance is shown in Fig. 2. As already mentioned, the singular behavior at T_{Ke} is to be interpreted as a crossover. In fact, above the Kondo temperature, the conductance is small but nonzero and can be calculated using perturbation theory.[38]

B. $S=1$ case

From the many possible representations of a spin 1 operator, we use a two spin 1/2 fermion representation that has proved to give good results when treated at the mean field level. Following Refs. 39 and 40, we define two states with quantum numbers $i=1,2$ and $\sigma=\uparrow,\downarrow$. The operators $f_{i\sigma}^\dagger$ create a fermion in these states. The physical Hilbert space corresponds to the subspace with $n_i=n_{i\uparrow}+n_{i\downarrow}=1$, with $n_{i\sigma}=f_{i\sigma}^\dagger f_{i\sigma}$. The spins of the states 1 and 2 are coupled ferromagnetically with an exchange constant J_H. Within this subspace, the three components of the spin 1 operator are given by

$$S_z = n_{1\uparrow}n_{2\uparrow} - n_{1\downarrow}n_{2\downarrow},$$

$$S^+ = n_1 S_2^+ + S_1^+ n_2,$$

$$S^- = S_1^- n_2 + n_1 S_2^-. \quad (19)$$

Here, $S_i^\pm$ are the (raising/lowering) spin operators of state i, which are defined as in Eq. (11).

As mentioned above, the effective Hamiltonian H_K for this case is described again by Eq. (9), but the definition of the coupling constant J_η is obtained by replacing $\varepsilon_M \rightarrow \varepsilon_M - 3J_H/4$ in Eqs. (6) and (7) and dividing Eq. (10) by 2. Defining bosonic fields as

$$\lambda_{\eta\sigma}^i = \frac{1}{\sqrt{N}} \sum_k c_{\eta k\sigma}^\dagger f_{i\sigma}, \quad (20)$$

we can write the transverse part of the spin product as

$$\frac{1}{N} \sum_{k,k'} (S^+ c_{\eta k\downarrow}^\dagger c_{\eta k'\uparrow} + S^- c_{\eta k\uparrow}^\dagger c_{\eta k'\downarrow}) = -\sum_{i\sigma} \lambda_{\eta-\sigma}^i \lambda_{\eta\sigma}^{i\dagger} n_{\bar i}, \quad (21)$$

with $\bar i=(i+1, \mathrm{mod}\ 2)$. As in the $S=1/2$ case, we treat this term in the mean field approximation. This gives

$$-\sum_{i\sigma} \lambda_{\eta\bar\sigma}^i \lambda_{\eta\sigma}^{i\dagger} n_{\bar i} \simeq - \sum_{i\sigma} (\lambda_{\eta\bar\sigma}^i \langle \lambda_{\eta\sigma}^{i\dagger}\rangle + \langle\lambda_{\eta\bar\sigma}^i\rangle\lambda_{\eta\sigma}^{i\dagger})\langle n_{\bar i}\rangle + \langle\lambda_{\eta\bar\sigma}^i\rangle$$
$$\times \langle\lambda_{\eta\sigma}^{i\dagger}\rangle n_{\bar i} - 2\langle\lambda_{\eta\bar\sigma}^i\rangle\langle\lambda_{\eta\sigma}^{i\dagger}\rangle\langle n_{\bar i}\rangle, \quad (22)$$

where $\bar\sigma=-\sigma$. In the absence of external magnetic fields, these quantities $\langle\lambda_{\eta\sigma}^i\rangle$ are spin independent.

The Kondo Hamiltonian is then given by

$$H_K = \sum_{\eta=e,o} -\frac{J_\eta}{\sqrt{N}} \sum_{i,k,\sigma} \langle\lambda_{\eta\bar\sigma}^{i\dagger}\rangle c_{\eta k\sigma}^\dagger f_{i\sigma} + \mathrm{H.c.}, \quad (23)$$

where we have taken $\langle n_i\rangle=1$. The total Hamiltonian also includes a term of the form $\sum_i \mu_i(n_i-1)+C$, where μ_i is a Lagrange multiplier introduced to preserve the number of f fermions and C is a constant. The quantities $\langle\lambda_{\eta\sigma}^{i\dagger}\rangle$ are calculated self-consistently. The symmetry of the Hamiltonian in the quantum number i may suggest that they are i independent. However, the most general solution is

$$\langle\lambda_{\eta\sigma}^{1+}\rangle = \Lambda_\eta, \quad \langle\lambda_{\eta\sigma}^{2+}\rangle = \Lambda_\eta e^{i\theta_\eta}, \quad (24)$$

with Λ_η a real number. For the one-channel case, the phase θ_e can be eliminated by a gauge transformation. However, as shown below, in the two-channel case the phase difference $\delta\theta = \theta_e - \theta_o$ plays an important role. With the notation defined above, the Hamiltonian [Eq. (23)] reads

$$H_K = -J_e\Lambda_e\sqrt{\frac{2}{N}}\sum_{k,\sigma} c_{ek\sigma}^\dagger f_{e\sigma} + \mathrm{H.c.}$$

$$-J_o\Lambda_o\sqrt{\frac{2}{N}}\sum_{k,\sigma} \cos\left(\frac{\delta\theta}{2}\right)\tilde c_{ok\sigma}^\dagger f_{e\sigma}$$

$$+ i\sin\left(\frac{\delta\theta}{2}\right)\tilde c_{ok\sigma}^\dagger f_{o\sigma} + \mathrm{H.c.}, \quad (25)$$

where $f_{e\sigma}=(f_{1\sigma}+e^{i\theta_e}f_{2\sigma})/\sqrt{2}$, $f_{o\sigma}=(f_{1\sigma}-e^{i\theta_e}f_{2\sigma})/\sqrt{2}$, and $\tilde c_{ok\sigma}^\dagger=e^{-i\delta\theta/2}c_{ok\sigma}^\dagger$. For $\delta\theta=0$, the two channels are mixed with the same fermion. Then, as in the $S=1/2$ case, one channel
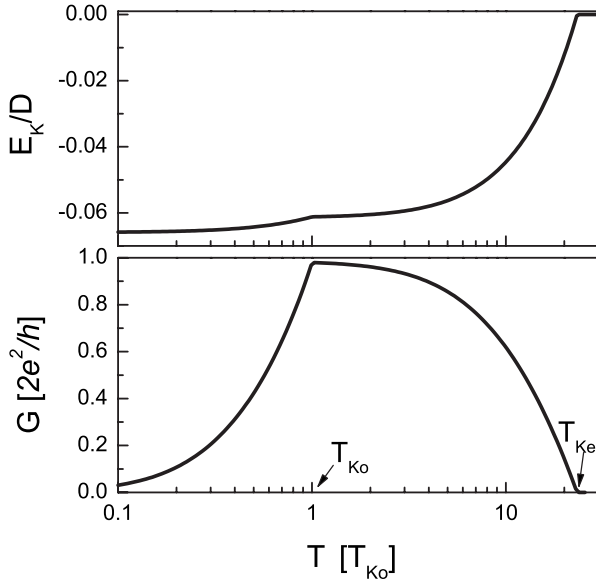
FIG. 3. Temperature dependence of the correlation energy (top) and the conductance (bottom) in the $S=1$ case. Parameters: $D=2$, $\rho J_e = 0.22$, and $\rho J_o = 0.13$.

decouples and does not contribute to the energy. For $\delta\theta = \pi$, the mean field problem reduces to the case of two channels, each one coupled with a resonant state and both contributing to lower the energy. It can be shown that for the general case with $J_e \neq J_o$, self-consistent solutions exist only for $\delta\theta = 0$ or $\pm\pi$. Without any loss of generality, we can take $\theta_e = 0$. Then, for $\delta\theta = \pm\pi$, we have

$$H_K = \sum_{\eta=e,o} -J_\eta \Lambda_\eta \sqrt{\frac{2}{N}} \sum_{k,\sigma} c^\dagger_{\eta k\sigma} f_{\eta\sigma} + \text{H.c.}, \qquad (26)$$

where the self-consistent parameters Λ_η are given by

$$1 = -J_\eta \rho \int_{-D}^{D} d\omega f(\omega) \frac{\omega}{\omega^2 + \Gamma_\eta^2}, \qquad (27)$$

with $\Gamma_\eta = \pi\rho q_\eta^2$ and $q_\eta = J_\eta \Lambda_\eta \sqrt{2}$. Accordingly, the zero temperature correlation energy is $E_K = -4J_e \Lambda_e^2 - 4J_o \Lambda_o^2$. As the two coupling constants are different, there are two characteristic energy scales given by the two Kondo temperatures T_{Ke} and T_{Ko}. The correlation energy as a function of temperature is shown in Fig. 3.

The conductance can be easily evaluated within the mean field approximation following the same line as in the $S=1/2$ case. The transmission function in this case is given by $T(\omega) = \text{Tr}[\Gamma_L G^a \Gamma_R G^r]$, where the Γ's and the propagators are 2×2 matrices since we now have two active channels coupled to the $S=1$ spin. In the even and odd base, we have

$$\Gamma_R = 2\pi\rho \begin{pmatrix} u^2 q_e q_e & uv q_e q_o \\ uv q_o q_e & v^2 q_o q_o \end{pmatrix},$$

$$\Gamma_L = 2\pi\rho \begin{pmatrix} v^2 q_e q_e & -uv q_e q_o \\ -uv q_o q_e & u^2 q_o q_o \end{pmatrix}. \qquad (28)$$

Finally, the conductance can be put as

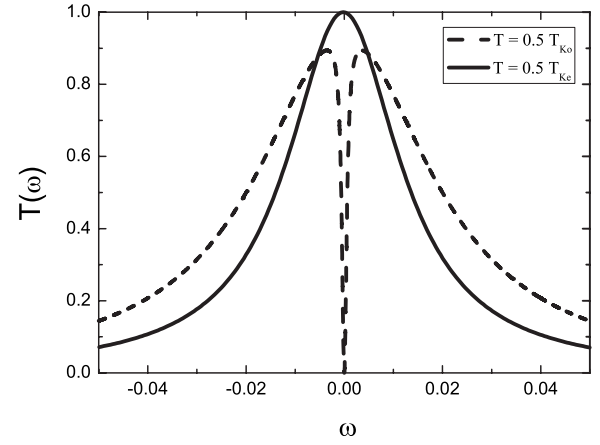FIG. 4. Transmission function $T(\omega)$ as a function of ω for an $S=1$ molecule. For $T_{Ko} < T < T_{Ke}$, the system shows the usual one-channel Kondo resonance (solid line), while for $T < T_{Ko}$ the odd channel becomes active and a zero-transmission dip appears at $\omega = 0$ (dashed line).

$$G = \frac{2e^2}{h} \int d\omega \left[-\frac{\partial f(\omega)}{\partial\omega} \right] 4u^2v^2 \left| \frac{\Gamma_e}{\omega + i\Gamma_e} - \frac{\Gamma_o}{\omega + i\Gamma_o} \right|^2. \qquad (29)$$

Here, $\Gamma_\eta = \pi\rho q_\eta^2$. The conductance as a function of temperature is shown in Fig. 3. Initially, the conductance increases as T decreases as in the usual one-channel case but it starts decreasing toward a zero value as T becomes smaller than T_{Ko}. This interference effect between the two channels is clearly seen as a dip at $\omega = 0$ in the transmission function (Fig. 4).

Interference effects in the context of "single impurity" Kondo physics have been extensively discussed in the literature.[25,41–44] In our case, the origin of the effect is clear, as discussed in detail by Pustilnik and Glazman.[35] In the low temperature Fermi liquid regime, the mean field approach presented here allows for a simple interpretation of the interference phenomena: the Hamiltonian [Eq. (25)] with $\delta\theta = \pi$ and nonzero Λ_e and Λ_o is equivalent to a two lead junction connected by two different paths. In this effective model, the phase difference of the two paths is π, leading to destructive interference and zero conductance at $T=0$.

IV. SUMMARY

We have analyzed the Kondo Hamiltonians for magnetic molecules with vibronic states in molecules with spin $S=1/2$ and $S=1$ within the slave boson mean field theory. We showed that in systems with no L-R symmetry in the electron-phonon coupling, there are two channels coupled to the molecular spin. For the case of $S=1/2$ molecules, the weakest coupled channel plays no role; at the mean field level, it is simply decoupled. For the $S=1$ case, the two channels screen the molecular spin at different energy scales. To fix ideas, we summarize the behavior of two simple cases with identical V_L and V_R.

(a) A Holstein-like mode with $\lambda \neq 0$ and $g_R = g_L$. The Kondo Hamiltonian includes a single channel and for the S

$=1/2$ case, the slave boson mean field approximation reproduces the known results. The electron-phonon coupling renormalizes the coupling constants. At T_K, the conductance increases to reach the unitary limit at zero temperature. In this case, it has been shown that for large electron-phonon coupling λ, the Kondo temperature is weakly dependent on gate voltages due to the anomalous dependence of coupling constants $J_{\alpha\alpha}$ with the molecular orbital energy ε_M.[27] For the $S=1$ case, a single channel can screen only half of the molecular spin. The zero temperature conductance also reaches the quantum of conductance value $2e^2/h$, although strictly speaking the system is not a Fermi liquid since there is an unscreened spin $1/2$ at the molecular junction.

(b) A molecule with inversion symmetry and a center of mass mode, $\lambda=0$ and $g_R=-g_L$. The resulting Kondo Hamiltonian includes two channels with different coupling constants. For the $S=1/2$ case, the usual behavior is reproduced as one channel decouples. In this simple model, electron-phonon coupling is just due to the modulation of the tunneling barriers or hybridizations $\hat{V}_\alpha$; in the lowest order, the molecular energies and Coulomb repulsion are not renormalized. For the $S=1$ case, the spin is screened by the two active channels with two characteristic energy scales T_{Ke} and T_{Ko}. For $T_{Ko} \ll T \ll T_{Ke}$, the conductance approaches the unitary limit and decreases for $T < T_{Ko}$ being zero at zero temperature. In the most general case with $\lambda \neq 0$ and $g_R \neq g_L$, the conductance is reduced by the prefactor $4u^2v^2$.

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