

A theoretical study of the single-molecule transistor

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The magnetic susceptibility χ , charge susceptibility χ_c , and spectral function ρ_{dd} of the single-molecule transistor at low temperatures were calculated using numerical renormalization-group methods. Relationships of χ to electron-phonon coupling, molecular deformability, and molecular energy level were determined. Susceptibility behavior was found to mirror across the particle-hole symmetric point of the transistor Hamiltonian so long as either electron-phonon coupling or molecular distortion (or both) was inactive. Spectral function analysis showed electron spin screening at the molecular energy site when phonon coupling was weak, and charge screening when phonon coupling was strong, both due to Kondo resonance.

I. INTRODUCTION

The Anderson model of dilute magnetic impurities in nonmagnetic metals treats each impurity as a localized electron level located in a Fermi sea of s-shell free electrons [1]. In recent years the model has been adapted to other physical systems. One such system is the molecular transistor — a single molecule connected to three electrical terminals: a source, a drain, and a gate [2–5]. By applying the numerical renormalization group (NRG) method [6], one can diagonalize and solve the Anderson Hamiltonian recursively for any number of eigenstates, with computational capacity being the sole limiting factor. We used the NRG method to study how varying certain conditions of the transistor, such as the gate voltage controlling the molecule’s energy level, and vibration of the molecule, affects its physical properties.

II. TRANSISTOR HAMILTONIAN

The modified Anderson Hamiltonian for the molecular transistor model consists of three parts:

$$\hat{H} = \hat{H}_M + \hat{H}_E + \hat{H}_{M-E}. \quad (1)$$

The first term, \hat{H}_M , represents the energy of the molecule itself:

$$\hat{H}_M = \epsilon_d n_d + U n_{d\uparrow} n_{d\downarrow} - \lambda (n_d - 1)(a + a^\dagger) + \omega_0 a^\dagger a \quad (2)$$

where ϵ_d is the single relevant electronic energy level of the molecule (relative to the Fermi energy of the two electrodes), n_d is the number of electrons in the molecular level, U is the Coulombic repulsion between two electrons in the molecular level, λ is the electron-phonon coupling constant, and $\omega_0 a^\dagger a$ is the vibrational energy of the molecule corresponding to a harmonic potential $V(x) = \frac{1}{2}m\omega_0^2 x^2$.

The second term of \hat{H} in Eq. (1) is

$$\hat{H}_E = \sum_{\alpha,k,\sigma} \epsilon_k c_{\alpha k \sigma}^\dagger c_{\alpha k \sigma} \quad (3)$$

where $\alpha = L, R$ represents the source and drain electrodes, respectively, which are assumed to be identical. The dispersion function ϵ_k describes the motion of electrons along each lead. We assume for simplicity that each lead has a density of states

$$\rho(\epsilon) = \sum_k \delta(\epsilon - \epsilon_k) = \begin{cases} \rho_0 & |\epsilon| < D \\ 0 & |\epsilon| \geq D \end{cases} \quad (4)$$

where D is the conduction half-bandwidth. The final term of \hat{H} represents the interaction of the molecule and the two terminals:

$$\hat{H}_{M-E} = \sum_{\alpha} [1 + g_{\alpha}(a + a^{\dagger})] V \sum_{k,\sigma} (d_{\sigma}^{\dagger} c_{\alpha k \sigma} + c_{\alpha k \sigma}^{\dagger} d_{\sigma}). \quad (5)$$

The term $\sum_k d_{\sigma}^{\dagger} c_{\alpha k \sigma}$ represents the ‘‘hopping’’ of an electron from terminal α to the molecule, and the second term, the Hermitian conjugate of the first, represents the opposite motion. V is the transistor-electrode tunneling parameter, and g_{α} describes the molecule’s deformability. The physical implications of this last parameter are twofold: if $g_L = g_R (= g)$, then the molecule is ‘‘breathing’’ (C_{60} molecules do this especially well); if $g_L = -g_R (= g)$, however, then the molecule exhibits center-of-mass motion between the two leads. This paper addresses the former case only.

The transistor model has a large number of parameters that can be varied. These parameters are summarized in Table I. We took the half-bandwidth $D = 1$ to be the fundamental

TABLE I: Parameters of the molecular transistor model

Parameter	Description
ϵ_d	energy of the molecule relative to Fermi energy
U	Coulombic interaction between electrons in the molecule
Δ	electron hybridization width, where $\Delta = 2\pi\rho_0 V^2$
g, g_{α}	molecular deformability
λ	electron-phonon coupling strength
ω_0	phonon vibrational frequency
D	half-bandwidth of the leads

energy scale in our calculations. Other parameters were divided by D and thus became dimensionless. We also changed as necessary a few other parameters in our programs which result purely from the numerical nature of the NRG method: the so-called band-discretization Λ ; the number of recursive diagonalizations of the Hamiltonian to perform; the maximum electronic energy value to retain during a given iteration; and the maximum number of

energy states to retain per iteration. The purpose of the latter two parameters was to control computation time. The time necessary to diagonalize matrices grows exponentially with their size, so we balanced these parameters so as to achieve maximum precision in our calculations in the least amount of time.

III. THE KONDO EFFECT

When the temperature of most nonmagnetic metals is decreased, the resistivity decreases as well. Some of these metals superconduct below a temperature T_c , at which point their resistivity sharply drops to zero. In the normal state, however, resistivity continues to decrease as $T \rightarrow 0$. However, a nonmagnetic metal doped with magnetic impurities reaches a temperature below which its resistivity actually begins to *increase* again. This temperature is called the *Kondo temperature*, T_K , and the phenomenon which causes ρ to increase at low temperatures is called the *Kondo effect*.

The Kondo effect is a purely quantum mechanical phenomenon. Suppose a magnetic impurity site (a single atom, for example), has only one energy level in its outer shell, and suppose the electrons in the nonmagnetic portion of the metal comprise a Fermi sea. If the energy of the impurity site is $-|\epsilon_d|$ with respect to the Fermi surface, and if a single electron is located at that energy level, it may tunnel off the impurity site and onto the Fermi surface, but the energy required to do so ($|\epsilon_d|$) must be “returned” within a very short amount of time, as required by the uncertainty principle. This energy comes from another electron at the Fermi surface which tunnels onto the impurity site to fill its vacancy. If the two electrons have the same spin, then nothing physically remarkable has occurred at the impurity. However, if they have *opposite* spin, then the total spin of the impurity has just changed. These exchange processes have the effect of correlating the spin of the impurity with the spins of the surrounding electrons. At temperatures below T_K the conductance electrons arrange themselves so that they effectively cancel or “screen” the spin- $\frac{1}{2}$ on the impurity level. This is the Kondo effect. Because the tunneling processes that cause the Kondo effect happen extremely quickly and frequently, the impurity site experiences a resonance of spin states, which is called the *Kondo resonance*.

The Kondo resonance only scatters electrons near the Fermi energy, so at high temperatures its effect on resistivity is negligible. However, at very low temperatures (≈ 10 K, for

example), it is these electrons which determine the properties of the metal, so the Kondo effect becomes very influential. The intense scattering of electrons at the impurity site is what increases the resistivity of the metal below T_K .

Since the single-molecule transistor behaves just like a magnetic impurity in a nonmagnetic metal, and since we focused our attention on very low-temperature situations, we expected the Kondo effect to play a dominant role in the transistor's physical properties. Specifically, for cases in which $\epsilon_d \ll -\Delta$, $U \gg \Delta$, and $\lambda = 0$ (setting $\lambda = 0$ negates all vibration effects of the molecule), the Coulombic repulsion U makes it favorable to have a single electron on the molecule, and thus the molecule should have a nonzero spin. However, for $T < T_K$ we expected nearby electrons in the leads to orient their spins antiferromagnetically, such that the spin of the electron at the molecular energy state would be effectively screened out.

However, when $\lambda \neq 0$, the third term of Eq. (2) shows that molecular vibrations (phonons) couple to the electron at the molecular energy state and lower its energy, but only if $n_d \neq 1$; since we assume the molecule has just one relevant energy state, it must have either zero or two electrons in order for the phonons to lower the energy of the system. For $n_d = 0$ or 2 the λ coupling effectively displaces the harmonic oscillator potential described by the last term in Eq. (2) from $x = 0$ to $x = x_0 \propto \lambda$. This does not change the energy levels of the harmonic oscillator, but changes the effective Coulombic repulsion from U to $U_{eff} = U - 2\lambda^2/\omega_0$. When $U_{eff} \ll -\Delta$, it becomes energetically favorable to have either zero or two electrons at the energy site. (The states $n_d = 0$ and 2 are degenerate for the special case $\epsilon_d = -U/2$ that we will focus on in this study.) In either case the molecule's actual spin is zero (the exclusion principle requires two electrons at the energy site to have opposite spins), but it instead develops a charge "pseudospin," which is -1 or $+1$ with respect to the single-occupancy state. For this case we expected this pseudospin to be screened out once again by surrounding electrons in the leads when $T < T_K$.

IV. BEHAVIOR OF MAGNETIC SUSCEPTIBILITY

We first studied how the magnetic susceptibility χ varies with the electron-phonon coupling constant λ . We used parameters set by Cornaglia *et al.* [2]: $\Delta = 0.016$, $U = 0.1$, and $\omega_0 = 0.05$. The results for this first case are shown in Fig. 1. For each plot shown in this

figure, $\epsilon_d = -U/2$ and $g = 0$.

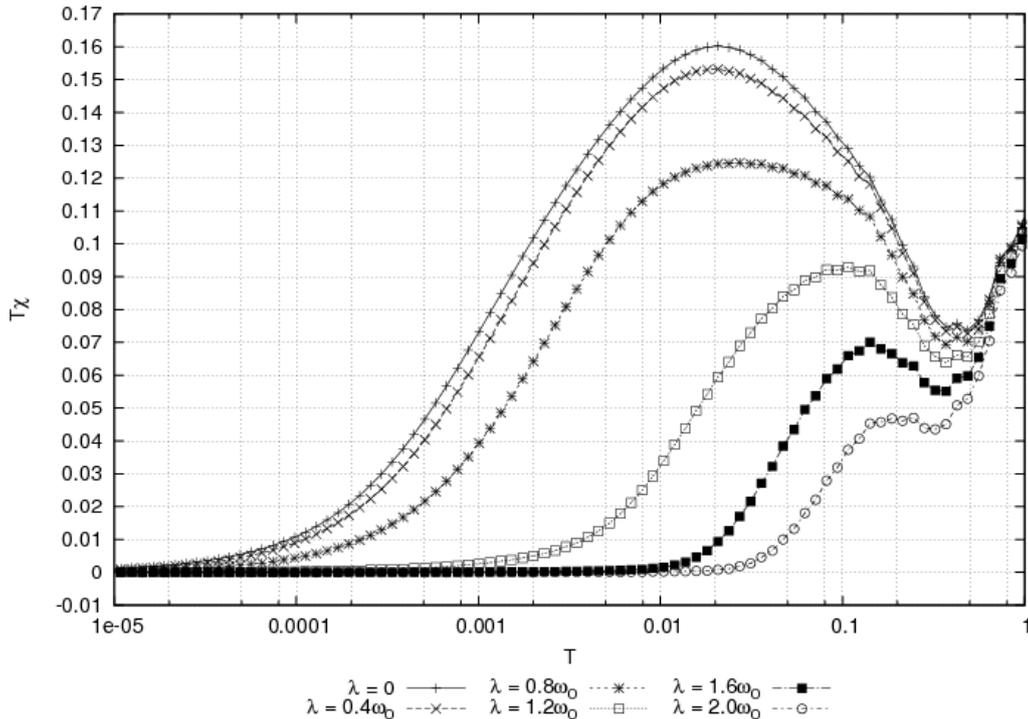


FIG. 1: Change in χ with change in λ .

The most distinct feature of Fig. 1 is that large values of λ heavily suppress the peak of $T\chi$. The maximum susceptibility value for $\lambda = 0$ is only $T\chi \approx 0.16$, whereas for $\lambda = 2.0\omega_0$ the peak is $T\chi \approx 0.05$. In Figs. 1-3, we define T_K as occurring at the point where $T\chi \approx 0.07$ (on the left side of each peak, not the right side). In this figure we see also that that increasing λ raises T_K . For example, at $\lambda = 0$, $T_K \approx 10^{-3}$, but at $\lambda = 1.6\omega_0$, $T_K \approx 0.2$.

Fig. 1 shows that the relationship between λ and T_K is not linear, however, even on a logarithmic temperature scale. The difference ΔT_K between $\lambda = 0$ and $\lambda = 0.4\omega_0$ is very small, whereas ΔT_K for $\lambda = 0.4\omega_0$ and $\lambda = 0.8\omega_0$ is quite large, and that of $\lambda = 0.8\omega_0$ and $\lambda = 1.2\omega_0$ is enormous. The susceptibility curve for $\lambda = 1.6\omega_0$ barely reaches $T\chi \approx 0.07$ at all, and that of $\lambda = 2.0\omega_0$ falls short entirely.

Next we studied how χ varies with the molecular energy level ϵ_d . Here we set $\lambda = 1.2\omega_0$ and $g = 0$. The results are displayed in Fig. 2. The influence ϵ_d has on χ is much less pronounced than that of λ . The value $\epsilon_d = -U/2$ (written “ $\epsilon_d/U = -0.5$ ” in the figure) is the particle-hole symmetric point of the transistor Hamiltonian in Eq. (1), and the susceptibility curve reaches its highest peak when ϵ_d has that value. Deviations from the

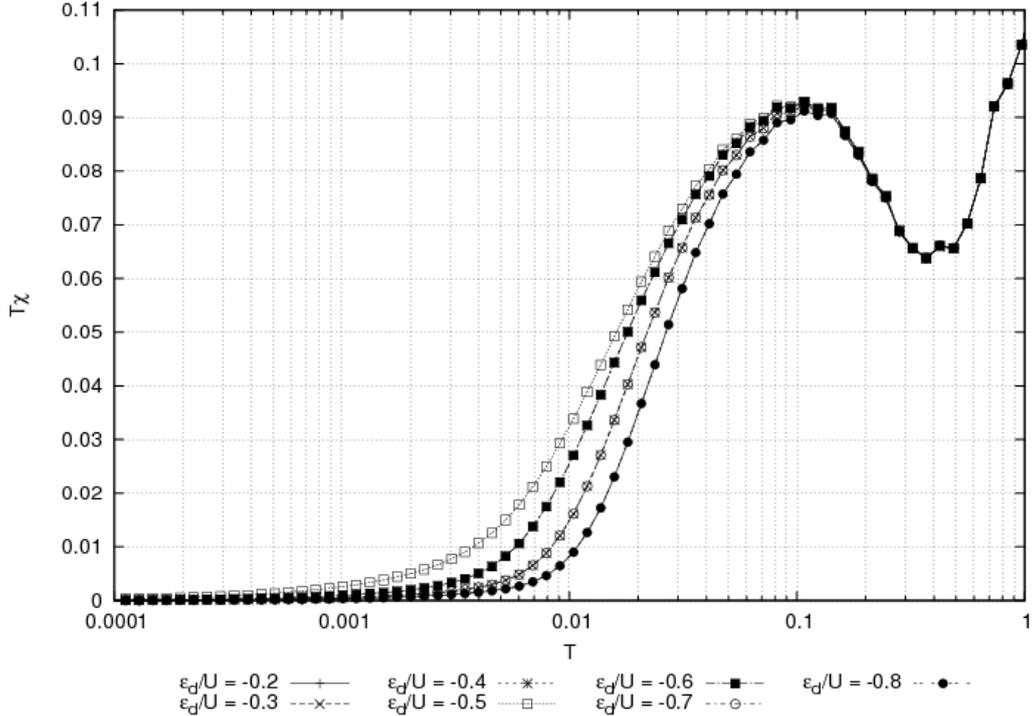


FIG. 2: Change in χ with change in ϵ_d .

symmetric point result in higher T_K and slightly lower peaks. The effect of ϵ_d on T_K appears more uniform than that of λ , but ΔT_K is still not exactly linear in Fig. 2.

One consequence of the symmetric nature of the Hamiltonian is that the data for values of ϵ_d which are larger or smaller *by the same amount* than $\epsilon_d = -U/2$ are identical. This is why Fig. 2 shows only four distinct lines instead of seven. The plots of $\epsilon_d/U = -0.6$ and $\epsilon_d/U = -0.4$ overlap exactly, as do those of -0.7 and -0.3 , and also -0.8 and -0.2 .

Finally we observed the effects of g , the molecular distortion constant, on χ . For this case we again set $\epsilon_d = -U/2$ and $\lambda = 1.2\omega_0$. Fig. 3 shows our results. The pattern in this figure resembles those of Figs. 1 and 2: increasing g (making the molecule deform more severely during electron acquisition and ejection) also increases the Kondo temperature T_K . Notice that in this case both λ and g are nonzero, so the particle-hole symmetry of the transistor Hamiltonian is broken. If we were to plot variation in χ with ϵ_d once again using one of the g values in Fig. 3, the curves would no longer mirror across $\epsilon_d = -U/2$, but rather across some other value of ϵ_d .

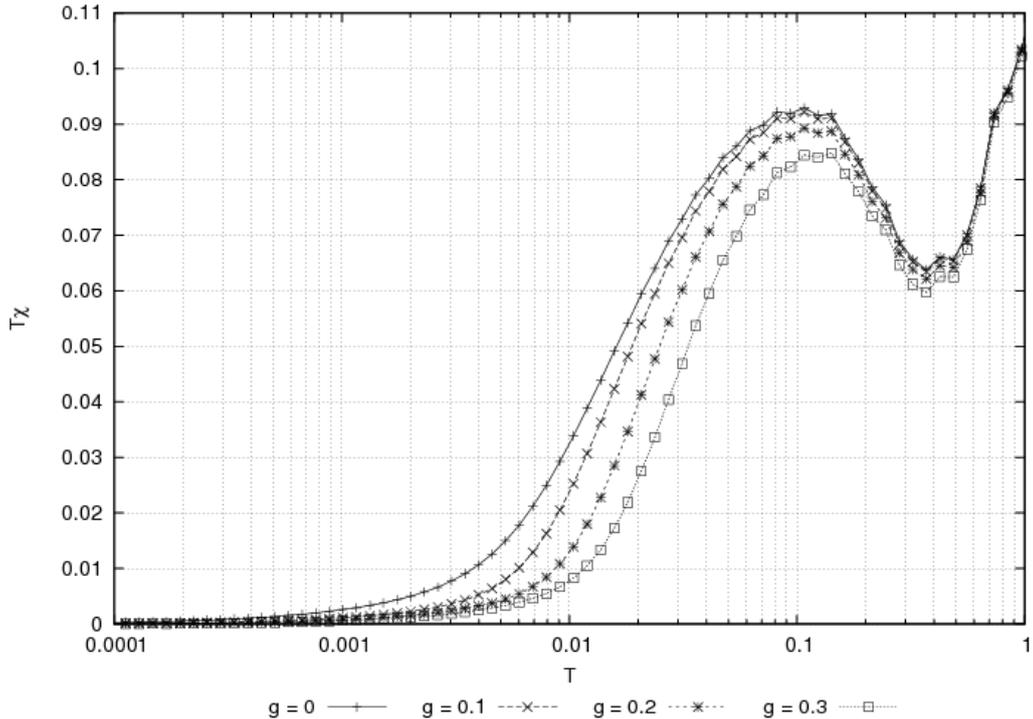


FIG. 3: Change in χ with change in g .

V. CHARGE AND SPIN SUSCEPTIBILITIES AND THE SPECTRAL FUNCTION

In Eq. (2), the term $n_d - 1$ causes the phonon operators $a + a^\dagger$ to couple to the electrons only if the energy state at the impurity site is unoccupied or doubly-occupied; if the site is singly-occupied, $n_d = 1$ and $n_d - 1 = 0$, so the whole third term of Eq. (2) is zero. When the electron-phonon coupling constant λ is small (that is, $2\lambda^2/\omega_0 \ll U$), $U_{eff} > 0$, and the two possible singly-occupied states (spin-up and spin-down) remain energetically more favorable than the empty and doubly-occupied states. The two singly-occupied states are also degenerate. However, when λ is large ($2\lambda^2/\omega_0 \gg U$), $U_{eff} < 0$, and the unoccupied and doubly-occupied states become favored (and degenerate in the special case $\epsilon_d = -U/2$).

The magnetic susceptibility χ is a measure of the oscillations of the spin on the impurity site, and the charge susceptibility χ_c is a measure of the oscillations of charge at the impurity site. For small λ , when the only possible energy state configuration is single-occupancy, the charge at the impurity site does not change (spin-up and spin-down electrons have the same charge), but the magnetic moment, caused by the spin direction, *does* change upon

application of a weak magnetic field. Conversely, at large λ , the magnetic moment does not change (an empty site and a doubly-occupied site both have a total spin of 0), but the charge *does* change upon the application of a weak electric field — it can change from +1 to -1 (relative to the singly-occupied state), depending on the electric field direction.

The Kondo effect drastically changes the charge and spin susceptibility behavior of the molecule at temperatures below the Kondo temperature. For weak or absent phonon coupling, where a single electron occupies the molecular energy state, Kondo resonance of electrons both at the impurity site and at sites along the leads nearest the molecule causes them to orient their spin directions and “amplitudes” such that there is a cancellation of total spin in an area surrounding the molecule. Thus, if an electron tries to pass through the molecular transistor, it will “see” no effective spin with which to interact.

For strong phonon coupling, where the empty and doubly-occupied states have lower energy than the singly-occupied states, the Kondo effect also plays an influential role, albeit in a slightly clandestine manner. The zero- and two-electron configurations have the same total spin (zero), but they have different charges. Thus, if the molecular site had two electrons, the sites along the leads near the molecule would resonate their *charges* instead of their *spins* (recall that the empty and doubly-occupied configurations are degenerate for $\epsilon_d = -U/2$), causing an effective cancellation of total charge in an area surrounding the molecule. Just as in the spin-resonance case, a traveling electron would “see” no effective charge as it passed through the transistor.

Consequently, we expected that the spectral function ρ_{dd} (an electron density-of-states function) would show that the temperature scale at which Kondo screening arose would match the temperature scale for spin screening predicted by χ for small λ ; for large λ we expected that ρ_{dd} would match the temperature scale predicted for charge screening by χ_c . Figs. 4 and 5 show this comparison on linear and logarithmic temperature scales, respectively. We see that, indeed, for small λ , T_{spin} and $T_{spectral}$ are very similar in value and are nearly parallel (Fig. 4), indicating that they differ only by some constant multiplicative factor which could be removed by re-calibrating our algorithms; for large λ , T_{charge} and $T_{spectral}$ are also very similar and nearly parallel (Fig. 5). For $2\lambda^2/\omega_0 \sim U$, ρ_{dd} deviates from both χ and χ_c .

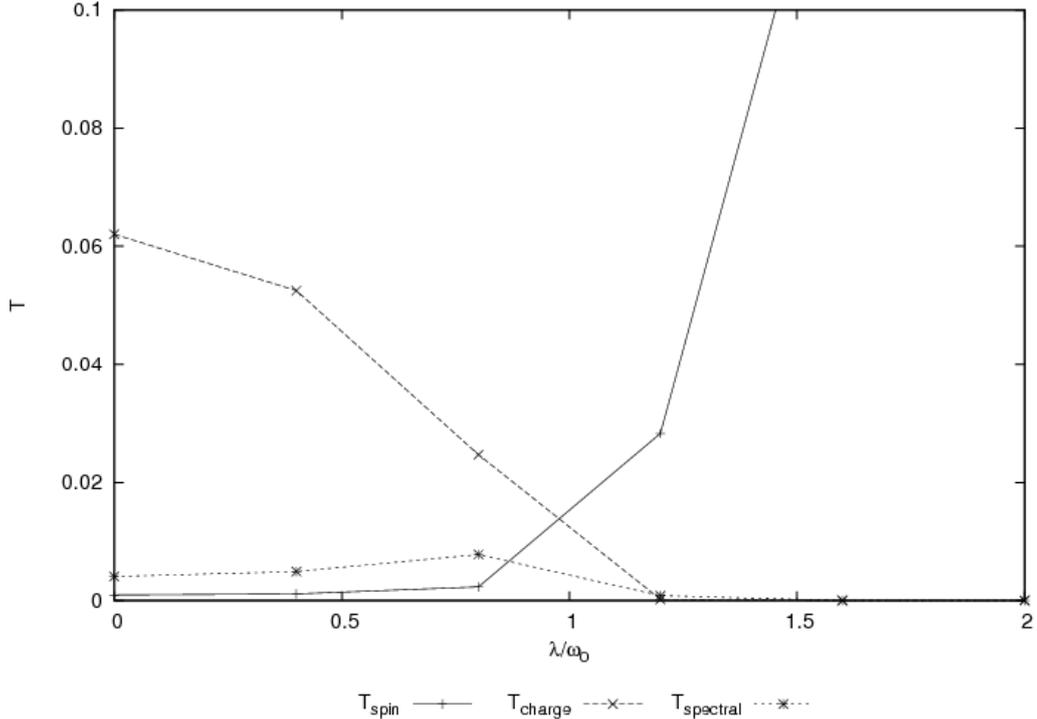


FIG. 4: Comparison of χ , χ_c and ρ_{dd} (linear scale).

VI. CONCLUSIONS

We found that the peak magnetic susceptibility χ of the single-molecule transistor is largest under the “simplest” circumstances — no electron-phonon coupling, no molecular distortion, and preserved particle-hole symmetry — and that activating such factors as these reduces the maximum value of χ and significantly raises the transistor’s Kondo temperature. We also found that Kondo resonance causes electrons on the molecule to have screened spins when phonon coupling is weak, and screened charges when phonon coupling is strong.

VII. ACKNOWLEDGMENTS

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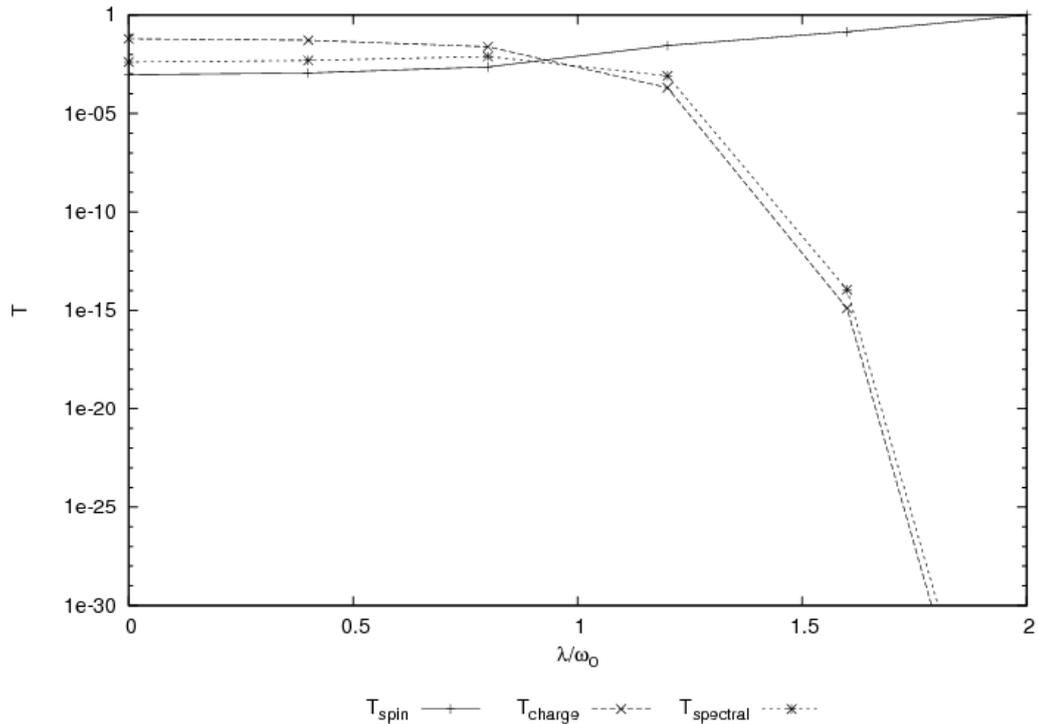


FIG. 5: Comparison of χ , χ_c and ρ_{dd} (logarithmic scale).

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