Enhancing the nonlinear thermoelectric response of a correlated quantum dot in the Kondo regime by asymmetrical coupling to the leads

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We study the low-temperature properties of the differential response of the current to a temperature gradient at finite voltage in a single-level quantum dot including electron-electron interaction, nonsymmetric couplings to the leads, and nonlinear effects. The calculated response is significantly enhanced in setups with large asymmetries between the tunnel couplings. In the investigated range of voltages and temperatures with corresponding energies up to several times the Kondo energy scale, the maximum response is enhanced nearly an order of magnitude with respect to symmetric coupling to the leads.

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I. INTRODUCTION

During the last decade, the study of nanodevices that convert heat into work has received great attention due to possible applications [1]. These quantum thermoelectric machines are usually considered to be composed of a system of a small number of degrees of freedom coupled to a set of macroscopic reservoirs. Among them, semiconducting [2–8] and molecular [9–18] quantum dots (QDs) play a fundamental role.

A permanent interest in enhancing efficiency and power of such devices exists. In this sense, the charge and heat currents through QDs have been the focus of intense research both experimentally [19–22] and theoretically [19,23–40].

Mahan and Sofo have shown that a delta shape of the transmission function maximizes the efficiency of thermoelectric devices [23]. Since then, other mechanisms for increasing the Seebeck coefficient (thermopower), S, have been proposed. Among them, a time-dependent gate voltage [30], orbital degeneracy [31,32], negative values of the Coulomb repulsion [29], quantum Hall bar with fractional filling factors [40], and nonlinear (NL) transport effects [27,35,39] have been investigated.

Recently, Dorda *et al.* studied the differential thermoelectric response of a correlated impurity in the nonequilibrium Kondo regime (KR) at finite voltage [35]. In addition to providing a fundamental understanding of the system, the authors point out the potential of QDs as possible nanoscale temperature sensors. The study was limited to symmetric coupling of the dot to both leads, and the authors state that further studies including asymmetric couplings to the leads are required to fully assess the potential of QD devices for nanoscale sensing applications.

In this paper, we consider a QD asymmetrically coupled to the leads and we show that for large asymmetry, which is expected for molecular QD [41,42], the differential response of the current to a temperature gradient at finite voltage is increased nearly by an order of magnitude with respect to the symmetric case.

Specifically, we investigate NL transport effects on the differential thermopower. When a bias voltage is applied to the system, a constant electric current in the steady state is established. Assuming this regime, we analyzed its response to an infinitesimal gradient of temperature between the leads, as sketched in Fig. 1. We restrict our study to the case in which transport is due to electrons. Vibrational effects were studied in Refs. [22,27,37], among others. The model is suitable for molecular QDs (for which asymmetric couplings are the most usual situation) and semiconducting QDs, in which the tunnel couplings can be tuned at will [8]. We find that the asymmetry of the tunneling couplings, $\alpha = \Delta_L/\Delta_R$, plays a nontrivial role and large values of α boost the differential thermopower in the NL regime. As it will be clarified below, the range of parameters for this enhancement are within or near the KR.

II. MODEL AND EXPRESSION FOR THE CURRENT

We employ the single impurity Anderson Hamiltonian to model the molecular or semiconducting QD. It is composed by a single dot level of energy E_d connected to two metallic reservoirs. The Hamiltonian is

$$H = E_d n_d + U n_{d\uparrow} n_{d\downarrow} + \sum_{\nu k\sigma} \epsilon_k^\nu c_{\nu k\sigma}^\dagger c_{\nu k\sigma} + \sum_{\nu k\sigma} \left(V_k^\nu d_\sigma^\dagger c_{\nu k\sigma} + \text{H.c.} \right), \quad (1)$$

where $n_d = \sum_\sigma n_{d\sigma}$, $n_{d\sigma} = d_\sigma^\dagger d_\sigma$, $d_\sigma^\dagger$ creates an electron with spin σ at the active level of the QD, $c_{\nu k\sigma}^\dagger$ creates a conduction electron at the left ($\nu = L$) or right ($\nu = R$) lead, and V_k^ν describe the hopping elements between the leads and the QD.

When the temperatures T_ν and/or chemical potentials μ_ν of the reservoirs are different, heat and electric (charge) currents flow from one lead to the other. The sign of such currents depend on the temperature and chemical potentials differences and they are constant in the steady state. As a reference, we assume $T_\nu = T + \gamma_\nu \Delta T/2$ and $\mu_\nu = -e\gamma_\nu \Delta V/2$ with

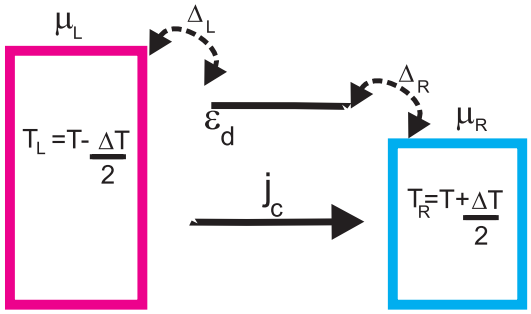

FIG. 1. Scheme of the model considered, with the electronic level of the QD and their hybridization to the leads.

the sign $\gamma_\nu = -(+)$ for $L(R)$ being $\Delta T > 0$ the temperature difference and ΔV the bias voltage.

The charge current through the QD is given by [43]

$$J_C = \frac{2e\pi}{h} A(\alpha)\Delta \int d\omega \rho(\omega)(f_L(\omega) - f_R(\omega)), \qquad (2)$$

where $\Delta = \Delta_L + \Delta_R$ is the total coupling of the QD to the leads with $\Delta_\nu = \pi \sum_k |V_k^\nu|^2 \delta(\omega - \epsilon_k^\nu)$ (assumed independent of energy), and $A(\alpha) = 4\alpha/(\alpha+1)^2$ represents the asymmetry factor. In addition, $f_\nu(\omega) = 1/(\exp(\frac{\omega-\mu_\nu}{T_\nu}+1))$ is the Fermi distribution associated to the lead ν, and the spectral function of the QD per spin is given by $\rho(\omega)$.

In the following, we assume $U \to \infty$, which is a realistic limit for most molecular QDs. In fact, renormalizing the Kondo energy scale T_K, the physics discussed here is the same for finite U as long as the Kondo peak (the one near the Fermi energy and of width $2T_K \ll \Delta$) in the spectral density of states is well separated from the charge-transfer peaks at E_d and $E_d + U$ and voltages and temperatures are such that the corresponding energy scales eV and T are much smaller than the charge-transfer excitations ($eV, T \ll |E_d|, E_d + U$ with the Fermi energy set as $\epsilon_F = 0$). Since the total width of the charge-transfer peaks in the KR $-E_d, E_d + U \gg \Delta$ are $\sim 4\Delta$ [44,45], and E_d can be tuned in QDs so that $E_d \sim -U/2$, our results are valid for systems such that $U \geqslant 8\Delta$.

III. NONCROSSING APPROXIMATION

To calculate the spectral function of the QD, we use the noncrossing approximation (NCA) in its nonequilibrium extension [46,47]. The NCA is equivalent to a sum of an infinite series of diagrams in perturbations in V_k^ν [48,49]. In the KR, it is known to reproduce correctly the relevant energy scale T_K and its dependence on the different parameters. The out-of-equilibrium NCA approach is one of the standard techniques for calculating the current in mixed valence systems within different regimes of the model, and especially within the KR, where the dot occupancy is near 1. It has proved to be a very valuable tool for calculating the differential conductance through different systems such as two-level QDs and C_{60} molecules displaying a quantum phase transition or a nanoscale Si transistor [17,50–53], among others. It also reproduces correctly the scaling of the conductance for small bias voltage V and temperature T [54], and is able to reproduce finite-energy features in systems, where the numerical renormalization group has difficulties, like the presence of a step in the conduction band [55].

Alternatives to NCA for nonequilibrium problems have some limitations. For example, renormalized perturbation theory is limited to small ω, V and T [33,56–58] and the method of the equation of motion [59–62] does not reproduce correctly the functional dependence of T_K on E_d [60,61].

The main limitations of the NCA for the Anderson model we consider take place for moderate positive E_d and finite moderate U. For positive E_d, the impurity self-energy has an unphysical positive imaginary part and as a consequence $\rho(\omega)$ presents a spurious peak at the Fermi energy. Similar spurious peaks exist for finite magnetic field [46]. For finite U, the NCA ceases to reproduce correctly the dependence of T_K with parameters, and vertex corrections should be included [63–65]. Since, in this paper, the parameters correspond to the KR $-E_d, E_d + U \gg \Delta$ and we take $U \to \infty$, we avoid these limitations. A minor problem is that the intensity of the Kondo peak is overestimated by about 15% compared to the value expected from the Friedel sum rule [66].

More details on the formalism and tricks that we use to solve the self-consistent integral equations can be found in Refs. [47,67].

IV. RESULTS

Without loss of generality, we choose our unity of energy to be $\Delta = 1$. We present results for $E_d = -4$, which corresponds to the KR. We choose a bandwidth of $2D$ with $D = 10$. We define the Kondo temperature (T_K) as the temperature for which the equilibrium conductance is half of the corresponding one for the unitary limit, $G(T = T_K) = G_0/2$ with $G_0 = 2A(\alpha)e^2/h$. For our parameters, this leads to $T_K = 0.0086$. Due to the universality of the model in the KR, the results presented here in units of T_K are quite general in this regime and do not depend on the particular values of Δ, E_d, or U. For simplicity, we also take the Boltzmann constant and absolute value of the electronic charge $k_B = e = 1$ so that the Seebeck coefficient S and V/T become dimensionless.

The Seebeck coefficient, S, and the electrical conductance, G, within the linear response regime, $\Delta T = \Delta V \to 0$, are commonly defined in terms of equilibrium properties [26], $S = -I_1(T)/[eTI_0(T)]$, $G = e^2 I_0(T)$ being

$$I_n(T) = \frac{2\pi}{h} A(\alpha)\Delta \int d\omega \omega^n \rho(\omega)(-f'(\omega)). \qquad (3)$$

Here, the asymmetry factor α does not modify the equilibrium spectral density due to the fact that both the charge-transfer peak near E_d and the Kondo one at the Fermi energy $\epsilon_F = 0$ depend on the total coupling $\Delta = \Delta_L + \Delta_R$ and not on the ratio $\alpha = \Delta_L/\Delta_R$. While the charge-transfer peak has a width of 4Δ in the KR [44,45], the width of the Kondo peak is of the order of $T_K \sim D\exp(\pi E_d/2\Delta)$ and its intensity is fixed by the Friedel sum rule $\rho(0) \sim 1/\pi\Delta$.

In Fig. 2(b), we show the spectral density for two extremely different values of α. As explained above, they are identical. Thus, the equilibrium conductance is strongly suppressed for

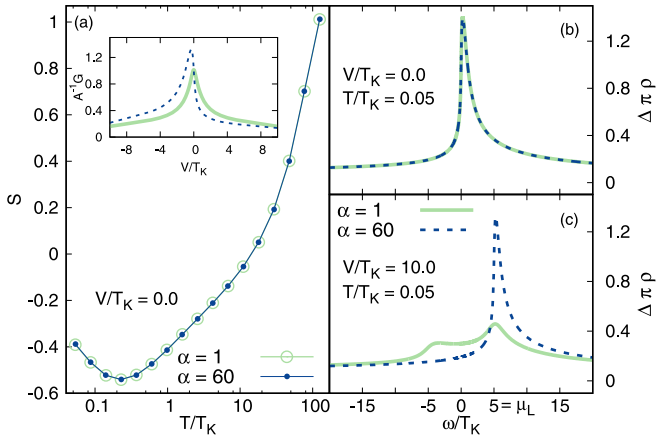

FIG. 2. (a) Thermopower as a function of temperature for two values of the asymmetry ratio α at equilibrium ($\Delta V = \Delta T = 0$). The inset shows the differential conductance as a function of bias voltage for two values of α (1 and 60). (b) Spectral density as a function of energy at equilibrium for the same α as in (a). (c) Spectral density as a function of energy for $V/T_K = 10$ for the same α as in (a). In all cases, $T/T_K = 0.05$.

high values of the asymmetry α [due to the factor $A(\alpha)$ in Eq. (2)] while the Seebeck coefficient remains unchanged due to the cancellation of $A(\alpha)$ in $I_1(T)/I_0(T)$ as it can be seen in the left panel of Fig. 2.

However, when finite values of the bias voltage are considered, nontrivial effects arise, which depend on α. The Kondo resonance in the spectral density splits in two peaks, located at μ_ν [46,51]. The weights of both peaks are affected by α. While they are approximately equal in the symmetric case, $\alpha = 1$, the one at μ_R (μ_L) decreases (increases) for increasing α. For $\alpha \gg 1$, the QD is nearly in equilibrium with the left lead and the spectral density shows the full Kondo resonance shifted to the chemical potential μ_L, see Fig. 2(c). On the other hand, the differential conductance, $G(\Delta V) = dJ_C/d(\Delta V)$, is an even function of the bias voltage for $\alpha = 1$ due to left-right reflection symmetry, but in the case of $\alpha \gg 1$ it mimics the spectral density, $G(\Delta V) \sim \frac{e^2}{h}\pi\Delta A(\alpha)\rho(-e\Delta V/2)$, see inset of Fig. 2(a). Similar conclusions were drown in Refs. [24,44].

In what follows, we focus on the analysis of NL effects on the differential Seebeck coefficient and its dependence on α. In analogy to bulk systems, when a temperature difference ΔT is applied between both sides of a QD, keeping $J_C = 0$, a voltage difference ΔV proportional to ΔT appears, $S = -\frac{\Delta V}{\Delta T}|_{J_C=0}$. NL effects following the line $J_C = 0$ have already been addressed [24,27,31,34,39]. However, Dorda *et al.* have recently analyzed the NL regime across the line $J_C \neq 0$,

$$\mathcal{S} = -\left.\frac{d(\Delta V)}{d(\Delta T)}\right|_{J_C=\text{const.}} = \frac{\partial J_C}{\partial(\Delta T)}\Big/\frac{\partial J_C}{\partial(\Delta V)}, \tag{4}$$

which is expected to be a measurable quantity that contributes to the better knowledge of the two decoherence processes generated by the bias voltage and temperature, and can be important for applications in nanoscale temperature sensing [35].

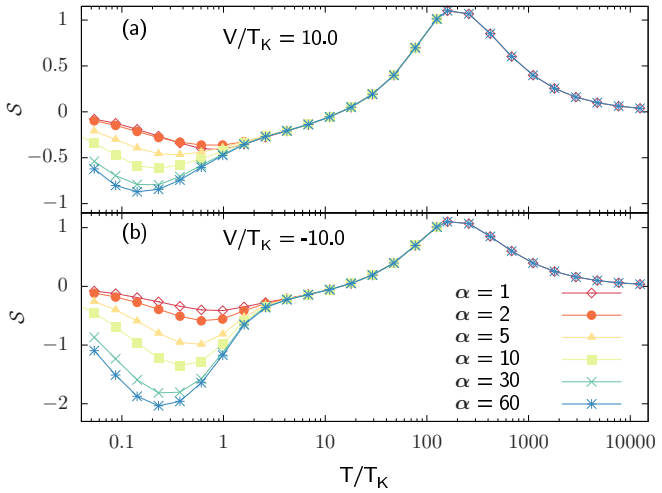

FIG. 3. Differential thermopower as a function of temperature for several values of the asymmetry α, (a) with $e\Delta V/T_K = 10$ and (b) with $e\Delta V/T_K = -10$.

We compute numerically both $\partial J_C/\partial(\Delta V)$ from Eq. (2) and $\partial J_C/\partial(\Delta T)$ using

$$\frac{\partial J_C}{\partial(\Delta T)} = \frac{2e\pi}{h}A(\alpha)\Delta\int d\omega\left[\frac{1}{2T}\rho(\omega)\sum_\nu(\omega-\mu_\nu)\frac{df_\nu}{d\omega}(\omega) + (f_L(\omega)-f_R(\omega))\frac{\partial\rho(\omega)}{\partial(\Delta T)}\right]. \tag{5}$$

We will show that the differential thermopower at finite bias voltage as described by Eq. (4) is largely enhanced for large asymmetry between the tunnel couplings.

In Fig. 3, we show the results for the differential Seebeck coefficient at finite voltage as a function of temperature and for several values of the asymmetry factor α. For $T \gg T_K$, $\mathcal{S}$ does not depend on α independently of the sign of the current. In fact, at high T there is no Kondo peak in the spectral density and the electronic transport is holelike, mediated by the charge transfer peak located at $\omega \sim E_d < 0$, that has a width of the order of 4Δ [44,45], and is nearly not affected for the bias voltage considered in the figure, of the order of a few T_K. For finite U, the other charge transfer peak at $\omega \sim E_d + U > 0$, neglected in our approach, can modify the results. However, we are interested in the regime of temperatures of the order of a few times T_K or less. For these temperatures, only the spectral density at low energies is relevant due to the small window of the Fermi functions. One can observe a significant increment of the magnitude of $\mathcal{S}$ for larger values of α as compared to the symmetric case. In particular for $V = -10T_K$ and temperatures of the order of T_K or below it, $|\mathcal{S}|$ is enhanced by a factor near 5 as the asymmetry α increases from 1 (symmetric case) to 60.

V. INTERPRETATION AND FURTHER RESULTS

To understand the behavior of the thermoelectric response as α is varied, we analyze qualitatively the low-temperature features of the charge current in Eq. (2). As we have showed in Fig. 2, for large enough asymmetry the dot tends to be in

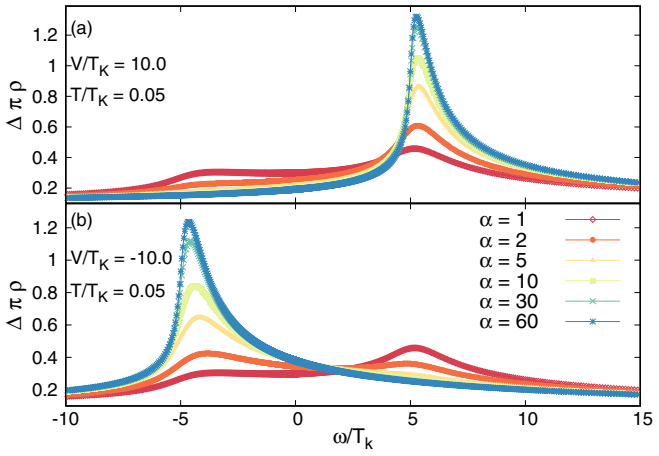

FIG. 4. Kondo resonance in the QD spectral density under a finite bias voltage for several values of the asymmetry ratio α. (a) Positive voltage, $\mu_L/T_K = 5$, $T_K = 0.008$. (b) Negative voltage, $\mu_L/T_K = -5$, $T_K = 0.01$.

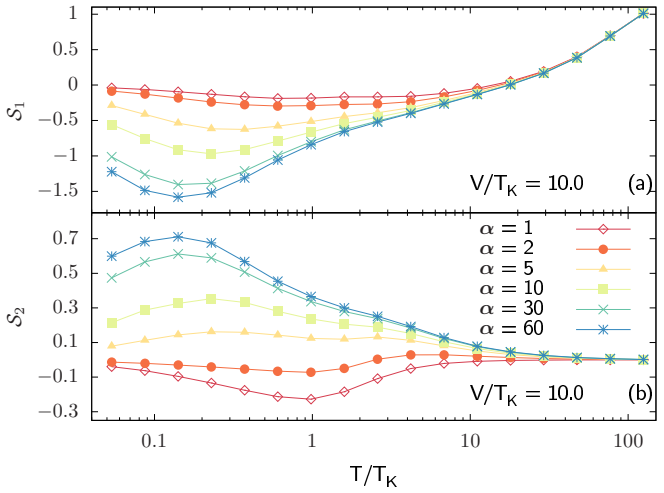

FIG. 5. Contributions to $\mathcal{S}$ of the first and second members of Eq. (5), $\mathcal{S}_1$ and $\mathcal{S}_2$, respectively, as a function of temperature and for positive bias voltage.

equilibrium with the left lead. The evolution of the spectral density with α is explicitly shown in Fig. 4 for both signs of the applied bias voltage.

If the dot is in equilibrium with the left lead, then $\int d\omega \rho(\omega) f_L(\omega)$ does not change with the applied voltage. Using this assumption and standard Sommerfeld expansion [22] for the current in Eq. (2), the low temperature behavior of the differential Seebeck coefficient reads as follows:

$$\mathcal{S}(T) \sim [\rho(\mu_R)]^{-1}\left[-\frac{\pi^2 T}{6e}\sum_v \rho'(\mu_v) + \int_{\mu_R}^{\mu_L} d\omega h(\omega) + \frac{\pi^2 T^2}{6e}(h'(\mu_L) - h'(\mu_R))\right], \quad (6)$$

being $h = \partial\rho/\partial\Delta T$ and $A' \equiv dA/d\omega$. Figure 4 demonstrates that $\sum_v \rho'(\mu_v)$ in the first term of the right-hand side of Eq. (6) increases as the coefficient α does. On the other hand, the value of $\rho(\mu_R)$ continuously decreases when α is increased. Interestingly, both tendencies contribute to boost the coefficient $\mathcal{S}$.

While the temperature dependence of $\mathcal{S}$ is qualitatively the same for positive as well as negative bias voltage, as it is shown in panel (a) ($\Delta V > 0$) and (b) ($\Delta V < 0$) of Fig. 3, the different intensity between them is related to the relative sign of the different contributions in Eq. (6). We have verified that for $\alpha > 5$, the magnitude $h(\omega)$ and $h'(\omega)$ are positive within the relevant energy range, and therefore, the second term of Eq. (6) is also positive.

In Fig. 5, we separately show for a positive value of voltage, the first and second contributions to $\mathcal{S}$ from Eq. (5), namely $\mathcal{S}_1$ and $\mathcal{S}_2$, respectively. While the total magnitude of $\mathcal{S}$ is still larger for the asymmetric case, it is clear that both contributions partially compensate each other. However, for negative voltage (not shown) both terms have the same negative sign and boost even further the magnitude of $\mathcal{S}$. The chain in sign is clearly due to the third (last) term in Eq. (6). Therefore, larger intensity of the differential response is obtained for $\mu_L < 0$, that is, when the current flows from the less coupled (right) lead to the other one. This observation can be used to determine experimentally, in a very simple way, to what side (L or R) the molecule or QD is closer or more coupled.

In Fig. 6, we show the behavior of the thermopower at two different temperatures and for several values of the asymmetry factor α as a function of the applied bias voltage. As a first observation, for the bias voltage considered here, $|e\Delta V| \sim T_K$, the sign of $\mathcal{S}$ is negative in agreement with Fig. 3 for $T < T_K$, due to the electronic character of the transport.

In the case of symmetric couplings, $\alpha = 1$, $\mathcal{S}$ as defined in Eq. (4) is characterized by an even function of the applied bias voltage [68]. The minimum at $e\Delta V = 0$ is due to finite temperature effects. From Eq. (5), $\mathcal{S}$ is expected to vanish in the zero temperature limit. This tendency can be observed by a comparison of the minimum value of $\mathcal{S}$ for the two selected temperatures in Fig. 6, $T = 0.2T_K$ and $T = 0.05T_K$. On the other hand, for large values of $e\Delta V$, the argument of Eq. (5) tends to be an odd function within the relevant

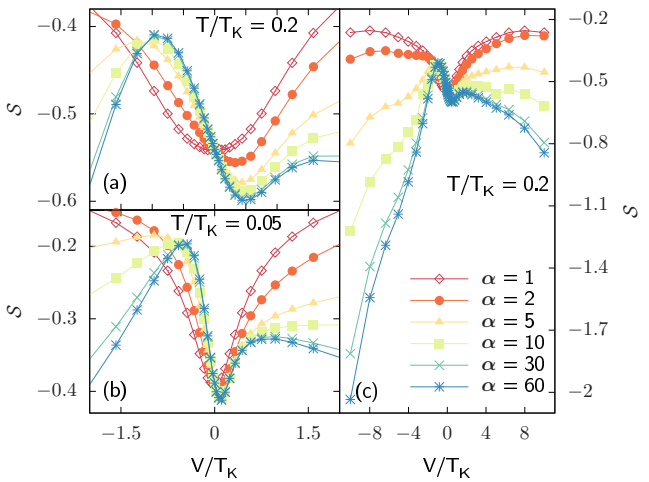

FIG. 6. Differential thermopower as a function of the bias voltage in units of T_K for several values of the asymmetry ratio α and at low temperature.

range of energies. Note that the latter can be written as $[\rho(\omega + e\Delta V/2) + \rho(\omega - e\Delta V/2)]\omega f'(\omega)$ in case of the first contribution [see Fig. 2(c)]. Regarding the second one, we note that $h_\nu(\omega)$ has structure at both μ_ν and, therefore, the product $(f_L(\omega) - f_R(\omega))h(\omega)$ approaches an odd function of the energy.

On the other hand, the case of $\alpha \gg 1$ is quite different. While the behavior of $\mathcal{S}$ for $|e\Delta V|/T_K \ll 1$ is still governed by temperature effects, its dependence on $e\Delta V$ has no parity. The situation of finite values of the bias voltage, particularly at values of a few times T_K, is more involved. As soon as $|e\Delta V|$ reaches T_K, the absolute value of $\mathcal{S}$ is largely increased. Once again, the mechanism behind this behavior is the displacement of $\rho(\omega)$ toward $\omega \sim \mu_L$. The same mechanism that explained the behavior of $\mathcal{S}$ in Fig. 3 applies in the case of the voltage dependence. Large values of $\mathcal{S}$ are obtained for large enough asymmetry. In particular, the increment is even larger when negative voltage is considered as explained before. Note that for negative V, an increase in $|\mathcal{S}|$ for more than an order of magnitude is obtained as α increases from 1 to 60.

VI. CONCLUSIONS

In summary, we have investigated theoretically the differential response of the electric current at finite bias voltage, when an infinitesimal gradient of temperature is applied to a system of a molecular or semiconducting QD coupled asymmetrically to two conducting leads. We have concentrated on the electronic contribution to the differential Seebeck coefficient $\mathcal{S}$, leaving aside phonon contributions.

We show that $\mathcal{S}$ is strongly enhanced for a large asymmetry between the tunnel couplings. In particular, we find an enhancement of $\mathcal{S}$ by an order of magnitude at temperatures of the order of a fraction of the Kondo temperature T_K and bias voltage eV of the order of several times $k_B T_K$. This becomes relevant for the standard cryogenic experimental conditions, for which the Kondo effect emerges. In Sec. V, we have provided an explanation of the nontrivial mechanism behind our findings and we believe that it could be useful for experimental purposes. Our findings can also be important for nanoscale temperature sensing.

Although the calculation of the figure of merit is beyond the scope of this paper, our results suggest that molecular QDs, for which large tunneling asymmetries are expected, or semiconducting QDs in which a large asymmetry can be tuned easily, would be the most efficient quantum machines operating as both heat engines or refrigerators.

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