Mechanism for large thermoelectric power in molecular quantum dots described by the negative-U Anderson model

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Mechanism for large thermoelectric power in molecular quantum dots described by the negative-U Anderson model

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We investigate with the aid of numerical renormalization group techniques the thermoelectric properties of a molecular quantum dot described by the negative-U Anderson model. We show that the charge Kondo effect provides a mechanism for enhanced thermoelectric power via a correlation induced asymmetry in the spectral function close to the Fermi level. We show that this effect results in a dramatic enhancement of the Kondo induced peak in the thermopower of negative-U systems with Seebeck coefficients exceeding $50\mu V/K$ over a wide range of gate voltages.

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Introduction.— Thermoelectric devices currently use bulk materials, e.g. Si-Ge, PbTe or Bi_2Te_3[1–3]. In future, devices made of nanoscale objects, such as quantum dots or molecules, could offer alternatives, particularly for low temperature applications, such as on-chip cooling of microprocessors or low temperature refrigeration. Nanoscale objects have some potential advantages over their bulk counterparts; for example, in scalability or in their high degree of tunability (e.g. via a gate voltage), allowing them to be operated at optimal thermoelectric efficiency. Molecular quantum dots, in particular, could be interesting to study, since a large variety of such systems could be fabricated and investigated for interesting thermoelectric properties[4].

The description of electrical and thermal transport through quantum dots is, however, a challenging theoretical task. Electrons tunneling from the leads through the quasi-localized levels of the dot typically experience a large Coulomb repulsion on the dot, giving rise to the spin Kondo effect[5]. The latter profoundly affects transport, resulting, for example, in the lifting of Coulomb blockade at low temperatures for a wide range of gate voltages and an enhanced conductance close to the unitary limit, $G \approx G_0 = 2e^2/h$, for symmetric coupling to the leads[6–10]. Recent experimental and theoretical work has also addressed the effects of Kondo correlations on the thermoelectric properties of such quantum dots[11–13]. However, the Kondo induced enhancement of the thermopower at the Kondo temperature T_K was found to be very small[13] suggesting that the spin Kondo effect, in its simplest manifestation, is ineffective for realizing efficient thermoelectric devices.

In this Rapid Communication we consider a molecular quantum dot with an *attractive* onsite Coulomb interaction, $U < 0$, described by a negative-U Anderson impurity model, Eq. (1) below. Such a model has been used to explain the dielectric properties of amorphous semiconductors[14], to describe highly polarized heavy fermion states[15] and to investigate the noise and non-equilibrium transport through negative-U molecules[16]. For a molecular quantum dot, several mechanisms could result in $U < 0$, for example, screening by electrons in metallic leads can reduce an initially repulsive local Coulomb interaction to negative values[17], or, a vibrating molecule with a local electron-phonon interaction could result in a net attractive Coulomb interaction[18,20]. For typically used metallic electrodes, such as gold, screening is expected to ensure the locality of the attractive interaction in Eq. (1).

A negative-U quantum dot supports a charge Kondo effect in which the role of spin up and spin down states in the conventional spin Kondo effect are played by the non-magnetic empty and doubly occupied states of the dot[15]. As in the usual spin Kondo effect, this charge Kondo effect results in a renormalized Fermi liquid at low temperatures which has important consequences for electrical and thermal transport. It is also believed to be the origin of superconductivity in PbTe doped with Tl, where the valence skipper Tl acts as a negative-U Centre[21,22]. While some aspects of the electrical transport through a negative-U molecule have been investigated[16], the most astonishing feature of such a system, elucidated below, lies in its remarkable low temperature Kondo induced thermoelectric response which has not been previously addressed.

Model and calculations.— Specifically, we consider a quantum dot described by the following two-lead Anderson impurity model

$$H = \sum_\sigma \varepsilon_d n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + \sum_{k\alpha\sigma} \epsilon_{k\alpha} c^\dagger_{k\alpha\sigma} c_{k\alpha\sigma} + \sum_{k\alpha\sigma} (t_\alpha c^\dagger_{k\alpha\sigma} d_\sigma + h.c.). \quad (1)$$

where, ε_d is the energy of the molecular level, $U < 0$ is the local Coulomb interaction, σ labels the spin, and

$\alpha = L, R$ labels left and right electron lead states with kinetic energies $\epsilon_{k\alpha}$. The couplings of the dot to the leads are denoted by $\Gamma_\alpha(\omega) = 2\pi\rho_\alpha(\omega)|t_\alpha|^2$, where $\rho_\alpha(\omega) = \sum_k \delta(\omega - \epsilon_{k\alpha})$ is the density of states of lead α.

The linear response transport properties can be calculated from the single-particle spectral function of the dot $A_\sigma(\omega) = -\mathrm{Im}[G_{d\sigma}(\omega + i\delta)]/\pi$, where $G_{d\sigma}(\omega + i\delta) = \langle\langle d_\sigma; d_\sigma^\dagger\rangle\rangle$ is the Fourier transform of the retarded single-particle Green function of (1). The thermopower is given by[12]

$$S = -\frac{1}{|e|T}\frac{\int d\omega\, \omega\mathcal{T}(\omega)\,(-\partial f/\partial\omega)}{\int d\omega\mathcal{T}(\omega)\,(-\partial f/\partial\omega)}, \qquad (2)$$

where f is the Fermi function, e is the electronic charge, and $\mathcal{T}(\omega) = 2\pi\Gamma(\omega)\sum_\sigma A_\sigma(\omega)$ is the transmission function of the dot with $\Gamma(\omega) = \frac{\Gamma_L(\omega)\Gamma_R(\omega)}{\Gamma_L(\omega)+\Gamma_R(\omega)}$. At low temperature, a Sommerfeld expansion leads to

$$S(T) = -\frac{\pi^2 k_B}{3|e|}k_B T\left(\frac{\Gamma'(\epsilon_F)}{\Gamma(\epsilon_F)} + \frac{\sum_\sigma A'_\sigma(\epsilon_F)}{\sum_\sigma A_\sigma(\epsilon_F)}\right) \qquad (3)$$

where $\epsilon_F = 0$ is the Fermi level of the leads. In the absence of a magnetic field $A_\uparrow(\omega) = A_\downarrow(\omega) = A(\omega)$ is spin independent. A large thermopower at low temperature can be achieved by either tailoring the band structure of the leads to give a highly asymmetric $\Gamma(\omega)$ at ϵ_F with a large slope $\Gamma'(\epsilon_F)$[23] or tailoring correlations to yield a highly asymmetric $A(\omega)$ at ϵ_F with a large slope $A'(\epsilon_F)$, or both. We concentrate on the latter which is robust to details of the lead density of states, and assume a smooth $\Gamma(\omega)$ around ϵ_F, i.e., we take $\Gamma(\omega) = \Gamma = 0.01$ (in units of the half bandwidth of the leads).

The frequency and temperature dependence of $A(\omega, T)$ is calculated by using the numerical renormalization group (NRG) method[24]. Results for $U/\Gamma = -8$ were obtained at gate voltages $-|e|V_g = (\varepsilon_d + U/2)$ in the range $|V_g| \leq 8\Gamma$ (setting $e = 1$). In addition, for $T = 0$, we have compared results for occupation numbers n_d with those from functional renormalization group (fRG)[25] and Bethe Ansatz[26] techniques (see Fig. 3 below). In the following, $T_K = \sqrt{|U|\Gamma/4}e^{-\pi|U|/4\Gamma}$[5], denotes the relevant low energy charge Kondo scale of (1). Due to the exponential dependence on U and Γ, T_K can vary by orders of magnitude, e.g. for positive-U systems from 1 K to 200 K[27]. For $U = -8\Gamma$, we have $T_K = 2.64 \times 10^{-3}\Gamma \ll \Gamma$.

Results.— Fig. 1 shows the $T = 0$ spectral function for several gate voltages. At $V_g = 0$ the pseudo-spin states $n_d = 0$ and $n_d = 2$ are degenerate, the spectral function is symmetric, with a Kondo resonance of width $\mathcal{O}(T_K)$ at $\omega = 0$ and two Hubbard satellite peaks at $\omega = \varepsilon_d > 0$ and $\omega = \varepsilon_d + U < 0$. A finite gate voltage V_g induces a splitting $\Delta E = -2V_g$ of the pseudo-spin states which is analogous to a magnetic field in the conventional spin Kondo effect, i.e. the spectral function becomes highly asymmetric due to the polarizing effect of V_g, with n_d changing substantially from its "perfectly screened" value of $n_d = 1$[28]. This asymmetry in the single-particle spectral function with a large slope at ϵ_F, for *both* spin components, is the origin of the large thermopowers to be discussed below. The analogy to the spin Kondo effect in a magnetic field, can be made precise for the case of particle-hole symmetric bands which we consider: a particle-hole transformation on the down spins, allows the negative-U Anderson model in absence of a local magnetic field to be mapped onto the positive-U symmetric Anderson model in a finite local magnetic field $B = 2\epsilon_d + |U| = -2V_g$[29], thereby explaining the highly asymmetric spectral function of (1) shown in Fig. 1. The polarizing effect of finite $V_g \sim B$ is strongest at $T = 0$ and diminishes for $T \gg T_K$ (see Fig. 1b). In terms of the above analogy, this corresponds to the quenching of the magnetization $M = (n_{d\uparrow} - n_{d\downarrow})/2$ at high temperatures in the corresponding positive-U model in a field B.

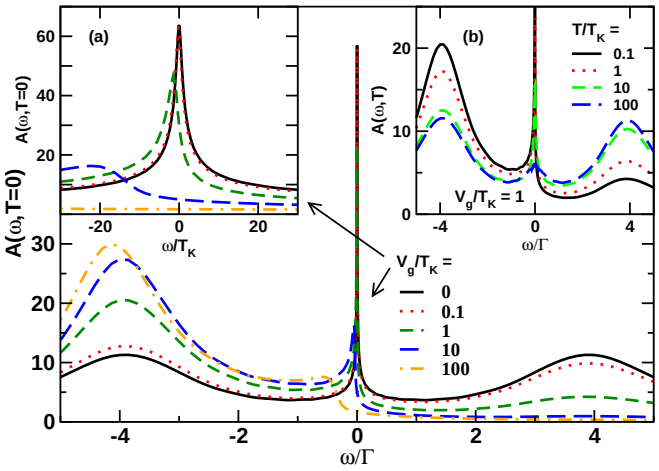

FIG. 1: *(Color online)* Main panel: $T = 0$ spectral function for $U/\Gamma = -8$ for different gate voltages V_g/T_K, inset (a): $A(\omega, T = 0)$ near $\omega = 0$, inset (b): temperature dependence of $A(\omega, T)$ for $V_g/T_K = 1$.

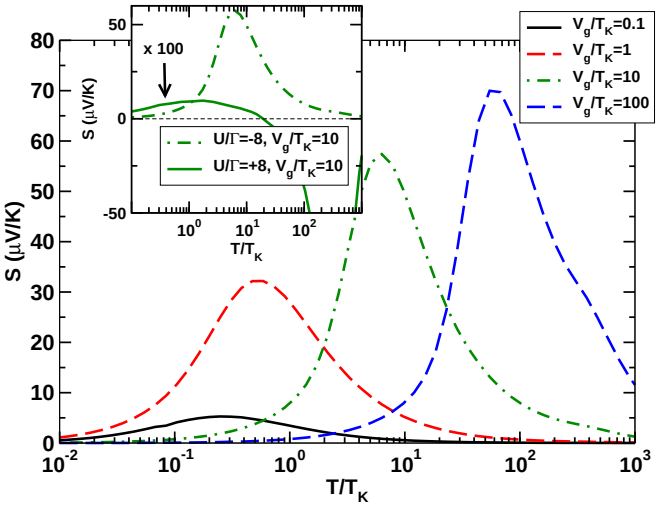

FIG. 2: *(Color online)* Thermopower S versus temperature at different gate voltages V_g/T_K and $U/\Gamma = -8$. Inset: comparison with $U > 0$ thermopower for $V_g/T_K = 10$.

Fig. 2 shows the main result of this Rapid Communication: a dramatic enhancement of the Seebeck coefficient induced by a finite gate voltage $V_g \gtrsim T_K$ exceeding $50\mu V/K$ for $V_g \gtrsim 2T_K$. The maximum in the thermopower occurs on a temperature scale which correlates with V_g and is therefore highly tunable. Corresponding Seebeck coefficients for $U > 0$ in the Kondo regime are insignificant (inset, Fig. 2). The large enhancement in S is due to the correlation induced asymmetry in the spectral function at finite V_g. At low temperatures, explicit calculations, within Fermi liquid theory[5], also shed light on this enhancement. In this limit, the thermopower may be expressed in terms of the occupancy n_d of the dot as

$$S(T) = -\frac{\pi\gamma T}{|e|}\cot(\pi n_d/2) \qquad (4)$$

with $\gamma T \ll 1$, and γ being the linear coefficient of specific heat of the dot[5] (with $\gamma \sim 1/T_K$ for $V_g = 0$). A finite $V_g \sim T_K$ polarizes the charge Kondo state, leading to $n_d \sim 2$ for $V_g > 0$. This enhances a nominally small ($\ll k_B/|e|$) thermopower by the large factor $\cot(\pi n_d/2) \gg 1$. Note also, that while a finite magnetic field for $U > 0$ also leads to asymmetric spectral functions $A_\uparrow(\omega)$ and $A_\downarrow(\omega)$ around ϵ_F, the asymmetry in the Kondo regime is opposite for spin up and spin down. Consequently, it largely cancels in the combination $\sum_\sigma A_\sigma$ entering (2) and the thermopower is not enhanced. (Furthermore, for $n_d \simeq 1$, the factor $\cot(\pi n_d/2)$ is very small.) Finally, note that $S(T)$ of the negative-U model in Fig. 2 does not exhibit a sign change with increasing temperature for any finite V_g, in contrast to the case of $U > 0$[13]: the sign change of the latter is due to a change in slope of the spectral function at the Fermi level, induced by a collapse of the Kondo resonance with increasing temperature. This cannot occur in the $U < 0$ model, since the spectral function remains polarized by a finite V_g at all relevant temperatures.

The gate voltage dependence of the thermopower and electrical conductance is shown in Fig. 3a-b at several temperatures. Except at $T \lesssim T_K$, a large Seebeck coefficient exceeding $50\mu V/K$ can always be realized by suitable choice of gate voltage. By tuning the gate voltage to positive or negative values about the charge Kondo state at $V_g = 0$ one can realize the p-type or n-type legs of a thermoelectric device. Note the absence of a Kondo plateau in $G(V_g)$ at $T \ll T_K$ in Fig. 3b, which contrasts with the $U > 0$ case, and the rapid drop on a scale $V_g \sim T_K$ of $G(V_g)$ due to the suppression of the Kondo state by finite gate voltage acting like a magnetic field in the conventional Kondo effect[16,18,19]. NRG results for $n_d(T = 0)$ versus V_g compare very well with fRG calculations at $U/\Gamma = -2, -4$ and with exact Bethe Ansatz (BA) calculations at $U/\Gamma = -8$ (see Fig. 3c). Fig. 3d shows that $G(T)$ exhibits the typical Kondo scaling behavior at small gate voltages $V_g \lesssim T_K$.

The thermoelectric efficiency of a nanoscale device is related to its dimensionless figure of merit defined by $ZT = PT/K$, where $P = S^2G$ is the power factor, and

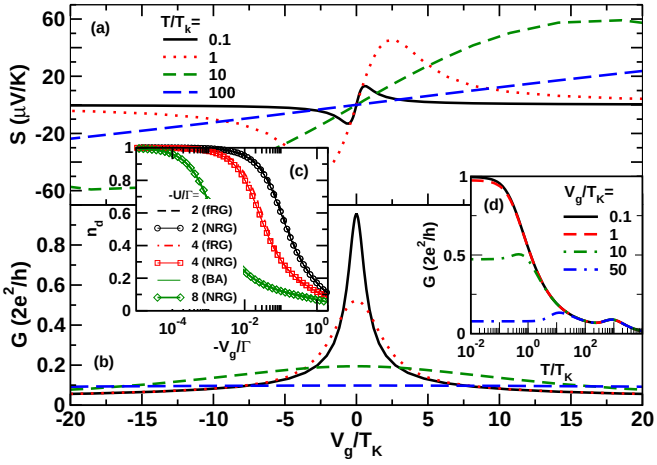

FIG. 3: *(Color online)* Gate voltage dependence of thermopower S (panel (a)) and conductance G (panel (b)) at typical temperatures T/T_K. Inset (c): dot occupation number n_d versus gate voltage for $U/\Gamma = -2, -4, -8$. fRG results for $U/\Gamma = -2, -4$ agree with NRG to less than 8% relative error, while for $U/\Gamma = -8$ NRG agrees with the Bethe Ansatz[26] very well. Inset (d): temperature dependence of G at selected gate voltages V_g/T_K.

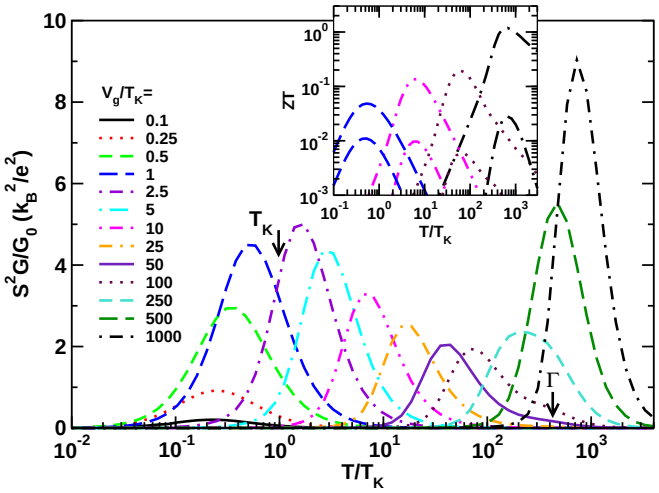

FIG. 4: *(Color online)* The power factor S^2G divided by $G_0 = 2e^2/h$ versus temperature and for a range of gate voltages V_g/T_K for $U/\Gamma = -8$. Location of T_K and Γ indicated by arrows. Inset: upper and lower bounds for ZT, as defined in the text, at several gate voltages.

$K = K_e + K_{ph}$ the thermal conductance due to electrons (e) and phonons (ph). For metallic leads, K_e will give the dominant contribution to K[30], while for semiconducting leads, K_{ph} will also be important. Since no calculation of K_{ph} in the presence of Kondo correlations is available, we discuss the efficiency of our system in terms of the power factor $P_{V_g}(T)$, shown in Fig. 4, and give upper and lower bound estimates for ZT below. The power factor is largely independent of details of the leads, making it a useful quantity for future comparison with

experiments. It is also a relevant quantity for on-chip cooling of a hot source in microelectronics[1]. For each V_g the power factor exhibits a maximum at a temperature which is related to V_g. The envelope of these curves has two maxima, one at $T \approx T_K$ for $V_g \approx 2T_K$ and another at high temperatures $T \approx 2\Gamma$ for $V_g \sim 4\Gamma \gg T_K$. In contrast, for $U > 0$, the power factor is vanishingly small in the Kondo regime, with larger values being obtained only at the border between mixed valence and Kondo regimes[13]. Turning to ZT, an upper bound estimate is obtained by setting $K_{ph} = 0$. A lower bound estimate is obtained by assuming that the molecule is transparent to phonons. In this case, each phonon mode contributes the maximum ballistic thermal conductance of $\kappa_0 = \pi^2 k_B T/3h$[31]. For three phonon modes we have $K_{ph} = 3\kappa_0$ resulting in a lower bound estimate for ZT. Both bounds (see inset to Fig. 4) show a maximum at a temperature T that correlates with V_g, with the upper bound exceeding 1 for $V_g/T_K \gg 1$ and $T/T_K \gg 1$. In a real device, phonons will be inelastically scattered, e.g. by vibrational modes of the molecule, thereby reducing K_{ph} below its ballistic value, especially at higher temperatures where anharmonic effects become important. Hence, our lower bound for ZT is likely too stringent so that a suitable choice of gate voltage could allow interesting values of $ZT \sim 0.5 - 1$ to be achieved at $T \sim 100T_K$.

Conclusions.— In summary, we investigated the thermoelectric properties of a negative-U molecular quantum dot exhibiting the charge Kondo effect. A small gate voltage $V_g \gtrsim T_K$ is found to polarize the charge on the dot creating a single-particle spectral function which is highly asymmetric about the Fermi level. This yields a large enhancement of the Seebeck coefficient exceeding $50\mu V/K$ on a temperature scale comparable to V_g. The device is highly tunable and allows large power factors to be achieved at virtually any temperature by suitable choice of the gate voltage. In addition to the mentioned possible realizations of such devices, molecular complexes similar to those in Ref. 27, but with valence skipping ions[32] such as Bi, Tl or In, acting as negative-U centers, and attached to gold leads, could be promising systems to look into in the future. Reducing the dimensionality of the leads, e.g. by using carbon nanotubes[33], could further enhance the power factor[23].

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