Tunable Charge and Spin Seebeck Effects in Magnetic Molecular Junctions

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We study the charge and spin Seebeck effects in a spin-1 molecular junction as a function of temperature, applied magnetic field, and magnetic anisotropy (D) using Wilson’s numerical renormalization group. A hard-axis magnetic anisotropy produces a large enhancement of the charge Seebeck coefficient \( S_c \) whose value only depends on the residual interaction between quasiparticles in the low temperature Fermi-liquid regime. In the underscreened spin-1 Kondo regime, the high sensitivity of the system to magnetic fields makes it possible to observe a sizable value for the spin Seebeck coefficient even for magnetic fields much smaller than the Kondo temperature. Similar effects can be obtained in \( C_{60} \) junctions where the control parameter, instead of \( D \), is the gap between a singlet and a triplet molecular state.

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The Seebeck effect refers to the generation of a charge current (or a voltage drop) by a temperature gradient applied across a metal [1]. The spin-Seebeck effect [2,3], concerns the thermal generation of pure spin currents. Applications of the Seebeck and spin-Seebeck effects at the nano-scale, with potential impact on a variety of new technologies, could profit from the scalability and tunability properties of nano-devices but still require a better understanding of thermopower effects in nanostructures and of the effect of strong electron-electron correlations on them. The recent experimental observation of the Seebeck effect in different nano-structures, in particular in molecular junctions [3] and quantum dots (QDs) [4], opened new routes to study these phenomena. Here we show that junctions with spin-1 molecules, like the Co(tpy-SH)\(_2\) complex [5] or the \( C_{60} \) buckyballs [6], give rise to a large and controllable enhancement of the Seebeck and spin Seebeck effects at low temperatures and low magnetic fields. We also show that thermoelectric experiments in these systems give access to valuable information on the residual interaction between quasiparticles in the low temperature Fermi-liquid regime [3], information that cannot be obtained by conventional techniques. This offers the opportunity to experimentally study these effects on the smallest possible lengths scales looking for the basic mechanisms of thermomagnetic effects in strongly correlated systems [10,12]—in particular in the regime where energy transfer is governed by spin fluctuations.

We start by describing the case of junctions with the organometallic molecule Co(tpy-SH)\(_2\) [see Fig. 1]. In this complex, the Co ion is located in an approximately octahedral environment and is found to be in the Co\(^{1+}\) 3d\(^8\) configuration with a total spin \( S = 1 \). When the molecule is mechanically stretched, the local environment of the Co ion is distorted and a magnetic anisotropy, with an easy plane, emerges due to the spin-orbit interaction. As the molecular orbitals reproduce the magnetic structure of the metallic ion, the molecular junction is modeled by the Hamiltonian \( \hat{H} = \hat{H}_M + \hat{H}_V + \hat{H}_l \) where

\[
\hat{H}_M = \sum_{\ell=a,b} \left[ U \hat{n}_{\ell \uparrow} \hat{n}_{\ell \downarrow} + \varepsilon (\hat{n}_{\ell \uparrow} + \hat{n}_{\ell \downarrow}) \right] + J \hat{S}_a \cdot \hat{S}_b - g \mu_B B S_z + D S_z^2,
\]

(1)
describes two degenerate orbitals (a and b) of the molecule with level energy \( \varepsilon \) and Coulomb repulsion \( U \), coupled through a spin exchange interaction \( J \). Here \( \hat{S} = \hat{S}_a + \hat{S}_b \) is the spin operator, \( \hat{S}_\ell = \sum_{\sigma \sigma'} d_{\ell \sigma}^\dagger \hat{\sigma}_{\sigma'} d_{\ell \sigma} \) where \( \hat{\sigma}_{\sigma'} \) the Pauli vector, and \( \hat{n}_{\ell \sigma} = d_{\ell \sigma}^\dagger d_{\ell \sigma} \) is the number operator. The molecular spin is coupled to an
external magnetic field $B$, and $D$ is the strength of the magnetic anisotropy. In this case, the orbitals describe the Cobalt $c_g$ levels and $J < 0$ is a Hund rule ferromagnetic coupling—in the $C_{g0}$ case, $J > 0$ is antiferromagnetic and $D = 0$. The hybridisation between the molecular orbitals and the leads’ states is described by $\hat{H} = \sum_{\kappa \sigma} V_{\kappa} \left( d_{\sigma}^\dagger c_{\kappa \sigma} + c_{\kappa \sigma} d_{\sigma} \right)$, where $\alpha = L, R$ stands for the left and right electrodes, respectively. Here we have assumed that a single conduction channel is active in order to describe the underscreened Kondo effect observed in Ref. [6], and we have considered, for simplicity, that only one of the molecular orbitals is coupled to the electrodes. The Hamiltonian of the metallic leads is given by $\hat{H}_l = \sum_{\alpha} \sum_{\sigma} \varepsilon_{\alpha} \hat{c}^\dagger_{\alpha \sigma} \hat{c}_{\alpha \sigma}$. We focus on the regime $\varepsilon < 0$, and $U \gg |\varepsilon|$ where only the single and double occupied states of the molecule are relevant for the low-temperature physics.

The presence of a voltage ($V$) and temperature drop ($\Delta T$) across the junction generates a charge current that in the linear response regime is given by

$$I_c = GV + GS_c \Delta T$$

(2)

where the conductance $G$ and charge Seebeck coefficient $S_c$ are given by

$$G = \frac{e^2}{h} T_0, \quad S_c = \frac{k_B}{|e|} \frac{T_1}{k_B T_0}$$

(3)

with $T_\sigma = \sum_\sigma T^\sigma_\sigma$ and $T_\sigma^\dagger = \int_\infty^{-\infty} \omega^n \left( \frac{\partial f(\omega)}{\partial \omega} \right) T_\sigma(\omega) d\omega$.

Here the quantity $T_\sigma(\omega)$ describes the tunneling of spin-$\sigma$ electrons across the junction and is given by $T_\sigma(\omega) = e^{i\omega \Gamma_{\alpha}} \rho_\sigma(\omega)$ where $\rho_\sigma(\omega)$ is the spin dependent spectral density of the molecular state. In the above expression $\Gamma_{\alpha} = \pi \rho_\alpha V^2$ is the contribution to the width of the molecular energy levels introduced by the coupling with the $\alpha$ lead, $\rho_\alpha$ is the electronic density of states per spin of the electrodes at the Fermi level and $f(\omega)$ is the Fermi function. In what follows we assume $\rho_\alpha$ to be constant, set the Fermi energy to zero ($\varepsilon_F = 0$) and choose the bandwidth of the leads $W$ as the unit of energy.

The molecular spectral density is evaluated using the numerical renormalization group (NRG), a non-perturbative technique known to give excellent results for the transport integrals [14, 15]. The total conductance and the charge Seebeck coefficient $S_c$ are shown in Fig. 2 for different values of the anisotropy parameter $D$ and $B = 0$. For the isotropic case ($D = 0$) the molecular spin is partially screened by the conduction electrons below a Kondo temperature $T_K$ (the under-screened Kondo effect) with $T_K$ ranging between 1K and 200K depending on the device [2]. The ground state of the system is a singular Fermi-liquid with a free (unscreened) spin $\frac{1}{2}$ [16, 17]. The development of Kondo correlations is associated with a monotonic increase in the conductance as $T$ is lowered (top panels Fig. 2). With a spin anisotropy $0 < D < k_BT_K$, as the temperature is lowered the conductance first increases following a universal behavior, goes through a maximum and decreases at a characteristic temperature $T^*_K = T_K \exp(-2\sqrt{\frac{k_BT_K}{D}})$ [18]. This new temperature scale can be identified with a second stage Kondo effect, induced by the magnetic anisotropy, in which the remaining spin $\frac{1}{2}$ is screened. In this regime the ground state of the system is a Fermi liquid.

Within this scenario, that has been confirmed by experiments and theory, the Seebeck coefficient shows novel features (bottom panels Fig. 2). For $D = 0$ it develops a large peak at very high temperatures (unphysical for magnetic molecules) and changes sign at a lower temperature. This behavior is similar to what is obtained for spin-$\frac{1}{2}$ quantum dots [11, 12]. For the stretched ($D > 0$) molecule [19], a second large peak develops at $T \lesssim T^*_K$. This low-$T$ peak is controlled by spin fluctuations and it is strongly dependent on the spin anisotropy. For small anisotropies ($D < k_BT_K$), the two characteristic energy scales $T^*_K$ and $T_K$ are far apart and $S_c$ is a function of $T/T_K$ at low temperature. For larger anisotropies, the scaling breaks down and the maximum value of $S_c$ decreases. In the scaling region, and for $T/T^*_K < 1$, the system is a Fermi-liquid and $S_c$ can be described by a simple analytical expression. In Fermi-liquids, the residual interaction between quasiparticles leads to a self-energy with an imaginary part proportional to $(\omega^2 + \pi^2T^2)$ [8, 20]. Using this result to estimate the spectral den-
FIG. 3. Spin Seebeck coefficient $S_s$ and spin current $I_s$ for an isotropic molecule ($D = 0$). Top panel: $S_s = S_{\uparrow} - S_{\downarrow}$ as a function of the magnetic field for different temperatures. Note that $S_s$ is significantly large even for $g\mu_BB \ll k_BT_K$. The maximum of $S_s$ occurs for $g\mu_BB \sim k_BT$. Bottom panel: Spin current as a function of $g\mu_BB$ in the zero charge current condition ($I_c = 0$).

sity $\rho_\sigma(\omega)$ we obtain \[ S_s = \frac{k_B}{|e|} \frac{2\pi^2(k_BT/\omega_0)}{\pi^2(1 + \gamma)(k_BT/\omega_0)^2 + 3}. \tag{4} \]

Here $\omega_0 = k_BT_K^\gamma \sin(\pi n/2)$, $n$ is the total occupation of the molecular orbitals and $\gamma > 0$ measures the strength of the quasiparticle interaction. Notably, the maximum of the Seebeck coefficient $S_c^{\text{max}} = (k_B/|e|)\pi/\sqrt{3(1 + \gamma)}$ depends only on universal constants and the parameter $\gamma$ that reduces the maximum value of the thermopower—the coupling to the leads, $D$ and other parameters that are both experimentally hard to determine and sample dependent, do not affect the value of $S_c^{\text{max}}$. The temperature behavior of the Seebeck coefficient is one of the central results of this work. Its measurement provides a direct access to the parameter $\gamma$ and can be used to quantitatively test Nozières local Fermi liquid ideas \[. \]

The fitting of the numerical results with Eq. (4) is excellent (see [21]) and gives $\gamma \simeq 2.8$ for the parameters used in our simulation. Therefore, in a junction with $T_K = 100K$, the Seebeck coefficient could be tuned to have a peak of the order of $k_BT/|e| \sim 100\mu V/K$ at a temperature in the range of 0-50K.

Let us now focus on the effect of an external magnetic field. There are now two control parameters, the magnetic field $B$ and the anisotropy $D$, leading to different magneto-thermal regimes for the junction. Defining the contribution to the charge current of the spin-$\sigma$ electrons as $I_\sigma = G_\sigma V + g_\sigma S_\sigma \Delta T$, where $G_\sigma$ is the $\sigma$-contribution to the total conductance [cf. Eq. (3)], the spin dependent Seebeck coefficient results, \[ S_\sigma = -\frac{k_B}{|e|} \frac{T_\sigma}{k_BT_0} \tag{5} \]

If the condition $I_c = 0$ is set, a voltage drop across the junction will develop as before but in addition, the temperature difference $\Delta T$ will also generate a pure spin current $I_s = (I_\uparrow - I_\downarrow)/|e|$ given by \[ I_s = (S_\uparrow - S_\downarrow) \frac{\Delta T}{|e|\mathcal{R}} \tag{6} \]

with $\mathcal{R} = \sum_\sigma G_\sigma^{-1}$. In this units $I_s$ gives the number of spins per second flowing though the junction. Note that with these definitions $S_{\sigma} = \sum_\sigma (G_\sigma/G)S_\sigma$. For $D = 0$, the under-screened Kondo regime, the system behaves as a singular Fermi-liquid with a divergent spin susceptibility as $T \to 0$ \[15\] and $\rho(\omega)$ shows a Kondo peak with a singular behavior at the Fermi energy $E_F$. As the ground state of the system contains a free $\uparrow$-spin, the presence of a magnetic field is a relevant perturbation in the renormalization group sense. Consequently, even a very small magnetic field is able to spin polarize the molecule and split the Kondo peak in $\rho(\omega)$ (see [21]). The magnetic field dependence of $S_s = S_\uparrow - S_\downarrow$ and $I_s$ is shown on Fig. 3. This spin polarization of the molecule results in the appearance of a pure spin current even for $g\mu_BB \ll k_BT_K$ (but $g\mu_BB \sim k_BT$), in clear contrast with the $S = 1$ case (Anderson model) where $g\mu_BB \sim k_BTK$ is required in order to observe a sizable spin polarizing effect \[12\].

Similar results are obtained for the stretched molecule only if $g\mu_BB \gtrsim k_BT_K$. For $g\mu_BB < k_BT_K$ the coefficient $S_s$ is small and a large charge Seebeck peak is recovered (see Fig 3) This behavior shows that with some spin anisotropy ($D \neq 0$) the voltage drop $V$ at the junction is very sensitive to the external field and can evolve from a large value (of the order of $k_BT/|e|$) for $B = 0$ to zero for $g\mu_BB \gtrsim k_BT_K$ \[22\]. The low temperature behavior of the spin dependent Seebeck coefficients $S_s$ can also be described using a local Fermi liquid theory. We obtain expressions similar to Eq. (4) where now $\omega_0$ is replaced by $\omega_0 = k_BT_K^\gamma \sin(\pi n_\sigma)$, with $n_\sigma = n/2 - \sigma m/2$ the total number of spin-$\sigma$ electrons in the molecular orbitals. As $n \simeq 2$, a small magnetization $m$ can change the sign of one of the energies $\omega_\sigma$ and consequently the sign of one of the spin dependent Seebeck coefficients $S_s$ leading to a large spin current.

C_{50} junctions present similar thermopower properties. A C_{50} molecule embedded in a junction may have a singlet $S = 0$ state and a triplet $S = 1$ state separated by a small singlet-triplet gap $J$ that can be controlled by gate voltages \[3\]. When the singlet state lies just below the triplet state the system shows a two stage
Kondo effect with a Kondo temperature $T_K$, of the order of 4K in [23], and a second stage temperature given by $T_K \propto T_K \exp(-k_B T_K/J)$ [23, 24]. While the global behavior of the conductance is similar to that of the anisotropic spin-1 case, its specific high $T$-dependence is different. By contrast, the temperature dependence of $S_c$ for $T \lesssim k_B T_K$ is the same as the one obtained for the Co-complex and it is well described by Eq (4) with a particular value for $\gamma$ that depends on the residual interaction in the $C_{90}$ case. If the triplet is the ground state, and for $J > T_K$, the system is described by the isotropic under-screened $S = 1$ Kondo model and the physical behavior corresponds to the $D = 0$ case discussed above. It is worth mentioning that other systems, like an artificial molecule build with a T-shape double Quantum Dot (2QD) may also show some similar effects. In these two cases, however, the Kondo temperatures are usually very small making it more difficult to experimentally observe them. In this sense, the stretched Co complex presents advantages over these systems that make it an excellent candidate to observe high charge and spin Seebeck effects at low or moderate fields and temperatures.

In summary we have presented a study of the charge and spin Seebeck effects for real molecular junctions that combines the $S = 1$ underscreened Kondo effect together with a controllable spin anisotropy $D$ or a single-triplet gap $J$. We found that these systems present a large charge Seebeck coefficient $S_c$, of the order of $k_B/|e|$, at a temperature that can be controlled either by stretching or gating the molecules. Quite remarkably, the maximum value of $S_c$ in the low $T$ regime, $(k_B/|e|)\pi/\sqrt{3(1+\gamma)}$, depends only on the Fermi liquid properties of the system (characterized by $\gamma$). It is important to emphasize that this low $T$ behavior is fully controlled by spin fluctuations. In the presence of a magnetic field these systems are able to filter the spin flow in a regime where Kondo correlations are fully developed and present moderate values of $S_c$ and $I_s$ even for magnetic fields such that the Zeeman energy is much smaller than the Kondo energy scale.

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