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Phonon-assisted thermoelectric effects in a two-level molecule

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ABSTRACT

Thermoelectric properties of a two-level molecule attached to the metallic electrodes are analyzed using the equation of motion technique within the Green function formalism. Results show that the electrical conductance is strongly dependent on the electron and phonon temperatures and the electron–phonon coupling strength. In addition, it is observed that the thermal conductance peaks in the electron–hole symmetry points are vanished in the presence of the strong electron–phonon interaction. It is also found that the figure of merit is strongly suppressed in the strong electron–phonon interaction. The violation of the Wiedemann–Franz law is also observed coming from the Coulomb interactions.

1. Introduction

Transport phenomena through molecular devices have been attracted a lot of attention during recent two decades. Experimental and theoretical results show that the electron transport through the molecular transistors results in novel and interesting effects such as Coulomb and spin blockade effects [1–4], Kondo effect [5–7], negative differential conductance [8–10], and so on. In addition, it has been predicted that the molecular devices can be efficient for conversion of heat into electric energy [11,12]. Thermoelectric efficiency of a device is indicated by a dimensionless quantity called figure of merit, $ZT = S^2 G_e T/\kappa$, where G_e is the electrical conductance and S is the thermopower. κ is the thermal conductance which is the sum of the electronic contribution, κ_e, and the lattice thermal conductance, κ_p, and T denotes the operating temperature. In bulky samples and according to the Wiedemann–Franz Law, the ratio of the electrical conductance to the thermal conductance is related to the operating temperature. Research shows that the strong Coulomb repulsions, discreteness of energy levels, interference effects etc. in nanostructures result in the violation of the Wiedemann–Franz law [13–15] and as a consequence, the increase of ZT. For these reasons, the investigation of the thermoelectric properties of the systems composed of a single or two quantum dots has attracted a lot of attention in recent years [15–26].

Electron–phonon interaction (EPI) is an interesting and important phenomenon in the molecular devices which can significantly affect the transport characteristics of the devices. The center of mass oscillation of the molecule [27], or thermally induced acoustic phonons [28] can be the origin of the coupling between the electronic degree of freedom and the vibrational degree of freedom. The influence of the EPI on the electronic characteristics of the molecular transistors and the carbon nanotube quantum dots has been extensively studied using both rate equation approach [29–33] and the Green function formalism [34–38]. However, the influence of the EPI on the thermoelectric properties of the molecular devices is an interesting issue needing more attention. Koch and co-workers [39] analyzed the thermopower in a single level molecule by means of the master equation. Furthermore, the effect of the EPI on the thermoelectric properties of a single-level quantum dot was studied in a few articles using the Green function formalism [40–42].

In this article, we consider a two-level molecule in which the electronic degree of freedom is coupled to the vibrational degree of freedom. Using the equation of motion technique within the Green function formalism and using the polaronic transformation, the density of the states of the molecule (DOS) and the thermoelectric properties of the device are analyzed. With respect to the fact that the phonon subsystem has a smaller heat capacity than the electron subsystem, it is completely probable an electron–phonon nonequilibrium thermodynamics is dominant so that the electron temperature,T_e, and phonon temperature, T_p, are different. The difference can result in the appearance of the phonon absorption sidebands in the DOS in the low electron temperatures which are not seen in the EP thermal equilibrium. The effects of the EP nonequilibrium and EP coupling strength on the thermoelectric properties of the system are analyzed in detail. In the next

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section, formalism is presented. Section 3 is devoted to the numerical results and in the end; some sentences are given as a summary.

2. Model and formalism

We consider a two-level molecule coupled to the normal metal electrodes. The Hamiltonian describing the system is given as

$$H=\sum_{\alpha k\sigma}\varepsilon_{\alpha k\sigma}c^{\dagger}_{\alpha k\sigma}c_{\alpha k\sigma}+\sum_{i=1,2\sigma}\varepsilon_{i\sigma}n_{i\sigma}+\frac{1}{2}\sum_{ij\sigma\sigma'}U_{ij}n_{i\sigma}n_{j\sigma'}$$
$$\omega a^{\dagger}a+\sum_{i\sigma}\lambda n_{i\sigma}[a^{\dagger}+a]+\sum_{\alpha k\sigma i}[V^{i}_{\alpha k\sigma}c^{\dagger}_{\alpha k\sigma}d_{i\sigma}+H.C.], \quad (1)$$

where $c^{\dagger}_{\alpha k\sigma}$ creates an electron with wave vector k, spin σ, and energy $\varepsilon_{\alpha k\sigma}$ in lead α. $d^{\dagger}_{i\sigma}$ creates an electron in the ith level of the molecule with energy $\varepsilon_{i\sigma}$, while U_{ii} stands for the on-site Coulomb repulsion and U_{ij} $(i\neq j)$ denotes the inter-level Coulomb repulsion. The energy levels of the molecule are tuned by a gate voltage thus we set $\varepsilon_{i\sigma}=\varepsilon^{0}_{i\sigma}+V_g$ so that $\varepsilon^{2}_{0}=\varepsilon^{0}_{1}+\Delta$ where Δ denotes the level spacing. $a^{\dagger}(a)$ is the creation (annihilation) operator for the phonons with energy ω and λ describes the electron–phonon coupling strength. The last term in the above equation describes the tunneling process between the electrodes and the molecule and $V^{i}_{\alpha k\sigma}$ is the coupling strength between the lead α and the ith energy level. $V^{i}_{\alpha k\sigma}$ induces a tunneling rate from the molecule to the electrode α, $\Gamma^{i}_{\alpha\sigma}=2\pi\sum_{k\in\alpha}\rho_{\alpha}|V^{i}_{\alpha k\sigma}|^{2}$ where ρ_{α} is the electronic density of the lead α.

The EPI can be eliminated using polaronic transformation [43], $\tilde{H}=e^{S}He^{-s}$, where $S=\exp(\sum_{i\sigma}\lambda n_{i\sigma}[a^{\dagger}-a])$. Thus, Eq. (1) becomes

$$\tilde{H}=\sum_{\alpha k\sigma}\varepsilon_{\alpha k\sigma}c^{\dagger}_{\alpha k\sigma}c_{\alpha k\sigma}+\sum_{i\sigma}\tilde{\varepsilon}_{i\sigma}n_{i\sigma}+\frac{1}{2}\sum_{ij\sigma\sigma'}\tilde{U}_{ij}n_{i\sigma}n_{j\sigma}$$
$$\omega a^{\dagger}a+\sum_{\alpha k\sigma i}[\tilde{V}^{i}_{\alpha k\sigma}c^{\dagger}_{\alpha k\sigma}d_{\sigma}+H.C], \quad (2)$$

where $\tilde{\varepsilon}_{i\sigma}=\varepsilon_{i\sigma}-\lambda^{2}/\omega$, and $\tilde{U}_{ij}=U_{ij}-2\lambda^{2}/\omega$. The polaronic transformation results in the renormalization of the molecule levels and Coulomb repulsions. In addition, the tunneling amplitude is transformed into $\tilde{V}^{i}_{\alpha k\sigma}=V^{i}_{\alpha k\sigma}X$ where $X=\exp(-\lambda/\omega[a^{\dagger}-a])$ is the phonon operator. In the following, we replace the operator X with its expectation value, $\langle X\rangle=\exp(-\lambda/\omega(N_p+1/2))$ [43] where N_p stands for the averaged number of phonons. This approximation is used in the localized polaron and is valid when the tunneling amplitude is smaller than the EPI, i.e. $V_{\alpha k\sigma}\ll\lambda$. Hence, the tunneling rate is renormalized according to $\tilde{\Gamma}^{i}_{\alpha\sigma}=\Gamma^{i}_{\alpha\sigma}\langle X\rangle^{2}$. $\langle X\rangle^{2}$ just narrows the tunneling rate.

In order to compute the electronic current, I_e, and the heat flux, I_Q, the Green function formalism is used so that the electronic current and heat current are expressed as [44,45]

$$I_e=\frac{-e}{h}\sum_{i\sigma}\int_{-\infty}^{\infty}d\varepsilon\frac{\Gamma^{i}_{L\sigma}\Gamma^{i}_{R\sigma}}{\Gamma^{i}_{L\sigma}+\Gamma^{i}_{R\sigma}}[f_L(\varepsilon)-f_R(\varepsilon)]\,\mathrm{Im}\,G^{r}_{i\sigma}(\varepsilon), \quad (3a)$$

$$I_Q=\frac{-1}{h}\sum_{i\sigma}\int_{-\infty}^{\infty}d\varepsilon\frac{\Gamma^{i}_{L\sigma}\Gamma^{i}_{R\sigma}}{\Gamma^{i}_{L\sigma}+\Gamma^{i}_{R\sigma}}(\varepsilon-\mu)[f_L(\varepsilon)-f_R(\varepsilon)]\,\mathrm{Im}\,G^{r}_{i\sigma}(\varepsilon), \quad (3b)$$

where $f_{\alpha}(\varepsilon)=(1+\exp((\varepsilon-\mu_{\alpha}))/kT_e)^{-1}$ is the Fermi distribution function and μ_{α}, and T_e are the chemical potential and electron temperature in the lead α. It is worth noting that Eq. (3) is computed with respect to the tunneling part of the Hamiltonian, Eq. (1), so the bare tunneling rates are used. However, the influence of the EPI on the electronic and heat currents is saved in the Green function, $G^{r}_{i\sigma}$. $-\mathrm{Im}\,G^{r}_{i\sigma}(\varepsilon)$ is the DOS of the level i composed of the phononic and electronic parts which can be computed by evaluating the phonon part of the trace by Feynman disentangling technique [43], and using the Keldysh equations [45] for the lesser and greater Green functions, as follows [34]:

$$\mathrm{Im}\,G^{r}_{i\sigma}(\varepsilon)=\sum_{\alpha=L,R}\sum_{n=-\infty}^{\infty}\frac{L_n}{\tilde{\Gamma}^{i}_{L\sigma}+\tilde{\Gamma}^{i}_{R\sigma}}[\tilde{\Gamma}^{i}_{\alpha\sigma}f_{\alpha}(\varepsilon+n\omega)\,\mathrm{Im}\,\tilde{G}^{r}_{i\sigma}(\varepsilon+n\omega)$$
$$+\tilde{\Gamma}^{i}_{\alpha\sigma}[1-f_{\alpha}(\varepsilon-n\omega)]\,\mathrm{Im}\,\tilde{G}^{r}_{i\sigma}(\varepsilon-n\omega)], \quad (4)$$

where L_n, for nonzero temperatures, is given as

$$L_n=e^{-(\lambda/\omega)^{2}(1+2N_{ph})}\left(\frac{N_{ph}+1}{N_{ph}}\right)^{n/2}I_n(2(\lambda/\omega)^{2}\sqrt{N_{ph}(N_{ph}+1)}), \quad (5)$$

where $I_n(x)$ are the Bessel functions of the complex argument, and $N_{ph}=(\exp(\omega/kT_p)-1)^{-1}$ is the averaged number of phonons and T_p stands for the phonon temperature. Indeed, the thermal equilibrium between the electrons in the electrodes and phonons in the molecule can be broken due to smaller heat capacity of the phonons. $\tilde{G}^{r}_{i\sigma}(\varepsilon)$ is the dressed retarded Green function governed by $\tilde{H}$. To compute $\tilde{G}^{r}_{i\sigma}$, we follow the procedure introduced by Chang and co-workers [46]. Therefore, $\tilde{G}^{r}_{i\sigma}$ is expressed as

$$\tilde{G}^{r}_{i\sigma}(\varepsilon)=\sum_{k=0}^{2}p_k\left(\frac{1-N_{i-\sigma}}{E_{i\sigma}-\Pi_k}+\frac{N_{i\sigma}}{E_{i\sigma}-U_{ii}-\Pi_k}\right) \quad (6)$$

where $E_{i\sigma}=\varepsilon-\varepsilon_{i\sigma}+1/2(\tilde{\Gamma}^{i}_{L\sigma}+\tilde{\Gamma}^{i}_{R\sigma})$, and, the summation is over all possible configurations in which the level $j(j\neq i)$ is empty, $p_0=1+\langle n_{j\sigma}n_{j-\sigma}\rangle-(N_{j\sigma}+N_{j-\sigma})$, singly, $p_1=N_{j\sigma}+N_{j-\sigma}$, or doubly, $p_2=\langle n_{j\sigma}n_{j-\sigma}\rangle$, occupied. p_k denotes the probability factor of a configuration expressed by one-particle $N_{i\sigma}=\langle d^{\dagger}_{i\sigma}d_{i\sigma}\rangle_{\tilde{H}}$ and two-particle $\langle n_{i\sigma}n_{i-\sigma}\rangle_{\tilde{H}}$ occupation numbers. Π_k denotes the sum of Coulomb repulsions seen by an electron in level i due to other electrons in configuration k, in which the level $j(j\neq i)$ is empty $\Pi_0=0$, singly, $\Pi_1=U_{12}$, or doubly, $\Pi_2=2U_{12}$ occupied.

In the linear response theory for the electronic current and heat flux (Eq. (3)), the electrical conductance is equal to $G_e=-e^{2}/T_eL_{11}$, thermopower is

$$S=-\frac{1}{eT_e}\frac{L_{12}}{L_{11}}$$

and the thermal conductance is given by

$$\kappa_e=\frac{1}{T_e^{2}}\left[L_{22}-\frac{L_{12}^{2}}{L_{11}}\right].$$

The linear response coefficients are given by Ref. [47]

$$L_{11}=\frac{T_e}{h}\sum_{i\sigma}\int d\varepsilon\frac{\Gamma^{i}_{L\sigma}\Gamma^{i}_{R\sigma}}{\Gamma^{i}_{L\sigma}+\Gamma^{i}_{R\sigma}}\mathrm{Im}\,G^{r}_{i\sigma}(\varepsilon)\left(-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right)_{T_e} \quad (7a)$$

$$L_{12}=\frac{T_e^{2}}{h}\sum_{i\sigma}\int d\varepsilon\frac{\Gamma^{i}_{L\sigma}\Gamma^{i}_{R\sigma}}{\Gamma^{i}_{L\sigma}+\Gamma^{i}_{R\sigma}}\mathrm{Im}\,G^{r}_{i\sigma}(\varepsilon)\left(\frac{\partial f(\varepsilon)}{\partial T_e}\right)_{\mu} \quad (7b)$$

$$L_{22}=\frac{T_e^{2}}{h}\sum_{i\sigma}\int d\varepsilon\frac{\Gamma^{i}_{L\sigma}\Gamma^{i}_{R\sigma}}{\Gamma^{i}_{L\sigma}+\Gamma^{i}_{R\sigma}}(\varepsilon-\mu)\,\mathrm{Im}\,G^{r}_{i\sigma}(\varepsilon)\left(\frac{\partial f(\varepsilon)}{\partial T_e}\right)_{\mu} \quad (7c)$$

For simulation purposes, we use bands of width, D, as energy unit and set $\omega=D/50$, and $U_{ii}=2U_{12}=D/10$. We also take the renormalized tunneling rate, $\tilde{\Gamma}^{i}_{\alpha\sigma}$ as an input parameter and ignore the narrowing the width of the tunneling rate due to the EPI and assume the wave functions of the molecular levels are the same, i.e. $\Gamma^{1}_{\alpha\sigma}=\Gamma^{2}_{\alpha\sigma}$. It has been shown that the EPI does not narrow the width of tunneling rate in some cases [48,49]. According to Refs. [48,49], the narrowing effect becomes important when the EPI is very strong i.e. $\lambda>\omega$, and the energy spacing between the QD's energy level and the Fermi energy of the leads is lesser than the phonon energy. The narrowing effect results in some quantitative but no important qualitative changes. On the other hand, the magnitude of the tunneling rate has no significant role in the thermoelectric properties of the system in the linear response regime used in this article.