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Variational polaron transformation approach toward the calculation of thermopower in organic crystals

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Based on the combination of the variational polaron transformation and the Green-Kubo formalism, a method toward the thermopower calculations in organic crystals is proposed, which covers a broad regime of electron-phonon interaction strengths and successfully recovers the small-polaron theory in the narrow-band limit and the modified Mott formula in the coherent limit, respectively. The application to a molecular chain reveals a crossover of thermopower with respect to the chemical potential and exhibits abnormal regions where the sign of thermopower is opposite to the sign of the carrier charge. This abnormal property may lead to a sign-inversion phenomenon of thermopower in terms of the temperature. It is also found that the incomplete dressing of the electron by the phonon cloud destroys the particle-hole symmetry and results in nonzero thermopower in a half-filled band.

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I. INTRODUCTION

In recent years, there has been growing interest in developing organic thermoelectric devices with high-energy conversion efficiencies [1–6]. As compared with traditional inorganic counterparts, organic thermoelectric materials have advantages of low thermal conductivity, mild manufacturing processes, soft mechanical properties, and good controllability in electronic properties. Up to now, however, the highest figure of merit ZT in organic materials [7] is only about 0.4 and the low ZT value severely limits their practical applications. Systematic and efficient improvements in ZT require further investigations of molecular thermoelectric properties both from experiment and from theory.

Theoretically, phenomenological models based on the hopping transport theory, pioneered by the work of Bässler [8], are commonly employed to investigate the thermoelectric effect in disordered organic semiconductors [9,10]. In these models, the carrier transport along the molecular chain is described by hopping events. The hopping rate is usually given by the Miller-Abrahams expression or the Marcus electron transfer theory and the density of states is assumed to have a Gaussian or exponential shape. Afterwards, the Mott formulas [11] are used for the calculation of the electrical conductivity and thermopower (i.e., Seebeck coefficient), either by deriving analytical expressions under some approximations [12,13] or by direct dynamical simulations via kinetic Monte Carlo techniques [14–16] or master equations [17–19]. Excellent agreement with experimental results has proven the validity of these models, although they are short of predictability owing to various parameters that need to be fitted by experimental results.

Besides phenomenological models, various efforts toward the first-principles description of the thermoelectric properties of organic crystals have been made recently. Some of them are the direct applications of conventional theories to organic systems. For example, the well-established Landauer formalism, which is generally used in calculating the coherent transport properties of nanostructures, has been applied to conducting polymers [20,21]. In this formalism, the electron motion is treated ballistically and the scattering channel from phonons is completely neglected. The other example is the application of the Boltzmann transport equation to organic semiconductors, traced back to Friedman's original work [22]. In this approach, the electron-phonon interaction is regarded as perturbation and its influence on the electron transport is grouped into a parameter called the relaxation time. Recently, the combination of the Boltzmann transport equation and first-principles calculations has been realized for several organic crystals. Under the rigid-band and constant-relaxation-time approximation, Gao *et al.* [23] have calculated thermopower of polythiophene and polyaminosquarine from electronic band structures. Utilizing the deformation potential theory, Shuai and coworkers [24–27] have explicitly calculated the relaxation time and investigated the thermoelectric properties of several conducting polymers and small organic molecules at different doping levels. Together with the thermal conductivity calculated from the nonequilibrium molecular dynamics, they have predicted a highest ZT value of 2.5 for α-form nickel phthalocyanine at room temperature [24].

It is known that both the Landauer formalism and the Boltzmann transport theory are only applicable to weak electron-phonon interactions. As an electron-phonon interaction is of the same magnitude as or much larger than the electronic coupling, a better way to describe the carrier transport process should be the polaron picture. The first attempt to calculate the thermoelectricity within the small-polaron model starts from the work of Schotte [28], who has demonstrated that the strong electron-phonon interaction only contributes a constant shift to thermopower and all of the dynamical

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effects vanish. Since then, however, not much attention [29,30] has been paid to the polaron description of thermopower until recently. Using the mixed quantum-classical approach together with the Langevin dynamics, de Oliveira Neto *et al.* [31] have calculated the drift velocity of the polaron in a polymer chain under a thermal gradient or an external electric field. From these drift velocities, thermopower is obtained. In this approach, quantum corrections to the final results are inevitable because organic molecules often consist of many high-frequency vibrational modes. Within Holstein's small-polaron model, Wang *et al.* [32] have proposed a theory for the case of strong electron-phonon interactions by applying the saddle-point approximation to the Green-Kubo formalism and a ZT value of as high as 15.2 for a one-dimensional molecular nanowire is predicted.

However, a general method is still missing for the calculation of thermopower in organic semiconductors suitable for a broad regime of electron-phonon interactions. The central difficulty for developing such an approach is that neither the electronic coupling nor the electron-phonon interaction can be considered as perturbation. In charge transport calculations, a powerful technique to overcome such a difficulty is the polaron transformation. For instance, by applying the full polaron transformation and the mean-field approximation to the Holstein Hamiltonian, a carrier mobility expression has been derived [33] which successfully bridges the coherent band transport at low temperatures and the incoherent hopping-type motion at high temperatures. The variational polaron transformation, which extends the validity of the full one, has also been introduced in the field of open quantum systems and has been successfully utilized to calculate transport properties [34–37], dynamical processes [38–41], thermal equilibrium properties [42], and linear absorption spectra [43]. The merit of the variational transformation lies in the fact that it decouples the electron and the phonon to a large extent via a variational procedure such that the residual interaction term may be considered as perturbation.

In this paper, we introduce the variational polaron transformation and mean-field approximation to the Green-Kubo formalism for the thermopower calculation. The pivotal process is very similar to the one adopted in Ref. [33] for carrier mobilities. We derive an analytical expression for the thermopower calculation, which correctly recovers conventional theories in both strong and weak electron-phonon interaction limits. From the thermopower expression, some novel phenomena are exhibited.

The paper is arranged as follows. In Sec. II, starting from a model Hamiltonian and the Green-Kubo formalism, we present the detailed derivation of formulas for the calculation of thermopower. We then discuss the asymptotic behaviors of these formulas in Sec. III and show an application in Sec. IV. Concluding remarks are given in Sec. V.

II. METHODOLOGY

A. Model Hamiltonian

To describe thermopower of organic crystals, we start from the following model Hamiltonian:

$$\hat{H} = \hat{H}_e + \hat{H}_{\text{ph}} + \hat{H}_{e\text{-ph}}. \tag{1}$$

Here, $\hat{H}_e$ is the electronic Hamiltonian

$$\hat{H}_e = \sum_l V_l \sum_n \hat{c}^\dagger_{n+l}\hat{c}_n, \tag{2}$$

where $\hat{c}^\dagger_n$ and $\hat{c}_n$ are the creation and annihilation operators, respectively, of the electron at site n, $V_l = V_{-l}$ is the electronic coupling, and $l = \pm 1, \pm 2, \ldots$ denotes the distance and direction of electron transfer. For the sake of simplicity, a one-dimensional molecular chain with repeated molecule units is considered, but the derivation processes outlined in the following can be easily extended to three-dimensional cases to account for anisotropy of thermopower without extra difficulty.

The phonon Hamiltonian $\hat{H}_{\text{ph}}$ that describes molecular vibrations is given by

$$\hat{H}_{\text{ph}} = \sum_n \sum_j \omega_j \left(\hat{b}^\dagger_{nj}\hat{b}_{nj} + \frac{1}{2}\right), \tag{3}$$

where $\hat{b}^\dagger_{nj}$ and $\hat{b}_{nj}$ are the creation and annihilation operators, respectively, of the jth phonon mode at site n with frequency ω_j. In the present paper we only consider intramolecular vibrational modes, which often reflect a high-frequency character.

The electron-phonon interaction $\hat{H}_{e\text{-ph}}$ is assumed to be

$$\hat{H}_{e\text{-ph}} = \sum_n \hat{F}_n \otimes \hat{c}^\dagger_n\hat{c}_n, \tag{4}$$

where the phonon operator reads

$$\hat{F}_n = \sum_j \omega_j g_j (\hat{b}^\dagger_{nj} + \hat{b}_{nj}), \tag{5}$$

and g_j is the dimensionless coupling constant, which is fully characterized by the spectral density defined as

$$J_{\text{SD}}(w) = \pi \sum_j \omega_j^2 g_j^2 \delta(\omega - \omega_j). \tag{6}$$

We adopt the same spectral density for each site. The periodic boundary condition is assumed and atomic units where $\hbar = 1$ are adopted throughout this paper.

B. Green-Kubo formalism

Within the Green-Kubo formalism, the electrical conductivity σ and thermopower S are expressed by different kinds of correlation functions [44]:

$$\sigma = \frac{1}{k_B T} M_{11}, \tag{7}$$

$$S = \frac{1}{T}\left(\frac{M_{12}}{M_{11}} - \frac{\mu}{e}\right), \tag{8}$$

with

$$M_{11} = \frac{1}{2L}\int_{-\infty}^{+\infty} dt \langle \hat{J}(t)\hat{J}(0)\rangle_H, \tag{9}$$

and

$$M_{12} = \frac{1}{2L}\int_{-\infty}^{+\infty} dt \langle \hat{J}_E(t)\hat{J}(0)\rangle_H. \tag{10}$$

Here, $\hat{J}$ and $\hat{J}_E$ are the electrical and energy currents, respectively. L is the total length of the molecular chain. e is the electron charge (which is negative) and μ is the chemical potential. The correlation functions are defined as $\langle \hat{A}(t)\hat{B}(0)\rangle_H \equiv \mathrm{Tr}\{e^{i\hat{H}t}\hat{A}e^{-i\hat{H}t}\hat{B}e^{-\beta(\hat{H}-\mu\hat{N})}/Z\}$, where $\hat{A}$ and $\hat{B}$ are two arbitrary operators, $\beta = 1/k_BT$ is the inverse temperature, $\hat{N} = \sum_n \hat{c}_n^\dagger \hat{c}_n$ is the total electron number operator, and $Z = \mathrm{Tr}e^{-\beta(\hat{H}-\mu\hat{N})}$ is the grand-canonical partition function.

The electrical and energy current operators are defined as the time derivatives of the electron-density polarization operator $\hat{P} = \sum_n r_n \hat{c}_n^\dagger \hat{c}_n$ and energy polarization operator $\hat{R}_E = \sum_n r_n \hat{h}_n$, respectively [44], where $r_n = na$, a is the distance between two nearest-neighbor sites, and $\hat{h}_n$ is the energy density at site n:

$$\hat{h}_n = \frac{1}{2}\sum_l V_l(\hat{c}_{n+l}^\dagger \hat{c}_n + \hat{c}_n^\dagger \hat{c}_{n+l}) + \sum_j \omega_j \hat{b}_{nj}^\dagger \hat{b}_{nj} + \hat{F}_n \otimes \hat{c}_n^\dagger \hat{c}_n \tag{11}$$

which satisfies $\hat{H} = \sum_n \hat{h}_n$. Then, from $\hat{J} = ie[\hat{H}, \hat{P}]$ and $\hat{J}_E = i[\hat{H}, \hat{R}_E]$, one obtains

$$\hat{J} = -iae\sum_l lV_l \sum_n \hat{c}_{n+l}^\dagger \hat{c}_n \tag{12}$$

and

$$\hat{J}_E = -\frac{ia}{2}\sum_{ll'}(l+l')V_lV_{l'}\sum_n \hat{c}_{n+l+l'}^\dagger \hat{c}_n - \frac{ia}{2}\sum_l lV_l \sum_n (\hat{F}_n + \hat{F}_{n+l})\hat{c}_{n+l}^\dagger \hat{c}_n. \tag{13}$$

Different from $\hat{J}$, which solely originates from the electron kinetic energy, $\hat{J}_E$ has two components. The first term in Eq. (13) emerges from the kinetic energy of the electrons, while the second term represents the flow of the electron-phonon interaction energy. Both of them enter in the calculation of thermopower.

C. Variational polaron transformation

The difficulty of rigorously calculating the correlation functions Eqs. (9) and (10) arises from the fact that the electronic coupling and the electron-phonon interaction may be of the same magnitude in organic crystals so that the perturbation theory fails. The variational polaron transformation has been proved to be a powerful technique to partially decouple the electronic and the vibrational degrees of freedom to a large extent such that nonperturbative calculations become possible. The unitary operator of this transformation is defined as

$$\hat{G} = e^{\sum_{n,j} f_j(\hat{b}_{nj}^\dagger - \hat{b}_{nj})\otimes \hat{c}_n^\dagger \hat{c}_n}, \tag{14}$$

where $\{f_j\}$ are parameters that need to be determined variationally and are implicit functions of the temperature and the chemical potential. In the special case when $f_j = g_j$, the variational polaron transformation recovers the full polaron transformation or the Lang-Firsov transformation [45], which completely diagonalizes the Hamiltonian in the atomic limit ($V_l = 0$).

It is easy to prove the following properties, $\hat{G}\hat{b}_{nj}^\dagger \hat{G}^\dagger = \hat{b}_{nj}^\dagger - f_j \hat{c}_n^\dagger \hat{c}_n$, $\hat{G}\hat{b}_{nj}\hat{G}^\dagger = \hat{b}_{nj} - f_j \hat{c}_n^\dagger \hat{c}_n$, $\hat{G}\hat{c}_n^\dagger \hat{G}^\dagger = \hat{c}_n^\dagger \hat{X}_n^\dagger$, and $\hat{G}\hat{c}_n\hat{G}^\dagger = \hat{c}_n\hat{X}_n$, where $\hat{X}_n$ is the phonon displacement operator at site n:

$$\hat{X}_n = e^{-\sum_j f_j(\hat{b}_{nj}^\dagger - \hat{b}_{nj})}. \tag{15}$$

After the transformation, the total Hamiltonian in the polaron representation is expressed as

$$\tilde{H} = \hat{G}\hat{H}\hat{G}^\dagger = -E_p\sum_n \hat{c}_n^\dagger \hat{c}_n + \sum_l V_l \sum_n \hat{X}_{n+l}^\dagger \hat{X}_n \hat{c}_{n+l}^\dagger \hat{c}_n + \hat{H}_{\mathrm{ph}} + \sum_{nj}\omega_j(g_j - f_j)(\hat{b}_{nj}^\dagger + \hat{b}_{nj})\hat{c}_n^\dagger \hat{c}_n, \tag{16}$$

where $E_p = \sum_j \omega_j(2g_jf_j - f_j^2)$ is the polaron self-energy.

The parameters $\{f_j\}$ are determined through a variational procedure suggested by Yarkony and Silbey [46]. For a general Hamiltonian that is divided into two parts, $\tilde{H} = \tilde{H}_0 + \tilde{H}'$, Bogoliubov's theorem states that the upper bound on the free energy is given by

$$\mathcal{A}_B = -\beta^{-1}\ln \mathrm{Tr}e^{-\beta(\tilde{H}_0 - \mu\hat{N})} + \langle \tilde{H}'\rangle_{\tilde{H}_0}, \tag{17}$$

where $\langle \tilde{H}'\rangle_{\tilde{H}_0} = \mathrm{Tr}\{\tilde{H}'e^{-\beta(\tilde{H}_0-\mu\hat{N})}\}/\mathrm{Tr}e^{-\beta(\tilde{H}_0-\mu\hat{N})}$. The variational parameters should be chosen so that they minimize $\mathcal{A}_B$. To utilize this theorem, we adopt the mean-field approximation to $\hat{X}_{n+l}^\dagger \hat{X}_n$ in Eq. (16):

$$\langle \hat{X}_{n+l}^\dagger \hat{X}_n\rangle_{\mathrm{ph}} = e^{-2\Gamma}, \tag{18}$$

where $\langle \hat{A}\rangle_{\mathrm{ph}} \equiv \mathrm{Tr}\{\hat{A}e^{-\beta\hat{H}_{\mathrm{ph}}}/Z_{\mathrm{ph}}\}$ with $Z_{\mathrm{ph}} = \mathrm{Tr}e^{-\beta\hat{H}_{\mathrm{ph}}}$, $e^{-2\Gamma} = \exp\{-\sum_j f_j^2(2n_j+1)\}$ is the Debye-Waller factor, and $n_j = 1/(e^{\beta\omega_j} - 1)$ is the Bose distribution function. Then, we define $\tilde{H}_0$ as

$$\tilde{H}_0 = -E_p\sum_n \hat{c}_n^\dagger \hat{c}_n + \sum_l \tilde{V}_l \sum_n \hat{c}_{n+l}^\dagger \hat{c}_n + \hat{H}_{\mathrm{ph}} \tag{19}$$

with the residual interaction $\tilde{H}'$:

$$\tilde{H}' = \sum_l V_l \sum_n (\hat{X}_{n+l}^\dagger \hat{X}_n - e^{-2\Gamma})\hat{c}_{n+l}^\dagger \hat{c}_n + \sum_{nj}\omega_{nj}(g_j - f_j)(\hat{b}_{nj}^\dagger + \hat{b}_{nj})\hat{c}_n^\dagger \hat{c}_n, \tag{20}$$

where $\tilde{V}_l = V_le^{-2\Gamma}$ is the phonon-dressed electronic coupling or the polaronic coupling, which may be much smaller than the bare electronic coupling.

By construction, $\langle \tilde{H}'\rangle_{\tilde{H}_0} = 0$, therefore we have

$$\mathcal{A}_B = -\beta^{-1}\ln \mathrm{Tr}e^{-\beta(\tilde{H}_0 - \mu\hat{N})}. \tag{21}$$

To obtain the analytical form of $\mathcal{A}_B$, we rewrite $\tilde{H}_0$ in the reciprocal space:

$$\tilde{H}_0 = \tilde{H}_e + \hat{H}_{\mathrm{ph}}, \tag{22}$$

where $\tilde{H}_e = \sum_k \tilde{\epsilon}_k \hat{c}_k^\dagger \hat{c}_k$, $k = \frac{2\pi m}{Na}$ $(m = 1, \ldots, N)$ is the crystal momentum, N is the total number of sites, $\tilde{\epsilon}_k = -E_p + \sum_l \tilde{V}_le^{-ikr_l}$ is the polaron band energy, and

$\hat{c}_k = \frac{1}{\sqrt{N}} \sum_n e^{-ikr_n} \hat{c}_n$ is the corresponding annihilation operator of the polaron. Then, we get

$$\mathcal{A}_B = -\beta^{-1} \sum_k \ln(1 + e^{-\beta(\tilde{\epsilon}_k - \mu)}) - \beta^{-1} \ln \mathrm{Tr} e^{-\beta \hat{H}_{\mathrm{ph}}}. \tag{23}$$

Taking the partial derivative of $\mathcal{A}_B$ and let $\frac{\partial \mathcal{A}_B}{\partial f_j} = 0$, we arrive at a self-consistent equation for $\{f_j\}$:

$$f_j = \frac{w_j g_j}{w_j - (2n_j + 1) \sum_k (\tilde{\epsilon}_k + E_p) P_k}, \tag{24}$$

where $P_k = \bar{n}_k / \sum_{k'} \bar{n}_{k'}$ and $\bar{n}_k = 1/(e^{\beta(\tilde{\epsilon}_k - \mu)} + 1)$ is the Fermi-Dirac distribution function. In practice, one should make an initial guess for each f_j and then solve this equation self-consistently. Different initial guesses may give different convergent results of Eq. (24) and therefore one should try various initial guesses in order to find the optimal set of variational parameters.

After the variational procedure, the residual interaction becomes small and therefore one can set $\tilde{H} \approx \tilde{H}_0$. There are two underlying assumptions to make this mean-field approximation valid. The first one is that the vibrational motion is faster than the electron transfer, i.e., the vibrational frequency is larger than the electronic coupling [47] (which is often satisfied in organic crystals). The second one is that the fluctuation of the polaronic coupling induced by the vibrational motion is smaller than its thermal average [48]. A similar approximation has been adopted in the mobility calculations [33].

The expressions for the electrical and energy current operators in the polaron representation are

$$\tilde{J} = -iae \sum_l lV_l \sum_n \hat{X}^\dagger_{n+l} \hat{X}_n \hat{c}^\dagger_{n+l} \hat{c}_n \tag{25}$$

and

$$\tilde{J}_E = -\frac{ia}{2} \sum_{ll'} (l + l') V_l V_{l'} \sum_n \hat{X}^\dagger_{n+l+l'} \hat{X}_n \hat{c}^\dagger_{n+l+l'} \hat{c}_n - \frac{ia}{2} \sum_l lV_l \sum_n (\hat{F}_n + \hat{F}_{n+l}) \hat{X}^\dagger_{n+l} \hat{X}_n \hat{c}^\dagger_{n+l} \hat{c}_n - \frac{\Delta_E}{e} \tilde{J}, \tag{26}$$

respectively, where $\Delta_E = \sum_j \omega_j g_j f_j$. In the case of the full polaron transformation, E_p and Δ_E coincide with each other, but in general cases $E_p > \Delta_E$. This discrepancy is ascribed to the incomplete dressing of the electron by the phonon cloud, due to the nonzero electron kinetic energy. In Sec. IV, it is demonstrated that this discrepancy leads to nonvanishing thermopower in a half-filled band.

We transform the electrical and energy current operators to the reciprocal space ulteriorly and obtain

$$\tilde{J} = -\frac{iae}{N} \sum_l lV_l \sum_n \sum_{k_1 k_2} e^{-ik_1 r_{n+l} + ik_2 r_n} \times \hat{X}^\dagger_{n+l} \hat{X}_n \hat{c}^\dagger_{k_1} \hat{c}_{k_2} \tag{27}$$

and

$$\tilde{J}_E = -\frac{ia}{2N} \sum_{ll'} (l + l') V_l V_{l'} \sum_n \hat{X}^\dagger_{n+l+l'} \hat{X}_n \times \sum_{k_1 k_2} e^{-ik_1 r_{n+l+l'} + ik_2 r_n} \hat{c}^\dagger_{k_1} \hat{c}_{k_2} - \frac{ia}{2N} \sum_l lV_l \sum_n (\hat{F}_n + \hat{F}_{n+l}) \hat{X}^\dagger_{n+l} \hat{X}_n \times \sum_{k_1 k_2} e^{-ik_1 r_{n+l} + ik_2 r_n} \hat{c}^\dagger_{k_1} \hat{c}_{k_2} - \frac{\Delta_E}{e} \tilde{J}, \tag{28}$$

respectively. Substituting Eqs. (22), (27), and (28) into the integrands in Eqs. (9) and (10) and using the properties $e^{i\tilde{H}t} \hat{c}_k e^{-i\tilde{H}t} = e^{-i\tilde{\epsilon}_k t} \hat{c}_k$ and $e^{i\tilde{H}t} \hat{b}_{nj} e^{-i\tilde{H}t} = e^{-i\omega_j t} \hat{b}_{nj}$, one obtains

$$\langle \hat{J}(t) \hat{J}(0) \rangle_H = -\frac{a^2 e^2}{N^2} \sum_{ll'} ll' V_l V_{l'} \sum_{nn'} \langle \hat{X}^\dagger_{n+l}(t) \hat{X}_n(t) \hat{X}^\dagger_{n'+l'} \hat{X}_{n'} \rangle_{\mathrm{ph}} \times \sum_{k_1 k_2 k_3 k_4} e^{-i(k_1 r_{n+l} - k_2 r_n + k_3 r_{n'+l'} - k_4 r_{n'})} e^{i(\tilde{\epsilon}_{k_1} - \tilde{\epsilon}_{k_2})t} \left\langle \hat{c}^\dagger_{k_1} \hat{c}_{k_2} \hat{c}^\dagger_{k_3} \hat{c}_{k_4} \right\rangle_{\tilde{H}_e}, \tag{29}$$

$$\langle \hat{J}_E(t) \hat{J}(0) \rangle_H = -\frac{a^2 e}{2N^2} \sum_{ll'l''} (l + l') l'' V_l V_{l'} V_{l''} \sum_{nn'} \langle \hat{X}^\dagger_{n+l+l'}(t) \hat{X}_n(t) \hat{X}^\dagger_{n'+l''} \hat{X}_{n'} \rangle_{\mathrm{ph}} \times \sum_{k_1 k_2 k_3 k_4} e^{-i(k_1 r_{n+l+l'} - k_2 r_n + k_3 r_{n'+l''} - k_4 r_{n'})} e^{i(\tilde{\epsilon}_{k_1} - \tilde{\epsilon}_{k_2})t} \left\langle \hat{c}^\dagger_{k_1} \hat{c}_{k_2} \hat{c}^\dagger_{k_3} \hat{c}_{k_4} \right\rangle_{\tilde{H}_e} - \frac{a^2 e}{2N^2} \sum_{ll'} ll' V_l V_{l'} \sum_{nn'} \langle [\hat{F}_n(t) + \hat{F}_{n+l}(t)] \hat{X}^\dagger_{n+l}(t) \hat{X}_n(t) \hat{X}^\dagger_{n'+l'} \hat{X}_{n'} \rangle_{\mathrm{ph}} \times \sum_{k_1 k_2 k_3 k_4} e^{-i(k_1 r_{n+l} - k_2 r_n + k_3 r_{n'+l'} - k_4 r_{n'})} e^{i(\tilde{\epsilon}_{k_1} - \tilde{\epsilon}_{k_2})t} \left\langle \hat{c}^\dagger_{k_1} \hat{c}_{k_2} \hat{c}^\dagger_{k_3} \hat{c}_{k_4} \right\rangle_{\tilde{H}_e} - \frac{\Delta_E}{e} \langle \hat{J}(t) \hat{J}(0) \rangle_H. \tag{30}$$

Here, a new notation $\langle\hat{A}\rangle_{\tilde{H}_e} \equiv \mathrm{Tr}\{\hat{A}e^{-\beta(\tilde{H}_e-\mu\hat{N})}/\tilde{Z}_e\}$ with $\tilde{Z}_e = \mathrm{Tr}\{e^{-\beta(\tilde{H}_e-\mu\hat{N})}\}$ is introduced, and

$$\hat{F}_n(t) = \sum_j \omega_j g_j (e^{i\omega_j t}\hat{b}^\dagger_{nj} + e^{-i\omega_j t}\hat{b}_{nj}), \tag{31}$$

$$\hat{X}_n(t) = e^{-\sum_j f_j (e^{i\omega_j t}\hat{b}^\dagger_{nj} - e^{-i\omega_j t}\hat{b}_{nj})}. \tag{32}$$

At this point, Eqs. (29) and (30) seem quite cumbersome. The simplification can be made by replacing thermal averages in these equations by the corresponding analytical expressions. These expressions are given in the next subsection.

D. Thermal average

The polaronic thermal average is easily obtained by the direct application of Wick's theorem:

$$\begin{aligned}\big\langle \hat{c}^\dagger_{k_1}\hat{c}_{k_2}\hat{c}^\dagger_{k_3}\hat{c}_{k_4}\big\rangle_{\tilde{H}_e} &= \delta_{k_1k_2}\delta_{k_3k_4}\bar{n}_{k_1}\bar{n}_{k_3}\\ &\quad + \delta_{k_1k_4}\delta_{k_2k_3}\bar{n}_{k_1}\big(1-\bar{n}_{k_2}\big).\end{aligned} \tag{33}$$

The first term in Eq. (33) represents the density correlations and usually has negligible contribution to transport properties (see the discussion in Appendix A). Hence, this term is omitted hereafter.

The derivation of the phononic thermal averages appearing in Eqs. (29) and (30) is straightforward but tedious. Here, we only display the final results and leave the detailed derivation process to Appendix B:

$$\begin{aligned}&\big\langle \hat{X}^\dagger_{n_1}(t)\hat{X}_{n_2}(t)\hat{X}^\dagger_{n_3}\hat{X}_{n_4}\big\rangle_{\mathrm{ph}}\\ &\quad = \exp\big\{-2\big(2-\delta_{n_1n_2}-\delta_{n_3n_4}\big)\Gamma - I^{n_3,n_4}_{n_1,n_2}L(t)\big\}\end{aligned} \tag{34}$$

and

$$\begin{aligned}&\big\langle \hat{F}_{n_0}(t)\hat{X}^\dagger_{n_1}(t)\hat{X}_{n_2}(t)\hat{X}^\dagger_{n_3}\hat{X}_{n_4}\big\rangle_{\mathrm{ph}}\\ &\quad = \big[\big(\delta_{n_0n_1}-\delta_{n_0n_2}\big)\Delta_E + i\big(\delta_{n_0n_3}-\delta_{n_0n_4}\big)L^{(1)}(t)\big]\\ &\qquad \times \big\langle \hat{X}^\dagger_{n_1}(t)\hat{X}_{n_2}(t)\hat{X}^\dagger_{n_3}\hat{X}_{n_4}\big\rangle_{\tilde{H}}.\end{aligned} \tag{35}$$

Here, $I^{n_3,n_4}_{n_1,n_2} = \delta_{n_1n_3} - \delta_{n_1n_4} - \delta_{n_2n_3} + \delta_{n_2n_4}$ is an integer, the value of which may be 0, ±1, or ±2. It also satisfies $I^{n_3,n_4}_{n_1,n_2} = I^{n_3+n,n_4+n}_{n_1+n,n_2+n}$, where n is an arbitrary integer. $L(t)$ and $L^{(1)}(t)$ have the following expressions:

$$L(t) = \sum_j f_j^2[(2n_j+1)\cos\omega_j t - i\sin\omega_j t] \tag{36}$$

and

$$L^{(1)}(t) = -\sum_j \omega_j g_j f_j[(2n_j+1)\sin\omega_j t + i\cos\omega_j t], \tag{37}$$

respectively. Note that $L(0) = 2\Gamma$.

E. Thermopower expressions

Substituting Eq. (34) into Eqs. (9) and (29), one obtains

$$\begin{aligned}M_{11} &= -\frac{a^2e^2}{2LN^2}\sum_{ll'} ll'V_lV_{l'}\sum_{k_1k_2}\bar{n}_{k_1}\big(1-\bar{n}_{k_2}\big)\\ &\quad \times \sum_{nn'} e^{-ik_1r_{n-n'+l}+ik_2r_{n-n'-l'}}\\ &\quad \times \int_{-\infty}^{+\infty} dt\, e^{i(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2})t-4\Gamma-I^{n'+l',n'}_{n+l,n}L(t)}.\end{aligned} \tag{38}$$

Using the fact that $I^{n'+l',n'}_{n+l,n} = I^{l',0}_{n-n'+l,n-n'}$, it is easy to figure out that the summation in Eq. (38) is only relevant to $n-n'$. Therefore, one of the dummy indices can be eliminated and Eq. (38) is simplified to

$$\begin{aligned}M_{11} &= -\frac{a^2e^2}{2LN}\sum_{ll'} ll'V_lV_{l'}\sum_{k_1k_2}\bar{n}_{k_1}\big(1-\bar{n}_{k_2}\big)\\ &\quad \times \sum_{n=1}^{N} e^{-ik_1r_{n+l}+ik_2r_{n-l'}}\\ &\quad \times \int_{-\infty}^{+\infty} dt\, e^{i(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2})t-4\Gamma-I^{l',0}_{n+l,n}L(t)},\end{aligned} \tag{39}$$

where the periodic boundary condition is used. Following the same procedure, the final expression for M_{12} is given by

$$M_{12} = -\frac{\Delta_E}{e}M_{11} + M^{(\mathrm{I})}_{12} + M^{(\mathrm{II})}_{12}, \tag{40}$$

where

$$\begin{aligned}M^{(\mathrm{I})}_{12} &= -\frac{a^2e}{4LN}\sum_{ll'l''}(l+l')l''V_lV_{l'}V_{l''}\sum_{k_1k_2}\bar{n}_{k_1}\big(1-\bar{n}_{k_2}\big)\\ &\quad \times \sum_{n=1}^{N} e^{-ik_1r_{n+l+l'}+ik_2r_{n-l''}}\\ &\quad \times \int_{-\infty}^{+\infty} dt\, e^{i(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2})t-4\Gamma-I^{l'',0}_{n+l+l',n}L(t)}\end{aligned} \tag{41}$$

and

$$\begin{aligned}M^{(\mathrm{II})}_{12} &= -\frac{ia^2e}{4LN}\sum_{l\neq-l'} ll'V_lV_{l'}\sum_{k_1k_2}\bar{n}_{k_1}\big(1-\bar{n}_{k_2}\big)\\ &\quad \times (e^{-ik_1r_{l+l'}} - e^{-ik_2r_{l+l'}})\\ &\quad \times \int_{-\infty}^{+\infty} dt\, L^{(1)}(t)e^{i(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2})t-4\Gamma+L(t)},\end{aligned} \tag{42}$$

respectively. Substituting Eq. (40) into Eq. (8), thermopower is finally expressed as

$$S = \frac{1}{T}\left(\frac{M^{(\mathrm{I})}_{12}+M^{(\mathrm{II})}_{12}}{M_{11}} - \frac{\mu+\Delta_E}{e}\right). \tag{43}$$

Equations (39), (41), (42), and (43) are the main results of this paper.

It is noted that in Eq. (40) the first term corresponds to the static contributions of the electron-phonon interaction to S because its effect is only to shift $-\frac{\mu}{eT}$ to $-\frac{\mu+\Delta_E}{eT}$, the third term is the dynamical contributions, and the second term accounts for the polaron kinetic energy.

III. ASYMPTOTIC LIMITS

A. Narrow-band limit

When the electron-phonon interaction is strong, the Debye-Waller factor rapidly decreases as the temperature rises. As a result, the dispersion of the polaron band fades away. Under this circumstance, it is appropriate to perform the narrow-band approximation and substitute $\tilde{\epsilon}_k$ and $\bar{n}_k$ in Eq. (39) by $-E_p$ and c, respectively, where $c = 1/(e^{-\beta(E_p+\mu)}+1)$ measures the carrier concentration. Then, invoking the fact that $\sum_k e^{ikr_n} = N\delta_{n,0}$, almost all of the terms in Eq. (39) vanish after the summation over k_1 and k_2 except those with $n = l' = -l$. Consequently, one finds that the electrical conductivity is fully characterized by electron hopping events:

$$M_{11}^{\rm NB} = \frac{1}{2}ae^2c(1-c)\sum_l l^2 k_l, \tag{44}$$

where

$$k_l = \left|V_l^2\right| \int_{-\infty}^{+\infty} dt e^{-4\Gamma+2L(t)} \tag{45}$$

is the electron transfer rate constant. Similarly, we have

$$M_{12}^{\rm NB} = \frac{\langle V^3\rangle}{2e\langle V^2\rangle}M_{11}^{\rm NB}, \tag{46}$$

where $\langle V^2\rangle \equiv \sum_l |lV_l|^2$ and $\langle V^3\rangle \equiv \sum_{ll'} |l+l'|^2 V_l V_{l'} V_{-(l+l')}$. Therefore, a very simple formula for thermopower under the narrow-band approximation is obtained:

$$S^{\rm NB} = \frac{1}{eT}\left(\frac{\langle V^3\rangle}{2\langle V^2\rangle} - \mu - \Delta_E\right). \tag{47}$$

It is worth noting that when only nearest-neighbor electronic coupling is taken into account one has $\langle V^3\rangle = 0$ and $S = -(\mu + \Delta_E)/eT$, which are just the results obtained by Schotte [28].

B. High-temperature approximation

At high temperatures, the Debye-Waller factor becomes small and it may be compensated by $L(0)$ to a large extent if the prefactor $I_{n_1n_2}^{n_3n_4}$ in Eqs. (39) and (41) is smaller than zero because $L(0) = 2\Gamma$. In this situation, the leading terms of the correlation functions are those which minimize $I_{n_1n_2}^{n_3n_4}$. For M_{11}, these terms correspond to $n = l' = -l$. Therefore, we have

$$M_{11} \approx \frac{a^2e}{2LN}\langle V^2\rangle \sum_{k_1k_2} \bar{n}_{k_1}\left(1-\bar{n}_{k_2}\right) \times \int_{-\infty}^{+\infty} dt e^{i(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2})t-4\Gamma+2L(t)}. \tag{48}$$

To analytically solve the time integral in Eq. (48), we use a short-time approximation for $L(t)$:

$$L(t) \approx 2\Gamma - \frac{\Lambda}{2}\left(\frac{t^2}{\beta} + it\right), \tag{49}$$

where $\Lambda = 2\sum_j f_j^2\omega_j$ plays a role similar to the reorganization energy in the Marcus theory of electron transfer. Then, Eq. (48) becomes

$$M_{11}^{\rm HT} = \frac{a^2e\langle V^2\rangle}{2LN}\sqrt{\frac{\pi}{k_BT\Lambda}}\sum_{k_1k_2}\bar{n}_{k_1}\left(1-\bar{n}_{k_2}\right)e^{-\frac{(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2}-\Lambda)^2}{4k_BT\Lambda}}. \tag{50}$$

This equation has a similar form as the Marcus formula for electron transfer.

Considering only the leading term with $n = l'' = -(l+l')$ in $M_{12}^{(\rm I)}$, it is easy to find that $M_{12}^{(\rm I),HT} = \frac{\langle V^3\rangle}{2e\langle V^2\rangle}M_{11}^{\rm HT}$. However, when only nearest-neighbor electronic coupling is considered, this term vanishes, and one must consider the next-leading terms with $n = l'' \neq -(l+l')$ or $n = -(l+l') \neq l''$. That is,

$$M_{12}^{(\rm I)} \approx -\frac{a^2e}{4LN}\sum_{ll'}\sum_{l''\neq-(l+l')}(l+l')l''V_lV_{l'}V_{l''} \times \sum_{k_1k_2}\bar{n}_{k_1}\left(1-\bar{n}_{k_2}\right)\left(e^{-ik_1r_{l+l'+l''}} + e^{-ik_2r_{l+l'+l''}}\right) \times \int_{-\infty}^{+\infty} dt e^{i(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2})t-4\Gamma+L(t)}. \tag{51}$$

The application of the high-temperature and short-time approximations to Eq. (51) results in

$$M_{12}^{(\rm I),HT} = -\frac{a^2e}{4LN}\sqrt{\frac{2\pi}{k_BT\Lambda}}\sum_{ll'}\sum_{l''\neq-l-l'}(l+l')l''V_lV_{l'}V_{l''} \times \sum_{k_1k_2}\bar{n}_{k_1}\left(1-\bar{n}_{k_2}\right)\left(e^{-ik_1r_{l+l'+l''}} + e^{-ik_2r_{l+l'+l''}}\right) \times e^{-2\Gamma-\frac{(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2}-\Lambda/2)^2}{2k_BT\Lambda}}. \tag{52}$$

Furthermore, under the same approximations, we have

$$L^{(1)}(t) \approx -\Lambda'\left(\frac{t}{\beta} + \frac{i}{2}\right), \tag{53}$$

where $\Lambda' = 2\sum_j \omega_j g_j f_j$. Substituting Eqs. (49) and (53) into Eq. (42) and solving the integral analytically, we finally get

$$M_{12}^{(\rm II),HT} = -\frac{a^2e\Lambda'}{4LN\Lambda}\sqrt{\frac{2\pi}{k_BT\Lambda}}\sum_{l\neq-l'}ll'V_lV_{l'} \times \sum_{k_1k_2}\bar{n}_{k_1}\left(1-\bar{n}_{k_2}\right)\left(e^{-ik_1r_{l+l'}} - e^{-ik_2r_{l+l'}}\right) \times \left(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2}\right)e^{-2\Gamma-\frac{(\tilde{\epsilon}_{k_1}-\tilde{\epsilon}_{k_2}-\Lambda/2)^2}{2k_BT\Lambda}}. \tag{54}$$

Equations (50), (52), and (54) are the results suitable for high temperatures and are very similar to the formulas derived by Wang *et al.* [32], although their work is based on the application of the full polaron transformation and the saddle-point approximation to the Green-Kubo formulas. It is noted that in their work the contribution of $M_{12}^{(\rm II)}$ is neglected, which may be of the same magnitude as the next-leading term of $M_{12}^{(\rm I)}$.

C. Coherent limit

On the basis of the physical picture, we can further separate Eqs. (39), (41), and (42) into coherent and incoherent contributions, as suggested in Ref. [33]. The coherent one dominates at low temperatures or weak electron-phonon interactions.

To extract the coherent part of the electrical conductivity and thermopower, we further apply the mean-field approximation to the electrical and energy current operators. Replacing $\hat{X}_{n+l}^{\dagger}\hat{X}_n$ in Eq. (25) by $e^{-2\Gamma}$, one obtains the phonon-cloud-dressed electrical current operator:

$$\tilde{J}_{\rm coh} = -iae\sum_n\sum_l l\tilde{V}_l\hat{c}_{n+l}^{\dagger}\hat{c}_n = e\sum_k \tilde{v}_k\hat{c}_k^{\dagger}\hat{c}_k, \tag{55}$$

where $\tilde{v}_k = \frac{\partial \tilde{\epsilon}}{\partial k} = -ia\sum_l l\tilde{V}_l e^{-ikr_l}$ is the group velocity of the polaron and the subscript "coh" indicates that no dissipative channel is presented under the full mean-field treatment so that the transport is completely coherent. Similarly, using the property

$$\langle(\hat{F}_n + \hat{F}_{n+l})\hat{X}^\dagger_{n+l}\hat{X}_n\rangle_{\rm ph} = 0, \tag{56}$$

which is easily proved by the technique shown in Appendix B, we have

$$\begin{aligned}\tilde{J}_{\rm E,coh} &= -\frac{ia}{2}\sum_{ll'}(l+l')V_lV_{l'}e^{-2\Gamma}\sum_n \hat{c}^\dagger_{n+l+l'}\hat{c}_n - \frac{\Delta_E}{e}\tilde{J}_{\rm coh}\\ &= \sum_k(\epsilon_k - \Delta_E)\tilde{v}_k\hat{c}^\dagger_k\hat{c}_k.\end{aligned} \tag{57}$$

Here, $\epsilon_k = \sum_l V_l e^{ikr_l}$ is the bare electronic band energy instead of the polaron band energy. Equation (57) implies that the electron-phonon interaction only reduces the polaron velocity but it does not change the relative energy carried by polarons during the transport.

It is easily shown that $\tilde{J}_{\rm coh}$ and $\tilde{J}_{\rm E,coh}$ are conserved quantities, $[\tilde{H}, \tilde{J}_{\rm coh}] = [\tilde{H}, \tilde{J}_{\rm E,coh}] = 0$, because the full mean-field treatment completely decouples the polaron from the phonon bath. Therefore, we have

$$\begin{aligned}\langle\tilde{J}_{\rm coh}(t)\tilde{J}_{\rm coh}(0)\rangle_{\tilde{H}} &= e^2\sum_{kk'}\tilde{v}_k\tilde{v}_{k'}\langle\hat{c}^\dagger_k\hat{c}_k\hat{c}^\dagger_{k'}\hat{c}_{k'}\rangle_{\tilde{H}}\\ &= e^2\left(\sum_k\tilde{v}_k\bar{n}_k\right)^2 + e^2\sum_k\tilde{v}_k^2\bar{n}_k(1-\bar{n}_k),\end{aligned} \tag{58}$$

where the second equality is obtained by using Eq. (33). Due to the symmetry of the first Brillouin zone, $\tilde{\epsilon}_k = \tilde{\epsilon}_{-k}$, $\tilde{v}_k = -\tilde{v}_{-k}$, the first term in Eq. (58) (corresponds to the density correlations) vanishes.

Similarly, we have

$$\langle\tilde{J}_{\rm E,coh}(t)\tilde{J}_{\rm coh}(0)\rangle_{\tilde{H}} = e\sum_k(\epsilon_k - \Delta_E)\tilde{v}_k^2\bar{n}_k(1-\bar{n}_k). \tag{59}$$

Substituting Eqs. (58) and (59) into Eqs. (9) and (10), respectively, we obtain

$$\begin{aligned}M_{11}^{\rm coh} &= \frac{1}{2L}\int_{-\infty}^{+\infty}dt\langle\tilde{J}_{\rm coh}(t)\tilde{J}_{\rm coh}(0)\rangle_{\tilde{H}}\\ &= \frac{\pi e^2}{L}\sum_k\tilde{v}_k^2\bar{n}_k(1-\bar{n}_k)\delta(\tilde{\epsilon}_k - \tilde{\epsilon}_k)\end{aligned} \tag{60}$$

and

$$\begin{aligned}M_{12}^{\rm coh} &= \frac{1}{2L}\int_{-\infty}^{+\infty}dt\langle\tilde{J}_{\rm E,coh}(t)\tilde{J}_{\rm coh}(0)\rangle_{\tilde{H}}\\ &= \frac{\pi e}{L}\sum_k(\epsilon_k - \Delta_E)\tilde{v}_k^2\bar{n}_k(1-\bar{n}_k)\delta(\tilde{\epsilon}_k - \tilde{\epsilon}_k).\end{aligned} \tag{61}$$

One may further replace the summation over k by the integration over the polaron energy, $\sum_k \to \int d\tilde{E}\tilde{g}(\tilde{E})$, where $\tilde{g}(\tilde{E}) = \sum_k\delta(\tilde{E} - \tilde{\epsilon}_k)$, and substitute $\bar{n}_k$ by the Fermi-Dirac distribution function $f(\tilde{E}) = 1/(1+e^{\beta(\tilde{E}-\mu)})$ to rewrite Eqs. (60) and (61) as

$$M_{11}^{\rm coh} = \frac{\pi e^2k_BT}{L}\int d\tilde{E}\tilde{g}(\tilde{E})\tilde{v}^2(\tilde{E})\delta(\tilde{E} - \tilde{E})\left(-\frac{\partial f}{\partial\tilde{E}}\right) \tag{62}$$

and

$$M_{12}^{\rm coh} = \frac{\pi ek_BT}{2L}\int d\tilde{E}(E - \Delta_E)\tilde{v}^2(\tilde{E})\delta(\tilde{E} - \tilde{E})\left(-\frac{\partial f}{\partial\tilde{E}}\right), \tag{63}$$

where the property $-\partial f/\partial\tilde{E} = f(\tilde{E})[1 - f(\tilde{E})]/k_BT$ is invoked. Finally, by defining the energy-dependent conductivity

$$\sigma(\tilde{E}) = \frac{\pi e^2}{L}\tilde{g}(\tilde{E})\tilde{v}^2(\tilde{E})\delta(\tilde{E} - \tilde{E}), \tag{64}$$

we obtain

$$\sigma_{\rm coh} = \int d\tilde{E}\sigma(\tilde{E})\left(-\frac{\partial f}{\partial\tilde{E}}\right) \tag{65}$$

and

$$S_{\rm coh} = \frac{1}{eT}\int d\tilde{E}(E - \Delta_E - \mu)\frac{\sigma(\tilde{E})}{\sigma}\left(-\frac{\partial f}{\partial\tilde{E}}\right), \tag{66}$$

where $E = (\tilde{E} + E_p)e^{2\Gamma}$. It may be appropriate to call Eqs. (65) and (66) the modified Mott formulas since they have very similar forms as the conventional Mott formulas [11] but they are suitable for the polaron transport.

It should be noted that in Eq. (66) $E_p \neq \Delta_E$ and $E \neq \tilde{E}$. The inconsistency between E_p and Δ_E is ascribed to the incomplete dressing of the electron to the phonon cloud and leads to a small shift of the energy carried by the polaron. As a result, the particle-hole symmetry is broken and thermopower is nonzero in a half-filled band where $\mu = -E_p$. It is noted that several investigations demonstrate zero thermopower for the Hubbard [49] and lattice-gas models [50] in a half-filled band without the consideration of electron-phonon interactions. A similar conclusion has also been obtained for the small-polaron model [29]. However, the present analysis shows that the above conclusion is not generally true as the carrier is partially dressed by the phonon cloud.

The inconsistency between E and $\tilde{E}$ is equivalent to an enlarged effect on the polaron energy by a factor of $e^{2\Gamma}$ if the polaron band energy is regarded as a reference. It will be shown in Sec. IV that this enlarged effect may result in a crossover behavior of thermopower in terms of the chemical potential and cause an abnormal sign-inversion phenomenon with respect to the temperature.

IV. RESULTS AND DISCUSSION

In numerical demonstrations, we mainly demonstrate the effects of the electron-phonon interaction strength, chemical potential, and temperature on thermopower. For this purpose, we use a model of a one-dimensional molecular chain with only nearest-neighbor electronic coupling ($V = 100$ cm^{-1}). The electron-phonon interaction is described by a super-Ohmic spectral density function:

$$J_{\rm SD}(\omega) = \frac{\pi E_p^0}{2}\left(\frac{\omega}{\omega_c}\right)^3e^{-\omega/\omega_c}. \tag{67}$$

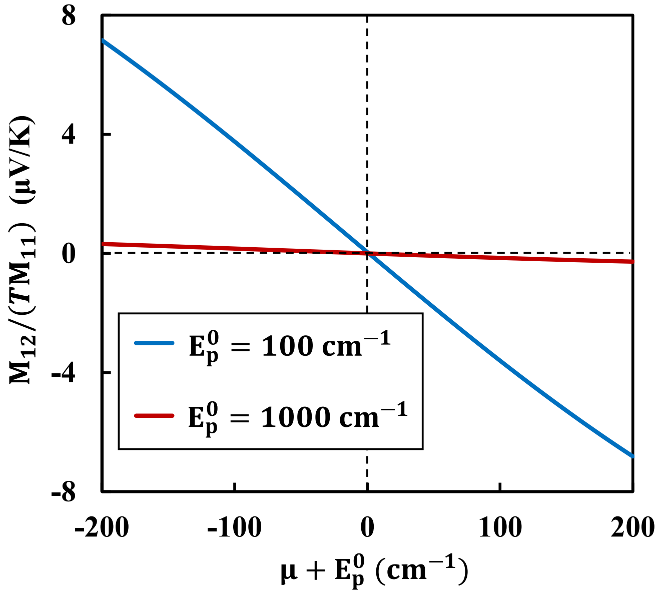

FIG. 1. Plot of $M_{12}/(TM_{11})$ vs the chemical potential. The temperature is 300 K.

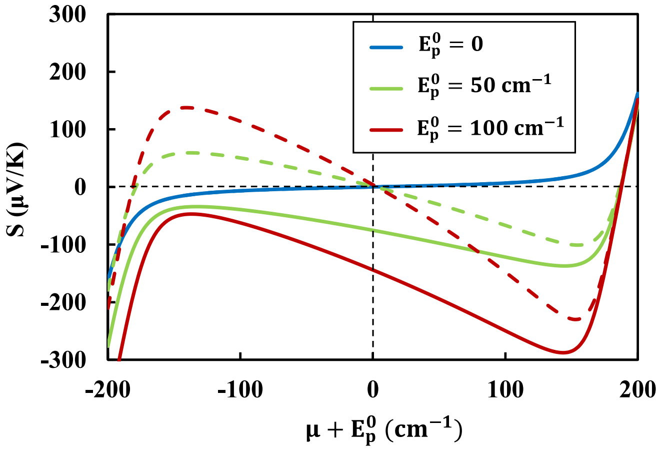

FIG. 2. Plot of thermopower vs the chemical potential. Solid and dashed color lines are S and $S - (E_p - \Delta_E)/eT$, respectively. The temperature is 10 K.

Here, E_p^0 is the polaron self-energy under the full polaron transformation and it determines the electron-phonon interaction strength. Generally, $E_p^0 \geqslant E_p \geqslant \Delta_E$. Due to the polaron self-trapping effect, a half-filled band corresponds to $\mu = -E_p \approx -E_p^0$, while n- and p-type doping correspond to $\mu + E_p^0 < 0$ and $\mu + E_p^0 > 0$, respectively. ω_c is the cutoff frequency that characterizes the relaxation time of the phonon bath and it is set to be $\omega_c = 300\ \mathrm{cm}^{-1}$, corresponding to an effective vibrational frequency [51] of about 1040 cm^{-1}, to resemble the high-frequency nature of intramolecular vibrations in organic crystals. To facilitate the calculations, we add a damping factor $e^{-\lambda t^2}$ in the integrands of Eqs. (39), (41), and (42), where λ may come from the homogeneous broadening of the energy levels. As λ is small enough, the calculated thermopower is independent of its value.

Figure 1 displays a thermopower component versus the chemical potential at room temperature for two different electron-phonon interaction strengths. It is seen that $M_{12}/(TM_{11})$ monotonously decreases with the increase of the chemical potential and it switches its sign from n-type to p-type doping. At a strong electron-phonon interaction strength, the magnitude of $M_{12}/(TM_{11})$ becomes quite small, which is consistent with the conclusion drawn in Sec. III A that in the narrow-band limit M_{12} completely vanishes when only nearest-neighbor electronic coupling is considered.

As discussed in Sec. III, the electron-phonon interaction may cause fruitful behaviors of thermopower, especially at very low temperature. Figure 2 shows thermopower in terms of the chemical potential at 10 K for several different electron-phonon interaction strengths. At a zero electron-phonon interaction, thermopower monotonously increases with respect to the chemical potential and has an inversion symmetry about $\mu = 0$. Consequently, it vanishes in a half-filled band. However, as the electron-phonon interaction is turned on, thermopower is no longer monotonous but exhibits a crossover behavior along with a downward shift by an amount of $-(E_p - \Delta_E)/eT$. The crossover behavior originates from the enlarged effect on the polaron energy, while the shift comes from the discrepancy between E_p and Δ_E. Due to this shift, thermopower is nonzero in a half-filled band. It should be noted that both E_p and Δ_E are functions of the temperature and the chemical potential. As a result, the shift is μ dependent and a smaller μ generally corresponds to a larger shift.

The joint action of the thermopower shift and the enlarged effect on the polaron energy gives rise to an abnormal p-type doping region where thermopower is negative, inconsistent with the sign of the carrier charge. With the increase of the electron-phonon interaction strength, this phenomenon is strengthened and even an abnormal n-type doping region with a positive thermopower occurs, as shown in Fig. 3(a) at $E_p^0 = 1000\ \mathrm{cm}^{-1}$. Nevertheless, this novel phenomenon only exists at extremely low temperatures and it quickly disappears as the temperature rises. The inset figure in Fig. 3(a) shows the results at 300 K and it can be seen that thermopower behaves normally in terms of the chemical potential.

To reveal the turning-over temperatures for these abnormal properties, we calculate the temperature dependence of thermopower in the four different doping regions partitioned in Fig. 3(a). The results are shown in Figs. 3(b)–3(e). In the normal regions I and IV [Figs. 3(b) and 3(e)], the absolute value of thermopower monotonously decreases with the increase of temperature, and no sign inversion occurs. However, in the abnormal regions II and III [Figs. 3(c) and 3(d)], the absolute value of thermopower rapidly vanishes as the temperature increases, followed up with a sign inversion, then rises again until it arrives at a maximum value, and finally ends with a slow decline. For the parameters adopted here, the turning-over temperatures are about 20 K for n-type doping and 40 K for p-type doping, respectively.

It should be emphasized that the abnormal behavior of thermopower caused by the electron-phonon interaction has not been reported yet to our best knowledge. However, a similar sign-inversion phenomenon caused by the intrasite Coulomb

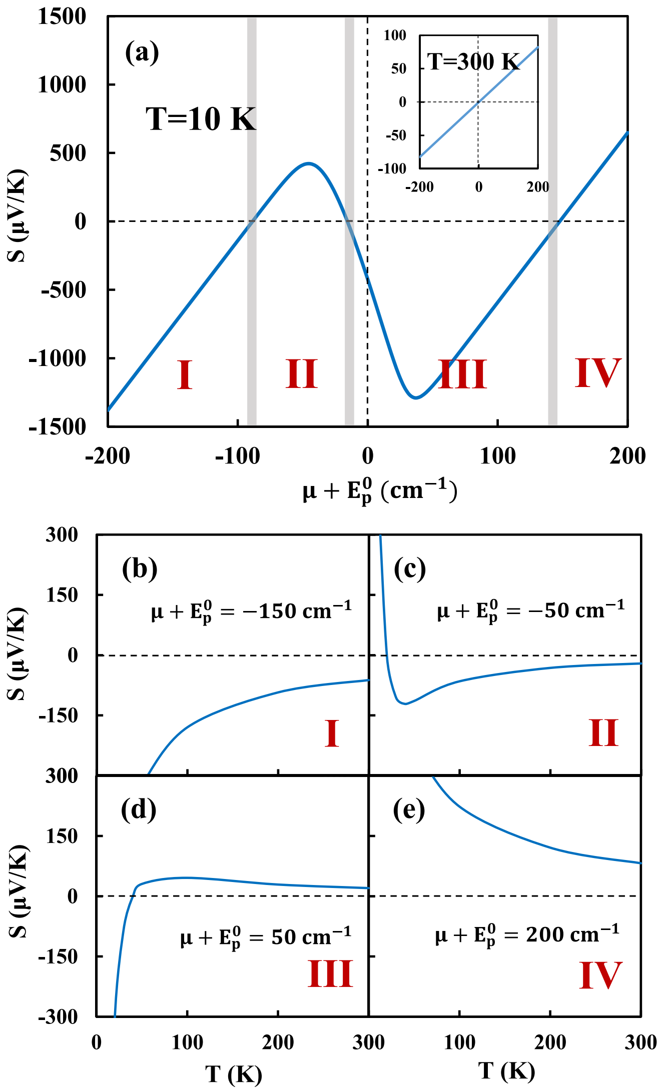

FIG. 3. (a) Plot of thermopower vs the chemical potential, $E_p^0 = 1000$ cm^{-1}, and the temperature is 10 K. The graph is divided into four regions according to the sign of thermopower. The inset shows the result at 300 K. (b)–(e) Plots of thermopower vs the temperature at different chemical potentials.

repulsion has been found in the single-band Hubbard model [30]. The model considered in this paper does not include the static disorder, which may have dominant effects on transport properties at low temperatures as the thermal fluctuations induced by electron-phonon interactions are weak. The presence of static disorders may also mask the phenomena shown here and make them hard to be detected by experiments. Therefore, to find these phenomena in experiments, it may be crucial to delicately prepare the sample to reduce static disorders as much as possible.

V. CONCLUSIONS

A variational polaron transformation approach is proposed to calculate thermopower in organic crystals. The method is applicable to a broad range of electron-phonon interaction strengths and temperatures. Detailed analysis illustrates that the present method naturally recovers several available methods in the narrow-band limit, the low-temperature or weak electron-phonon interaction limit, and the high-temperature limit. In numerical demonstrations with a one-dimensional molecular chain, it is found that at very low temperatures the electron-phonon interaction may lead to abnormal regions of the doping level where the sign of thermopower is opposite to the sign of the carrier charge. These abnormal properties are explained with the polaron transport energy enhancement by the reciprocal of the Debye-Waller factor. In addition, the incomplete dressing of the electron by the phonon cloud destroys the particle-hole symmetry and results in a nonzero value of thermopower in a half-filled band.

In this paper, only the local electron-phonon interaction is considered and attentions are mainly made on thermoelectric phenomena of organic crystals. Nevertheless, as suggested in Ref. [37], it is straightforward to incorporate static disorder as well as nonlocal electron-phonon interactions into the Hamiltonian and treat them in the spirit of the self-consistent Born approximation. Following this scheme, the extension of our approach is now underway. Connecting our method to phenomenological models for disordered organic semiconductors is an attractive subject and will be left as a future work.

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APPENDIX A: CONTRIBUTIONS OF THE DENSITY CORRELATIONS

In this Appendix, we discuss the contributions of the density correlations to the correlation function. The density correlation part of the polaronic thermal average is

$$\langle \hat{c}_{k_1}^\dagger \hat{c}_{k_2} \hat{c}_{k_3}^\dagger \hat{c}_{k_4} \rangle_{\tilde{H}}^{\mathrm{DC}} = \delta_{k_1 k_2} \delta_{k_3 k_4} \bar{n}_{k_1} \bar{n}_{k_3}. \tag{A1}$$

Substituting it into Eqs. (29) and (30) and simplifying the expressions by the same procedure used in Sec. II, one can get the following extra terms to the correlation function:

$$M_{11}^{\mathrm{DC}} = -\frac{a^2 e^2}{2LN} \sum_{ll'} l l' V_l V_{l'} \left(\sum_{k_1 k_2} \bar{n}_{k_1} \bar{n}_{k_2} e^{-ik_1 r_l - ik_2 r_{l'}} \right) \times \sum_{n=1}^{N} \int_{-\infty}^{+\infty} dt\, e^{-4\Gamma - I_{n+l,n}^{l',0} L(t)}, \tag{A2}$$

$$M_{12}^{\mathrm{DC}} = -\frac{a^2 e}{4LN} \sum_{ll'l''} (l + l') l'' V_l V_{l'} V_{l''} \times \left(\sum_{k_1 k_2} \bar{n}_{k_1} \bar{n}_{k_2} e^{-ik_1 r_{l+l'} - ik_2 r_{l''}} \right) \times \sum_{n=1}^{N} \int_{-\infty}^{+\infty} dt\, e^{-4\Gamma - I_{n+l+l',n}^{l'',0} L(t)}. \tag{A3}$$

It is obvious that in both expressions the reciprocal indices k_1 and k_2 are decoupled from the site index n such that k_1 and k_2 enter in these expressions on an almost equal footing, completely different from the expressions given in Sec. II E. As a result, most of the terms in the summation cancel out with each other. In numerical calculations, it is found that M_{11}^{DC} and M_{12}^{DC} are always several orders of magnitudes smaller than the results from Eqs. (39), (41), and (42) in broad regimes of the temperature and the concentration of the charge carrier.

APPENDIX B: PHONONIC THERMAL AVERAGE

To derive the analytical expressions of the two phononic thermal averages, we first introduce a set of displacement operators:

$$\hat{D}_{nj}(\alpha) = e^{\alpha \hat{b}_{nj}^{\dagger} - \alpha^{*} \hat{b}_{nj}}, \tag{B1}$$

where α is a complex number. Then, the phonon displacement operator [Eq. (32)] can be expressed as

$$\hat{X}_n(t) = \prod_j \hat{D}_{nj}(-f_j e^{i\omega_j t}). \tag{B2}$$

Considering the generality of the following derivation, we expand the variational parameters $\{f_j\}$ to a larger set $\{f_{mj}^{(n)}\}$ and let $f_{mj}^{(n)} = \delta_{nm} f_j$. Thereby, $\hat{X}_n(t)$ is reexpressed as

$$\hat{X}_n(t) = \prod_m \prod_j \hat{D}_{mj}\big(-f_{mj}^{(n)} e^{i\omega_j t}\big). \tag{B3}$$

Using this expression, the first kind of the phononic thermal average is written as

$$\begin{aligned}
&\big\langle \hat{X}_{n_1}^{\dagger}(t) \hat{X}_{n_2}(t) \hat{X}_{n_3}^{\dagger} \hat{X}_{n_4} \big\rangle_{\mathrm{ph}} \\
&\quad= \prod_m \prod_j \langle \hat{D}_{mj}\big(f_{mj}^{(n_1)} e^{i\omega_j t}\big) \hat{D}_{mj}\big(-f_{mj}^{(n_2)} e^{i\omega_j t}\big) \\
&\qquad \times \hat{D}_{mj}\big(f_{mj}^{(n_3)}\big) \hat{D}_{mj}\big(-f_{mj}^{(n_4)}\big)\rangle_{\mathrm{ph}}.
\end{aligned} \tag{B4}$$

To go further, two properties of the displacement operator are invoked:

$$\hat{D}_{mj}(\alpha_1) \cdots \hat{D}_{mj}(\alpha_M) = e^{i \sum_{i_1 < i_2} \mathrm{Im}(\alpha_{i_1} \alpha_{i_2}^{*})} \hat{D}_{mj}\left(\sum_i \alpha_i\right) \tag{B5}$$

and

$$\langle \hat{D}_{mj}(\alpha) \rangle_{\mathrm{ph}} = e^{-|\alpha|^2 (n_j + \frac{1}{2})}. \tag{B6}$$

The first property is easily proved by Glauber's formula and mathematical induction and the second property is just the Bloch identity [52]. From these two properties, we have

$$\begin{aligned}
&\langle \hat{D}_{mj}(\alpha_1) \cdots \hat{D}_{mj}(\alpha_M) \rangle_{\mathrm{ph}} \\
&\quad= \exp\left\{ i \sum_{i_1 < i_2} \mathrm{Im}\big(\alpha_{i_1} \alpha_{i_2}^{*}\big) - \left(n_j + \frac{1}{2}\right) \sum_i |\alpha_i|^2 \right. \\
&\qquad \left. -(2n_j + 1) \sum_{i_1 < i_2} \mathrm{Re}\big(\alpha_{i_1} \alpha_{i_2}^{*}\big) \right\},
\end{aligned} \tag{B7}$$

where Re and Im represent taking the real and the imaginary part, respectively. Applying Eq. (B7) to Eq. (B4), one readily obtains

$$\begin{aligned}
&\big\langle \hat{X}_{n_1}^{\dagger}(t) \hat{X}_{n_2}(t) \hat{X}_{n_3}^{\dagger} \hat{X}_{n_4} \big\rangle_{\mathrm{ph}} \\
&\quad= \prod_m \prod_j \exp\Big\{ -\big(f_{mj}^{(n_1)} - f_{mj}^{(n_2)}\big)\big(f_{mj}^{(n_3)} - f_{mj}^{(n_4)}\big) \\
&\qquad \times [(2n_j + 1)\cos\omega_j t - i \sin\omega_j t] \\
&\qquad - \left(n_j + \frac{1}{2}\right)\Big[\big(f_{mj}^{(n_1)} - f_{mj}^{(n_2)}\big)^2 + \big(f_{mj}^{(n_3)} - f_{mj}^{(n_4)}\big)^2\Big]\Big\}.
\end{aligned} \tag{B8}$$

Finally, substituting $f_{mj}^{(n)} = \delta_{nm} f_j$ into Eq. (B8), the compact expression Eq. (34) is obtained.

For the second kind of the phononic thermal average, two extra properties are needed:

$$\langle \hat{b}_{mj}^{\dagger} \hat{D}_{mj}(\alpha) \rangle_{\mathrm{ph}} = -\alpha^{*} n_j \langle \hat{D}_{mj}(\alpha) \rangle_{\mathrm{ph}} \tag{B9}$$

and

$$\langle \hat{b}_{mj} \hat{D}_{mj}(\alpha) \rangle_{\mathrm{ph}} = \alpha(n_j + 1) \langle \hat{D}_{mj}(\alpha) \rangle_{\mathrm{ph}}. \tag{B10}$$

Combining the above four properties of the displacement operator, we have

$$\begin{aligned}
&\langle (\gamma \hat{b}_{mj}^{\dagger} + \gamma^{*} \hat{b}_{mj}) \hat{D}_{mj}(\alpha_1) \cdots \hat{D}_{mj}(\alpha_M) \rangle_{\mathrm{ph}} \\
&\quad= \left\{ -i\mathrm{Im}\left[\gamma\left(\sum_i \alpha_i^{*}\right)\right](2n_j + 1) + \mathrm{Re}\left[\gamma\left(\sum_i \alpha_i^{*}\right)\right] \right\} \\
&\qquad \times \langle \hat{D}_{mj}(\alpha_1) \cdots \hat{D}_{mj}(\alpha_M) \rangle_{\mathrm{ph}},
\end{aligned} \tag{B11}$$

where γ is a complex number. To utilize this result, the electron-phonon coupling constants are expanded to a larger set, $g_{mj}^{(n)} = \delta_{nm} g_j$, as is done for $\{f_j\}$. Rewriting Eq. (31) as

$$\hat{F}_n(t) = \sum_{mj} \omega_j g_{mj}^{(n)} \big(e^{i\omega_{nj} t} \hat{b}_{nj}^{\dagger} + e^{-i\omega_{nj} t} \hat{b}_{nj}\big), \tag{B12}$$

and using Eqs. (B3) and (B11), we obtain the following expression:

$$\begin{aligned}
\big\langle \hat{F}_{n_0}(t) \hat{X}_{n_1}^{\dagger}(t) \hat{X}_{n_2}(t) \hat{X}_{n_3}^{\dagger} \hat{X}_{n_4} \big\rangle_{\mathrm{ph}} &= \sum_{mj} \big\{ -i\omega_j g_{mj}^{(n_0)} \big(f_{mj}^{(n_3)} - f_{mj}^{(n_4)}\big)\big[(2n_j + 1)\sin\omega_j t + i\cos\omega_j t\big] + w_j g_{mj}^{(n_0)} \big(f_{mj}^{(n_1)} - f_{mj}^{(n_2)}\big) \big\} \\
&\quad \times \big\langle \hat{X}_{n_1}^{\dagger}(t) \hat{X}_{n_2}(t) \hat{X}_{n_3}^{\dagger} \hat{X}_{n_4} \big\rangle_{\mathrm{ph}}.
\end{aligned} \tag{B13}$$

Finally, replacing $g_{mj}^{(n)}$ by $\delta_{mn} g_j$, we obtain Eq. (35) from the above expression.

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