Theoretical model obtained in momentum space for charge transport in a system consisting of noninteracting polarons

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We have developed a theory of charge transport in a system of noninteracting polarons. The theory is conducted to a compact relation through a nonperturbative method based on electron-phonon Hamiltonian. The derived final result represents two different limits of band and phonon-assisted transport, which depends on temperature and electron-phonon coupling strength.

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I. INTRODUCTION

Charge carrier transport phenomena coupled to harmonic vibration of lattice are of great interest in quantum solid-state physics. The coupling of the charge movement to the vibrational states results in the dressing of the charge carriers by phonon clouds, or polaron formation. Polaron mass becomes larger with increasing electron-lattice coupling strength, while this heavy quasiparticle is much less mobile than a bare electron or hole. The state of the art of theoretical condensed-matter and computational modeling in the last decades made it possible to develop a comprehensive understanding of charge transport mechanism of various materials using first principle methods including density functional theory (DFT).[1–6] Using DFT has the advantage of mapping a system of interacting electrons into a system of noninteracting electrons with the same ground-state density. The aim of this work is to present a theoretical model to calculate charge transport in a system with electron-phonon interaction of arbitrary strength. The recent works from Hannewald *et al.*[7–13] provided a unified approach beyond Holstein formalism for calculating conductivity of organic materials consisting of polarons of arbitrary size and temperature using tight-binding model. They have performed an analytical evaluation of Kubo formula using the method of canonical transformation incorporating the electron-phonon interaction in a nonperturbative manner.[13] Especially, they simplified the complicated time evolution of the electron and phonon creation and annihilation operators by employing an approximated Hamiltonian resulting from thermal averaging over phonon substates. Therefore, they could separate polaron and phonon terms in the transformed Hamiltonian.[10] According to Ref. 13, the predicted mobility resulting from this model has well reproduced the available experimental results. So in our nonperturbative theoretical method, we have applied the same approximations as have been used in Ref. 13. Consistent with Refs. 11 and 13, the final result of our model shows two different transport behaviors depending on the temperature and electron-phonon coupling strength. In low temperature limit, band transport is the dominant phenomena. If the coupling strength is strong enough, with increasing temperature a phonon-assisted charge transport behavior gradually begins to be observed. Therefore, the complicated dual behavior of charge transport in terms of the temperature for a system with strong coupling can be explained by our model.

This article is organized in seven main sections. The methodology of our analytical work and applied-approximations are described through Sec. II. In Sec. III, the Hamiltonian of the system is investigated and a displacement transformation is applied to decouple the electronic part of the Hamiltonian from its phononic counterpart. Following Refs. 7–13 in Sec. IV, by averaging over the phononic substates, we derive a diagonal Hamiltonian for each electronic level . This diagonal Hamiltonian will be used to approximate the time evolution of creation and annihilation operators in Sec. V, in which we will derive a compact relation for mobility in k space. The different aspects of transport, depending on coupling strength and temperature, are discussed in Sec. VI, and finally a brief summary and conclusion is presented in Sec. VII.

II. METHODOLOGY

There is a substantial difference between this work and the Hannewald *et al*. model. Their theory has been constructed in real space within a tight-binding model. This will impose some complications in deriving relations, especially in calculating the anisotropic effects of coupling on mobility. In contrast, our theory is established and developed in reciprocal space using many body techniques. Consequently, our final result depends directly on momentum vectors and can be used in a much simpler way in simulating of charge transport within the DFT framework using plane wave basis set. Another advantage of the present work is generalization of the theory to both acoustical and optical phonons. Acoustical phonons have a more important role in lower temperatures and often have to be ignored for the sake of simplicity in simulation by tight-binding model in real space. However, in order to be analytically traceable, we approximate Bloch electrons by plane waves and at the same time change the electron mass m into the effective mass m^*. This approximation is best valid for translational-invariant media, when the spatial extension of the polaron is large compared to the lattice parameter

(Fröhlich-type polarons, where the bandwidth is large). For other systems, which are characterized by localized polaron, this model must be used with more caution.

III. HAMILTONIAN DESCRIPTION OF A SYSTEM UNDERGOING INTERACTION WITH PHONONS

The initial Hamiltonian of noninteracting electrons coupled to longitudinal phonons has the form of

$$H = H_{\rm e} + H_{\rm ph} + H_{\rm e-ph}, \tag{1}$$

where

$$H_{\rm e} = \sum_{n\mathbf{k}} \varepsilon_n(\mathbf{k}) a^+_{n\mathbf{k}} a_{n\mathbf{k}}, \tag{2}$$

$$H_{\rm ph} = \sum_{\lambda\mathbf{Q}} \hbar\omega^{\lambda}_{\mathbf{Q}} \left(b^+_{\mathbf{Q}\lambda} b_{\mathbf{Q}\lambda} + \frac{1}{2} \right), \tag{3}$$

$$H_{\rm e-ph} = \sum_{\substack{n\lambda \\ \mathbf{kQ}}} \hbar\omega_{\lambda Q} g^{\lambda}_{\mathbf{k}-\mathbf{Qk}} \times (b^+_{\mathbf{Q}\lambda} + b_{-\mathbf{Q}\lambda}) a^+_{n\mathbf{k}-\mathbf{Q}} a_{n\mathbf{k}}. \tag{4}$$

Here we neglect electron-electron interaction, since we suppose the system constructed from N_c noninteracting charge carriers within DFT framework. $a_{\mathbf{k}}(a^+_{\mathbf{k}})$ are annihilation (creation) operators of electrons with wave vector $\mathbf{k}$; $b_{\mathbf{Q}}(b^+_{\mathbf{Q}})$ are phonon operators with wavevector $\mathbf{Q}$; $g^{\lambda}_{\mathbf{k}-\mathbf{Qk}}$ is the matrix element of the electron-phonon interaction; $\varepsilon_n(\mathbf{k})$ illustrates the energy of an electron in state $\mathbf{k}$ in band energy level n; and $\omega^{\lambda}_{\mathbf{Q}}$ represents phonon frequency in the mode λ with wave vector $\mathbf{Q}$. For simplicity, we will neglect electron band and phonon mode indices in the rest of the article. By applying Lang-Firsov displacement transformation,[14] $\tilde{H} = e^U H e^{-U}$, we treat electron-phonon interaction in a nonperturbative manner using an anti-Hermitian operator $(-U = U^+)$

$$U = \sum_{\mathbf{kQ}} g_{\mathbf{k}-\mathbf{Qk}} (b^+_{\mathbf{Q}} - b_{-\mathbf{Q}}) a^+_{\mathbf{k}-\mathbf{Q}} a_{\mathbf{k}}. \tag{5}$$

We also introduce matrix C with matrix elements $C_{\mathbf{k}'\mathbf{k}}$ determined with

$$C_{\mathbf{k}'\mathbf{k}} = g_{\mathbf{k}'\mathbf{k}} (b^+_{\mathbf{k}-\mathbf{k}'} - b_{\mathbf{k}'-\mathbf{k}}). \tag{6}$$

Under this transformation and by means of Baker-Campbell-Hausdorff formula,[15] $e^U a_{\mathbf{k}} e^{-U} = a_{\mathbf{k}} + [U, a_{\mathbf{k}}] + \frac{1}{2!}[U,[U,a_{\mathbf{k}}]] + \cdots$, the transformed electron and phonon creation and annihilation operators would be in the form

$$\tilde{a}^+_{\mathbf{k}} = e^U a^+_{\mathbf{k}} e^{-U} = \sum_{\mathbf{k}'} (e^C)_{\mathbf{k}'\mathbf{k}} a^+_{\mathbf{k}'}, \tag{7}$$

and

$$\tilde{b}^+_{\mathbf{Q}} = e^U b^+_{\mathbf{Q}} e^{-U} = b^+_{\mathbf{Q}} - \sum_{k} g_{\mathbf{k}+\mathbf{Qk}} a^+_{\mathbf{k}+\mathbf{Q}} a_{\mathbf{k}}. \tag{8}$$

We therefore obtain the transformed Hamiltonian as

$$\tilde{H} = \tilde{H}_{\rm e} + \tilde{H}_{\rm ph} + \tilde{H}_{\rm e-ph}, \tag{9}$$

with

$$\tilde{H}_{\rm e} = e^U H_{\rm e} e^{-U} = \sum_{\mathbf{kk}'\mathbf{k}''} (e^C)_{\mathbf{k}'\mathbf{k}} \varepsilon_{\mathbf{kk}} (e^{-C})_{\mathbf{kk}''} a^+_{\mathbf{k}'} a_{\mathbf{k}''}, \tag{10}$$

where we introduced a diagonal matrix ε with its elements defined as

$$\varepsilon_{\mathbf{kk}'} = \delta^{\mathbf{k}}_{\mathbf{k}'} \varepsilon_{\mathbf{kk}} = \varepsilon(\mathbf{k}). \tag{11}$$

$$\tilde{H}_{\rm ph} = e^U H_{\rm ph} e^{-U} = H_{\rm ph} - \sum_{\mathbf{kQ}} \hbar\omega_{\mathbf{Q}} g_{\mathbf{k}-\mathbf{Qk}} (b^+_{\mathbf{Q}} + b_{-\mathbf{Q}}) a^+_{\mathbf{k}-\mathbf{Q}} a_{\mathbf{k}} + \sum_{\mathbf{k}} \hbar\omega_{\mathbf{Q}} g_{\mathbf{kk}-\mathbf{Q}} g_{\mathbf{k}-\mathbf{Qk}} a^+_{\mathbf{k}} a_{\mathbf{k}}, \tag{12}$$

and

$$\tilde{H}_{\rm int} = \sum_{\substack{\mathbf{kQ} \\ \mathbf{k}_1\mathbf{k}_2}} \hbar\omega_{\mathbf{Q}} [(e^C)_{\mathbf{k}_1\mathbf{k}-\mathbf{Q}} g_{\mathbf{k}-\mathbf{Qk}} (e^{-C})_{\mathbf{kk}_2} a^+_{\mathbf{k}_1} a_{\mathbf{k}_2}] (b^+_{\mathbf{Q}} + b_{-\mathbf{Q}}) - 2 \sum_{\substack{\mathbf{kQ} \\ \mathbf{k}_1 \ldots \mathbf{k}_3}} \hbar\omega_{Q} [(e^C)_{\mathbf{k}_1\mathbf{k}-\mathbf{Q}} g_{\mathbf{k}-\mathbf{Qk}} (e^{-C})_{\mathbf{kk}_2} a^+_{\mathbf{k}_1} a_{\mathbf{k}_2}] \times (g_{\mathbf{k}_3+\mathbf{Qk}_3} a^+_{\mathbf{k}_3+\mathbf{Q}} a_{\mathbf{k}_3}). \tag{13}$$

But

$$\sum_{\mathbf{k}} (e^C)_{\mathbf{k}_1\mathbf{k}-\mathbf{Q}} g_{\mathbf{k}-\mathbf{Qk}} (e^{-C})_{\mathbf{kk}_2} = [e^C g^{(\mathbf{Q})} e^{-C}]_{\mathbf{k}_1\mathbf{k}_2}, \tag{14}$$

where we defined matrix $g^{(\mathbf{Q})}$ with elements $g^{(\mathbf{Q})}_{\mathbf{kk}'} = g_{\mathbf{kk}'} \delta^{\mathbf{k}'}_{\mathbf{k}+\mathbf{Q}}$. If anisotropic coupling has a weak feature compared to isotropic coupling,[16] approximately we have $[C, g^{(\mathbf{Q})}] \approx 0$. As a result we find

$$[e^C g^{(\mathbf{Q})} e^{-C}]_{\mathbf{k}_1\mathbf{k}_2} = g_{\mathbf{k}_1\mathbf{k}_2} \delta^{\mathbf{k}_2}_{\mathbf{k}_1+\mathbf{Q}} + [C, g^{(\mathbf{Q})}]_{\mathbf{k}_1\mathbf{k}_2} + \cdots \approx g_{\mathbf{k}_1\mathbf{k}_2} \delta^{\mathbf{k}_2}_{\mathbf{k}_1+\mathbf{Q}}. \tag{15}$$

Under the above assumption, Eq. (13) will be simplified to

$$\tilde{H}_{\rm int} = \sum_{\mathbf{kQ}} \hbar\omega_{\mathbf{Q}} g_{\mathbf{kk}+\mathbf{Q}} (b^+_{\mathbf{Q}} + b_{-\mathbf{Q}}) a^+_{\mathbf{k}} a_{\mathbf{k}+\mathbf{Q}} - 2 \sum_{\mathbf{Qkk}'} \hbar\omega_{\mathbf{Q}} g_{\mathbf{kk}+\mathbf{Q}} g_{\mathbf{k}'+\mathbf{Qk}'} a^+_{\mathbf{k}} a_{\mathbf{k}+\mathbf{Q}} a^+_{\mathbf{k}'+\mathbf{Q}} a_{\mathbf{k}'}. \tag{16}$$

We also assume for a system of low density carriers and therefore approximate $a^+_{\mathbf{k}} a_{\mathbf{k}+\mathbf{Q}} a^+_{\mathbf{k}'+\mathbf{Q}} a_{\mathbf{k}'} \approx a^+_{\mathbf{k}} a_{\mathbf{k}'} \delta^{\mathbf{k}}_{\mathbf{k}'}$, and finally from Eqs.(10)–(16) we find the total Hamiltonian as

$$\tilde{H} = H_{\rm p} + H_{\rm ph}, \tag{17}$$

with polaron part in the form of

$$H_p = \sum_{\mathbf{kk}'} \tilde{E}_{\mathbf{kk}'} a^+_k a_{\mathbf{k}'}, \tag{18}$$

where

$$\tilde{E}_{\mathbf{kk}'} = \sum_{\mathbf{k}_1} (e^C)_{\mathbf{kk}_1} \varepsilon_{\mathbf{k}_1\mathbf{k}_1} (e^{-C})_{\mathbf{k}_1\mathbf{k}'} - \delta^{\mathbf{k}}_{\mathbf{k}'} \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} g_{\mathbf{kk}+\mathbf{Q}} g_{\mathbf{k}+\mathbf{Qk}}. \tag{19}$$

According to Eq. (19), in addition to get dressed by phonon momentum, the polaron energy is shifted down (red shift) with the value of $\sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} g_{\mathbf{kk}+\mathbf{Q}} g_{\mathbf{k}+\mathbf{Qk}}$.

IV. THERMAL AVERAGING OF POLARON ENERGY

Still Hamiltonian Eq. (17) is not diagonal and the polaron part includes phonon operators. It is not possible to solve this

Hamiltonian exactly. However, one can continue by making an average over phononic terms for each electronic band structure and find the effective influence of the electron-phonon interaction on the electronic levels. This procedure was first introduced by Holstein[7,18] and will help us to evaluate mobility analytically. We use this approximation and replace the polaron operator with its expectation value in phonon space:

$$\begin{aligned}\bar{\tilde{E}}(\mathbf{k}) &= \prec \tilde{E}_{\mathbf{k}\mathbf{k}'} \succ_{\mathrm{Ph}} = \bar{\tilde{\varepsilon}}(\mathbf{k}) - \Delta(\mathbf{k}),\\ \bar{\tilde{\varepsilon}}(\mathbf{k}) &= \prec \sum_{\mathbf{k_1}} (e^{C})_{\mathbf{k}\mathbf{k_1}} \varepsilon_{\mathbf{k_1}\mathbf{k_1}} (e^{-C})_{\mathbf{k_1}\mathbf{k}'} \succ_{\mathrm{Ph}}\\ &= \prec (e^{C} \varepsilon e^{-C})_{\mathbf{k}\mathbf{k}'} \succ_{\mathrm{Ph}},\\ \Delta(\mathbf{k}) &= \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} g_{\mathbf{k}\mathbf{k}+\mathbf{Q}} g_{\mathbf{k}+\mathbf{Q}\mathbf{k}}. \end{aligned} \tag{20}$$

Now we expand the quantity $\bar{\tilde{\varepsilon}}(\mathbf{k})$ in a power series of matrix elements $C_{\mathbf{k}\mathbf{k}'}$ introduced in Eq. (6), $\bar{\tilde{\varepsilon}}(\mathbf{k}) = \sum_{m=0}^{+\infty} \frac{1}{m!} \bar{\tilde{\varepsilon}}^{(m)}_{\mathbf{k}\mathbf{k}'}$, with $\bar{\tilde{\varepsilon}}^{(m)}_{\mathbf{k}\mathbf{k}'} = \prec [C,[C,\ldots[C,\varepsilon]]\ldots]_{\mathbf{k}\mathbf{k}'} \succ_{\mathrm{Ph}}$. For simplicity, we remove the bracket indices, $\prec \ldots \succ_{\mathrm{Ph}}$. Using Baker-Campbell-Hausdorff formula with "m" number of commutators for $m > 0$ and from Eq. (11) we find the zeroth order as

$$\bar{\tilde{\varepsilon}}^{(0)}_{\mathbf{k}\mathbf{k}'} = \prec \varepsilon_{\mathbf{k}\mathbf{k}'} \succ = \varepsilon(\mathbf{k}) \delta^{\mathbf{k}}_{\mathbf{k}'}, \tag{21}$$

which is simply the energy of electron in the absence of electron-phonon interaction. Since the creation and annihilation operators of odd orders have zero average, only even orders give rise to a nonzero contribution and must be calculated.

The second order has been calculated as

$$\begin{aligned}\bar{\tilde{\varepsilon}}^{(2)}_{\mathbf{k}\mathbf{k}'} &= \prec [C,(C,\varepsilon)]_{\mathbf{k}\mathbf{k}'} \succ\\ &= 2\delta^{\mathbf{k}}_{\mathbf{k}'} \sum_{\mathbf{k_1}} |g_{\mathbf{k}\mathbf{k_1}}|^2 \big(2N_{\mathbf{k_1}-\mathbf{k}} + 1\big)[\varepsilon(\mathbf{k_1}) - \varepsilon(\mathbf{k})], \end{aligned} \tag{22}$$

where at a given temperature T, phonon population follows Bose-Einstein statistic, $N_{\mathbf{Q}} = \prec b^{+}_{\mathbf{Q}} b_{\mathbf{Q}} \succ = \frac{1}{\exp(\frac{\hbar\omega_{\mathbf{Q}}}{k_B T}) - 1}$, with k_B as the Boltzmann constant. Here we introduce new auxiliary functions $\bar{G}(\mathbf{k}) = \sum_{\mathbf{k_1}} |g_{\mathbf{k}\mathbf{k_1}}|^2 (2N_{\mathbf{k_1}-\mathbf{k}} + 1)$, $G_{\mathbf{k}\mathbf{k_1}} = |g_{\mathbf{k}\mathbf{k_1}}|^2 (2N_{\mathbf{k_1}-\mathbf{k}} + 1)$, and $X_{\mathbf{k}\mathbf{k_1}} = -\bar{G}(\mathbf{k}) \delta^{\mathbf{k_1}}_{\mathbf{k}} + G_{\mathbf{k}\mathbf{k_1}}$. By substituting in Eq. (22), we get a simpler form for $\bar{\tilde{\varepsilon}}^{(2)}_{\mathbf{k}\mathbf{k}'}$:

$$\bar{\tilde{\varepsilon}}^{(2)}_{\mathbf{k}\mathbf{k}'} = \delta^{\mathbf{k}}_{\mathbf{k}'} \sum_{\mathbf{k_1}} \varepsilon(\mathbf{k_1}) (2X)_{\mathbf{k}\mathbf{k_1}}. \tag{23}$$

By means of the linked cluster expansion method,[19] higher-order $\bar{\tilde{\varepsilon}}^{(2m)}_{\mathbf{k}\mathbf{k}'}$ is evaluated by

$$\bar{\tilde{\varepsilon}}^{(2m)}_{\mathbf{k}\mathbf{k}'} = \delta^{\mathbf{k}}_{\mathbf{k}'} \sum_{\mathbf{k_1}} \varepsilon(\mathbf{k_1}) [(2X)^m]_{\mathbf{k}\mathbf{k_1}} \times (2m-1)(2m-3)\ldots 3.1. \tag{24}$$

Using identity $(2m-1)(2m-3).3.1 = \frac{(2m)!}{2^m m!}$, which shows the number of different arrangements of the m number of bubbles in Feynman diagrams, the whole power series can be summed up to give a compact result:

$$\bar{\tilde{\varepsilon}}_{\mathbf{k}\mathbf{k}'} = \delta^{\mathbf{k}}_{\mathbf{k}'} \sum_{\mathbf{k_1}} \varepsilon(\mathbf{k_1}) \sum_{m} \frac{1}{2m!} \frac{2m!}{2^m m!} [(2X)^m]_{\mathbf{k}\mathbf{k_1}}. \tag{25}$$

Finally, by replacing the average polaron energy over phononic states, the Hamiltonian Eq. (17) would be changed into a diagonal form of

$$\tilde{H}' = \sum_{\mathbf{k}} \bar{\tilde{E}}(\mathbf{k}) a^{+}_{\mathbf{k}} a_{\mathbf{k}} + \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} \left(N_{\mathbf{Q}} + \frac{1}{2} \right), \tag{26}$$

with

$$\begin{aligned}\bar{\tilde{E}}(\mathbf{k}) &= \bar{\tilde{\varepsilon}}(\mathbf{k}) - \Delta(\mathbf{k})\\ &= e^{-\bar{G}(\mathbf{k})} \sum_{\mathbf{k_1}} \varepsilon(\mathbf{k_1}) (e^{G})_{\mathbf{k}\mathbf{k_1}} - \sum_{\mathbf{k_1}} \hbar\omega_{\mathbf{k}-\mathbf{k_1}} |g_{\mathbf{k_1}\mathbf{k}}|^2. \end{aligned} \tag{27}$$

Now the polaron part of Hamiltonian Eq. (26), which is consistent with the deduced Hamiltonian in Ref. 8, contains no phonon operators. The phonon effective influences on the energy of state $\mathbf{k}$ are collected in $e^{-\bar{G}(\mathbf{k})}$ and $(e^{G})_{\mathbf{k}\mathbf{k_1}}$ terms. Also, Eq. (27) shows two interesting features. First, Similar to Eq. (19), the polaronic band energy is shifted down (red shift) compared to the original value. Second, a bandwidth narrowing effect is introduced through the exponential term $\bar{G}(\mathbf{k})$, which depends on the temperature and the second power of the electron-phonon coupling strength. This means that the electronic coupling bandwidth can be reduced by lattice thermal fluctuation from its value at zero temperature and in fixed geometry. This effect may change the nature of the transport phenomena from band-like mechanism into hopping motion.

Thermal averaging has a great advantage of making the analytical solution traceable. The disadvantage of removing phonon operators from Hamiltonian Eq. (17) is neglecting thermal broadening of polaron spectral bandwidth resulting from residual polaron-phonon interaction. This interaction is actually responsible for scattering of polarons by phonons, which leads to a finite polaron lifetime, and according to the uncertainty principle to a polaron finite bandwidth as well. In addition to polaron-phonon interaction, other passivation procedures like crystal disorder, impurities, and finite lifetime of the optical phonons associated with the crystal anharmonicity reduce the polaron lifetime.[20] These effects can be introduced into the final result via τ as a finite lifetime.[9,21] Sometimes scattering of such properties are assumed by a Gaussian characteristic function and may enter in a phenomenological approach into the final result in the form of $e^{-(t/\tau)^2}$.[22]

V. DERIVING MOBILITY

This section describes the construction of the main part of our work, while we are interested only in the dc conductivity or long wavelength and zero frequency limit. By means of Kubo formula, dc conductivity can be obtained from current-current correlation function within linear response function theory

$$\sigma_{\alpha\beta} = \frac{1}{2k_B T} \lim_{\substack{\omega \to 0 \\ q \to 0}} \int_{-\infty}^{+\infty} dt e^{i\omega t} \prec j_{\alpha}(q,t) j_{\beta}(-q,0) \succ_{H}. \tag{28}$$

Mobility of charge carriers in the above-mentioned system is defined as $\mu = \frac{\sigma}{eN_c}$, where e represents elementary charge. μ as a very useful quantity can be directly measured by time-

of-flight experiment.[17] From Eq. (28) the dc mobility ($q \to 0$ limit) at a given temperature T is given by

$$\mu_{\alpha\beta} = \frac{1}{eN_c}\frac{1}{2k_BT}\lim_{q\to 0}\int_{-\infty}^{+\infty} dt \prec j_\alpha(q,t)j_\beta(-q,0)\succ_H. \tag{29}$$

The current-current correlation function, $\prec j_\alpha(q,t)j_\beta(-q,0)\succ_H$, will be evaluated from the elementary definition of $\prec A\succ_H = \frac{Tr[Ae^{-\beta H}]}{Tr[e^{-\beta H}]}$ and using Wick's theorem.[19] We are proceeding this section with electronic current derivation in k space and in the absence of a magnetic field. In such a framework and from second quantization formalism, the particle current (paramagnetic current) is obtained as follows:

$$\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi}\{\boldsymbol{\psi}^+(\mathbf{r})\nabla\boldsymbol{\psi}(\mathbf{r}) - \nabla\boldsymbol{\psi}^+(\mathbf{r})\boldsymbol{\psi}(\mathbf{r})\}, \tag{30}$$

with particle mass m and Planck's constant $\hbar$. $\boldsymbol{\psi}(\mathbf{r})$ and $\boldsymbol{\psi}^+(\mathbf{r})$ are second quantization field operators. These two latter can be expanded in terms of the basis sets

$$\boldsymbol{\psi}^+(\mathbf{r},t) = \sum_{\mathbf{k}} a^+_{\mathbf{k}}(t)\varphi^*_{\mathbf{k}}(\mathbf{r}), \tag{31}$$

$$\boldsymbol{\psi}(\mathbf{r},t) = \sum_{\mathbf{k}} a_{\mathbf{k}}(t)\varphi_{\mathbf{k}}(\mathbf{r}). \tag{32}$$

$\varphi(\mathbf{r})$ and $\varphi^*(\mathbf{r})$ are ordinary first quantization wave functions. Working with a periodic lattice, it is often convenient to use plane wave as the basis set.

$$\boldsymbol{\psi}^+(\mathbf{r},t) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{k}} a^+_{\mathbf{k}}(t)e^{-i\mathbf{k}.\mathbf{r}}, \tag{33}$$

$$\boldsymbol{\psi}(\mathbf{r},t) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{k}} a_{\mathbf{k}}(t)e^{i\mathbf{k}.\mathbf{r}}, \tag{34}$$

where Ω denotes primitive cell volume. In addition to translational-invariant property, using plane wave makes the analytical study of transport model traceable. However, it may not be a suitable basis set for localized small polarons.

Inserting Eqs. (33) and (34) into Eq. (30) we get the momentum representation of current,

$$j_\alpha(\mathbf{r}) = \frac{\hbar e}{m\Omega}\sum_{\mathbf{k}\mathbf{k}'}(k+k')_\alpha e^{-i(\mathbf{k}-\mathbf{k}').\mathbf{r}}a^+_{\mathbf{k}}a_{\mathbf{k}'}. \tag{35}$$

Finally, by performing the Fourier transformation of Eq. (35), together with $\int d\mathbf{r}e^{-i(\mathbf{k}-(\mathbf{k}'+\mathbf{q})).\mathbf{r}} = \Omega\delta_{\mathbf{k},\mathbf{k}'+\mathbf{q}}$, we obtain the second quantization current operator in k-space representation

$$j_\alpha(\mathbf{q}) = \frac{\hbar e}{m}\sum_{\mathbf{k}} a^+_{\mathbf{k}+\mathbf{q}}a_{\mathbf{k}}\left(k+\frac{q}{2}\right)_\alpha. \tag{36}$$

Now we apply the Lang-Firsov transformation on each side of Eq. (36) and use expression $e^Ue^{-U} = 1$. The current operator is transformed into

$$\tilde{j}_\alpha(\mathbf{q}) = \frac{\hbar e}{m_\alpha}\sum_{\mathbf{k}} \tilde{a}^+_{\mathbf{k}+\mathbf{q}}\tilde{a}_{\mathbf{k}}\left(k+\frac{q}{2}\right)_\alpha. \tag{37}$$

In the effective mass approximation, m would be replaced with polaron effective mass m^*, which can be calculated from the polaron energy dispersion curve

$$\frac{1}{m^*_\alpha} = \frac{1}{\hbar^2}\frac{\partial^2\bar{\tilde{E}}(k)}{\partial k^2_\alpha}. \tag{38}$$

Hamiltonian Eq. (9) is responsible for time evolution of Eq. (37) according to

$$\begin{aligned}\tilde{j}(\mathbf{q},t) &= e^{(\frac{i\tilde{H}t}{\hbar})}\tilde{j}(\mathbf{q},0)e^{(\frac{-i\tilde{H}t}{\hbar})}\\ &\approx e^{(\frac{i\tilde{H}'t}{\hbar})}\tilde{j}(\mathbf{q},0)e^{(\frac{-i\tilde{H}'t}{\hbar})}.\end{aligned} \tag{39}$$

In contrast to $\tilde{H}$, the Hamiltonian given by Eq. (26), namely $\tilde{H}'$, is diagonal in both the polaron and phonon operators and enables us to trace an analytical solution for our problem. The disadvantage imposed by this assumption is only neglecting some effects due to the finite polaron bandwidths, as described in the previous section. The great advantage of this approximation lies in fully separable polaron and phonon parts of the Hamiltonian. We rewrite the transformed current-current correlation function presented in Eq. (29) in a new form of

$$\begin{aligned}\prec\tilde{j}_\alpha(\mathbf{q},t)\tilde{j}_\beta(\mathbf{q}',0)\succ_{\tilde{H}} &\approx \prec\tilde{j}_\alpha(\mathbf{q},t)\tilde{j}_\beta(\mathbf{q}',0)\succ_{\tilde{H}'}\\ &= \frac{e^2\hbar^2}{m^*_\alpha m^*_\beta}\sum_{kk'}\left(k+\frac{q}{2}\right)_\alpha\left(k'+\frac{q'}{2}\right)_\beta\\ &\times\sum_{\mathbf{k}_1\ldots\mathbf{k}_4}\prec a^+_{\mathbf{k}_1}(t)a_{\mathbf{k}_2}(t)a^+_{\mathbf{k}_3}(0)a_{\mathbf{k}_4}(0)\succ_{\tilde{H}'}\\ &\times\prec(e^{C(t)})_{\mathbf{k}_1\mathbf{k}+\mathbf{q}}(e^{-C(t)})_{\mathbf{k}\mathbf{k}_2}\\ &\times(e^{C(0)})_{\mathbf{k}_3\mathbf{k}'+\mathbf{q}'}(e^{-C(0)})_{\mathbf{k}'\mathbf{k}_4}\succ_{\tilde{H}'},\end{aligned} \tag{40}$$

in which the time evolution of polaron and phonon operators can be easily computed from the polaron and phonon band energy in Eq. (26) using the following relations:

$$\begin{aligned}a^+_{\mathbf{k}}(t) &= e^{(\frac{i\tilde{H}'t}{\hbar})}a^+_{\mathbf{k}}e^{(-\frac{i\tilde{H}'t}{\hbar})} = a^+_{\mathbf{k}}e^{\frac{i\bar{\tilde{E}}_{\mathbf{k}}t}{\hbar}},\\ C_{\mathbf{k}'\mathbf{k}}(t) &= g_{\mathbf{k}'\mathbf{k}}e^{(\frac{i\tilde{H}'t}{\hbar})}(b^+_{\mathbf{k}-\mathbf{k}'} - b_{\mathbf{k}'-\mathbf{k}})e^{(-\frac{i\tilde{H}'t}{\hbar})}\\ &= g_{\mathbf{k}'\mathbf{k}}(b^+_{\mathbf{k}-\mathbf{k}'}e^{i\omega_{\mathbf{k}-\mathbf{k}'}t} - b_{\mathbf{k}'-\mathbf{k}}e^{-i\omega_{\mathbf{k}'-\mathbf{k}}t}).\end{aligned} \tag{41}$$

An interesting feature in construction of this theory is that the obligation of $\mathbf{q}' = -\mathbf{q}$ and conservation laws will appear automatically. Using Wick's theorem, first we simply treat the polaronic part, while for convenience we will again drop the bracket indices, $\prec\ldots\succ_{\tilde{H}'}$, in the rest of the paper.

$$\begin{aligned}&\prec a^+_{\mathbf{k}_1}(t)a_{\mathbf{k}_2}(t)a^+_{\mathbf{k}_3}(0)a_{\mathbf{k}_4}(0)\succ\\ &= \prec a^+_{\mathbf{k}_1}(t)a_{\mathbf{k}_2}(t)\succ\prec a^+_{\mathbf{k}_3}(0)a_{\mathbf{k}_4}(0)\succ\\ &\quad+\prec a^+_{\mathbf{k}_1}(t)a_{\mathbf{k}_4}(0)\succ\prec a_{\mathbf{k}_2}(t)a^+_{\mathbf{k}_3}(0)\succ,\\ &= n_{\mathbf{k}_1}n_{\mathbf{k}_3}\delta^{\mathbf{k}_1}_{\mathbf{k}_2}\delta^{\mathbf{k}_3}_{\mathbf{k}_4} + e^{\frac{it}{\hbar}[\bar{\tilde{E}}(\mathbf{k}_1)-\bar{\tilde{E}}(\mathbf{k}_2)]}n_{\mathbf{k}_1}(1-n_{\mathbf{k}_2})\delta^{\mathbf{k}_1}_{\mathbf{k}_4}\delta^{\mathbf{k}_3}_{\mathbf{k}_2}.\end{aligned} \tag{42}$$

Compared to $n(1-n)$, the term n^2 is negligible. According to Fermi-Dirac distribution $n_{\mathbf{k}} = \prec a^+_{\mathbf{k}}a_{\mathbf{k}}\succ = \frac{1}{exp(\frac{\bar{\tilde{E}}(\mathbf{k})-\zeta}{k_BT})+1}$ with $\zeta = \zeta(T,N_c)$ presented as chemical potential. Here we introduce new matrices $K^{(\alpha,\mathbf{q})}$ and $K^{(\beta,\mathbf{q}')}$ with elements defined as $K^{(\alpha,\mathbf{q})}_{\mathbf{k}\mathbf{k}'} = (k+k')_\alpha\delta^{\mathbf{k}'}_{\mathbf{k}-\mathbf{q}}$ and $K^{(\beta,\mathbf{q}')}_{\mathbf{k}\mathbf{k}'} = (k+k')_\beta\delta^{\mathbf{k}'}_{\mathbf{k}-\mathbf{q}'}$,

respectively. With the aid of these new matrices, Eq. (39) will be reduced to:

$$\begin{aligned}&\prec\tilde{j}_\alpha(\mathbf{q},t)\tilde{j}_\beta(\mathbf{q}',0)\succ\\&=\frac{e^2\hbar^2}{m_\alpha^* m_\beta^*}\sum_{\mathbf{k_1k_2}} e^{\frac{it}{\hbar}[\tilde{\bar{E}}(\mathbf{k_1})-\tilde{\bar{E}}(\mathbf{k_2})]} n_{\mathbf{k_1}}(1-n_{\mathbf{k_2}})\\&\times\frac{1}{4}\prec[(e^{C(t)})K^{\alpha,\mathbf{q}}(e^{-C(t)})]_{\mathbf{k_1k_2}}\\&\times[(e^{C(0)})K^{\beta,\mathbf{q}'}(e^{-C(0)})]_{\mathbf{k_2k_1}}\succ,\end{aligned}\tag{43}$$

and we are left with evaluating $X_{\mathbf{k_1k_2}}(t)$ with

$$\begin{aligned}X_{\mathbf{k_1k_2}}(t)=\sum_m\frac{1}{m!}(X^{(m)})_{\mathbf{k_1k_2}}=\frac{1}{4}\prec[(e^{C(t)})K^{\alpha,\mathbf{q}}(e^{-C(t)})]_{\mathbf{k_1k_2}}\\\times[(e^{C(0)})K^{\beta,\mathbf{q}'}(e^{-C(0)})]_{\mathbf{k_2k_1}}\succ.\end{aligned}\tag{44}$$

Compared to how the electronic part is treated in Eq. (42), calculation of this term is a very elaborate task. We follow the similar approach introduced to calculate $\tilde{\bar{E}}_{\mathbf{kk}'}=\prec\tilde{E}_{\mathbf{kk}'}\succ$ in Sec. IV. We apply the Baker-Campbell-Hausdorff theorem to the right-hand side of Eq. (44) and then regroup all terms into a single power series. Again, only even orders have nonzero contributions. The zeroth order is given by

$$\begin{aligned}X^{(0)}_{\mathbf{k_1k_2}}&=\frac{1}{4}(k_1+k_2)_\alpha(k_1+k_2)_\beta\delta^{\mathbf{k_2}}_{\mathbf{k_1}-\mathbf{q}}\delta^{\mathbf{k_1}}_{\mathbf{k_2}-\mathbf{q}'}\\&=\left(k_1+\frac{q}{2}\right)_\alpha\left(k_1+\frac{q}{2}\right)_\beta\delta^{\mathbf{k_2}}_{\mathbf{k_1}-\mathbf{q}}\delta^{-\mathbf{q}}_{\mathbf{q}'},\end{aligned}\tag{45}$$

and if inserted into Eq. (43), the resulting mobility is simply the well-known Boltzmann transport equation. We will discuss this limit in detail in the next section. As indicated in the right-hand side of Eq. (45), from now on the obligation of $\delta^{-\mathbf{q}}_{\mathbf{q}'}$ comes automatically into our relations. The second term itself is composed of three parts:

$$\begin{aligned}X^{(2)}_{\mathbf{k_1k_2}}&=\frac{1}{2}[\prec[C(t),K^{(\alpha,\mathbf{q})}]_{\mathbf{k_1k_2}}[C(0),K^{(\beta,\mathbf{q}')}]_{\mathbf{k_2k_1}}\succ\\&+K^{(\beta,\mathbf{q}')}_{\mathbf{k_2k_1}}\prec\frac{1}{2!}[C(t),[C(t),K^{(\alpha,\mathbf{q})}]_{\mathbf{k_1k_2}}\succ\\&+K^{(\alpha,\mathbf{q})}_{\mathbf{k_1k_2}}\prec\frac{1}{2!}[C(0),[C(0),K^{(\beta,\mathbf{q}')}]_{\mathbf{k_2k_1}}\succ].\end{aligned}\tag{46}$$

The first part is evaluated as follows:

$$\begin{aligned}&-2\Bigg\{\left[\left(k_2+\frac{q}{2}\right)_\alpha\left(k_1-\frac{q}{2}\right)_\beta\right]\left[g_{\mathbf{k_1k_2+q}}g_{\mathbf{k_2k_1-q}}\right]\phi_{\mathbf{k_2}-(\mathbf{k_1}-\mathbf{q})}(t)\delta^{\mathbf{q}}_{-\mathbf{q}'}\\&-\left[\left(k_2+\frac{q}{2}\right)_\alpha\left(k_2+\frac{q}{2}\right)_\beta\right]\left[g_{\mathbf{k_1k_2+q}}g_{\mathbf{k_2+qk_1}}\right]\phi_{\mathbf{k_2}-(\mathbf{k_1}-\mathbf{q})}(t)\delta^{\mathbf{q}}_{-\mathbf{q}'}\\&-\left[\left(k_1-\frac{q}{2}\right)_\alpha\left(k_1-\frac{q}{2}\right)_\beta\right]\left[g_{\mathbf{k_1-qk_2}}g_{\mathbf{k_2k_1-q}}\right]\phi_{\mathbf{k_2}-(\mathbf{k_1}-\mathbf{q})}(t)\delta^{\mathbf{q}}_{-\mathbf{q}'}\\&+\left[\left(k_1-\frac{q}{2}\right)_\alpha\left(k_2+\frac{q}{2}\right)_\beta\right]\left[g_{\mathbf{k_1-qk_2}}g_{\mathbf{k_2+qk_1}}\right]\phi_{\mathbf{k_2}-(\mathbf{k_1}-\mathbf{q})}(t)\delta^{\mathbf{q}}_{-\mathbf{q}'}\Bigg\},\end{aligned}\tag{47}$$

where the thermal average $\prec C(t)C(t')\succ$ has been done through Eq. (48), and the auxiliary function ϕ is defined according to Eq. (49) for phonon frequency $\omega_{\mathbf{Q}}$ and occupation number $N_{\mathbf{Q}}$.

$$\begin{aligned}&\prec(b^+_{\mathbf{Q}}(t)-b_{-\mathbf{Q}}(t))(b^+_{\mathbf{Q}'}(t')-b_{-\mathbf{Q}'}(t'))\succ,\\&=-\prec b^+_{\mathbf{Q}}(t)b_{-\mathbf{Q}'}(t')\succ-\prec b_{-\mathbf{Q}}(t)b^+_{\mathbf{Q}'}(t')\succ,\\&=-\delta^{\mathbf{Q}}_{-\mathbf{Q}'}[N_{\mathbf{Q}}e^{i\omega_{\mathbf{Q}}(t-t')}+(1+N_{\mathbf{Q}})e^{-i\omega_{\mathbf{Q}}(t-t')}],\end{aligned}\tag{48}$$

$$\phi_{\mathbf{Q}}(t)=N_{\mathbf{Q}}\exp[i\omega_{\mathbf{Q}}t]+(1+N_{\mathbf{Q}})\exp(-i\omega_{\mathbf{Q}}t).\tag{49}$$

From here we continue with the limit of small $\mathbf{q}$ ($\mathbf{q}\to 0$), or long wavelength condition in our relations. So the Eq. (47) will be simplified to

$$2(k_2-k_1)_\alpha(k_2-k_1)_\beta\left|g_{\mathbf{k_1k_2}}\right|^2\phi_{\mathbf{k_2}-\mathbf{k_1}}(t).\tag{50}$$

The sum of the two last terms in the right-hand side of Eq. (46) is given by:

$$\begin{aligned}&-2\delta^{\mathbf{k_2}}_{\mathbf{k_1}}\times\Bigg\{(k_1)_\alpha(k_2)_\beta\sum_{\mathbf{k}}[\phi_{\mathbf{k}-\mathbf{k_1}}(0)|g_{\mathbf{k_1k}}|^2+\phi_{\mathbf{k}-\mathbf{k_2}}(0)|g_{\mathbf{k_2k}}|^2]\\&+(k_2)_\alpha\sum_{\mathbf{k}}\phi_{\mathbf{k}-\mathbf{k_1}}(0)|g_{\mathbf{k_1k}}|^2k_\beta\\&+(k_1)_\beta\sum_{\mathbf{k}}\phi_{\mathbf{k}-\mathbf{k_1}}(0)|g_{\mathbf{k_2k}}|^2k_\alpha\Bigg\}\end{aligned}\tag{51}$$

Within the first Brillouin zone, the average contributions of the two last terms of the relation Eq. (51) are negligible compared to the first term. The auxiliary matrices $\bar{F}(\mathbf{k_1})$ and $F(t)$ are introduced as follows:

$$\bar{F}(\mathbf{k_1})=2\sum_{\mathbf{k}}\phi_{\mathbf{k}-\mathbf{k_1}}(0)|g_{\mathbf{k_1k}}|^2,\tag{52}$$

and

$$F_{\mathbf{k_1k_2}}(t)=\left|g_{\mathbf{k_1k_2}}\right|^2\phi_{\mathbf{k_2}-\mathbf{k_1}}(t).\tag{53}$$

We therefore obtain

$$\begin{aligned}X^{(0)}_{\mathbf{k_1k_2}}&=\delta^{\mathbf{k_1}}_{\mathbf{k_2}}(k_1)_\alpha(k_2)_\beta,\\X^{(2)}_{\mathbf{k_1k_2}}&=-2(k_1)_\alpha(k_2)_\beta\bar{F}(\mathbf{k_1})\quad\text{for}\quad\mathbf{k_1}=\mathbf{k_2},\\X^{(2)}_{\mathbf{k_1k_2}}&=2(k_2-k_1)_\alpha(k_2-k_1)_\beta F(t)\quad\text{for}\quad\mathbf{k_1}\neq\mathbf{k_2}.\end{aligned}\tag{54}$$

Similar to what was done in Sec. IV, we apply linked cluster expansion to evaluate the correlation function. This leads to

$$\begin{aligned}X^{(2m)}_{\mathbf{k_1k_2}}&=(k_1)_\alpha(k_2)_\beta[-2\bar{F}(\mathbf{k_1})]^m\\&\times(2m-1)(2m-3)\ldots3.1\quad\text{for}\quad\mathbf{k_1}=\mathbf{k_2},\\X^{(2m)}_{\mathbf{k_1k_2}}&=(k_2-k_1)_\alpha(k_2-k_1)_\beta([2F(t)]^m)_{\mathbf{k_1k_2}}\\&\times(2m-1)(2m-3)\ldots3.1\quad\text{for}\quad\mathbf{k_1}\neq\mathbf{k_2}.\end{aligned}\tag{55}$$

Therefore, we find

$$X_{\mathbf{k_1k_2}}=(k_1)_\alpha(k_2)_\beta e^{-\bar{F}(\mathbf{k_1})},\quad\text{for}\quad\mathbf{k_1}=\mathbf{k_2},\tag{56}$$

and

$$X_{\mathbf{k_1k_2}}=(k_2-k_1)_\alpha(k_2-k_1)_\beta[e^{F(t)}]_{\mathbf{k_1k_2}},\quad\text{for}\quad\mathbf{k_1}\neq\mathbf{k_2}.\tag{57}$$

If inserted to Eq. (29), we are left with a compact surprising relation for mobility in phase space, while anisotropic effect

of coupling has been considered as far as possible.

$$\mu_{\alpha\beta} = \mu^{(I)}_{\alpha\beta} + \mu^{(II)}_{\alpha\beta}, \tag{58}$$

where

$$\mu^{(I)}_{\alpha\beta} = \frac{1}{2k_BT}\frac{e\hbar^2}{N_c m^*_\alpha m^*_\beta}\sum_{\mathbf{k_1k_2}}(k_1)_\alpha(k_2)_\beta n_{\mathbf{k_1}}\left(1-n_{\mathbf{k_2}}\right)e^{-\bar{F}(\mathbf{k_1})}\delta^{\mathbf{k_1}}_{\mathbf{k_2}} \times \int_{-\infty}^{+\infty} dt e^{\frac{it}{\hbar}[\tilde{\bar{E}}(\mathbf{k_1})-\tilde{\bar{E}}(\mathbf{k_2})]}. \tag{59}$$

$$\mu^{(II)}_{\alpha\beta} = \frac{1}{2k_BT}\frac{e\hbar^2}{N_c m^*_\alpha m^*_\beta} \times \sum_{\mathbf{k_1}\neq\mathbf{k_2}}(k_2-k_1)_\alpha(k_2-k_1)_\beta n_{\mathbf{k_1}}\left(1-n_{\mathbf{k_2}}\right) \times \int_{-\infty}^{+\infty} dt e^{\frac{it}{\hbar}[\tilde{\bar{E}}(\mathbf{k_1})-\tilde{\bar{E}}(\mathbf{k_2})]}\left[(e^{F(t)})_{\mathbf{k_1k_2}}\right]. \tag{60}$$

Equation (58) contains coherent band transport and incoherent scattering, including phonon-assisted current, and can be better applicable for wide-bandwidth materials with the Fröhlich type of electron-phonon coupling.

VI. DISCUSSION

A. Coherent band transport

The transport expression $\mu^{(I)}$ in Eq. (59) can be inferred as a scattering event from an initial state $\mathbf{k}_1$ into a final state $\mathbf{k}_2$. For a given coupling strength, such a scattering event can happen with probability $n_{\mathbf{k_1}}$ for the initial state to be filled, and $(1-n_{\mathbf{k_2}})$ for the final state to be empty. $e^{-\bar{F}(\mathbf{k}_1)}$ shows the decreasing rate of the probability by increasing the temperature. This expression, which exists only for $\mathbf{k_1}=\mathbf{k_2}$, can be interpreted as band transport contribution. From the time integration, the energy of the initial polaron, $\tilde{\bar{E}}_{\mathbf{k_1}}$, must be equal to the energy of the final polaron, $\tilde{\bar{E}}_{\mathbf{k_2}}$, which provides energy conservation. The Kronecker delta term can be interpreted as momentum conservation. In general, these two obligations can be completely satisfied simultaneously for an elastic coherent transport process, see Fig. 1(a). Approximately similar to what was introduced by Ref. 9, we write the resulting mobility as

$$\mu^{(I)}_{\alpha\beta} = \frac{1}{2k_BT}\frac{e}{N_c}\sum_{\mathbf{k}}\frac{\hbar k_\alpha}{m^*_\alpha}\frac{\hbar k_\beta}{m^*_\beta}n_{\mathbf{k}}(1-n_{\mathbf{k}})e^{-\bar{F}(\mathbf{k}_1)}, \tag{61}$$

or

$$\mu^{(I)}_{\alpha\beta} = \frac{1}{2k_BT}\frac{e}{N_c}\sum_{\mathbf{k}}\tilde{v}_\alpha(\mathbf{k})\tilde{v}_\beta(\mathbf{k})n_{\mathbf{k}}(1-n_{\mathbf{k}})e^{-\bar{F}(\mathbf{k}_1)}, \tag{62}$$

where the polaron band velocity

$$\tilde{v}_\alpha(\mathbf{k}) = \frac{\hbar k_\alpha}{m^*_\alpha} \tag{63}$$

has been introduced through polaron effective mass m^*_α. Apart from exponential term, Eq. (62) is the reminiscent of the expression derived from Boltzmann transport equation. However, the main difference arises from generalizing the transport equation for polaron quasiparticles rather than bare electrons. The exponential term in this equation emphasizes the reduction of the band transport with increasing the temperature via electron-phonon interaction. If there is no electron-phonon coupling, this term disappears and infinite lifetime coherent transport could be the main mechanism.

B. Incoherent transport

The second part of the mobility, $\mu^{(II)}$, contains the exponential term $(e^{F(t)})_{\mathbf{k_1k_2}}$, which can be expanded into a power series in terms of the function $F(t)$ introduced by Eq. (53),

$$(e^{F(t)})_{\mathbf{k_1k_2}} = \sum_{\mathbf{k}_1^{(m)}\ldots\mathbf{k}_{m-1}^{(m)}}\frac{1}{m!}[F(t)]_{\mathbf{k_1}\mathbf{k}_1^{(m)}}[F(t)]_{\mathbf{k}_1^{(m)}\mathbf{k}_2^{(m)}}\ldots[F(t)]_{\mathbf{k}_{m-1}^{(m)}\mathbf{k_2}}. \tag{64}$$

Equation (64) represents a transport event with electron-phonon scattering processes, including all possible combinations of intermediate wave vectors through phonon emission or absorption. Therefore, the energy conservation mechanism is not the same as the coherent band transport discussed in the previous section. It will be accounted for all vibrational energies through $\phi_{\mathbf{Q}}(t)$ included in term F(t) in Eq. (60). The polaron momentum after scattering (k_2) is not the same as the initial value (k_1) and has been affected by the momentum transferred via absorption or emission of phonons. Since each scattering event is statistically independent, the whole process can be regarded as stochastically independent, in which the phase coherence due to the particles is destroyed through each event. Zeroth order, $m=0$, in Eq. (64) results in $[F(t)]^0_{\mathbf{k_1k_2}} = \delta^{\mathbf{k_1}}_{\mathbf{k_2}}$ and gives a zero contribution in mobility through (k_2-k_1) coefficients. First order, $m=1$, gives $F(t)_{\mathbf{k_1k_2}} = |g_{\mathbf{k_1k_2}}|^2\phi_{\mathbf{k_2}-\mathbf{k_1}}(t)$ and leads to a single-phonon

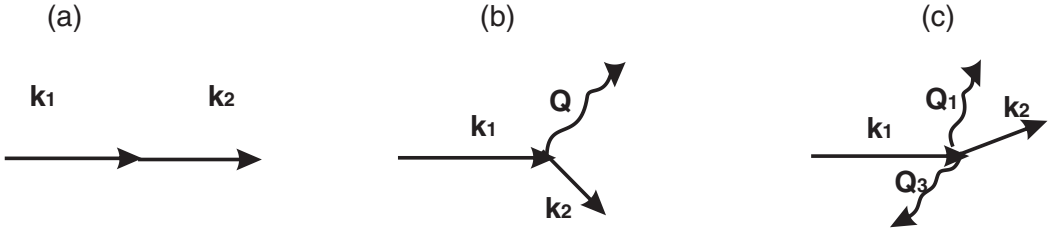

FIG. 1. (a) Typical coherent process. (b and c) Incoherent processes including one (first-order incoherent process) and two phonons (second-order), respectively.

absorption or emission event with phonon wavevector $\mathbf{Q} = \mathbf{k}_2 - \mathbf{k}_1$. In this case, the energy conservation is also provided by means of $e^{\frac{it}{\hbar}[\tilde{\tilde{E}}(\mathbf{k_1})-\tilde{\tilde{E}}(\mathbf{k_2})]} \times e^{\pm i\omega_{\mathbf{Q}}t}$. Second order, namely $m = 2$, may involve two-phonon absorption or emission events and so on for higher orders; see Figs. 1(b) and 1(c). For weak electron-phonon interaction, the incoherent transport contribution will nearly vanish. The next important incoherent feature observed in Eq. (60) is temperature-assisted charge transport due to electron-phonon coupling via exponential term $e^{F(t)}$, while according to Eq. (52) apart from a vibrational term the rest of the power term in $e^{F(t)}$ is positive. Therefore, although phonon coupling into electrons motion increases electron mass and reduces the band transport mobility, as was considered in the previous section, it can provide a transport promotion for higher temperatures.

VII. RESULTS AND CONCLUSION

By means of Kubo formula, we have presented an analytical solution for the charge transport theory based on a nonperturbative treatment of electron-phonon Hamiltonian in a system composed of noninteracting particles. The Lang-Firsov transformation was applied to separate the electronic from the phononic part of the Hamiltonian. Thermal averaging over the polaron band energy led to a diagonal Hamiltonian and was used for time evolution of polaron and phonon operators in separate parts. Using Wick's theorem enabled us to derive a compact relation for polaron transport, while anisotropic effects were conserved as much as possible. All these were done before the coupling of the electron motion was known to be limited to a special optical or acoustical phonon mode. However, since plane wave basis sets were used to expand field operators, this model is most valuable as a translational-invariant and wide-bandwidth medium. The resulting relation shows two different mechanisms based on the electron-phonon coupling strength and temperature. In the case of weak coupling and low temperature, band transport is the dominant event and the relation reduces to the well-known Boltzmann expression. By increasing temperature and coupling strength, the transport event changes feature and decreases by an exponential behavior. For higher temperatures, another limiting feature by using phonon-assisted transport character is also observed. In addition to deriving a compact relation while conserving all possible properties of polaron transport, this work has the advantage of fully deriving relations in the reciprocal space and simplifies future simulations of the charge transport in a complicated medium using available codes within the DFT framework.

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