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Anisotropy effects in phonon-assisted charge-carrier transport in organic molecular crystals

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We present a theoretical description of polaron dc conductivities in organic molecular crystals. Our approach is based on a rigorous evaluation of the Kubo formula for electrical conductivity within a mixed Holstein-Peierls model. It generalizes the result of Holstein's local-coupling theory by treating both local and nonlocal electron-phonon interactions nonperturbatively. The general theory is supplemented by an application to a simplified model crystal in order to emphasize the essential physics. Accompanied by an illustrative numerical example, special emphasis is put on the emergence of anisotropy effects in the temperature dependence of the conductivity tensor. These anisotropy effects are shown to originate from phonon-assisted currents due to the nonlocal electron-lattice interaction which demonstrates the importance to go beyond local-coupling theories in order to describe the experimental observations.

I. INTRODUCTION

During the last decade, research on organic semiconductors has regained considerable interest as these materials have become very promising candidates for low-cost and easy-to-process electronic and optoelectronic applications such as organic light-emitting devices and solar cells.[1–7] Apart from semiconducting polymers, a particularly interesting class of organic semiconductors are high-purity crystals of organic molecules. Not only do they have a large technological potential as materials for thin-film transistors,[8–10] organic molecular crystals are also considered ideal candidates for fundamental studies of optical and transport properties of organic semiconductors. In comparison to polymers, disorder-related effects are strongly reduced in these crystals which makes it possible to study directly their intrinsic excitations and charge-carrier transport mechanisms. Consequently, several fundamental experimental and theoretical studies have been performed in recent years, e.g., on oligoacene crystals such as pentacene.[11–17]

An important contribution towards the understanding of the intrinsic charge-carrier transport mechanisms in organic molecular crystals has been made by Holstein[18] who studied the influence of the electron-lattice interaction on bandwidths and mobilities for a one-dimensional model system. In comparison to covalently bonded inorganic semiconductors, organic molecular crystals exhibit weak intermolecular van der Waals bonds and, hence, narrower electron bands and stronger electron-phonon interaction. As a consequence, polaron effects become important which led Holstein to predict a temperature-dependent band narrowing as well as a crossover from bandlike conduction into phonon-assisted hopping transport at elevated temperatures. Twenty years later, this interplay between band and hopping transport in organic solids was, indeed, observed in naphthalene crystals,[19,20] and some experimental data could be fitted to Holstein's theory.[21,22]

From the theoretical point of view, it is important to stress that Holstein's molecular crystal model is based on the assumption that the *local* (or on-site) electron-phonon coupling is the dominant interaction between electronic excitations and lattice vibrations. However, it is well known, e.g., from the work of Su, Schrieffer, and Heeger,[23] that in organic semiconductors also the *nonlocal* electron-phonon coupling, i.e., the influence of lattice vibrations on the electron transfer between different sites, may be very important. Consequently, a number of theoretical studies on different aspects of nonlocal coupling have been performed in the past.[24–28] In this paper, we extend those ideas and develop a theoretical description of polaron dc conductivities in organic molecular crystals, including both local and nonlocal electron-phonon coupling.

Our approach is based on a rigorous evaluation of the Kubo formula for electrical conductivity and incorporates both local and nonlocal electron-phonon couplings in a nonperturbative manner. It generalizes both the result of Holstein's local-coupling theory[18] as well as previous evaluations of the Kubo formula based either on *ad hoc* assumptions[25] or Fermi's golden rule.[26] Our method can be best compared to Munn and Silbey's nonperturbative calculation of polaron diffusion coefficients[27] but it is difficult to establish a direct connection between both approaches due to the different formalisms used and the overall complexity of the problem. As already recognized by the authors of Refs. 25–27, charge-carrier transport in the presence of nonlocal coupling may exhibit qualitatively new properties due to phonon-assisted currents absent in local-coupling theories. By means of our theory, we will demonstrate explicitly how these additional nonlocal contributions give rise to anisotropy effects in the temperature dependence of polaron dc conductivities, as commonly observed in experiment.[19–22] Furthermore, the explicit expression we shall derive for the conductivity tensor may, in principle, also be utilized to make quantitative statements about the polaron conductivities once all the material-specific parameters are determined. As these parameters can be obtained from *ab initio* calculations—as recently demonstrated for oligoacene crystals[29,30]—our theory does also represent an important step towards a fully microscopic description of charge-carrier conductivities in organic molecular crystals.

The paper is organized as follows. In Sec. II, we introduce a mixed Holstein-Peierls model used in this paper for the description of local *and* nonlocal interactions between electrons and phonons. In Sec. III, we briefly review some of our previous results on the polaron band structure within this model. This serves mainly as a preparation for the actual calculation of the polaron dc conductivity in Sec. IV. Starting from the basic definitions and equations of charge-carrier transport (Sec. IV A), we derive in Sec. IV B an explicit expression for the polaron dc conductivity by evaluating the Kubo formula for the Holstein-Peierls model. In Sec. IV C, this general result is applied to a simplified model crystal in order to emphasize the basic physics contained in our theory. Especially, we will demonstrate that our solution of the Holstein-Peierls model can be used to explain anisotropy effects in the temperature dependence of the polaron conductivities. In Sec. IV D, these effects are traced back to phonon-assisted currents due to the nonlocal electron-lattice interaction which demonstrates the importance to go beyond local-coupling theories. Our analysis is concluded by a brief discussion in Sec. IV E on the limitations of the present approach. Finally, a summary is given in Sec. V.

II. THE HOLSTEIN-PEIERLS MODEL

We consider a mixed Holstein-Peierls model for the interaction between electrons and phonons. Using a tight-binding description, this corresponds to a Hamiltonian of the form

$$H = \sum_{mn} \hat{E}_{mn} a_m^\dagger a_n + \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \tfrac{1}{2}), \quad (1)$$

$$\hat{E}_{mn} = \varepsilon_{mn} + \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} g_{\mathbf{Q}mn} B_{\mathbf{Q}}^+, \quad B_{\mathbf{Q}}^+ = b_{\mathbf{Q}}^\dagger + b_{-\mathbf{Q}}, \quad (2)$$

where electron-electron interaction has been neglected which is justified for the case of low charge-carrier densities considered in this work. The operators $a_m^{(\dagger)}$ and $b_{\mathbf{Q}}^{(\dagger)} := b_{\mathbf{q}\lambda}^{(\dagger)}$ annihilate (create) an electron at site $\mathbf{R}_m$ with energy ε_{mm} and a phonon with wave vector $\mathbf{q}$ in the mode λ, respectively. Due to Hermiticity and symmetry requirements, the parameters of the above Hamiltonian fulfill the relations

$$\hbar \omega_{\mathbf{Q}} = \hbar \omega_{-\mathbf{Q}}, \quad g_{\mathbf{Q}mn} = g_{\mathbf{Q}nm} = g_{-\mathbf{Q}nm}^*, \quad \varepsilon_{mn} = \varepsilon_{nm}, \quad (3)$$

where $\omega_{\mathbf{Q}}$, $g_{\mathbf{Q}mn}$, and ε_{mn} are the phonon frequencies, electron-phonon coupling values, and transfer integrals, respectively. Furthermore, we will henceforth assume all onsite energies ε_{mm} to be equal, i.e., all molecules of the crystal are equivalent.

The electron-phonon interaction described by the second term in Eq. (2) contains, in general, coupling terms of both local ($m = n$, Holstein model) and nonlocal nature ($m \neq n$, Peierls model). In order to treat these coupling terms in a nonperturbative manner, we will often make use of nonlocal canonical transformations of the type

$$A \rightarrow \tilde{A} = e^S A e^{S^\dagger}, \quad S = \sum_{mn} C_{mn} a_m^\dagger a_n, \quad (4)$$

$$C_{mn} = \sum_{\mathbf{Q}} g_{\mathbf{Q}mn} B_{\mathbf{Q}}^-, \quad B_{\mathbf{Q}}^- = b_{\mathbf{Q}}^\dagger - b_{-\mathbf{Q}}, \quad (5)$$

where A is an arbitrary operator. This transformation may be looked upon as a generalization of the local transformation $S = \Sigma_m C_{mm} a_m^\dagger a_m$ used for the solution of the original Holstein model of purely local coupling. Due to the identity $S^\dagger = -S$, the transformed operators (4) can be calculated explicitly by means of the Baker-Campbell-Hausdorff theorem

$$\tilde{A} = e^S A e^{-S} = \sum_{k=0}^{\infty} \frac{1}{k!} \underbrace{[S, [S, \cdots, [S, A] \cdots]]}_{k \text{ commutators}}. \quad (6)$$

Especially, it turns out to be useful to introduce the transformed operators $\tilde{a}_m^{(\dagger)} = e^S a_m^{(\dagger)} e^{S^\dagger}$ and $\tilde{b}_{\mathbf{Q}}^{(\dagger)} = e^S b_{\mathbf{Q}}^{(\dagger)} e^{S^\dagger}$ which may be interpreted as annihilation (creation) operators of a polaron and a phonon of the distorted lattice, respectively. For the explicit evaluation via the Baker-Campbell-Hausdorff theorem (6), we follow Ref. 29 and assume henceforth $[g_{\mathbf{Q}}, g_{\mathbf{Q}'}]_{mn} = 0$ for all pairs $\mathbf{Q}$ and $\mathbf{Q}'$ which was shown to yield reliable results despite its approximative nature.[30] Then, the transformed operators are straightforwardly found as

$$\tilde{a}_m = \sum_n (e^{-C})_{mn} a_n, \quad \tilde{b}_{\mathbf{Q}} = b_{\mathbf{Q}} - \sum_{mn} g_{\mathbf{Q}mn} a_m^\dagger a_n, \quad (7)$$

$$\tilde{a}_m^\dagger = \sum_n a_n^\dagger (e^C)_{nm}, \quad \tilde{b}_{\mathbf{Q}}^\dagger = b_{\mathbf{Q}}^\dagger - \sum_{mn} g_{-\mathbf{Q}mn} a_m^\dagger a_n, \quad (8)$$

where we introduced a compact matrix notation for the exponential operators involved. Again, these relations may be looked upon as generalizations of the local transformations $\tilde{a}_m = e^{-C_{mm}} a_m$ and $\tilde{b}_{\mathbf{Q}} = b_{\mathbf{Q}} - \Sigma_m g_{\mathbf{Q}mm} a_m^\dagger a_m$ corresponding to the Holstein model, see also Ref. 27.

III. POLARON BAND STRUCTURE

Prior to calculating the polaron dc conductivity within the Holstein-Peierls model, it is instructive to discuss the polaron band structure, as both calculations proceed in a similar way and involve comparable approximations. Therefore, we summarize our findings from Ref. 29 and make the reader familiar with the basic ideas and our slightly revised notation.

If the electron-lattice interaction is neglected, the electron band structure is solely determined by the on-site energies ε_{mm} and transfer integrals ε_{mn}. In order to calculate the modifications induced by the electron-phonon interaction, the Hamiltonian (1) has to be diagonalized which requires a disentangling of the electron and phonon operators in Eq. (2). This can be achieved approximately by applying the nonlocal canonical transformation (4) to the Hamiltonian H which (at low carrier densities) yields the transformed Hamiltonian

$$\tilde{H} = \sum_{mn} \tilde{E}_{mn} a_m^\dagger a_n + \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \tfrac{1}{2}), \quad (9)$$

$$\tilde{E}_{mn} = (e^C E e^{-C})_{mn}, \quad E_{mn} = \varepsilon_{mn} - \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (g_{\mathbf{Q}} g_{-\mathbf{Q}})_{mn}.$$

(10)

Expanding the quantities $\tilde{E}_{mn} = \Sigma_{k=0}^{\infty} (1/k!) \tilde{E}_{mn}^{(k)}$ into a power series of the transformation matrices C_{mn} from Eq. (5), we find by means of the Baker-Campbell-Hausdorff theorem (6)

$$\tilde{E}_{mn}^{(k)} = \sum_{\mathbf{Q}_1 \cdots \mathbf{Q}_k} [g_{\mathbf{Q}_1}, \ldots, [g_{\mathbf{Q}_k}, E] \cdots]_{mn} B_{\mathbf{Q}_1}^- \cdots B_{\mathbf{Q}_k}^-.$$

(11)

Following the original work of Holstein,[18] we replace the quantities $\tilde{E}_{mn}^{(k)}$ by their thermal averages $\langle \tilde{E}_{mn}^{(k)} \rangle$. This implies that bandlike conduction prevails over hopping conduction which is a reasonable approximation for the calculation of the polaron band structure. As a result, we obtain the desired approximate diagonalization of the Hamiltonian $\tilde{H}$. The non-vanishing orders $\langle \tilde{E}_{mn}^{(2l)} \rangle$ are calculated by means of Wick's theorem and utilizing $\langle B_{\mathbf{Q}}^- B_{-\mathbf{Q}'}^- \rangle = -(1 + 2N_{\mathbf{Q}}) \delta_{\mathbf{QQ}'}$, where $N_{\mathbf{Q}} = \langle b_{\mathbf{Q}}^{\dagger} b_{\mathbf{Q}} \rangle$ are the phonon occupation numbers, and the result can be expressed as

$$\langle \tilde{E}_{mn}^{(2l)} \rangle = \frac{(-1)^l (2l)!}{2^l l!} \sum_{\mathbf{Q}_1, \ldots, \mathbf{Q}_l} (1 + 2N_{\mathbf{Q}_1}) \cdots (1 + 2N_{\mathbf{Q}_l})$$
$$\times [g_{\mathbf{Q}_1}, [g_{-\mathbf{Q}_1}, \ldots, [g_{\mathbf{Q}_l}, [g_{-\mathbf{Q}_l}, E]] \cdots]]_{mn}.$$

(12)

As demonstrated in Ref. 29, the right-hand side (rhs) of Eq. (12) can be significantly simplified by taking into account only its most important contributions which are the terms proportional to E_{jj} and E_{mn}.[31] As a consequence, the evaluation of the commutators in Eq. (12) becomes analytically tractable, and one obtains the compact results

$$\langle \tilde{E}_{mm} \rangle = E_{mm},$$

(13)

$$\langle \tilde{E}_{mn} \rangle = E_{mn} \exp\left(-\frac{1}{2} \sum_{\mathbf{Q}} G_{\mathbf{Q}mn} (1 + 2N_{\mathbf{Q}}) \right),$$

(14)

where we have introduced for brevity the quantities

$$G_{\mathbf{Q}mn} = |g_{\mathbf{Q}mm} - g_{\mathbf{Q}nn}|^2 + \sum_{k \neq m} |g_{\mathbf{Q}mk}|^2 + \sum_{k \neq n} |g_{\mathbf{Q}nk}|^2.$$

(15)

Compared to the Holstein model, the exponential renormalization of the transfer integrals is now determined by both local and nonlocal coupling. Qualitatively, however, the solution (14) for the full Holstein-Peierls model is very similar to Holstein's result for purely local coupling. This is especially evident in the case of a single dispersionless phonon mode. Then, we can replace $N_{\mathbf{Q}} \to N_{\mathrm{ph}} = (e^{\hbar \omega_{\mathrm{ph}}/k_B T} - 1)^{-1}$ and $g_{\mathbf{Q}mn} \to (1/2\sqrt{N}) g_{mn} (e^{-i\mathbf{q} \cdot \mathbf{R}_m} + e^{-i\mathbf{q} \cdot \mathbf{R}_n})$ where N denotes the number of sites (molecules).[32] Assuming all on-site coupling values $g_{mm} := g_0$ to be equal, the above expression (14) for the polaron transfer integrals becomes

$$\langle \tilde{E}_{mn} \rangle = E_{mn} e^{-g_{\mathrm{eff}}^2 (1 + 2N_{\mathrm{ph}})}, \quad g_{\mathrm{eff}}^2 := g_0^2 + \frac{1}{2} \sum_{k \neq m} (g_{mk})^2,$$

(16)

where we have introduced an effective coupling constant g_{eff} in order to emphasize the analogy with Holstein's result given by

$$\langle \tilde{E}_{mn} \rangle = \varepsilon_{mn} e^{-g_0^2 (1 + 2N_{\mathrm{ph}})}.$$

(17)

By comparison of the solutions for both models it can be seen immediately that the difference between them is only of quantitative nature, namely, the replacements $\varepsilon_{mn} \leftrightarrow E_{mn}$ and $g_0 \leftrightarrow g_{\mathrm{eff}}$. This explains why the much simpler Holstein model combined with a phenomenological (or fitted) coupling constant can work reasonably well in practice. However, for quantitative *ab initio* predictions of the polaron band structure as a function of temperature, the solution of the full Holstein-Peierls model has to be used, as demonstrated in Ref. 29.

A specific qualitative feature of the polaron transfer integrals (16) and (17) in the presence of nonlocal and/or local coupling is that the exponents do not depend on the actual values of m and n.[33] Consequently, if the transfer integrals were used directly to mimic the charge-carrier conductivities, the temperature dependence would be independent of the crystallographic direction, in contrast to the experimental observations.[19–22] Thus, in order to describe the anisotropic temperature dependence of polaron mobilities, the bandlike-conduction picture employed in this section is apparently not sufficient and one should include hopping processes as well. This will be done in the following sections where we calculate the polaron dc conductivity directly from the Kubo formula. Most importantly, it will turn out that this approach yields qualitatively different results for the Holstein model and the Holstein-Peierls model. Especially, phonon-assisted currents due to nonlocal electron-lattice interaction are shown to play a crucial role for the anisotropic temperature dependence of polaron transport in organic molecular crystals.

IV. POLARON dc CONDUCTIVITY

A. Charge-carrier transport: Basic equations

The electrical conductivity of charge carriers in solids can be described by the conductivity tensor $\sigma_{\alpha\beta}(\omega)$ which relates the electric field $\mathbf{E}(\omega)$ present in a sample to the current $\mathbf{J}(\omega)$ that is induced by this field,

$$J_{\alpha}(\omega) = \sum_{\beta} \sigma_{\alpha\beta}(\omega) E_{\beta}(\omega).$$

(18)

Here, the indices correspond to the components of $\mathbf{J}$ and $\mathbf{E}$ in the real-space directions $\mathbf{e}_{\alpha,\beta} = \mathbf{e}_{x,y,z}$. In this paper, we are only interested in the dc conductivity which is obtained from Eq. (18) as the zero-frequency limit,

$$\sigma_{\alpha\beta}^{\mathrm{dc}} := \lim_{\omega \to 0} \sigma_{\alpha\beta}(\omega).$$

(19)

In thermal equilibrium, this quantity can be evaluated by means of the Kubo formalism for linear-response theory, as described, e.g., in the textbook of Mahan.[34] As a result, one obtains a general relation between the dc conductivity and the microscopic current-current correlation function, namely,

$$\sigma_{\alpha\beta}^{dc} = \frac{1}{2k_B T} \lim_{\omega \to 0} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle j_\alpha(t) j_\beta(0) \rangle. \qquad (20)$$

This relation is usually referred to as the Kubo formula for electrical conductivity. Note that the rhs does not contain the experimentally measured macroscopic current **J** from Eq. (18) but the quantum-mechanical current operator $\mathbf{j}(t) = e^{(i/\hbar)Ht} \mathbf{j}\, e^{-(i/\hbar)Ht}$ where **j** is obtained from the polarization operator **P** via

$$\mathbf{j} = \frac{d\mathbf{P}}{dt} = \frac{1}{i\hbar}[\mathbf{P}, H], \qquad (21)$$

and H denotes the Holstein-Peierls Hamiltonian from Eq. (1). Within the tight-binding formalism from the previous sections, the polarization can be expressed as $\mathbf{P} = e_0 \Sigma_m \mathbf{R}_m a_m^\dagger a_m$, where e_0 equals the negative (positive) elementary charge in case of electron (hole) conduction. If inserted into Eq. (21), the component j_α of the current in direction $\mathbf{e}_\alpha$ is found to be

$$j_\alpha = \frac{e_0}{i\hbar} \sum_{mn} (R_{\alpha m} - R_{\alpha n}) \hat{E}_{mn} a_m^\dagger a_n = \frac{e_0}{i\hbar} \sum_{mn} [R_\alpha, \hat{E}]_{mn} a_m^\dagger a_n, \qquad (22)$$

where we introduced the shorthand matrix notation $\mathbf{R}_{mn} := \mathbf{R}_m \delta_{mn}$.

At this point, it is important to stress that the current in Eq. (22) consists of two different contributions, $j_\alpha := j_\alpha^{(I)} + j_\alpha^{(II)}$, originating from the two terms in the definition (2) of $\hat{E}_{mn}$. The first contribution

$$j_\alpha^{(I)} = \frac{e_0}{i\hbar} \sum_{mn} (R_{\alpha m} - R_{\alpha n}) \varepsilon_{mn} a_m^\dagger a_n, \qquad (23)$$

which contains only electron operators is often used as an *ad hoc* starting point in transport theories. However, this choice can only be justified if the electron-lattice interaction is either completely neglected or assumed to be purely local as in the original Holstein model. In contrast, if also the nonlocal electron-phonon coupling is taken into account, the second contribution

$$j_\alpha^{(II)} = \frac{e_0}{i\hbar} \sum_{mn\mathbf{Q}} (R_{\alpha m} - R_{\alpha n}) \hbar \omega_\mathbf{Q} g_{\mathbf{Q}mn} B_\mathbf{Q}^+ a_m^\dagger a_n \qquad (24)$$

is nonzero and gives rise to phonon-assisted currents which have no counterpart in local-coupling theories, as already pointed out in previous literature.[25,26] While the terms $j_\alpha^{(II)}$ significantly complicate the actual evaluation of the Kubo formula (20), we will show in the following sections that they are the essential ingredient to understand the anisotropic behavior of charge-carrier transport in organic molecular crystals.

We conclude this section by introducing the transformed current operators $\tilde{j}_\alpha = e^S j_\alpha e^{S^\dagger}$, in accordance with Eq. (4). In the limit of low charge-carrier densities, the explicit evaluation via the Baker-Campbell-Hausdorff theorem (6) can be easily performed using the relations $[e^{\pm C}, b_\mathbf{Q}]_{mn} = \mp(e^{\pm C} g_\mathbf{Q})_{mn} = [e^{\pm C}, b_{-\mathbf{Q}}^\dagger]_{mn}$ which can be proven using our approximation from Sec. II that all matrices $g_{\mathbf{Q}mn}$ commute with each other. As a result, the transformed currents adopt the form

$$\tilde{j}_\alpha = \frac{e_0}{i\hbar} \sum_{mn} (e^C [R_\alpha, \hat{E}] e^{-C})_{mn} a_m^\dagger a_n, \qquad (25)$$

in close analogy to relation (22) for the original currents.

B. Evaluation of the Kubo formula

In this section, we calculate the dc conductivity of polarons within the Holstein-Peierls model. Our approach is based on the evaluation of the Kubo formula (20) and generalizes the results of Holstein's theory of purely local coupling.[18] In fact, our derivation is in close analogy to the one presented in Mahan's textbook[34] who evaluates the Kubo formula for the Holstein model following an original work of Lang and Firsov.[35]

In order to calculate $\sigma_{\alpha\beta}^{dc}$, we must determine the current-current correlation function on the rhs of Eq. (20). The evaluation of this quantity is quite complicated but can be considerably simplified if one employs the canonical transformations introduced in the previous sections, and in particular, Eqs. (9) and (25) for the Hamiltonian $\tilde{H}$ and the current $\tilde{\mathbf{j}}$, respectively. The use of the transformed operators is favorable since it provides a convenient way to include the electron-phonon interaction nonperturbatively and, hence, allows us to go beyond previous evaluations of the current-current correlation function based either on an educated guess[25] or Fermi's golden rule.[26]

In technical terms, we rewrite the current-current correlation function according to

$$\langle j_\alpha(t) j_\beta(0) \rangle := \langle e^{(i/\hbar)Ht} j_\alpha e^{-(i/\hbar)Ht} j_\beta \rangle_H$$
$$= \langle e^{(i/\hbar)\tilde{H}t} \tilde{j}_\alpha e^{-(i/\hbar)\tilde{H}t} \tilde{j}_\beta \rangle_{\tilde{H}}$$
$$\approx \langle e^{(i/\hbar)\tilde{H}'t} \tilde{j}_\alpha e^{-(i/\hbar)\tilde{H}'t} \tilde{j}_\beta \rangle_{\tilde{H}'}, \qquad (26)$$

where the bracket indices indicate which Hamiltonian is used in the thermal average, e.g., $\langle A \rangle_H := \text{Tr}(e^{-H/k_B T} A)/\text{Tr}(e^{-H/k_B T})$. The first equality in Eq. (26) is just the definition from Sec. IV A whereas the second equality follows after insertion of several factors $1 = e^{-S} e^S = e^{S^\dagger} e^S$ and using the cyclic properties of the trace. The third step involves the replacement

$$\tilde{H} \to \tilde{H}' = \sum_m E_{mm} a_m^\dagger a_m + \sum_\mathbf{Q} \hbar \omega_\mathbf{Q} \left(b_\mathbf{Q}^\dagger b_\mathbf{Q} + \frac{1}{2} \right), \qquad (27)$$

as discussed by Mahan.[34] While this approximation partially neglects effects due to the finite polaron bandwidths (see also our discussion in Sec. IV E), it has the major advantage that

$\tilde{H}'$ is diagonal in both the electron and phonon operators which allows us to perform their thermal averages separately, as shown in the following paragraph.

Inserting the transformed currents (25) into Eq. (26) and using the identity

$$e^{(i/\hbar)\tilde{H}'t} f(a_m^\dagger, a_n, b_\mathbf{Q}^\dagger, b_{\mathbf{Q}'}) e^{-(i/\hbar)\tilde{H}'t}$$
$$= f(a_m^\dagger e^{(i/\hbar)E_{mm}t}, a_n e^{-(i/\hbar)E_{nn}t}, b_\mathbf{Q}^\dagger e^{i\omega_\mathbf{Q}t}, b_{\mathbf{Q}'} e^{-i\omega_{\mathbf{Q}'}t}),$$
$$(28)$$

which is easily proven for any function f by means of the Baker-Campbell-Hausdorff theorem (6), the current-current correlation function acquires the form

$$\langle j_\alpha(t) j_\beta(0) \rangle = -\frac{e_0^2}{\hbar^2} \sum_{mnm'n'} \langle a_m^\dagger a_n a_{m'}^\dagger a_{n'} \rangle$$
$$\times \langle \{ e^{C(t)} [R_\alpha, \hat{E}(t)] e^{-C(t)} \}_{mn}$$
$$\times \{ e^{C(0)} [R_\beta, \hat{E}(0)] e^{-C(0)} \}_{m'n'} \rangle. \quad (29)$$

For convenience, we have now dropped again the bracket indices $\langle \cdots \rangle_{\tilde{H}'}$ on the rhs and introduced the definitions

$$\hat{E}_{mn}(t) = \varepsilon_{mn} + \sum_\mathbf{Q} \hbar \omega_\mathbf{Q} g_{\mathbf{Q}mn} B_\mathbf{Q}^+(t),$$

$$B_\mathbf{Q}^+(t) = b_\mathbf{Q}^\dagger e^{i\omega_\mathbf{Q}t} + b_{-\mathbf{Q}} e^{-i\omega_\mathbf{Q}t}, \quad (30)$$

$$C_{mn}(t) = \sum_\mathbf{Q} g_{\mathbf{Q}mn} B_\mathbf{Q}^-(t), \quad B_\mathbf{Q}^-(t) = b_\mathbf{Q}^\dagger e^{i\omega_\mathbf{Q}t} - b_{-\mathbf{Q}} e^{-i\omega_\mathbf{Q}t}, \quad (31)$$

which may be regarded as the time-dependent generalizations of Eqs. (2) and (5), respectively. In Eq. (29), the electronic and phononic parts of the thermal average are now, indeed, completely separated. First, we evaluate the electronic part which is easily done applying Wick's theorem

$$\langle a_m^\dagger a_n a_{m'}^\dagger a_{n'} \rangle = cc \delta_{mn} \delta_{m'n'} + c(1-c) \delta_{mn'} \delta_{m'n}, \quad (32)$$

where $c = N_c/N$ is the charge-carrier concentration in the sample (N_c is the number of charge carriers, N is the number of molecules). The first term on the rhs of Eq. (32) can be straightforwardly shown to give no contribution in Eq. (29) whereas the second term which contains the familiar Pauli-blocking factor $c(1-c)$ does always contribute unless the band is completely empty ($c=0$) or completely filled ($c=1$). As a result, the dc conductivity (20) can be written as

$$\sigma_{\alpha\beta}^{\text{dc}} = -\frac{e_0^2 c(1-c)}{2k_B T \hbar^2} \lim_{\omega \to 0} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle \hat{X}_{\alpha\beta}(t) \rangle, \quad (33)$$

where the phonon-related terms are condensed into the quantity

$$\hat{X}_{\alpha\beta}(t) = \sum_{mn} \{ e^{C(t)} [R_\alpha, \hat{E}(t)] e^{-C(t)} \}_{mn}$$
$$\times \{ e^{C(0)} [R_\beta, \hat{E}(0)] e^{-C(0)} \}_{nm}. \quad (34)$$

Compared to the electronic part, the thermal average $\langle \hat{X}_{\alpha\beta}(t) \rangle$ over the phononic part is much more difficult and very technical. For its evaluation, we follow a strategy that is very similar to the calculation of $\langle \tilde{E}_{mn} \rangle$ in Sec. III, Eqs. (10)–(16).

First, we note that the two terms on the rhs of Eq. (34) allow the application of the Baker-Campbell-Hausdorff theorem (6). While all operators $B_\mathbf{Q}^-(t)$ do commute with each other, the nonvanishing commutators $[B_\mathbf{Q}^+(t), B_{-\mathbf{Q}'}^-(t)] = 2\delta_{\mathbf{QQ}'}$ make the explicit evaluation somewhat complicated. Nonetheless, after some algebra and appropriate regrouping, one ends up with the expansions

$$\{ e^{C(t)} [R_\alpha, \hat{E}(t)] e^{-C(t)} \}_{mn}$$
$$= \sum_{i=0}^\infty \frac{1}{i!} \sum_{\mathbf{Q}_1, \cdots, \mathbf{Q}_i} [g_{\mathbf{Q}_1}, \ldots, [g_{\mathbf{Q}_i}, \hat{V}^\alpha(t)] \cdots]_{mn}$$
$$\times B_{\mathbf{Q}_1}^-(t) \cdots B_{\mathbf{Q}_i}^-(t), \quad (35)$$

$$\{ e^{C(0)} [R_\beta, \hat{E}(0)] e^{-C(0)} \}_{nm}$$
$$= \sum_{j=0}^\infty \frac{1}{j!} \sum_{\mathbf{Q}_1, \cdots, \mathbf{Q}_j} B_{\mathbf{Q}_1}^-(0) \cdots B_{\mathbf{Q}_j}^-(0)$$
$$\times [g_{\mathbf{Q}_1}, \ldots, [g_{\mathbf{Q}_j}, \hat{W}^\beta(0)] \cdots]_{nm}. \quad (36)$$

Here, we have introduced the operators

$$\hat{V}_{mn}^\alpha(t) = [R_\alpha, \hat{E}(t)]_{mn} - v_{mn}^\alpha, \quad (37)$$

$$\hat{W}_{nm}^\beta(0) = [R_\beta, \hat{E}(0)]_{nm} - w_{nm}^\beta, \quad (38)$$

where $v_{mn}^\alpha = 2\Sigma_\mathbf{Q} (g_{-\mathbf{Q}} [R_\alpha, \hbar \omega_\mathbf{Q} g_\mathbf{Q}])_{mn}$ and $w_{nm}^\beta = 2\Sigma_\mathbf{Q} ([R_\beta, \hbar \omega_\mathbf{Q} g_\mathbf{Q}] g_{-\mathbf{Q}})_{nm}$. Note that the definition (38) is actually redundant since $w_{nm}^\beta = -v_{mn}^\beta$ and, hence, $\hat{W}_{nm}^\beta(0) = -\hat{V}_{mn}^\beta(0)$. However, the interchange in indices due to the different orders of operators in Eqs. (35) and (36) simplifies both the notation and systematics in the following analysis.

After the above preparatory considerations, we insert the expansions (35) and (36) into the definition of $\hat{X}_{\alpha\beta}(t)$ and regroup all terms into a single power series according to $\hat{X}_{\alpha\beta}(t) = \Sigma_{k=0}^\infty (1/k!) \hat{X}_{\alpha\beta}^{(k)}(t)$ where $k = i+j$. The lowest orders are easily evaluated and give

$$\hat{X}_{\alpha\beta}^{(0)}(t) = \sum_{mn} \hat{V}_{mn}^\alpha(t) \hat{W}_{nm}^\beta(0), \quad (39)$$

$$\hat{X}_{\alpha\beta}^{(1)}(t) = \sum_{mn} \sum_{\mathbf{Q}} [g_{\mathbf{Q}}, \hat{V}^{\alpha}(t)]_{mn} [B_{\mathbf{Q}}^{-}(t) - B_{\mathbf{Q}}^{-}(0)] \hat{W}_{nm}^{\beta}(0),$$
(40)

where the latter formula is obtained by rearranging all commutators so that they appear in front of the B^{-} operators. This procedure can be generalized to the higher-order terms, and, as a result, we obtain for arbitrary k the expression

$$\hat{X}_{\alpha\beta}^{(k)}(t) = \sum_{mn} \sum_{\mathbf{Q}_1, \ldots, \mathbf{Q}_k} [g_{\mathbf{Q}_1}, \ldots, [g_{\mathbf{Q}_k}, \hat{V}^{\alpha}(t)] \cdots]_{mn}$$

$$\times T\{\Delta B_{\mathbf{Q}_1}^{-}(t,0) \cdots \Delta B_{\mathbf{Q}_k}^{-}(t,0)\} \hat{W}_{nm}^{\beta}(0), \quad (41)$$

where we defined $\Delta B_{\mathbf{Q}}^{-}(t,0) = B_{\mathbf{Q}}^{-}(t) - B_{\mathbf{Q}}^{-}(0)$ and introduced a time-ordering symbol T which moves operators at time t to the left of those with time 0. This time-ordering procedure does not only simplify the notation but provides also a more systematic way to perform the thermal averages as outlined below. Note also that expression (41) is the analogon to Eq. (11) in our theory for the polaron band structure from Sec. III.

In order to perform the thermal average in Eq. (41), we define the auxiliary functions

$$\Phi_{\mathbf{Q}}(t) = (1 + N_{\mathbf{Q}})(1 - e^{-i\omega_{\mathbf{Q}}t}) + N_{\mathbf{Q}}(1 - e^{i\omega_{\mathbf{Q}}t}), \quad (42)$$

$$\Phi_{\mathbf{Q}}^{\pm}(t) = (1 + N_{\mathbf{Q}})e^{-i\omega_{\mathbf{Q}}t} \pm N_{\mathbf{Q}}e^{i\omega_{\mathbf{Q}}t}, \quad (43)$$

which appear in the basic thermal averages of the following two-operator products

$$\langle T\{\Delta B_{\mathbf{Q}}^{-}(t,0) \Delta B_{-\mathbf{Q}'}^{-}(t,0)\}\rangle = -2\Phi_{\mathbf{Q}}(t)\delta_{\mathbf{Q}\mathbf{Q}'}, \quad (44)$$

$$\langle B_{\mathbf{Q}}^{+}(t) \Delta B_{-\mathbf{Q}'}^{-}(t,0)\rangle = \langle \Delta B_{\mathbf{Q}}^{-}(t,0) B_{-\mathbf{Q}'}^{+}(0)\rangle$$

$$= [1 - \Phi_{\mathbf{Q}}^{-}(t)]\delta_{\mathbf{Q}\mathbf{Q}'}, \quad (45)$$

$$\langle B_{\mathbf{Q}}^{+}(t) B_{-\mathbf{Q}'}^{+}(0)\rangle = \Phi_{\mathbf{Q}}^{+}(t)\delta_{\mathbf{Q}\mathbf{Q}'}. \quad (46)$$

Furthermore, for technical reasons it is helpful to rewrite the above definitions (37) and (38) according to

$$\hat{V}_{mn}^{\alpha}(t) = V_{mn}^{0\alpha} + \sum_{\mathbf{Q}} [R_{\alpha}, \hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]_{mn} B_{\mathbf{Q}}^{+}(t), \quad (47)$$

$$\hat{W}_{nm}^{\beta}(0) = W_{nm}^{0\beta} + \sum_{\mathbf{Q}} [R_{\beta}, \hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]_{nm} B_{\mathbf{Q}}^{+}(0), \quad (48)$$

where we have split off the time-independent and operator-free terms $V_{mn}^{0\alpha} = [R_{\alpha}, \varepsilon]_{mn} - v_{mn}^{\alpha}$ and $W_{nm}^{0\beta} = [R_{\beta}, \varepsilon]_{nm} - w_{nm}^{\beta}$. By this, the zeroth-order thermal average $\langle \hat{X}_{\alpha\beta}^{(0)}(t)\rangle$ is readily obtained by application of Eqs. (46)–(48) to Eq. (39),

$$\langle \hat{X}_{\alpha\beta}^{(0)}(t)\rangle = \sum_{mn} V_{mn}^{0\alpha} W_{nm}^{0\beta}$$

$$+ \sum_{mn\mathbf{Q}} [R_{\alpha}, \hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]_{mn} [R_{\beta}, \hbar\omega_{\mathbf{Q}}g_{-\mathbf{Q}}]_{nm} \Phi_{\mathbf{Q}}^{+}(t).$$
(49)

The evaluation of the higher-order thermal averages by means of Wick's theorem is more complicated, especially due to the "mixed-operator" terms originating from Eq. (45). For methodical reasons, it is therefore advantageous to neglect those terms first and to include them later on. Following this strategy, it is sufficient to consider first exclusively the thermal averages of the even orders since the odd orders always contain such a "mixed-operator" factor. By doing this, we find in generalization of Eq. (49),

$$\langle \hat{X}_{\alpha\beta}^{(2l)}(t)\rangle = (-1)^l \frac{(2l)!}{l!} \sum_{\mathbf{Q}_1, \ldots, \mathbf{Q}_l} \Phi_{\mathbf{Q}_1}(t) \cdots \Phi_{\mathbf{Q}_l}(t) \times \left(\sum_{mn} [g_{\mathbf{Q}_1}, [g_{-\mathbf{Q}_1}, \cdots, [g_{\mathbf{Q}_l}, [g_{-\mathbf{Q}_l}, V^{0\alpha}]], \cdots,]]_{mn} W_{nm}^{0\beta} \right.$$

$$\left. + \sum_{mn\mathbf{Q}} [g_{\mathbf{Q}_1}, [g_{-\mathbf{Q}_1}, \cdots, [g_{\mathbf{Q}_l}, [g_{-\mathbf{Q}_l}, [R_{\alpha}, \hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]]] \cdots]]_{mn} [R_{\beta}, \hbar\omega_{\mathbf{Q}}g_{-\mathbf{Q}}]_{nm} \Phi_{\mathbf{Q}}^{+}(t) \right). \quad (50)$$

Note here again the similarity between this result and its pendant in the band structure theory, Eq. (12). As in Sec. III, we proceed by taking into account only the most important contributions in Eq. (50), namely, terms proportional to $V_{mn}^{0\alpha}$ and terms proportional to $[R_{\alpha}, \hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]_{mn}$. As a consequence, the evaluation of the commutators in Eq. (50) becomes analytically tractable, and the dc conductivity (33) can be expressed as

$$\sigma_{\alpha\beta}^{\text{dc}} = -\frac{e_0^2 c(1-c)}{2k_B T\hbar^2} \lim_{\omega \to 0} \int_{-\infty}^{+\infty} dt\, e^{i\omega t}$$

$$\times \sum_{mn} \exp\left(-\sum_{\mathbf{Q}} G_{\mathbf{Q}mn} \Phi_{\mathbf{Q}}(t) \right) \{V_{mn}^{0\alpha} W_{nm}^{0\beta}$$

$$+ [R_{\alpha}, \hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]_{mn} [R_{\beta}, \hbar\omega_{\mathbf{Q}}g_{-\mathbf{Q}}]_{nm} \Phi_{\mathbf{Q}}^{+}(t)\}, \quad (51)$$

where the exponent contains the same quantity $G_{\mathbf{Q}mn}$ as defined previously in Eq. (15) for the band-structure theory.

So far, we have neglected the "mixed-operator" terms originating from Eq. (45). If these terms are taken into account, the above calculation becomes much more lengthy and tedious, and we skip the detailed presentation of it. Yet, the final result can be put into the same form as in Eq. (51) but with the replacement

$$V_{mn}^{0\alpha} \rightarrow V_{mn}^{0\alpha} + \sum_{\mathbf{Q}} \ [g_{-\mathbf{Q}},[R_\alpha,\hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]]_{mn}[1-\Phi_{\mathbf{Q}}^-(t)]$$

$$\approx \left(R_\alpha,\varepsilon - \sum_{\mathbf{Q}} \ \hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}g_{-\mathbf{Q}}\right)_{mn} = [R_\alpha,E]_{mn} \quad (52)$$

and analogously for $W_{nm}^{0\beta} = -V_{mn}^{0\beta}$. Here, in the second line of Eq. (52), we simplified the expression by taking into account only the dominant band structure term, in accordance with the definition (10) given above.[36]

If the substitutions (52) are applied to Eq. (51), we see that the summations over m and n can be replaced by a single summation according to $\Sigma_{mn} \rightarrow N\Sigma_{n \neq m}$. Furthermore, in the limit of low charge-carrier concentrations ($c \ll 1$), we may simplify $Nc(1-c) \approx Nc \equiv N_c$. If finally the remaining commutators are evaluated and the limit $\omega \rightarrow 0$ is taken, we obtain our primary result for the dc conductivity of polarons within the Holstein-Peierls model,

$$\sigma_{\alpha\beta}^{\mathrm{dc}} = \frac{N_c e_0^2}{2k_B T\hbar^2} \sum_{n \neq m} \ (R_{\alpha m}-R_{\alpha n})(R_{\beta m}-R_{\beta n})$$

$$\times \int_{-\infty}^{+\infty} dt F_{mn}(t)e^{-\Gamma_{mn}(t)}. \quad (53)$$

Here we have introduced the abbreviations

$$F_{mn}(t) = (E_{mn})^2 + \sum_{\mathbf{Q}} \ |\hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}mn}|^2\Phi_{\mathbf{Q}}^+(t), \quad (54)$$

$$\Gamma_{mn}(t) = \sum_{\mathbf{Q}} \ G_{\mathbf{Q}mn}\Phi_{\mathbf{Q}}(t), \quad (55)$$

where $\Phi_{\mathbf{Q}}(t)$ and $\Phi_{\mathbf{Q}}^+(t)$ are defined in Eqs. (42) and (43), respectively. While the above equations can, in principle, be used to calculate the polaron dc conductivity for arbitrary phonon dispersions and coupling matrix elements, the essential physics can already be learned if one considers the simple model of a single dispersionless phonon mode, as introduced in Sec. III. Then, we can replace again $N_{\mathbf{Q}} \rightarrow N_{\mathrm{ph}} = (e^{\hbar\omega_{\mathrm{ph}}/k_B T}-1)^{-1}$ and $g_{\mathbf{Q}mn} \rightarrow (1/2\sqrt{N})g_{mn}(e^{-i\mathbf{q}\cdot\mathbf{R}_m} + e^{-i\mathbf{q}\cdot\mathbf{R}_n})$, and the above quantities $F_{mn}(t)$ and $\Gamma_{mn}(t)$ simplify into

$$F_{mn}(t) = (E_{mn})^2 + \tfrac{1}{2}(\hbar\omega_{\mathrm{ph}}g_{mn})^2\Phi_{\mathrm{ph}}(t), \quad (56)$$

$$\Gamma_{mn}(t) = 2g_{\mathrm{eff}}^2[1+2N_{\mathrm{ph}}-\Phi_{\mathrm{ph}}(t)] =: \Gamma_{\mathrm{ph}}(t), \quad (57)$$

where we used again the concept of an effective coupling constant, cf. Eq. (16). This, in turn, makes the rhs of Eq. (57)

independent of m and n and allows us to rename $\Gamma_{mn}(t)$ into $\Gamma_{\mathrm{ph}}(t)$. Furthermore, we defined the time-dependent auxiliary function

$$\Phi_{\mathrm{ph}}(t) = (1+N_{\mathrm{ph}})e^{-i\omega_{\mathrm{ph}}t} + N_{\mathrm{ph}}e^{i\omega_{\mathrm{ph}}t}, \quad (58)$$

which basically describes the hopping contribution to the dc conductivity. In fact, if the terms containing $\Phi_{\mathrm{ph}}(t)$ are neglected in Eqs. (56) and (57), the integrand in Eq. (53) becomes $[E_{mn}e^{-g_{\mathrm{eff}}^2(1+2N_{\mathrm{ph}})}]^2$ and we recover our previous result (16) from the bandlike-conduction picture of Sec. III.

Finally, we incorporate line-broadening effects which are always present to some extent in a real system, e.g., due to the presence of static disorder. Here, these effects are accounted for by the introduction of an extra factor $e^{-\Gamma^2 t^2}$ in Eq. (53) which corresponds to an inhomogeneous line broadening characterized by the phenomenological parameter Γ.

C. Anisotropy effects

In this section, we apply the general theory from the preceding section to a simplified model system in order to understand the basic physics contained in our approach. Accompanied by an illustrative numerical example, special emphasis is put on the emergence of anisotropy effects in the temperature dependence of the polaron dc conductivity.

We consider an orthorhombic crystal characterized by the three lattice vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$. Then, the basis vectors $\{\mathbf{e}_\alpha\}$ corresponding to the definition (18) of the conductivity tensor coincide with the crystal axes, or strictly speaking, with the normalized lattice vectors, and we can identify $\{\mathbf{e}_\alpha\} = \{\mathbf{e}_x,\mathbf{e}_y,\mathbf{e}_z\} = \{\boldsymbol{a}/a,\boldsymbol{b}/b,\boldsymbol{c}/c\}$. Furthermore, we assume that in the tight-binding Hamiltonian (1) only one transfer integral per crystallographic direction is nonvanishing, namely, $\{\varepsilon_{mn}\} = \{\varepsilon_a,\varepsilon_b,\varepsilon_c\} \equiv \{\varepsilon_\alpha\}$ corresponding to $\mathbf{R}_m-\mathbf{R}_n = \pm\boldsymbol{a}$, $\pm\boldsymbol{b}$, and $\pm\boldsymbol{c}$, respectively. The same holds true for the quantities E_{mn} and g_{mn} in Eq. (56).

For the above model crystal, the dc conductivity tensor (53) becomes diagonal, $\sigma_{\alpha\beta}^{\mathrm{dc}} = \sigma_\alpha^{\mathrm{dc}}\delta_{\alpha\beta}$, and we can identify $\{\sigma_\alpha^{\mathrm{dc}}\} = \{\sigma_{a,b,c}^{\mathrm{dc}}\}$ with the dc conductivities in the three crystallographic directions. As a result, we obtain by means of Eqs. (53) and (56),

$$\sigma_\alpha^{\mathrm{dc}} \propto \frac{\alpha^2}{T} \int_{-\infty}^{+\infty} dt \left[E_\alpha^2 + \frac{1}{2}(\hbar\omega_{\mathrm{ph}}g_\alpha)^2\Phi_{\mathrm{ph}}(t) \right] e^{-\Gamma_{\mathrm{ph}}(t)}e^{-\Gamma^2 t^2}$$

$$(\alpha = a,b,c), \quad (59)$$

where we dropped all prefactors which neither depend on the temperature nor on the crystallographic direction.

From Eq. (59), we see that the directionally dependent quantities α, E_α, and g_α contribute differently to the anisotropy of the conductivities $\sigma_\alpha^{\mathrm{dc}}$. While the prefactor α^2 causes an anisotropy in the overall magnitudes, it does not influence the actual temperature dependence itself. In contrast, the terms in the square brackets may influence both the overall values as well as the temperature dependence of $\sigma_\alpha^{\mathrm{dc}}$. The latter effect is due to the extra factor $\Phi_{\mathrm{ph}}(t)$ in the second term and explains how anisotropy effects in the T depen-
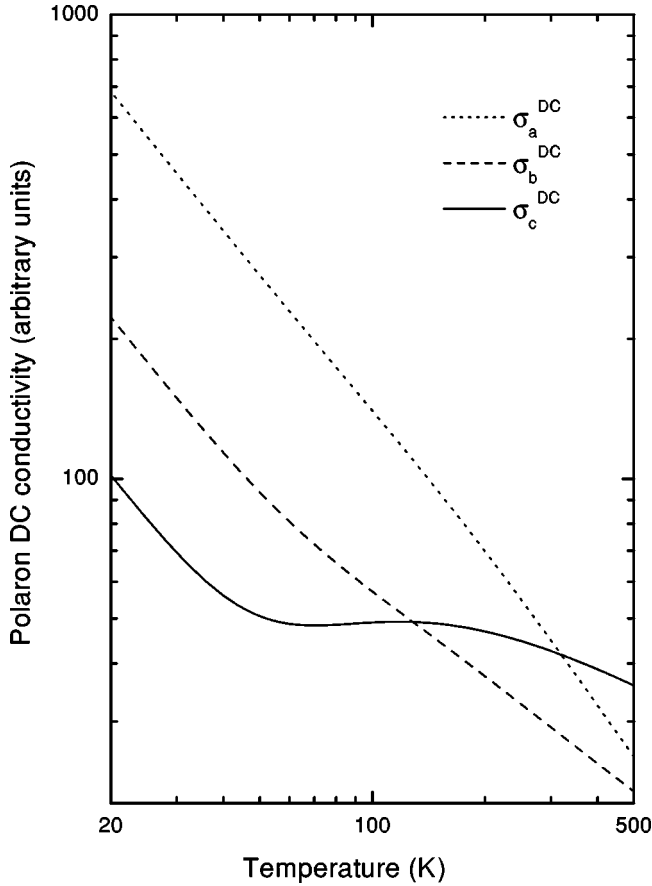
FIG. 1. Polaron dc conductivities $\sigma^{\mathrm{dc}}_{a,b,c}$ along the three principal axes of an orthorhombic model crystal, calculated as a function of temperature by means of Eq. (59) using $\hbar\omega_{\mathrm{ph}} = 15.0$ meV, $g_{\mathrm{eff}} = 1.0$, and $\hbar\Gamma = 0.1$ meV. The directionally dependent parameters are $a = 7$ Å, $E_a = 10.0$ meV, $g_a = 0.2$ (dotted line); $b = 8$ Å, $E_b = 5.0$ meV, $g_b = 0.3$ (dashed line); and $c = 9$ Å, $E_c = 3.0$ meV, $g_c = 0.4$ (solid line).

dence of polaron dc conductivities can arise within the Holstein-Peierls model. The strength of this anisotropy is basically determined by the ratios $r_\alpha := E_\alpha / \hbar\omega_{\mathrm{ph}} g_\alpha$ which, in general, may be different for different directions.

In order to visualize the anisotropy effects arising from the solution (59), we present in Fig. 1 an illustrative numerical example. For the phonon frequency and the effective coupling constant, we choose values of $\hbar\omega_{\mathrm{ph}} = 15.0$ meV and $g_{\mathrm{eff}} = 1.0$, respectively, which correspond to the typical values found in organic molecular crystals. Furthermore, we assume a very small value of $\hbar\Gamma = 0.1$ meV for the line broadening since we are primarily interested in the conductivity of charge carriers in high-purity crystals. The values of the directionally dependent quantities α, E_α, and g_α are chosen intentionally in such a way that distinct anisotropy effects in the dc conductivities become visible. Here, this is achieved by assuming that increasing lattice constants ($a = 7$ Å, $b = 8$ Å, $c = 9$ Å) go along with decreasing transfer integrals ($E_a = 10.0$ meV, $E_b = 5.0$ meV, $E_c = 3.0$ meV) and rising electron-phonon coupling strength ($g_a = 0.2$, $g_b = 0.3$, $g_c = 0.4$). While this might not always be fulfilled so ideally

for real crystals, it does serve the purpose to provide insight into some general phenomena described by our theory.

From Fig. 1, it can be seen at first glance that the different choice of parameters leads also to significant differences in the polaron dc conductivities for the three directions. In the low temperature region, these differences are of purely *quantitative* nature. Here, all conductivity curves scale like T^{-1} and only the overall values exhibit an anisotropy which is mainly determined by the values $\alpha^2 E_\alpha^2$. In contrast, for higher temperatures we observe also *qualitative* differences between the three curves. This is a consequence of the significantly different ratios $r_\alpha = E_\alpha / \hbar\omega_{\mathrm{ph}} g_\alpha$ introduced above. If this ratio is smaller than unity, the phonon-assisted hopping term $\propto \Phi_{\mathrm{ph}}(t)$ in Eq. (59) becomes increasingly important for higher temperatures. As a result, the dc conductivity exhibits the typical temperature dependence expected for thermally activated charge-carrier transport. Here, this is nicely seen in the c direction ($r_c = 0.50$) for $T \approx 100$ K where the conductivity increases with rising temperature. For the b direction, the ratio $r_b = 1.11$ is close to unity which makes the term $\propto \Phi_{\mathrm{ph}}(t)$ less important. Correspondingly, we do not observe anymore a temperature region where the conductivity rises with increasing temperature. Yet, the influence of the hopping term is still visible as a change from the T^{-1} power law at low temperatures into a $T^{-0.5}$ dependence at elevated temperatures. Finally, in the a direction, the large ratio $r_a = 3.33$ makes the term $\propto E_a^2$ the dominant contribution in Eq. (59) and a T^{-1} behavior is observed in almost the entire range of relevant temperatures. Nevertheless, even in this case there is still an interplay between band and hopping terms due to the factor $e^{-\Gamma_{\mathrm{ph}}(t)}$ in Eq. (59). However, for our choice of $g_{\mathrm{eff}} = 1.0$ this factor does not play a significant role but it may become more important for larger values of g_{eff} (not shown).

D. Importance of phonon-assisted currents

In the preceding section, we have shown that our theory of polaron dc conductivities can, in principle, describe anisotropy effects in the temperature dependence of $\sigma^{\mathrm{dc}}_{\alpha\beta}$ as observed in experiments. In this section, we proceed with a more detailed physical analysis of the origin of this anisotropy.

Much insight is gained if we compare the full theory developed above to a simplified version where the phonon-assisted currents $j_\alpha^{(\mathrm{II})}$ defined in Eq. (24) are not taken into account. Then, the evaluation of the Kubo formula (20) is much easier and, compared to the full theory, nothing but a nice exercise. Here, we will not repeat all the details of this calculation but rather focus on the most important changes. First, we can replace $\hat{E}_{mn} \to \varepsilon_{mn}$ in Eqs. (22) and (25) for the current operators $\mathbf{j}$ and $\tilde{\mathbf{j}}$, respectively. As a consequence, the definition of $\hat{X}_{\alpha\beta}(t)$ in Eq. (34) is changed accordingly and its subsequent evaluation becomes significantly simpler due to the disappearance of the extra operator $B_{\mathbf{Q}}^+$. The result of this evaluation can be expressed in the same way as Eq. (41) but with the operators $\hat{V}_{mn}^\alpha(t)$ and $\hat{W}_{nm}^\beta(0)$ replaced by the operator-free expressions $[R_\alpha, \varepsilon]_{mn}$ and $[R_\beta, \varepsilon]_{nm}$, respec-

tively. Then, the thermal average is readily performed using Wick's theorem since just one type of average appears [Eq. (44)] and only the even orders $\langle \hat{X}_{\alpha\beta}^{(2l)}(t) \rangle$ contribute. The result reads like Eq. (50) but without the term $\propto \Phi_{\mathbf{Q}}^{+}(t)$ and including the replacements $V_{mn}^{0\alpha} \to [R_\alpha, \varepsilon]_{mn}$ and $W_{nm}^{0\beta} \to [R_\beta, \varepsilon]_{nm}$. Taking into account only the dominant terms proportional to $[R_\alpha, \varepsilon]_{mn}$, we can readily sum up the whole power series $\langle \hat{X}_{\alpha\beta}(t) \rangle = \Sigma_{l=0}^{\infty} [1/(2l)!] \langle \hat{X}_{\alpha\beta}^{(2l)}(t) \rangle$ and insert the result into Eq. (33). From this, we obtain the polaron dc conductivity tensor without the phonon-assisted currents,

$$\sigma_{\alpha\beta}^{dc} = \frac{N_c e_0^2}{2 k_B T \hbar^2} \sum_{n \neq m} (R_{\alpha m} - R_{\alpha n})(R_{\beta m} - R_{\beta n})$$

$$\times \int_{-\infty}^{+\infty} dt (\varepsilon_{mn})^2 e^{-\Gamma_{mn}(t)}, \tag{60}$$

which equals the solution (53) of the full theory except for the replacement $F_{mn}(t) \to (\varepsilon_{mn})^2$. Note that in Eq. (60) the electron-phonon coupling enters only via the quantity $\Gamma_{mn}(t)$ which we can replace by $\Gamma_{ph}(t) = 2 g_{eff}^2 [1 + 2 N_{ph} - \Phi_{ph}(t)]$ in the case of a single dispersionless phonon mode. By this, Eq. (60) becomes qualitatively equivalent to the result of Holstein's theory of purely local coupling which is obtained by simply interchanging $g_{eff} \leftrightarrow g_0$ in $\Gamma_{ph}(t)$.

In order to visualize the important qualitative difference between the theories with and without the phonon-assisted current $j_\alpha^{(II)}$, we apply Eq. (60) to the model crystal of Sec. IV C, namely, an orthorhombic crystal with just one nonzero transfer integral per crystallographic direction, i.e., $\{\varepsilon_{mn}\} = \{\varepsilon_a, \varepsilon_b, \varepsilon_c\} \equiv \{\varepsilon_\alpha\}$. As a result, the dc conductivities in the three directions are given by

$$\sigma_\alpha^{dc} \propto \frac{\alpha^2}{T} \int_{-\infty}^{+\infty} dt \varepsilon_\alpha^2 e^{-\Gamma_{ph}(t)} e^{-\Gamma^2 t^2} \quad (\alpha = a, b, c), \tag{61}$$

which corresponds to Eq. (59) in the full theory. In contrast to Eq. (59), the simplified result (61) does not give rise to an anisotropic temperature dependence of the conductivities σ_α^{dc}. The only anisotropy in Eq. (61) arises from the factors $\alpha^2 \varepsilon_\alpha^2$ which determine the absolute values of σ_α^{dc} but not the actual T dependence itself. In other words, the additional term $\propto \Phi_{ph}(t)$ in Eq. (59) which stems from the phonon-assisted currents $j_\alpha^{(II)}$ is, indeed, the essential contribution to the anisotropy in the T dependence of polaron dc conductivities.[37] Since the currents $j_\alpha^{(II)}$ originate solely from the nonlocal electron-lattice interaction, this means also that local-coupling theories can, in general, not be expected to yield completely satisfying results.[38]

The above analysis can be further deepened if the time integrals in Eqs. (59) and (61) are explicitly evaluated. This is achieved by means of the following expansion into modified Bessel functions I_l of order l,

$$e^{+2 g_{eff}^2 \Phi_{ph}(t)} = e^{+z_{ph} \cos \Theta_{ph}} = \sum_{l=-\infty}^{+\infty} I_l(z_{ph}) e^{-il\Theta_{ph}}, \tag{62}$$

where $z_{ph} = 4 g_{eff}^2 \sqrt{N_{ph}(1 + N_{ph})}$ and $\Theta_{ph} = \omega_{ph} t + i(\hbar \omega_{ph}/2 k_B T)$. Then, in the limit $\Gamma \to 0$, the remaining time integrations $\int_{-\infty}^{+\infty} dt e^{-il\omega_{ph}t}$ result in δ functions at multiple integers l of the phonon frequency ω_{ph} corresponding to the effective emission ($l > 0$) or absorption ($l < 0$) of $|l|$ phonons.[39] As a result, the dc conductivities can be written as

$$\sigma_\alpha^{dc} \propto \frac{\alpha^2}{T} e^{-2 g_{eff}^2 (1 + 2 N_{ph})} \sum_{l=-\infty}^{+\infty} f_\alpha^{(l)} e^{l\hbar\omega_{ph}/2 k_B T} 2 \pi \delta(l\omega_{ph}), \tag{63}$$

where the quantities $f_\alpha^{(l)}$ are defined either as $f_\alpha^{(l)} := \varepsilon_\alpha^2 I_l(z_{ph})$ if $j_\alpha^{(II)}$ is neglected [Eq. (61)] or $f_\alpha^{(l)} := E_\alpha^2 I_l(z_{ph}) + \frac{1}{2}(\hbar\omega_{ph}g_\alpha)^2 [I_{l-1}(z_{ph}) + I_{l+1}(z_{ph})] \sqrt{N_{ph}(1 + N_{ph})}$ if $j_\alpha^{(II)}$ is taken into account [Eq. (59)]. From the latter formula, the fundamental importance of the phonon-assisted currents $j_\alpha^{(II)}$ is strikingly visible due to the explicit appearance of the phonon occupation numbers via the factor $\sqrt{N_{ph}(1 + N_{ph})}$. Therefore, the corresponding term in $f_\alpha^{(l)}$ gains weight at higher T which eventually causes the temperature dependence of σ_α^{dc} to become anisotropic as discussed above.

In practice, the singularities arising from the δ functions in Eq. (63) are removed by the inhomogeneous line broadening Γ which can be accounted for by the replacement $2 \pi \delta(l\omega_{ph}) \to (\sqrt{\pi}/\Gamma) e^{-l^2 \omega_{ph}^2/2\Gamma^2}$, in accordance with the factor $e^{-\Gamma^2 t^2}$ used in time domain. For crystals of high purity, i.e., little static disorder, it holds that $\Gamma \ll \omega_{ph}$ and the term with $l = 0$ becomes the dominant contribution to σ_α^{dc}. Within this approximation, the polaron dc conductivities (63) simplify into

$$\sigma_\alpha^{dc} \propto \frac{\alpha^2}{T} \frac{\sqrt{\pi}}{\Gamma} e^{-2 g_{eff}^2 (1 + 2 N_{ph})} f_\alpha^{(0)}, \tag{64}$$

where, additionally, in the full theory including $j_\alpha^{(II)}$ the above-defined quantity $f_\alpha^{(0)}$ can be transformed into

$$f_\alpha^{(0)} = E_\alpha^2 I_0(z_{ph}) + (\hbar\omega_{ph}g_\alpha)^2 I_1(z_{ph}) \sqrt{N_{ph}(1 + N_{ph})} \tag{65}$$

by means of the identity $I_{-1}(z_{ph}) = I_1(z_{ph})$. Here, it is worthwhile to note that the simplified expressions (64) and (65) exhibit some similarities to results on polaron diffusion coefficients obtained by Munn and Silbey[27] but it is difficult to establish a direct relation to our findings due to the different formalisms involved and the overall complexity of the problem. These authors also pointed out the importance of phonon-assisted currents arising from nonlocal electron-lattice interaction but could not explicitly demonstrate the resulting anisotropy effects since their analysis was restricted to a one-dimensional system.

Finally, it is interesting to discuss some limiting cases of the above formulas (64) and (65). The low-temperature limit is easily performed. Using $I_0(z_{ph}) \to 1$ and $I_{l \neq 0}(z_{ph}) \to 0$ for $z_{ph} \to 0$, we obtain immediately $\sigma_\alpha^{dc} \propto \alpha^2 E_\alpha^2 T^{-1}$, in agreement with our numerical findings from Fig. 1. In this limit, the second term in Eq. (65) approaches zero and, apart from the small change in the transfer integrals $\varepsilon_\alpha \to E_\alpha$, the current $j_\alpha^{(II)}$ does not contribute to the conductivity, as expected for

phonon-assisted transport. We note that the divergence for zero temperature is an unphysical artifact originating from the approximation made in Eqs. (26) and (27) which will be discussed in more detail in Sec. IV E.

The high-temperature limit is somewhat more complicated but can be performed using the asymptotic expansions for the modified Bessel functions $I_l(z_{ph} \rightarrow \infty) \approx e^{z_{ph}}/\sqrt{2\pi z_{ph}}$ for arbitrary order l as well as $1 + 2N_{ph} \approx 2k_BT/\hbar\omega_{ph}$ and $1 + 2N_{ph} - 2\sqrt{N_{ph}(1+N_{ph})} \approx \hbar\omega_{ph}/4k_BT$ for large T. If inserted into Eqs. (64) and (65), the conductivity can be written as

$$\sigma_\alpha^{dc} \propto \frac{\alpha^2}{T^{1.5}}\left[E_\alpha^2 + (\hbar\omega_{ph}g_\alpha)^2 \frac{k_BT}{\hbar\omega_{ph}}\right]e^{-\Delta/k_BT}, \quad (66)$$

where we dropped all irrelevant prefactors and introduced an "activation energy" $\Delta = \frac{1}{2}\hbar\omega_{ph}g_{eff}^2$. The asymptotic behavior found in Eq. (66) is in agreement with our numerical results in Fig. 1 and supports our discussion at the end of Sec. IV C. Especially, we obtain a factor $e^{-\Delta/k_BT}$ which causes thermal activation as seen in the c direction, and we recover the ultimate $T^{-0.5}$ dependence for high enough temperatures as seen in the b direction. However, for large ratios $r_\alpha = E_\alpha/\hbar\omega_{ph}g_\alpha$, this $T^{-0.5}$ dependence will be established only for extremely high T, and in the relevant temperature range one may instead observe just a gradual change from the T^{-1} power law at low temperatures into a $T^{-1.5}$ dependence at elevated temperatures as seen in the a direction in Fig. 1. At this stage, it is important to note that the exponents obtained within our model of a single dispersionless optical phonon mode may be subject to changes due to effects beyond this model, in particular, due to additional optical and/or acoustical modes as well as temperature-dependent homogeneous line broadening. However, as far as the anisotropy effects are concerned, the general picture presented here will remain valid.

E. Limitations of the present approach

In the previous sections, we have presented a theoretical description of polaron dc conductivities in organic molecular crystals based on the evaluation of the Kubo formula within a mixed Holstein-Peierls model. Due to the inclusion of both local and nonlocal electron-phonon interactions, our approach may be looked upon as the generalization of Holstein's original theory of purely local coupling. As a key result, we found that the Holstein-Peierls model can account for anisotropy effects in the temperature dependence of the conductivities whereas they are absent in local-coupling theories. Yet, despite this significant improvement, there are still some limitations of the present approach. In this section, we conclude our analysis by a brief discussion of these limitations and how they might be overcome.

As far as the physics is concerned, the most important approximation of our derivation is made in Eqs. (26) and (27) by the replacement $\tilde{H} \rightarrow \tilde{H}'$ for the calculation of the thermal averages. As discussed in Mahan's textbook,[34] this approximation is also made in the corresponding solution for the pure Holstein model and basically serves as a convenient

method to calculate the electronic part of the thermal average. In fact, the use of Eqs. (28) and (32) strongly simplifies our derivation but relies on the diagonality of $\tilde{H}'$ with respect to the electron operators. In this way, effects due to the finite polaron bandwidths are partially neglected. In a first step, this drawback may be overcome if instead of the substitution $\tilde{E}_{mn} \rightarrow \langle\tilde{E}_{mm}\rangle\delta_{mn}$ corresponding to $\tilde{H} \rightarrow \tilde{H}'$ just the replacement $\tilde{E}_{mn} \rightarrow \langle\tilde{E}_{mn}\rangle$ is made, in accordance with our polaron band-structure theory of Sec. III, Eq. (14). Yet, even this improvement would take into account only the real part of the polaron bands whereas effects due to the imaginary part and here, in particular, the homogeneous line broadening (which may be temperature dependent) would still remain unaddressed. Obviously, the latter deficiency could only be overcome by calculating the thermal average with respect to the full Hamiltonian $\tilde{H}$ without further approximations. However, to our knowledge, this has not even been achieved so far for the much simpler Holstein model.

In any case, once the diagonality in the electron operators is lifted, the use of the real-space representation for the thermal averaging of the electronic part in $\langle j_\alpha(t)j_\beta(0)\rangle$ becomes disadvantageous. In principle, this problem could be solved by switching to the reciprocal space but then, in turn, the thermal average over the phononic part becomes more complicated, and to our knowledge, the only attempt for a rigorous solution has been made by Munn and Silbey.[27] Recently, for local coupling, an *ad hoc* solution has been proposed by Kenkre and co-workers.[40,41] Even though their treatment of the problem is quite simplistic, it allowed them to capture an important modification due to the finite bandwidths, namely, the disappearance of the unphysical singularity at $T=0$ K. This is achieved by taking into account the thermal (Fermi) distribution of the charge carriers within the band which (at low densities and low temperatures) basically introduces an additional factor $\propto k_BT$ corresponding to the spectral width of the distribution.

On the other hand, from the practical point of view, the region of very low temperatures is anyway more difficult to describe since there are further effects beyond our model that may play an important role, especially acoustic-phonon and impurity scattering. Only if these effects are included microscopically as well can one expect to make exact *quantitative* predictions for low-T conductivities. We hope that our present theory will stimulate further research into this direction which would ultimately result in a fully microscopic description of charge-carrier conductivities in organic molecular crystals.

V. SUMMARY

In summary, we have presented a theoretical description of polaron dc conductivities in organic molecular crystals within a mixed Holstein-Peierls model. Our approach is based on a rigorous evaluation of the Kubo formula for electrical conductivity and incorporates both the local and nonlocal electron-lattice interactions nonperturbatively. As a key result, we have derived an explicit expression for the dc conductivity tensor that generalizes both the result of Holstein's

local-coupling theory as well as previous evaluations of the Kubo formula including nonlocal coupling.

The general theory has been applied to a simplified model crystal, namely, an orthorhombic crystal with one nonzero transfer integral per crystallographic direction. Accompanied by an illustrative numerical example, we have demonstrated that the Holstein-Peierls model can account for anisotropy effects in the temperature dependence of polaron conductivities. These anisotropy effects are solely caused by phonon-assisted currents arising from the nonlocal electron-phonon coupling. This proves the importance to go beyond local-coupling theories in order to describe the experimentally observed anisotropy of charge-carrier conductivities in organic molecular crystals.

While the actual evaluation of the Kubo formula turned out to be rather complicated, our final expressions for the polaron dc conductivity, Eqs. (53)–(58), are comparably easy to comprehend. As all the material-specific input parameters can be obtained from *ab initio* calculations—as recently demonstrated for oligoacene crystals[29,30]—our theory does also represent a significant step towards quantitative calculations of polaron conductivities and may pave the way for a fully microscopic description of charge-carrier transport in organic molecular crystals.

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[32] Strictly speaking, this choice of the coupling matrix elements $g_{\mathbf{Q}mn}$ can only be justified for crystals with one molecule per unit cell. However, in practice, one may also treat crystals containing several equivalent molecules per unit cell by means of the same formulas if an appropriately enlarged Brillouin zone is used, as successfully demonstrated in Ref. 29.

[33] If the terms discussed in Ref. 31 are taken into account, the exponents within the Holstein-Peierls model become slightly dependent on the indices m and n. However, the resulting anisotropy effects are found to be of minor importance, as discussed in Ref. 29.

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dispersionless phonons as used in this paper, the neglected terms $-\Sigma_{\mathbf{Q}}[g_{-\mathbf{Q}}[R_{\alpha},\hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]]_{mn}\Phi_{\mathbf{Q}}^{-}(t)$ can be shown to vanish if, in consistency with previous approximations, again only the terms proportional to $[R_{\alpha},\hbar\omega_{\mathbf{Q}}g_{\mathbf{Q}}]_{mn}$ are taken into account.

[37] Note also that there is another change due the inclusion of $j_{\alpha}^{(\mathrm{II})}$, namely, the shift $\varepsilon_{\alpha}\rightarrow E_{\alpha}$ of the transfer integrals, in agreement with the band-structure theory from Sec. III, Eq. (10). However, it has been shown in Ref. 30 that these shifts are usually small and, hence, of minor importance.

[38] In Ref. 22, the anisotropy of the mobilities in naphthalene crystals was theoretically described by fitting the experimental data to the Holstein model using directionally dependent effective coupling constants. Despite the apparent success of this procedure, the validity of such an approach is not ensured since it is intrin-

sically inconsistent with the Holstein model which actually predicts the same T dependence of $\sigma_{\alpha}^{\mathrm{dc}}$ in all crystallographic directions.

[39] Note that due to the availability of many phonon wave vectors the effective emission (absorption) of $|l|$ phonons is not equivalent to the total emission (absorption) of $|l|$ phonons but rather means that the total number of emitted (absorbed) phonons exceeds the total number of absorbed (emitted) phonons by a value of $|l|$. This difference is especially important for the term $l=0$ which must not be misinterpreted as a purely coherent contribution with no phonons being involved.

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