PHYSICAL REVIEW B **69**, 144302 (2004)

Nonlocal electron-phonon coupling: Consequences for the nature of polaron states

Vladimir M. Stojanović,* P. A. Bobbert, and M. A. J. Michels
Group Polymer Physics, Eindhoven Polymer Laboratories and Dutch Polymer Institute, Technische Universiteit Eindhoven,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 10 July 2003; revised manuscript received 30 January 2004; published 12 April 2004)

We develop a variational approach to an extended Holstein model, comprising both local and nonlocal electron-phonon coupling. The approach is based on the minimization of a Bogoliubov bound to the Helmholtz free energy. The ambivalent character of nonlocal coupling, which both promotes and hinders transport, is clearly observed. Furthermore, a salient feature of our results is that the local and nonlocal couplings can compensate each other, leading to a reduction of polaronic effects and a quasi-free character of the excitation. Our findings have implications for organic crystals of π-conjugated molecules, where this electron-phonon coupling mechanism plays an important role.

DOI: 10.1103/PhysRevB.69.144302 PACS number(s): 71.38.−k, 63.20.Kr

I. INTRODUCTION

Coupled electron-phonon or exciton-phonon (hereafter e-ph) systems have long been an active research area in condensed-matter physics. A significant portion of the research effort has been dedicated to the study of a single electron or exciton interacting with the lattice vibrations through a short-range, nonpolar potential that is linear in the lattice displacements and accounts for the dependence of the electronic or excitonic on-site energies on the lattice degrees of freedom. This physical situation, termed local linear e-ph coupling, is traditionally described by what became known as the Holstein Hamiltonian, after Holstein's groundbreaking work on this Hamiltonian.[1] The Lang-Firsov unitary transformation of the displacement-operator type[2–4] was another theoretical milestone. Later, the field received further developments in the theoretical analysis, including those of computational nature.[5–7]

In a recent work,[8] we showed that in organic molecular crystals of polyacenes (naphthalene, anthracene, and tetracene) there is a strong coupling of optical phonons, especially those of rotational provenance (librons), to the electronic transfer integrals (nonlocal e-ph coupling), dominating the local-coupling mechanism. Nonlocal (Peierls' type) coupling is also expected to play an important role in the crystals of other π-conjugated molecules. In particular, nonlocal exciton-phonon coupling appears to be important for the description of excimers in, e.g., pyrene and α-perylene.[9–11] Perhaps the best known model dealing with nonlocal coupling is the Su-Schrieffer-Heeger (SSH) model,[12,13] introduced to describe solitons and polarons in the quasi-one-dimensional conductive polymer *trans*-polyacetylene. However, in its original form, the model leans on a classical treatment of the lattice dynamics, which is allowed only in the case when a typical electronic transfer integral is much smaller than a typical phonon energy (antiadiabatic limit). There are a few accounts of a quantum-mechanical treatment of the lattice together with nonlocal e-ph coupling mechanism.[14–18] In our previous work,[8,19] we generalized the Lang-Firsov transformation to account for both local and nonlocal e-ph coupling. We showed that, after some approximations, a rather simple expression can be obtained for the temperature-dependent polaron transfer integrals, closely analogous to the equivalent expression for the Holstein Hamiltonian. An additional term appears, however, which is related to the promotion of transport by nonlocal e-ph coupling.

In this previous work,[8,19] we assumed that a full nonlocal transformation should be performed for an approximate decoupling of polaronic and phononic degrees of freedom. In other words, we assumed a full "dressing" of the electron by a phonon cloud forming a polaron. In the present work, we go beyond that assumption. Our approach utilizes the method of temperature-dependent, variationally optimized canonical transformations.[20] The variational principle used is based upon the Bogoliubov bound to the Helmholtz free energy of the e-ph system under consideration. For local coupling, a similar approach was followed by Yarkony and Silbey[21] and it is in this sense that our treatment constitutes a generalization of their work. A variational treatment of combined local and nonlocal coupling performed by Zhao *et al.*[22] makes use of Toyozawa's Ansatz states, commonly employed in local-coupling theory.[23–25] However, the latter variational analysis is limited to the ground-state polaron structure, whereas our treatment also covers the regime of finite temperatures.

The outline of the paper is as follows. In Sec. II we introduce the Hamiltonian of our coupled e-ph system and the canonical transformation to be used throughout. In Sec. III we first give a short exposition of the variational principle employed, then demonstrate its application to the coupled e-ph system, and, finally, specialize to a one-dimensional model with dispersionless (Einstein) phonons. Section IV provides the numerical results obtained for this model system. We discuss the zero- and finite-temperature results for the optimal dressing parameter and present phase diagrams for the parameter regions of strong and weak dressing. Possible implications of our work to optical and transport properties are briefly touched upon in Sec. V. Finally, the main conclusions are summarized in Sec. VI. Some cumbersome derivations are relegated to the Appendices.

II. MODEL

The system under study consists of an excess electron (hole, exciton) interacting with harmonic lattice vibrations

0163-1829/2004/69(14)/144302(13)/$22.50

(nonpolar optical phonons). Both local and nonlocal e-ph coupling are taken into account, within the framework of an extended Holstein Hamiltonian, encompassing an electronic part (H_e), a phonon part (H_{ph}), and the interaction (e-ph) part ($H_{e\text{-}ph}$):

$$H = H_e + H_{ph} + H_{e\text{-}ph}\,. \tag{1}$$

The respective forms of the three read ($\hbar = 1$ in what follows)

$$H_e = \sum_{m,n} \varepsilon_{mn} a_m^\dagger a_n\,, \tag{2}$$

$$H_{ph} = \sum_{\mathbf{q}} \omega_{\mathbf{q}} \left(b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2} \right), \tag{3}$$

$$H_{e\text{-}ph} = \sum_{\mathbf{q},m,n} \omega_{\mathbf{q}} g_{mn}^{\mathbf{q}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^\dagger) a_m^\dagger a_n\,, \tag{4}$$

wherein $a_m^\dagger$ and $b_{\mathbf{q}}^\dagger$ create an electron in the Wannier state at site m (position $\mathbf{R}_m$) and a phonon with wave vector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$, respectively. ε_{mn} is a compact notation for the electronic on-site energies ($\varepsilon_{mm} \equiv \varepsilon$) and transfer integrals ($\varepsilon_{mn}, m \neq n$). Like in our previous work[8,19] we assume the form

$$g_{mn}^{\mathbf{q}} = \frac{g_{mn}}{2\sqrt{N}} (e^{-\imath \mathbf{q}\cdot\mathbf{R}_m} + e^{-\imath \mathbf{q}\cdot\mathbf{R}_n}) \tag{5}$$

for the $\mathbf{q}$-dependent e-ph coupling constants, where g_{mn} depends only on $|\mathbf{R}_m - \mathbf{R}_n|$ (abbreviated in the following as $|m-n|$), and where N is the number of sites. This form obeys the property $(g_{mn}^{\mathbf{q}})^* = g_{nm}^{-\mathbf{q}}$ required for the Hermiticity of $H_{e\text{-}ph}$ and satisfies the translational symmetry. In the case $m=n$ one recovers $g_{mm}^{\mathbf{q}} = g e^{-\imath \mathbf{q}\cdot\mathbf{R}_m}/\sqrt{N}$, the usual choice for the $\mathbf{q}$-dependent local-coupling constants.

In order to account for both local and nonlocal e-ph coupling, we utilize a unitary transformation $H \to \tilde{H} = e^S H e^{-S}$ of the initial Hamiltonian, the generator of which is given by

$$S = \sum_{m,n,\mathbf{q}} A_{mn}^{\mathbf{q}} (b_{\mathbf{q}}^\dagger - b_{-\mathbf{q}}) a_m^\dagger a_n\,. \tag{6}$$

Being also of the displacement-operator type,[20] it represents an obvious nonlocal generalization of the Lang-Firsov canonical transformation. The transformation parameters have to meet the same conditions as the $\mathbf{q}$-dependent e-ph coupling constants, in order to satisfy the anti-Hermiticity of S ($S^\dagger = -S$) and translational invariance. As can straightforwardly be demonstrated, the latter property guarantees the invariance of the total crystal momentum, defined as

$$\mathbf{P} = \sum_{\mathbf{k}} \mathbf{k} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \sum_{\mathbf{q}} \mathbf{q} b_{\mathbf{q}}^\dagger b_{\mathbf{q}}\,, \tag{7}$$

i.e., the validity of the relation $e^S \mathbf{P} e^{-S} = \mathbf{P}$. Our particular choice of the transformation parameters reads $A_{mn}^{\mathbf{q}} = \lambda g_{mn}^{\mathbf{q}}$, wherein λ is the as yet undetermined (implicitly temperature dependent) variational parameter, representing a measure of the phonon dressing of the excitation. The generator of the transformation can be recast in the form

$$S = \sum_{m,n} C_{mn} a_m^\dagger a_n\,, \tag{8}$$

where $C_{mn} = C_{mn}(\{b_{\mathbf{q}}^\dagger; b_{\mathbf{q}}\})$ stands for the operator

$$C_{mn} = \sum_{\mathbf{q}} A_{mn}^{\mathbf{q}} (b_{\mathbf{q}}^\dagger - b_{-\mathbf{q}}) = \lambda \sum_{\mathbf{q}} g_{mn}^{\mathbf{q}} (b_{\mathbf{q}}^\dagger - b_{-\mathbf{q}}). \tag{9}$$

Once transformed, the electronic and phononic operators read, respectively,[8,19]

$$e^S a_m e^{-S} = \sum_n (e^{-C})_{mn} a_n\,, \tag{10}$$

$$e^S b_{\mathbf{q}} e^{-S} = b_{\mathbf{q}} + \sum_{m,n} [(e^C b_{\mathbf{q}} e^{-C})_{mn} - b_{\mathbf{q}} \delta_{mn}] a_m^\dagger a_n\,. \tag{11}$$

Leaving out the terms describing two-particle interactions, which is valid for the low electron densities we are interested in, the transformed Hamiltonian $\tilde{H}$ acquires the form

$$\tilde{H} = \sum_{m,n} \tilde{\varepsilon}_{mn} a_m^\dagger a_n + \sum_{\mathbf{q}} \omega_{\mathbf{q}} \left(b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2} \right) + \sum_{m,n,\mathbf{q}} \omega_{\mathbf{q}} (\tilde{b}_{\mathbf{q}}^\dagger \tilde{g}^{\mathbf{q}} + \tilde{g}^{\mathbf{q}} \tilde{b}_{-\mathbf{q}} + \tilde{b}_{\mathbf{q}}^\dagger \tilde{b}_{\mathbf{q}} - b_{\mathbf{q}}^\dagger b_{\mathbf{q}})_{mn} a_m^\dagger a_n\,, \tag{12}$$

wherein $\tilde{\varepsilon}_{mn} = (e^C \varepsilon e^{-C})_{mn}$, $\tilde{g}_{mn}^{\mathbf{q}} = (e^C g^{\mathbf{q}} e^{-C})_{mn}$, $\tilde{b}_{mn}^{\mathbf{q}} = (e^C b^{\mathbf{q}} e^{-C})_{mn}$, and $(b_{\mathbf{q}}^\dagger b_{\mathbf{q}})_{mn}$ is a shorthand notation for $b_{\mathbf{q}}^\dagger b_{\mathbf{q}} \delta_{mn}$. For further use, it is convenient to rewrite the Hamiltonian as

$$\tilde{H} = \sum_{m,n} \tilde{V}_{mn} a_m^\dagger a_n + \sum_{\mathbf{q}} \omega_{\mathbf{q}} \left(b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2} \right), \tag{13}$$

where $\tilde{V}_{mn} = \tilde{V}_{mn}(\{b_{\mathbf{q}}^\dagger; b_{\mathbf{q}}\})$ stands for

$$\tilde{V}_{mn} = \tilde{\varepsilon}_{mn} + \sum_{\mathbf{q}} \omega_{\mathbf{q}} (\tilde{b}_{\mathbf{q}}^\dagger \tilde{g}^{\mathbf{q}} + \tilde{g}^{\mathbf{q}} \tilde{b}_{-\mathbf{q}} + \tilde{b}_{\mathbf{q}}^\dagger \tilde{b}_{\mathbf{q}} - b_{\mathbf{q}}^\dagger b_{\mathbf{q}})_{mn}\,. \tag{14}$$

The presence of phonon operators in $\tilde{V}_{mn}$ necessitates the use of the transformation (6) in the sense of a temperature-dependent optimal transformation.[20]

We point to the following difference with the bare local-coupling case: while the Lang-Firsov transformation, when applied to the Holstein Hamiltonian, introduces only a constant shift of the electronic on-site energies (usually referred to as polaronic shift, or polaron binding energy), the transformation (6) brings about the presence of a remnant of the e-ph coupling in the corresponding term of $\tilde{H}$. In other words, in the transformed on-site term, the electronic and phononic degrees of freedom are not completely decoupled.

III. FREE-ENERGY MINIMIZATION

A. Variational principle

The Helmholtz-free-energy (henceforth free energy) of a system with a Hamiltonian H that acts upon states in a separable Hilbert space $\mathcal{H}$ is defined by ($\beta\equiv 1/k_B T$)

$$F=-\beta^{-1}\ln Z=-\beta^{-1}\ln[\mathrm{Tr}(e^{-\beta H})]. \tag{15}$$

In view of the well-known relation between the free energy and the ground-state energy of the system (denoted by E_0), given by

$$\lim_{T\to 0} F(T)=E_0, \tag{16}$$

the free-energy minimization is a natural finite-temperature generalization of the ground-state variational principle of quantum mechanics (used by Zhao *et al.*[22] in the study of zero-temperature polaron structure). Owing to the Jensen convexity of the function $f(x)=e^{-\beta x}$, the following theorem holds true (Bogoliubov's inequality):[26,27]

For an arbitrary splitting of the Hamiltonian $H=H_0+(H-H_0)$, under the condition that $e^{-\beta H}$ and $e^{-\beta H_0}$ have finite traces for $\beta>0$, an upper bound to the free energy F is given by

$$F\leqslant F_0+\langle H-H_0\rangle_{H_0}, \tag{17}$$

where $F_0=-\beta^{-1}\ln[\mathrm{Tr}(e^{-\beta H_0})]$ is the free energy corresponding to the Hamiltonian H_0 and $\langle H-H_0\rangle_{H_0}=\mathrm{Tr}[e^{-\beta H_0}(H-H_0)]/\mathrm{Tr}(e^{-\beta H_0})$ stands for the thermal average of $H-H_0$ with respect to H_0.

The theorem has proved useful in the treatment of many problems in condensed-matter theory and statistical physics.[26,27] As regards its use in the present paper, the following two properties are of major importance.

(a) If the Hamiltonian $H=H_0+V$ is transformed by means of a unitary transformation $U=e^S$, so that $\tilde{H}=e^S He^{-S}=\tilde{H}_0+\tilde{V}$, the above inequality adopts the form

$$F\leqslant -\beta^{-1}\ln \mathrm{Tr}(e^{-\beta\tilde{H}_0})+\langle\tilde{V}\rangle_{\tilde{H}_0}. \tag{18}$$

(b) If the Hilbert space $\mathcal{H}$ of the system is partitioned into the mutually orthogonal subspaces, each invariant to the unitary transformation employed, then the preceding result holds for each of these subspaces separately.

B. Application to the coupled e-ph system

In order to make practical use of the Bogoliubov inequality, one has to have the possibility to perform an independent averaging over the electronic and phononic degrees of freedom. To that end, we make use of the splitting

$$\tilde{H}=\tilde{H}_0+\tilde{V} \tag{19}$$

of our transformed Hamiltonian, with

$$\tilde{H}_0=\sum_{m,n}\langle\tilde{V}_{mn}\rangle_{ph}a_m^{\dagger}a_n+\sum_{\mathbf{q}}\omega_{\mathbf{q}}\left(b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}}+\frac{1}{2}\right), \tag{20}$$

$$\tilde{V}=\sum_{m,n}(\tilde{V}_{mn}-\langle\tilde{V}_{mn}\rangle_{ph})a_m^{\dagger}a_n, \tag{21}$$

where $\langle\cdots\rangle_{ph}$ denotes a thermal phonon average. The noninteracting Hamiltonian $\tilde{H}_0$ can be rewritten as

$$\tilde{H}_0=\sum_{\mathbf{k}}\epsilon(\mathbf{k})a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+\sum_{\mathbf{q}}\omega_{\mathbf{q}}\left(b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}}+\frac{1}{2}\right), \tag{22}$$

with $\epsilon(\mathbf{k})=\epsilon+\langle\tilde{V}_{\mathbf{kk}}\rangle_{ph}$, where $\langle\tilde{V}_{\mathbf{kk}}\rangle_{ph}$ stands for the Fourier transform of $\langle\tilde{V}_{mn}\rangle_{ph}$, given by

$$\langle\tilde{V}_{\mathbf{kk}}\rangle_{ph}=\sum_{m}\langle\tilde{V}_{mn}\rangle_{ph}e^{i\mathbf{k}\cdot(\mathbf{R}_m-\mathbf{R}_n)}. \tag{23}$$

In what follows, we make use of the bounds that can be derived for the free energies pertaining to the subspaces of the total Hilbert space that correspond to different values of the total momentum; namely, the total-crystal-momentum invariance practically translates into the possibility to divide the total Hilbert space $\mathcal{H}$ of our e-ph system into orthogonal sectors, each of which is characterized by the particular eigenvalue of the total momentum operator and is invariant under the canonical transformation employed. As shown in what follows, this enables one to isolate the contributions $F_{\mathbf{K}}$ to the overall free energy originating from the subspaces $\mathcal{H}_{\mathbf{K}}$ (which correspond to different eigenvalues $\mathbf{K}$ of the total momentum) and find the corresponding Bogoliubov bounds. In order to find $F_{\mathbf{K}}$, one has to take traces in the general formulas pertaining to the Bogoliubov inequality, but only over the states $|\mathbf{K}-\mathbf{Q};\{n_{\mathbf{q}}\}\rangle$ with the total momentum equal to $\mathbf{K}$, where $\{n_{\mathbf{q}}\}$ denotes the set of phonon occupation numbers and $\mathbf{Q}$ is the phonon contribution to the total momentum:

$$\mathbf{Q}=\sum_{\mathbf{q}}\mathbf{q}n_{\mathbf{q}}. \tag{24}$$

Along these lines, in the case of the splitting (19), one obtains the bound[21]

$$F_{\mathbf{K}}=-\beta^{-1}\ln Z_{ph}-\beta^{-1}\ln(e^{-\beta\tilde{\mathbf{V}}})_{mm}, \tag{25}$$

where $\tilde{\mathbf{V}}$ is the matrix with the elements $(\tilde{\mathbf{V}})_{mn}\equiv\langle\tilde{V}_{mn}\rangle_{ph}$, depending on $|m-n|$ only. On account of the fact that[21]

$$(e^{-\beta\tilde{\mathbf{V}}})_{mm}=N^{-1}\sum_{\mathbf{k}}\exp[-\beta\epsilon(\mathbf{k})], \tag{26}$$

Eq. (25) can be given the form

$$F_{\mathbf{K}}=-\beta^{-1}\ln Z_{ph}-\beta^{-1}\ln\left[N^{-1}\sum_{\mathbf{k}}\exp[-\beta\epsilon(\mathbf{k})]\right], \tag{27}$$

thereby evincing that at finite temperatures the bound $F_{\mathbf{K}}$ does not bear any $\mathbf{K}$ dependence.

The thermal phonon average of $\tilde{V}_{mn}$ can be calculated approximately, at the level of second-order cumulant expansion (Appendix A). In the Einstein (dispersionless) phonon limit with one phonon mode of frequency ω, the result reads

$$\langle \tilde{V}_{mm} \rangle_{ph} = \varepsilon + (\lambda^2 - 2\lambda)\Delta, \tag{28}$$

and for $m \neq n$ one has

$$\langle \tilde{V}_{mn} \rangle_{ph} = \varepsilon_{mn} e^{-\lambda^2 U_{mn}} + \left[\frac{e^{-\lambda^2 U_{mn}} - 1}{U_{mn}} + \sqrt{\frac{\pi}{U_{mn}}} (\lambda - 1) \mathrm{erf}(\lambda \sqrt{U_{mn}}) \right] \Delta_{mn}, \tag{29}$$

wherein the auxiliary quantities Δ, Δ_{mn}, and U_{mn} are defined as

$$\Delta_{mn} \equiv \omega \sum_{\mathbf{q}} (g^{\mathbf{q}} g^{-\mathbf{q}})_{mn}, \tag{30}$$

$$\Delta_{mm} \equiv \Delta, \tag{31}$$

$$U_{mn} \equiv \left(\frac{1}{2} + N_T \right) \Gamma_{mn}, \tag{32}$$

$$\Gamma_{mn} \equiv G_{mm} + G_{nn} - g_{mn}^2, \tag{33}$$

$$G_{mm} \equiv g_{mm}^2 + \frac{1}{2} \sum_{k \neq m} g_{mk}^2, \tag{34}$$

with $N_T = (e^{\beta\omega} - 1)^{-1}$ being the thermally averaged phonon occupation number.

It is important to point out that, strictly speaking, the variational scheme we employ is not the most general possible. The more typical use of the Bogoliubov inequality in conjunction with the method of canonical transformations involves not only the dependence of a canonical transformation on a certain set of variational parameters, but also a dependence of the splitting of the initial Hamiltonian on one or more parameters, a common place in the variational mean-field theories.[26] In our case such an approach could be conveyed through the more general splitting $\tilde{H} = \tilde{H}_0(\mu) + \tilde{V}(\mu)$ of the initial Hamiltonian, with $\tilde{H}_0(\mu)$ and $\tilde{V}(\mu)$ being given by

$$\tilde{H}_0(\mu) = \mu \sum_{m,n} \langle \tilde{V}_{mn} \rangle_{ph} a_m^\dagger a_n + \sum_{\mathbf{q}} \omega_{\mathbf{q}} \left(b_{\mathbf{q}}^\dagger b_{\mathbf{q}} + \frac{1}{2} \right), \tag{35}$$

$$\tilde{V}(\mu) = \sum_{m,n} (\tilde{V}_{mn} - \mu \langle \tilde{V}_{mn} \rangle_{ph}) a_m^\dagger a_n . \tag{36}$$

This would subsequently lead to the corresponding set of the Girardeau-Huber-type equations[20,26] involving λ and the new variational parameter μ. Yet, in order to alleviate the calculational burden, we elect a somewhat less flexible variational scheme with $\mu = 1$, which also bears certain technical advantages, stemming from the fact that $\langle \tilde{V}(\mu = 1) \rangle_{ph} = 0$.

C. One-dimensional model with Einstein phonons

We now resort to a one-dimensional situation, where we assume only nearest-neighbor coupling with transfer integral $\varepsilon_{m,m\pm1} \equiv J > 0$, local coupling constant $g_{m,m} \equiv g$, and nonlocal coupling constant $g_{m,m\pm1} \equiv \phi$. The nonlocal part of the electron-phonon coupling Hamiltonian then reads

$$\omega \phi \sum_m (u_m + u_{m+1}) a_m^\dagger a_{m+1} + \text{H.c.}, \tag{37}$$

with $u_m \equiv b_m^\dagger + b_m$ (phonon-displacement operators). It corresponds to the case of *symmetric* nonlocal coupling.[22] Furthermore, we define $\Gamma_{m,m\pm1} \equiv \Gamma_1$, $U_{m,m\pm1} \equiv U_1$, $\Delta_{m,m\pm1} \equiv \Delta_1$, $\tilde{V}_{m,m\pm1} \equiv \tilde{V}_1$, and $\mathbf{R}_m - \mathbf{R}_{m\pm1} = \mp \mathbf{a}$. In Appendix B we derive the equalities

$$\Gamma_1 = 2g^2 + \phi^2, \tag{38}$$

$$\Delta = \omega(g^2 + \phi^2), \tag{39}$$

$$\Delta_1 = \omega g \phi. \tag{40}$$

The Hamiltonian $\tilde{H}_0$ of the preceding section reduces to the form (22), with

$$\epsilon(\mathbf{k}) = \epsilon + 2 \langle \tilde{V}_1 \rangle_{ph} \cos(\mathbf{k} \cdot \mathbf{a}), \tag{41}$$

where

$$\langle \tilde{V}_1 \rangle_{ph} = J e^{-\lambda^2 U_1} + \left[\frac{e^{-\lambda^2 U_1} - 1}{U_1} + \sqrt{\frac{\pi}{U_1}} (\lambda - 1) \mathrm{erf}(\lambda \sqrt{U_1}) \right] \Delta_1 . \tag{42}$$

Hence, the $\mathbf{k}$ sum in the expression (27) takes the form

$$N^{-1} \sum_{\mathbf{k}} \exp[-\beta \epsilon(\mathbf{k})] = e^{-\beta\epsilon} N^{-1} \sum_{\mathbf{k}} \exp[-2\beta \langle \tilde{V}_1 \rangle_{ph} \cos(\mathbf{k} \cdot \mathbf{a})]. \tag{43}$$

Upon replacing this sum by an integral over the Brillouin zone and recalling that[32]

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} e^{z \cos\theta} d\theta = I_0(z), \tag{44}$$

where $I_0(z)$ is the zeroth-order modified Bessel function of the first kind, one finds

$$N^{-1} \sum_{\mathbf{k}} \exp[-\beta \epsilon(\mathbf{k})] = e^{-\beta\epsilon} I_0(2\beta \langle \tilde{V}_1 \rangle_{ph}), \tag{45}$$

and, consequently,

$$F_{\mathbf{K}} = \varepsilon + (\lambda^2 - 2\lambda)\Delta - \beta^{-1} \ln Z_{ph} - \beta^{-1} \ln I_0(2\beta \langle \tilde{V}_1 \rangle_{ph}). \tag{46}$$

The value of λ that minimizes Eq. (46) satisfies the equation

$$\lambda-1=\frac{1}{\Delta}\,\frac{I_1(2\beta\langle\tilde{V}_1\rangle_{ph})}{I_0(2\beta\langle\tilde{V}_1\rangle_{ph})}\,\frac{d}{d\lambda}(\langle\tilde{V}_1\rangle_{ph}), \tag{47}$$

where use has been made of the identity $dI_0/dx=I_1(x)$. The pure local-coupling limit of the last equation reads

$$\lambda\left(1+\frac{2J}{\omega}e^{-g^2\lambda^2[(1/2)+N_T]}\,\frac{I_1(2\beta Je^{-g^2\lambda^2[(1/2)+N_T]})}{I_0(2\beta Je^{-g^2\lambda^2[(1/2)+N_T]})}\right)=1, \tag{48}$$

equivalent to what was found by Yarkony and Silbey.[21] Owing to the asymptotic relation for the modified Bessel functions,[32]

$$I_\nu(x)\sim\frac{e^x}{\sqrt{2\pi x}}\quad(x\gg1), \tag{49}$$

and to the fact that the zero-temperature ($\beta\to+\infty$) limit of $\langle\tilde{V}_1\rangle_{ph}$ is finite,

$$\langle\tilde{V}_1\rangle_{ph}\to Je^{-(1/2)\lambda^2\Gamma_1}+\left[2\frac{e^{-(1/2)\lambda^2\Gamma_1}-1}{\Gamma_1}+\sqrt{\frac{2\pi}{\Gamma_1}}\,(\lambda-1)\mathrm{erf}\left(\lambda\sqrt{\frac{\Gamma_1}{2}}\right)\right]\Delta_1, \tag{50}$$

one has

$$\frac{I_1(2\beta\langle\tilde{V}_1\rangle_{ph})}{I_0(2\beta\langle\tilde{V}_1\rangle_{ph})}\to1. \tag{51}$$

As a consequence of Eqs. (50) and (51) one obtains the following self-consistency equation for the zero-temperature, bottom-of-the-band situation:

$$\lambda-1=\sqrt{\frac{2\pi}{\Gamma_1}}\frac{\Delta_1}{\Delta}\mathrm{erf}\left(\sqrt{\frac{\Gamma_1}{2}}\lambda\right)-\left(\frac{J}{\Delta}\Gamma_1\lambda+2\frac{\Delta_1}{\Delta}\right)e^{-(1/2)\Gamma_1\lambda^2}. \tag{52}$$

In the limit of pure local coupling ($\phi\to0$, and consequently $\Gamma_1\to2g^2$, $\Delta_1\to0$, $\Delta\to\omega g^2$) the last equation goes over into

$$\lambda\left(1+\frac{2J}{\omega}e^{-g^2\lambda^2}\right)=1, \tag{53}$$

equivalent to what was derived by Yarkony and Silbey[21] in the zero-temperature bottom-of-the-band situation. In the limit of pure nonlocal coupling one finds a similar equation

$$\lambda\left(1+\frac{J}{\omega}e^{-(1/2)\phi^2\lambda^2}\right)=1. \tag{54}$$

The transcendental equations (47) and (52) can be solved numerically for different choices of values of the parameters (J,ω,g,ϕ,T). The numerical results thereby obtained are presented in the following section.

As for the allowed values of the variational parameter λ, a remark has to be made here: unlike the case of the Holstein Hamiltonian, where in the limit of vanishing electronic transfer integrals ($J=0$) the Lang-Firsov transformation yields the exact diagonalization (and, consequently, possible optimal values of the variational parameter are bound from above by one[21]) our transformation does not possess such a plausible limit. Rephrasing, there is no *a priori* physical reason for the optimal values of λ to be always smaller than one.

IV. RESULTS AND DISCUSSION

A. Zero-temperature case

The self-consistency equation (52) for the optimal value of λ (denoted by λ^*) is apparently determined by the parameters J/ω, ϕ, g. Since we are interested in the effects inherent to nonlocal coupling we can adopt as our parameters J/ω and ϕ, with g being fixed. In the presence of both local and nonlocal coupling, the relative sign of the corresponding coupling constants plays a role. For definiteness, we keep g positive, and let ϕ take on both positive and negative values.

In Fig. 1(a) we plot the value of λ^* which gives the minimal free energy at zero temperature for five different values of J/ω between 0.25 and 4.0, and $g=0.25$. The dependence of λ^* on ϕ is clearly nonmonotonous, with the minimum equal zero at $\phi/g=1$ and the limiting value of one realized at higher values of ϕ. The dependence is smooth and continuous for small values of J/ω, whereas for larger values an abrupt transition occurs between "weakly dressed" and "strongly dressed" states. In the latter case, the free energy of the system has two minima (as a function of λ). At a certain coupling strength the free energies of the two minima become equal, marking the onset of the abrupt transition between the weakly dressed and strongly dressed states. As stressed elsewhere,[22] the discontinuities registered in such transitions might be the result of the changes in the polaron structure occurring too rapidly to be accurately accounted for by the variational entities used, and our method is not devoid of that. In order to illustrate the character of the dependence on g, in Fig. 1(b) we present the same information for $g=0.5$. For negative ϕ the behavior is qualitatively similar, whereas for positive ϕ the abrupt transitions appear already for rather small values of J/ω. For $g=0$ [Fig. 1(c)] the dependence of λ^* on ϕ is monotonous and does not depend on the sign of ϕ.

The most interesting feature that we observe is the existence of a "dressing minimum" at $\phi=g$. While the value of the relative coupling strength at which it appears, and the absolute value of the minimum might be at least partly an artifact (i.e., the consequence of the approximations made in the derivation of the expression for the bound on free energy to be minimized), the very existence of this minimum seems to be a robust characteristic. When $g\to0$ the feature related to the minimum becomes narrower and narrower, and a singularity remains for $g=0$ [not displayed in Fig. 1(c)].

B. Finite-temperature case

While the zero-temperature self-consistency equation (47) depends on J and ω only through their ratio, its finite-temperature counterpart (52) depends both on J/ω and ω itself (through the Boltzmann factor $e^{-\beta\omega}$ incoming into the expression for U_1). Therefore, it seems natural to look at the solution to this equation for fixed values of J/ω and g, and different nonlocal coupling strengths, expressing temperature in units ω/k_B.

The dependence of λ^* on the temperature for $J/\omega=1$, and different nonlocal coupling strengths (both positive and negative) is depicted in Figs. 2(a)–2(e) for $g=0$, 0.25 and 0.5. What can be clearly observed is that when g and ϕ have the same sign this dependence is monotonous, i.e., λ^* increases monotonously as temperature is increased. However, when $g=0$, or g and ϕ have opposite signs, the dependence is nonmonotonous for smaller absolute values of ϕ, and becomes monotonous for larger absolute values of ϕ.

The variational parameter λ does not have a direct physical meaning. Its implicit dependence on temperature and the parameters of the model (J,ω,g,ϕ) illustrates only the nontrivial character of the phonon dressing of the excitation. To that end, it is of interest to examine the character of the temperature dependence of the renormalized transfer integral $J_{eff}=\langle \tilde{V}_1\rangle_{ph}$, where $\langle \tilde{V}_1\rangle_{ph}$ is given by the expression (42). Figures 3(a)–3(c) depict the ratio J_{eff}/J in the case $J/\omega=1$ for $g=0$ and $g=0.25$ (in the latter case both for positive and negative nonlocal-coupling strengths). It can be observed that for smaller nonlocal-coupling strengths ($|\phi|=0.25,0.5$) the temperature-dependent renormalization is mild (at least up to the higher temperatures $T\simeq 4\omega/k_B$), whereas for larger values of ϕ it becomes much stronger. We also register cases when simultaneous local and nonlocal coupling changes the sign of the electronic transfer integrals [Fig. 3(b)], and when the ratio J_{eff}/J at low temperatures acquires values slightly larger than one [Fig. 3(c)]. While the first feature we ascribe to the nonlocal coupling being an additional transport mechanism, the second one might be, at least to a certain extent, an artifact of the approximations made.

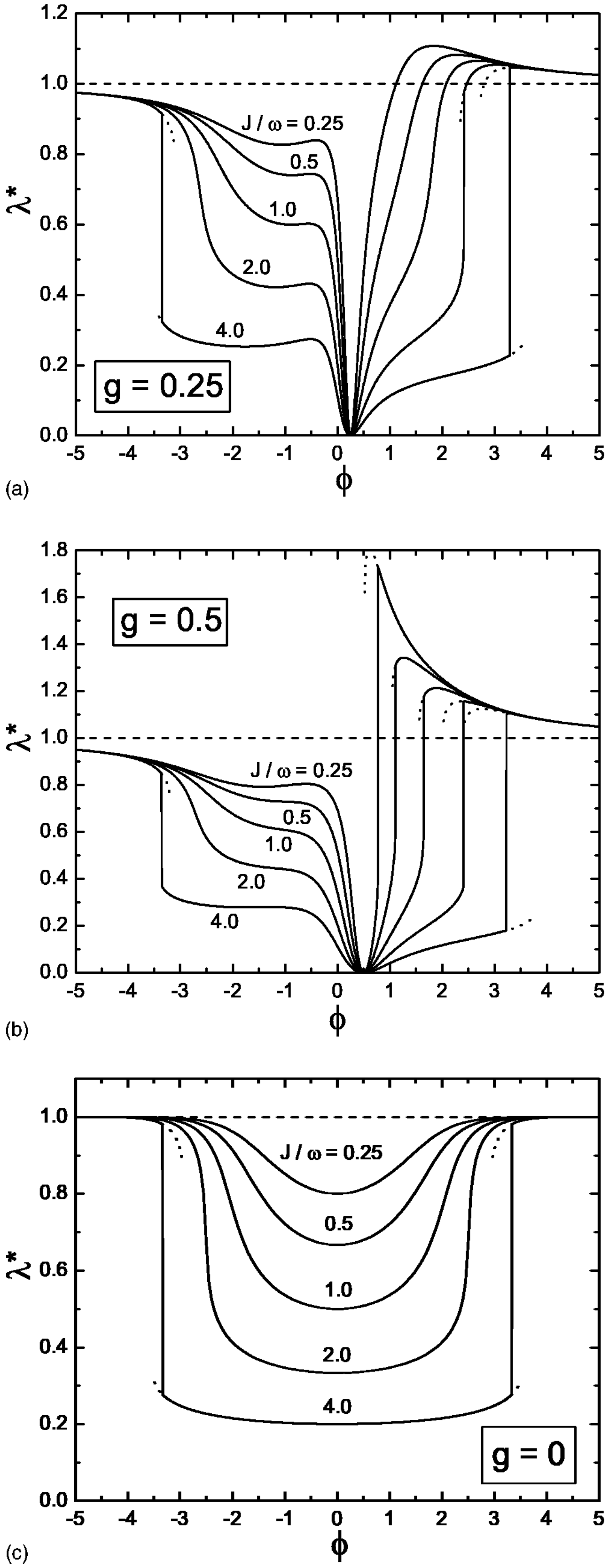

FIG. 1. Optimal dressing parameter λ^* as a function of the nonlocal-coupling strength ϕ, at $T=0$ K, for different values of J/ω and local-coupling strengths (a) $g=0$, (b) $g=0.25$, and (c) $g=0.5$. The dashed line indicates the limiting value $\lambda^*=1$.

C. Phase diagrams

We define the phase boundaries between regions of weak dressing and strong dressing as the parameter values for which $\lambda^*=0.5$ (obviously, there is some arbitrariness in this choice). In Figs. 4(a)–4(c) we plot these phase boundaries in the T-ϕ plane for different values of the ratio J/ω and fixed values of the local-coupling strength ($g=0,0.25,0.5$, respectively). For any particular pair of boundary curves (i.e., for any fixed value of J/ω and the two possible signs of nonlocal-coupling strength) the region between them represents weak dressing and the outer region depicts strong dressing.

For positive values of g, we see that the curves for $J/\omega=1.0,2.0,4.0$ look qualitatively the same. The obvious trend is that when J/ω becomes larger, the weak dressing region becomes more and more extended, which is to be expected. However, for smaller J/ω equal to 0.5 this region is confined to a small, "tonguelike" shaped, closed domain in the T-ϕ plane.

For nonzero g phase boundaries for negative values of ϕ exhibit differences with respect to that of positive values of ϕ in the region of low temperatures ($k_BT\lesssim\omega$). The region

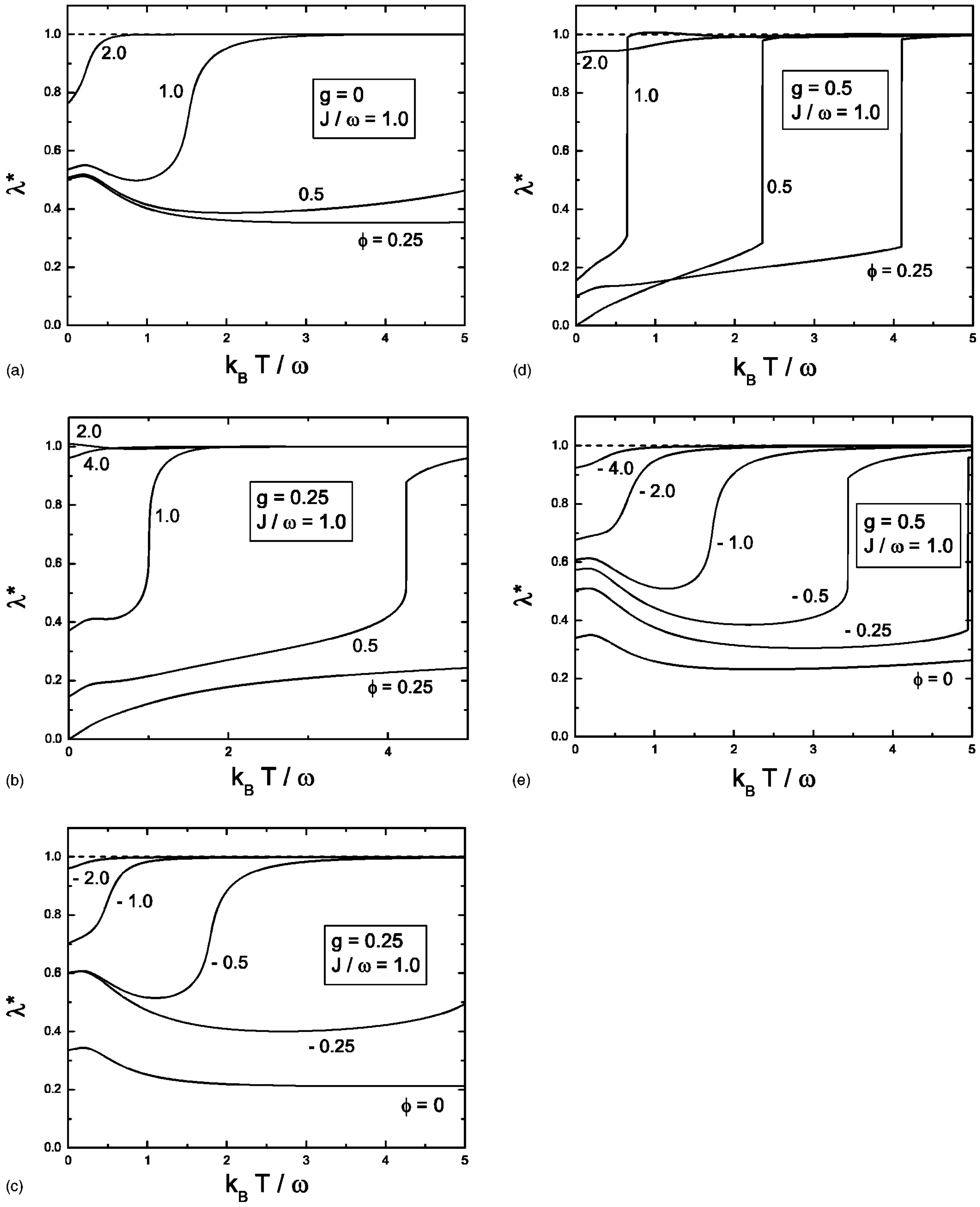

FIG. 2. Optimal dressing parameter λ^* as a function of temperature, at $J/\omega=1$ and different values of the nonlocal-coupling strength ϕ, for local-coupling strengths (a) $g=0$, (b) $g=0.25$ ($\phi>0$), (c) $g=0.25$ ($\phi\leqslant 0$), (d) $g=0.5$ ($\phi>0$), and (e) $g=0.5$ ($\phi\leqslant 0$). The dashed line indicates the limiting value $\lambda^*=1$.

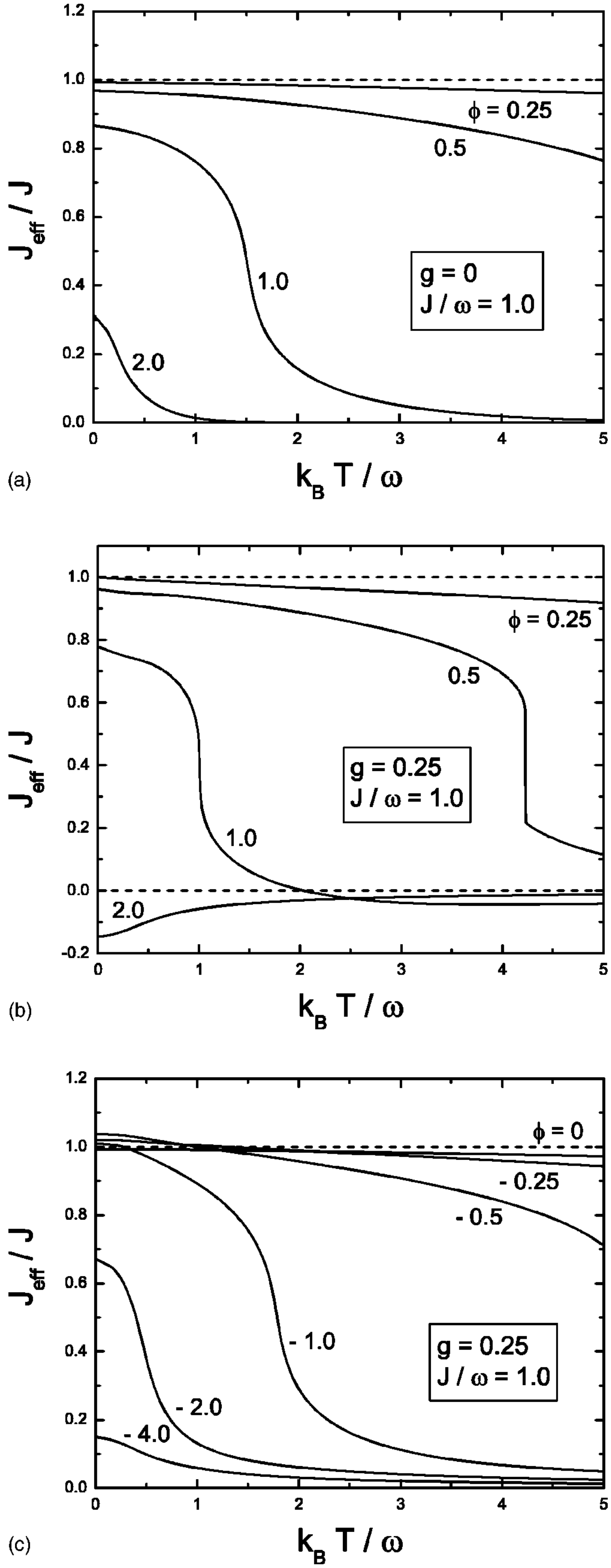

FIG. 3. Relative renormalization J_{eff}/J of the electronic transfer integral as a function of temperature, at $J/\omega = 1$ and different values of the nonlocal-coupling strength ϕ, for local-coupling strengths (a) $g = 0$, (b) $g = 0.25$ ($\phi > 0$), and (c) $g = 0.25$ ($\phi \leqslant 0$).

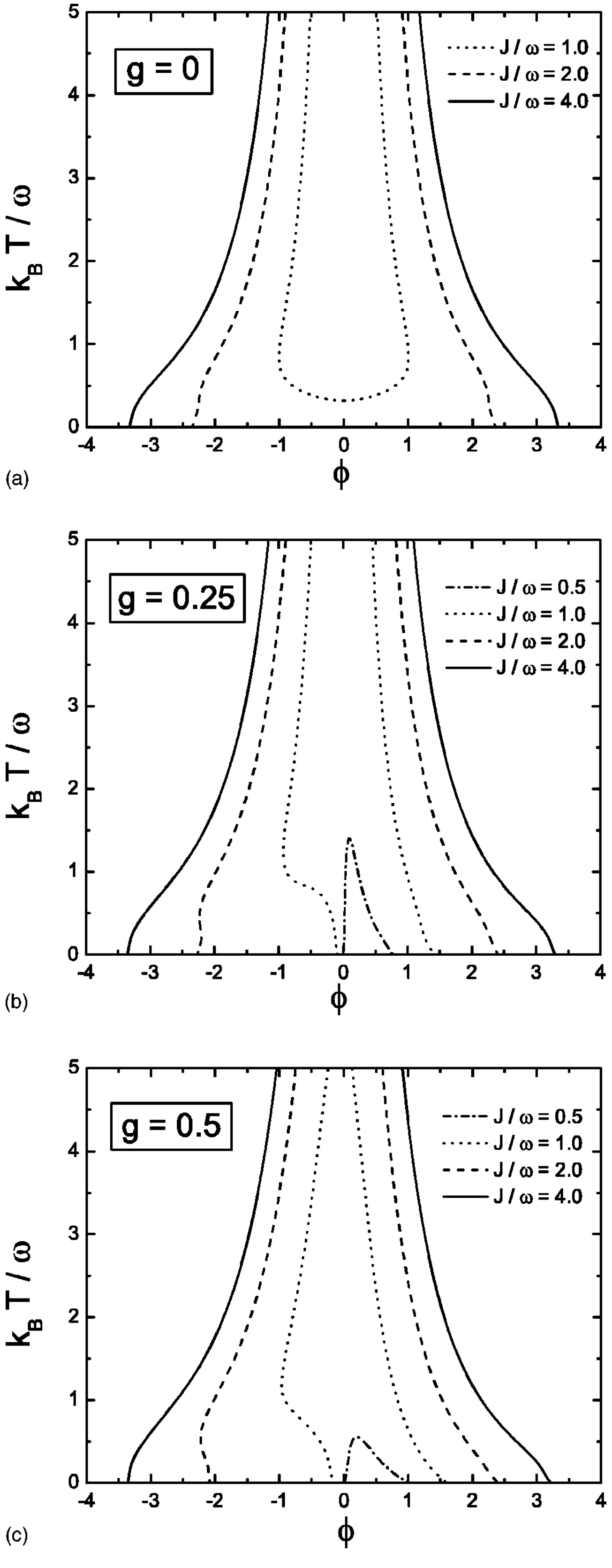

FIG. 4. Phase diagrams indicating regions of strong dressing ($\lambda^* > 0.5$) and weak dressing ($\lambda^* < 0.5$) in the T-ϕ plane, for different values of J/ω and local-coupling strengths (a) $g = 0$, (b) $g = 0.25$, and (c) $g = 0.5$.

corresponding to weak dressing is less extended, the last feature being more and more pronounced as J/ω becomes smaller. However, in the region of higher temperatures the behavior is similar, regardless of the sign of ϕ (i.e., the relative sign of g and ϕ).

V. IMPLICATIONS FOR OPTICAL AND TRANSPORT PROPERTIES

Within the framework of Kubo's linear-response theory, transport coefficients are determined by the corresponding time-correlation functions.[28,29] In particular, dc conductivity is expressed through the current-current autocorrelation function $\langle j(t)j(0)\rangle_H$, where $\langle\cdots\rangle_H$ stands for the thermal expectation value with respect to Hamiltonian H of the system. In the zero-temperature limit, it reduces to the ground-state expectation value.

The utility of the method of canonical transformations in this context is based on the simple property of thermal averages $[\tilde{j}=\exp(S)j\exp(-S),\ \tilde{H}=\exp(S)H\exp(-S)]$

$$\langle j(t)j(0)\rangle_H=\langle\tilde{j}(t)\tilde{j}(0)\rangle_{\tilde{H}}, \tag{55}$$

being an immediate consequence of the relation[20] $\langle A\rangle_H=\langle\tilde{A}\rangle_{\tilde{H}}$ [with $\tilde{A}=\exp(S)A\exp(-S)$], which is valid for an arbitrary operator A and an arbitrary unitary transformation $U=\exp(S)$. When H stands for the local-coupling Holstein Hamiltonian, the corresponding current operator is given by

$$j=ieJ\sum_m a_{m+1}^{\dagger}a_m+\text{H.c.}, \tag{56}$$

and the use of the relation (55) is supplemented by an additional assumption that the thermal average over $\tilde{H}$ can be approximated by taking thermal average over the Hamiltonian in which the electronic transfer term, as transformed by the Lang-Firsov transformation (non-adiabatic terms), is removed.[20] This is justified at least in the adiabatic strong-coupling regime. However, in case nonlocal coupling is taken into account, the current operator adopts the form (the "+" and "−" signs correspond to the symmetric and antisymmetric nonlocal couplings, respectively)

$$j=ie\sum_m [J+\phi(u_{m+1}\pm u_m)]a_{m+1}^{\dagger}a_m+\text{H.c.}, \tag{57}$$

i.e., it depends explicitly on phonon operators through $u_m\equiv b_m^{\dagger}+b_m$. Besides, our generalized canonical transformation does not yield an exact diagonalization in any limit. As a consequence, the straightforward generalization of the aforementioned procedure would necessitate uncontrollable approximations, and is therefore rather unwieldy.

However, the problem can be addressed by computational means, through the device of Lanczos-diagonalization-based calculation of dynamical correlations. This was done by Capone *et al.*[30] for the case of the quantal version of the SSH model (antisymmetric nonlocal coupling), with optical instead of acoustic phonons. They found an evidence for the occurrence of a new, high-energy absorption feature (at energy $4E_p$, where E_p is the polaron binding energy), not present in the local-coupling case, and gave a plausible physical explanation of its nature, in terms of the bond character of nonlocal coupling. In our forthcoming publication[31] we study the extended Holstein model by means of Lanczos-diagonalization, both for symmetric and antisymmetric nonlocal coupling. We calculate the optical conductivity corresponding to this model and corroborate results of Capone *et al.*[30] in the case of antisymmetric nonlocal coupling. We also show that in the case of symmetric nonlocal coupling an analogous high-energy absorption feature does not exist, which is to be expected from the physical circumstances inherent to symmetric coupling. More elaborate discussion we defer to this forthcoming publication.

VI. SUMMARY AND CONCLUSIONS

In the present work we have investigated the influence of simultaneous local and nonlocal electron-phonon (e-ph) coupling on the nature of polaron states, mainly through analytical means. As our point of departure, we have adopted an extended Holstein Hamiltonian and a generalized canonical transformation of the displacement-operator type. In order to allow for an additional flexibility of the transformation parameters, use has been made of the variational principle based upon the Bogoliubov inequality for the Helmholtz free energy of the system. The variational parameter introduced is a measure for the phonon dressing of the polaron. The appealing feature of the variational approach is that it does away with the need to make any assumption about the relative magnitude of the electronic transfer integral J and the phonon energy ω.

We have mainly been interested in the changes of polaron structure resulting from the inclusion of nonlocal e-ph coupling. We find nonmonotonous dependence of the optimal value for the dressing parameter on the nonlocal-coupling strength. Moreover, we observe the existence of a dressing minimum, which in the zero-temperature case goes down to zero, indicating the absence of the bandwidth reduction. We interpret this dressing minimum as a compensation phenomenon between the local and nonlocal e-ph couplings. This compensation phenomenon could be of importance in the area of organic crystals, since weak dressing implies large bandwidths and high mobilities, registered in these narrow-band materials.

The general message of this paper is that the presence of nonlocal e-ph coupling introduces, in certain regimes of the involved physical parameters, qualitative changes into the nature of polaron states. The approximate character of the present treatment makes the obtained results inevitably qualitative. An independent corroboration and quantitative improvement utilizing the computational methods akin to those employed in the local-coupling context[5–7] is needed.

ACKNOWLEDGMENTS

One of the authors (V.M.S.) is indebted to Dr. Franz X. Bronold, and Professor Holger Fehske of the Ernst-Moritz-Arndt-Universität Greifswald for illuminating discussions, and to colleagues Frank Pasveer, Henk Vocks, and Dr. Paul van der Schoot for their congeniality and support throughout the endeavor of making this paper. Likewise, he is grateful to Professor Sava Milošević of the University of Belgrade, whose lectures on quantum statistical physics have been an important source of inspiration behind the methodology brought to bear in the present work.

APPENDIX A: CALCULATION OF THERMAL AVERAGES

While an exact evaluation is not possible, the thermal averages required in this paper are amenable to an approximate calculation at the level of second-order cumulant expansion.[27,33] For an arbitrary operator V and an arbitrary sort of averaging involved, the expansion up till the second-order cumulant reads

$$\langle \exp V\rangle \simeq \exp\{\langle V\rangle + \tfrac{1}{2}(\langle V^2\rangle - \langle V\rangle^2)\}, \tag{A1}$$

which in the case $\langle V\rangle = 0$ goes over to

$$\langle \exp V\rangle \simeq \exp(\tfrac{1}{2}\langle V^2\rangle). \tag{A2}$$

An example when this expansion is exact rather than approximate is the thermal average of $\exp A$, where $A = c_1\hat{a} + c_2\hat{a}^\dagger$ is a linear combination of the harmonic-oscillator creation and annihilation operators, in which case it reduces to the well-known Bloch identity.[34] The multiphonon operators appearing in the nonadiabatic terms of the transformed Holstein Hamiltonian assume such form, with $c_2 = -c_1^*$, characteristic of the displacement operator which generates coherent states when acting on the linear-harmonic-oscillator vacuum.[35] However, in our case one is confronted with the more complicated thermal expectation values.

One type of thermal average we have to perform is

$$\langle \tilde{f}_{mm'}\rangle_{ph} = \langle (e^{C} f e^{-C})_{mm'}\rangle_{ph}, \tag{A3}$$

where $f_{mm'}$ is a number matrix, that is,

$$\langle \tilde{f}_{mm'}\rangle_{ph} = \sum_{n,n'} \Lambda^{nn'}_{mm'} f_{nn'}, \tag{A4}$$

with

$$\Lambda^{nn'}_{mm'} = \langle (e^{C})_{mn}(e^{-C})_{n'm'}\rangle_{ph} = \langle (e^{C-C'})_{mn,n'm'}\rangle_{ph} \tag{A5}$$

representing the shorthand notation in which the primed matrix elements of C are invoked every time C' is encountered. Up to the second-order cumulant (A2), one has (because the odd order cumulants are equal zero, in particular $\langle C\rangle_{ph} = 0$),

$$\begin{aligned}\Lambda^{nn'}_{mm'} &\simeq \exp\langle \tfrac{1}{2}[(C-C')^2]_{mn,n'm'}\rangle_{ph}\\ &= \exp\langle \tfrac{1}{2}(C^2)_{mn}\rangle_{ph}\ \exp\langle \tfrac{1}{2}(C'^2)_{n'm'}\rangle_{ph}\\ &\quad\times \exp\langle -(CC')_{mn,n'm'}\rangle_{ph},\end{aligned} \tag{A6}$$

where, as can routinely be derived,

$$\begin{aligned}\left\langle \frac{1}{2}(C^2)_{mn}\right\rangle_{ph} &= -\lambda^2 \sum_{\mathbf{q},k} g^{\mathbf{q}}_{mk} g^{-\mathbf{q}}_{kn}\left(\frac{1}{2} + N_{\mathbf{q},T}\right),\\ \left\langle \frac{1}{2}(C'^2)_{n'm'}\right\rangle_{ph} &= -\lambda^2 \sum_{\mathbf{q},k'} g^{\mathbf{q}}_{n'k'} g^{-\mathbf{q}}_{k'm'}\left(\frac{1}{2} + N_{\mathbf{q},T}\right),\\ \langle -(CC')_{mn,n'm'}\rangle_{ph} &= 2\lambda^2 \sum_{\mathbf{q}} g^{\mathbf{q}}_{mn} g^{-\mathbf{q}}_{n'm'}\left(\frac{1}{2} + N_{\mathbf{q},T}\right),\end{aligned} \tag{A7}$$

with $N_{\mathbf{q},T}$ representing the thermally averaged phonon occupations.

If the elements of the matrix f depend only on $m-m'$ (translational invariance) one can define $F_{m-m'} \equiv f_{mm'}$ and rewrite Eq. (A4) in the form

$$\langle \tilde{F}_m\rangle_{ph} = \sum_n T_{mn} F_n, \tag{A8}$$

wherein

$$T_{mn} = \sum_{n'} \Lambda^{m0}_{n+n',n'}. \tag{A9}$$

If we assume that in Eq. (A7) the most important contributions come from the terms with $m=n$ and $m'=n'$,[8,19] the matrix T_{mn} becomes diagonal, with elements given by

$$T_{mm} = \exp\left[-\lambda^2 \sum_{\mathbf{q}} \left(\frac{1}{2} + N_{\mathbf{q},T}\right) G^{\mathbf{q}}_{m0}\right], \tag{A10}$$

$$G^{\mathbf{q}}_{mn} \equiv |g^{\mathbf{q}}_{mm} - g^{\mathbf{q}}_{nn}|^2 + \sum_{k\neq m,n} (|g^{\mathbf{q}}_{mk}|^2 + |g^{\mathbf{q}}_{nk}|^2). \tag{A11}$$

Hence, in the Einstein phonon limit ($\omega_{\mathbf{q}} \to \omega$; $N_{\mathbf{q},T} \to N_T$) one obtains

$$\langle \tilde{f}_{mm}\rangle_{ph} \simeq f_{mm}, \tag{A12}$$

$$\langle \tilde{f}_{mn}\rangle_{ph} \simeq e^{-\lambda^2[(1/2)+N_T]\Gamma_{mn}} f_{mn} \quad (m\neq n), \tag{A13}$$

with Γ_{mn} given by

$$\Gamma_{mn} \equiv \sum_{\mathbf{q}} G^{\mathbf{q}}_{mn} = G_{mm} + G_{nn} - g^2_{mn}, \tag{A14}$$

$$G_{mm} \equiv g^2_{mm} + \frac{1}{2}\sum_{k\neq m} g^2_{mk}. \tag{A15}$$

We now turn to the phonon average $\langle \tilde{V}_{mn}\rangle_{ph}$ appearing in Eq. (20):

$$\begin{aligned}\langle \tilde{V}_{mn}\rangle_{ph} = \langle \tilde{\epsilon}_{mn}\rangle_{ph} + \sum_{\mathbf{q}} \omega_{\mathbf{q}} \langle (&\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}} + \tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}} + \tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}}\\ &- b^\dagger_{\mathbf{q}} b_{\mathbf{q}})_{mn}\rangle_{ph}.\end{aligned} \tag{A16}$$

In order to find the thermal average of $(\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}}+\tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}}+\tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}}-b^\dagger_{\mathbf{q}}b_{\mathbf{q}})_{mn}$, we first calculate $\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}}+\tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}})_{mn}\rangle_{ph}$ starting from the operator identity

$$\frac{d}{dx}\langle[e^{xC}(b^\dagger_{\mathbf{q}}g^{\mathbf{q}}+g^{\mathbf{q}}b_{-\mathbf{q}})e^{-xC}]_{mn}\rangle_{ph} =\langle(e^{xC}[C,b^\dagger_{\mathbf{q}}g^{\mathbf{q}}+g^{\mathbf{q}}b_{-\mathbf{q}}]e^{-xC})_{mn}\rangle_{ph}. \tag{A17}$$

On account of the fact that $[C,b^\dagger_{\mathbf{q}}]=[C,b_{-\mathbf{q}}]=-\lambda g^{-\mathbf{q}}$, this can easily be reduced to

$$\frac{d}{dx}\langle[e^{xC}(b^\dagger_{\mathbf{q}}g^{\mathbf{q}}+g^{\mathbf{q}}b_{-\mathbf{q}})e^{-xC}]_{mn}\rangle_{ph}=-2\lambda\langle(\tilde{g}^{\mathbf{q}}\tilde{g}^{-\mathbf{q}})_{mn}\rangle_{ph}. \tag{A18}$$

Upon integrating the last equation between 0 and 1, one finds

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}}+\tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}})_{mn}\rangle_{ph}=-2\lambda\int_0^1 dx\langle(\tilde{g}^{\mathbf{q}}\tilde{g}^{-\mathbf{q}})_{mn}\rangle_{ph}. \tag{A19}$$

As a special case of Eqs. (A12) and (A13), it holds that

$$\langle(\tilde{g}^{\mathbf{q}}\tilde{g}^{-\mathbf{q}})_{mm}\rangle_{ph}=(g^{\mathbf{q}}g^{-\mathbf{q}})_{mm}, \tag{A20}$$

$$\langle(\tilde{g}^{\mathbf{q}}\tilde{g}^{-\mathbf{q}})_{mn}\rangle_{ph}=e^{-\lambda^2[(1/2)+N_T]\Gamma_{mn}}(g^{\mathbf{q}}g^{-\mathbf{q}})_{mn}\quad (m\neq n). \tag{A21}$$

On performing the integral in Eq. (A19), making use of the last two equations, it follows that

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}}+\tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}})_{mm}\rangle_{ph}=-2\lambda(g^{\mathbf{q}}g^{-\mathbf{q}})_{mm} \tag{A22}$$

and for $m\neq n$,

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}}+\tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}})_{mn}\rangle_{ph}=-\sqrt{\frac{\pi}{U_{mn}}}\,\mathrm{erf}(\lambda\sqrt{U_{mn}})(g^{\mathbf{q}}g^{-\mathbf{q}})_{mn}, \tag{A23}$$

where $\mathrm{erf}x=(2/\sqrt{\pi})\int_0^x e^{-t^2}\,dt$ is the error function, and the abbreviation $U_{mn}\equiv(1/2+N_T)\Gamma_{mn}$ has been introduced.

The expression for the thermal average $\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}}-b^\dagger_{\mathbf{q}}b_{\mathbf{q}})_{mn}\rangle_{ph}$ can be obtained in a similar manner: the operator identity

$$\frac{d}{dx}\langle[e^{xC}(b^\dagger_{\mathbf{q}}b_{\mathbf{q}})e^{-xC}]_{mn}\rangle_{ph} =-\lambda\langle[e^{xC}(b^\dagger_{\mathbf{q}}g^{\mathbf{q}}+g^{\mathbf{q}}b_{-\mathbf{q}})e^{-xC}]_{mn}\rangle_{ph}, \tag{A24}$$

when integrated between 0 and 1, leads to

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}}-b^\dagger_{\mathbf{q}}b_{\mathbf{q}})_{mn}\rangle_{ph} =-\lambda\int_0^1 dx\langle[e^{xC}(b^\dagger_{\mathbf{q}}g^{\mathbf{q}}+g^{\mathbf{q}}b_{-\mathbf{q}})e^{-xC}]_{mn}\rangle_{ph}. \tag{A25}$$

On making the replacement $C\rightarrow xC$ in Eqs. (A22) and (A23), one obtains

$$\langle[e^{xC}(b^\dagger_{\mathbf{q}}g^{\mathbf{q}}+g^{\mathbf{q}}b_{-\mathbf{q}})e^{-xC}]_{mm}\rangle_{ph}=-2\lambda x(g^{\mathbf{q}}g^{-\mathbf{q}})_{mm} \tag{A26}$$

for $m=n$ and

$$\langle[e^{xC}(b^\dagger_{\mathbf{q}}g^{\mathbf{q}}+g^{\mathbf{q}}b_{-\mathbf{q}})e^{-xC}]_{mn}\rangle_{ph} =-\sqrt{\frac{\pi}{U_{mn}}}\,\mathrm{erf}(\lambda\sqrt{U_{mn}}x)(g^{\mathbf{q}}g^{-\mathbf{q}})_{mn} \tag{A27}$$

for $m\neq n$. Upon executing the integral in Eq. (A19), with the aid of Eqs. (A26) and (A27), respectively, it follows that

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}}-b^\dagger_{\mathbf{q}}b_{\mathbf{q}})_{mm}\rangle_{ph}=\lambda^2(g^{\mathbf{q}}g^{-\mathbf{q}})_{mm} \tag{A28}$$

and for $m\neq n$,

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}})_{mn}\rangle_{ph}=\left[\sqrt{\frac{\pi}{U_{mn}}}\lambda\,\mathrm{erf}(\lambda\sqrt{U_{mn}})+\frac{e^{-\lambda^2U_{mn}}-1}{U_{mn}}\right] \times(g^{\mathbf{q}}g^{-\mathbf{q}})_{mn}, \tag{A29}$$

where the last equation has been derived by making use of the identity

$$\int_0^a \mathrm{erf}\,u\,du=a\,\mathrm{erf}\,a+\frac{1}{\sqrt{\pi}}(e^{-a^2}-1). \tag{A30}$$

Summing up the results (A22) and (A28), one finds

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}}+\tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}}+\tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}}-b^\dagger_{\mathbf{q}}b_{\mathbf{q}})_{mm}\rangle_{ph} =(\lambda^2-2\lambda)(g^{\mathbf{q}}g^{-\mathbf{q}})_{mm}. \tag{A31}$$

Similarly, from Eqs. (A23) and (A29) it follows that

$$\langle(\tilde{b}^\dagger_{\mathbf{q}}\tilde{g}^{\mathbf{q}}+\tilde{g}^{\mathbf{q}}\tilde{b}_{-\mathbf{q}}+\tilde{b}^\dagger_{\mathbf{q}}\tilde{b}_{\mathbf{q}}-b^\dagger_{\mathbf{q}}b_{\mathbf{q}})_{mn}\rangle_{ph} =\left[\frac{e^{-\lambda^2U_{mn}}-1}{U_{mn}}+\sqrt{\frac{\pi}{U_{mn}}}(\lambda-1)\mathrm{erf}(\lambda\sqrt{U_{mn}})\right] \times(g^{\mathbf{q}}g^{-\mathbf{q}})_{mn}. \tag{A32}$$

Upon inserting Eqs. (A31) and (A32), along with Eqs. (A12) and (A13), into the expression (42), one finally obtains

$$\langle\tilde{V}_{mm}\rangle_{ph}=\varepsilon+(\lambda^2-2\lambda)\Delta \tag{A33}$$

and, likewise, for $m\neq n$,

$$\langle\tilde{V}_{mn}\rangle_{ph}=\varepsilon_{mn}e^{-\lambda^2U_{mn}}+\left[\frac{e^{-\lambda^2U_{mn}}-1}{U_{mn}} +\sqrt{\frac{\pi}{U_{mn}}}(\lambda-1)\mathrm{erf}(\lambda\sqrt{U_{mn}})\right]\Delta_{mn}, \tag{A34}$$

wherein Δ_{mn} and Δ are given by

$$\Delta_{mn}\equiv\omega\sum_{\mathbf{q}}\;(g^{\mathbf{q}}g^{-\mathbf{q}})_{mn}\,, \tag{A35}$$

$$\Delta\equiv\Delta_{mm}\,. \tag{A36}$$

APPENDIX B: EXPRESSIONS FOR Γ_1, Δ, AND Δ_1

We begin by noting that the general expression (A11) in the case of $G^{\mathbf{q}}_{m,m\pm1}$ reduces to

$$G^{\mathbf{q}}_{m,m\pm1}=|g^{\mathbf{q}}_{mm}-g^{\mathbf{q}}_{m\pm1,m\pm1}|^2+|g^{\mathbf{q}}_{m,m\pm1}|^2+|g^{\mathbf{q}}_{m\pm1,m\pm2}|^2. \tag{B1}$$

On taking into account that $|g^{\mathbf{q}}_{m,m\pm1}|^2=|g^{\mathbf{q}}_{m\pm1,m\pm2}|^2$, the last equation can be rewritten as

$$G^{\mathbf{q}}_{m,m\pm1}=|g^{\mathbf{q}}_{mm}-g^{\mathbf{q}}_{m\pm1,m\pm1}|^2+2|g^{\mathbf{q}}_{m,m\pm1}|^2. \tag{B2}$$

With the general form of the **q**-dependent e-ph coupling constants, and the notation $g_{mm}\equiv g$, $g_{m,m\pm1}\equiv\phi$, it is straightforward to obtain

$$|g^{\mathbf{q}}_{mm}-g^{\mathbf{q}}_{m\pm1,m\pm1}|^2=2g^2N^{-1}[1-\cos(\mathbf{q}\cdot\mathbf{a})], \tag{B3}$$

$$|g^{\mathbf{q}}_{m,m\pm1}|^2=\phi^2N^{-1}[1+\cos(\mathbf{q}\cdot\mathbf{a})]/2, \tag{B4}$$

which routinely leads to

$$G^{\mathbf{q}}_{m,m\pm1}=N^{-1}[2g^2+\phi^2-(2g^2-\phi^2)\cos(\mathbf{q}\cdot\mathbf{a})]. \tag{B5}$$

Hence, one readily obtains

$$\Gamma_1\equiv\sum_{\mathbf{q}}\;G^{\mathbf{q}}_{m,m\pm1}=2g^2+\phi^2. \tag{B6}$$

For $\Delta_{m,m}\equiv\Delta$ and $\Delta_{m,m\pm1}\equiv\Delta_1$ one has, respectively,

$$\Delta=\omega\sum_{\mathbf{q}}\;(g^{\mathbf{q}}_{m,m+1}g^{-\mathbf{q}}_{m+1,m}+g^{\mathbf{q}}_{m,m-1}g^{-\mathbf{q}}_{m-1,m}+g^{\mathbf{q}}_{m,m}g^{-\mathbf{q}}_{m,m}), \tag{B7}$$

$$\Delta_1=\omega\sum_{\mathbf{q}}\;(g^{\mathbf{q}}_{mm}g^{-\mathbf{q}}_{m,m\pm1}+g^{\mathbf{q}}_{m,m\pm1}g^{-\mathbf{q}}_{m\pm1,m\pm1}), \tag{B8}$$

which can easily be reduced to

$$\Delta=\omega N^{-1}\sum_{\mathbf{q}}\;\{\phi^2[1+\cos(\mathbf{q}\cdot\mathbf{a})]+g^2\}, \tag{B9}$$

$$\Delta_1=\omega N^{-1}\sum_{\mathbf{q}}\;g\phi[1+\cos(\mathbf{q}\cdot\mathbf{a})]. \tag{B10}$$

Upon executing the **q** sums in the last two equations, one finally finds

$$\Delta=\omega(g^2+\phi^2), \tag{B11}$$

$$\Delta_1=\omega g\phi. \tag{B12}$$

---

*Author to whom correspondence should be addressed. Electronic mail: v.s.stojanovic@tue.nl

[1] T. Holstein, Ann. Phys. (N.Y.) **8**, 343 (1959).

[2] I.G. Lang and Yu.A. Firsov, Zh. Éksp. Teor. Fiz. **43**, 1843 (1962). [Sov. Phys. JETP **16**, 1301 (1963)].

[3] Yu.A. Firsov, *Polarons* (Mir, Moscow, 1975) (in Russian).

[4] Yu.A. Firsov, Semiconductors **29**, 515 (1995).

[5] H. De Raedt and A. Lagendijk, Phys. Rev. B **30**, 1671 (1984).

[6] G. Wellein and H. Fehske, Phys. Rev. B **58**, 6208 (1998).

[7] E. Jeckelmann and S.R. White, Phys. Rev. B **57**, 6376 (1998).

[8] K. Hannewald, V.M. Stojanović, J.M.T. Schellekens, P.A. Bobbert, G. Kresse, and J. Hafner, Phys. Rev. B **69**, 075211 (2004).

[9] M. Pope and C.E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, Oxford, 1999).

[10] T.-M. Wu, D.W. Brown, and K. Lindenberg, Phys. Rev. B **47**, 10 122 (1993).

[11] K.S. Song and R.T. Williams, *Self-Trapped Excitons* (Springer-Verlag, Berlin, 1996).

[12] W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).

[13] A.J. Heeger, S. Kivelson, J.R. Schrieffer, and W.P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[14] L. Friedman, Phys. Rev. **140**, A1649 (1965).

[15] P. Gosar and S.-I. Choi, Phys. Rev. **150**, 529 (1966).

[16] H. Sumi, Solid State Commun. **28**, 309 (1978); J. Chem. Phys. **70**, 3775 (1979).

[17] R.W. Munn and R. Silbey, J. Chem. Phys. **83**, 1843 (1985); **83**, 1854 (1985).

[18] Y. Zhao, D.W. Brown, and K. Lindenberg, J. Chem. Phys. **100**, 2335 (1993).

[19] K. Hannewald, P.A. Bobbert, and V.M. Stojanović, J. Phys.: Condens. Matter **16**, 2023 (2004).

[20] M. Wagner, *Unitary Transformations in Solid State Physics* (North-Holland, Amsterdam, 1986).

[21] D. Yarkony and R. Silbey, J. Chem. Phys. **65**, 1042 (1976).

[22] Y. Zhao, D.W. Brown, and K. Lindenberg, J. Chem. Phys. **106**, 2728 (1997).

[23] Y. Toyozawa, Prog. Theor. Phys. **26**, 29 (1961).

[24] Y. Zhao, D.W. Brown, and K. Lindenberg, J. Chem. Phys. **107**, 3159 (1997).

[25] Li-Chung Ku, S.A. Trugman, and J. Bonča, Phys. Rev. B **65**, 174306 (2002).

[26] M.D. Girardeau and R.M. Mazo, in *Advances in Chemical Physics*, edited by I. Prigogine and S.A. Rice (Wiley, New York, 1973), Vol. XXIV.

[27] S. Milošević, *Quantum Statistical Physics* (Belgrade, 2000).

[28] D.N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974).

[29] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, New York, 2001).

[30] M. Capone, W. Stephan, and M. Grilli, Phys. Rev. B **56**, 4484 (1997).

[31] H. Vocks and V.M. Stojanović (unpublished).

[32] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic Press, New York, 1980).

[33] Th. Niemeyer and J.M.J. van Leeuwen, Physica **71**, 17 (1974).

[34] G. Grosso and G.P. Parravicini, *Solid State Physics* (Academic Press, San Diego, 2000).

[35] W.M. Zhang, D.H. Feng, and R. Gilmore, Rev. Mod. Phys. **62**, 867 (1990).