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## Variational considerations in the study of carrier transport in organic crystals

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A variational approach is used to investigate consequences of electron-phonon interactions between a charge carrier and multiple (specifically two) phonon branches. Phase diagrams are obtained and the nature of the transition from undressed to dressed phases of the carrier is studied with their help. No sharp transition between singly dressed and doubly dressed phases occurs. The effective carrier bandwidth, reduced by strong coupling to the high-frequency branch is found to be stable with respect to small to intermediate values of additional coupling to the low-frequency branch. This finding lends support to transport calculations based on the idea that carriers in a polaron band are dressed by one phonon mode and scattered by another.

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### I. INTRODUCTION

Despite intense investigations carried out by a number of researchers over the years,<sup>1-12</sup> several questions concerning charge carrier transport in organic crystals have remained unanswered. Some of them concern general issues while others deal with specific materials. An example of the latter, generally considered solved in the literature,<sup>13-15</sup> is the nature of the charge carrier in the particular aromatic hydrocarbon crystal naphthalene. Initial debates regarding the possibility of a band-to-hopping transition in this system<sup>16</sup> evolved into questions about the degree to which charge transport was polaronic, i.e., clothed by the vibrational modes of the crystal. An extensive study<sup>9,10</sup> carried out a couple of decades ago led to the conclusion<sup>10,13</sup> that charge carriers in naphthalene are indeed polaronic, and that the temperature dependence of the vibrationally narrowed band plays an important role in determining the corresponding temperature dependence of the mobilities. Similar questions have been raised<sup>15,17</sup> about the nature of carriers in specific disordered materials. Recently, studies have led to the conclusion that carriers are also polaronic<sup>18</sup> in those disordered materials.

The purpose of the present paper is an investigation of a general rather than such a material-specific issue. We have recently constructed<sup>19</sup> a detailed theory of transport of a carrier which is dressed by phonons of one branch while being scattered by phonons of another branch. The present investigation addresses the issue of to what extent such a picture can be justified. We study here what happens when a carrier interacts strongly with more than one phonon branch in such a way that, by itself, one branch interaction would lead to carrier dressing (polaronic transport of the carrier), while the other, by itself, would lead to mere scattering (free carrier transport).<sup>20</sup> We use a variational approach.

Common to most of the previous variational treatments<sup>1-4,6,8</sup> is the finding that two qualitatively different kinds of variational solution may result, depending upon the magnitude of the parameters of interest. These parameters include the bare intersite transfer matrix element  $V_0$ , the dimensionless carrier-phonon coupling constant  $g$ , the phonon frequency (equivalently energy<sup>21</sup>)  $\omega$ , and the tem-

perature  $T$ . For small coupling  $g \ll 1$  and large bandwidths  $V_0 > \omega$ , variational solutions predict weakly dressed, essentially free, carrier states with an effective intersite matrix element  $V_{\text{eff}} \approx V_0$  that is, to lowest order, insensitive to the magnitude of  $g$  and  $\omega$ . By contrast, for large coupling  $g$  and small  $V_0 < \omega$ , variational treatments predict the existence of strongly narrowed polaron states with an effective intersite matrix element that is fully dressed, or very nearly so

$$V_{\text{eff}} \approx V_0 \exp[-g^2 \coth(\beta\omega/2)]. \quad (1)$$

In some of these treatments, as  $g$  is increased at fixed  $\omega$ ,  $V_0$ , and  $T$ , a transition is predicted to occur.<sup>2</sup> What this means is that, at a critical coupling  $g$ , the effective matrix element  $V_{\text{eff}}$  is predicted to collapse from its bare value  $V_0$  to the strongly reduced value associated with the vibrationally narrowed polaron bandwidth. The existence (and sharpness) of such a transition has been a subject of some debate. Conventional wisdom based upon the adiabatic approximation is that in one dimension, all polaron states should have a finite radius, but that in dimensions greater than one a sharp transition exists between free and self-trapped states. Extensive recent studies by the authors of Ref. 4, suggest, however, that the zero temperature “self-trapping transition” in all dimensions is actually a smooth, but possibly rapid, crossover from large polaron states at low coupling to small polaron states at large coupling. In other treatments, it has been argued<sup>8</sup> that in higher dimensions there exists an extended regime where both kinds of states can coexist, with smoothly varying free energy differences and populations in each, in which the two states exchange majority/minority status in the neighborhood of the “transition.” We will follow the standard practice in the literature and use the term “transition” to refer to the crossover between these characteristically different regimes.

In the present paper, we consider a carrier in three dimensions interacting with two narrow-bandwidth optical phonon branches of mean frequencies  $\omega_1$  and  $\omega_2$  via respective coupling constants  $g_1 > 1$  and  $g_2 < g_1$ . For the sake of simplicity, both phonon bandwidths are assumed to be zero (Einstein oscillators.) Even within this highly simplified model, interesting questions arise regarding the interplay of the two phonon modes, and the kinds of bare-dressed transitions that can

occur as the coupling constants  $g_1$  and  $g_2$  are varied. Do regimes exist in which  $g_1$  and  $g_2$  are individually not large enough to produce a narrowed band, but do so in combination? Our studies, which are carried out through a straightforward generalization of the temperature dependent variational treatment of Yarkony and Silbey,<sup>2</sup> indeed confirm the existence of such a regime. If  $g_1$  is large enough to narrow the band, and  $g_2$  is not, is the variationally determined bandwidth associated with  $g_1$  *stable* with respect to changes in  $g_2$ ? Specifically, will a collapse occur to a doubly narrowed regime only after  $g_2$  increases to a critical value, or will the addition of a small additional coupling  $g_2$  to an already narrowed band lead to further reduction in bandwidth as a function of  $g_2$ ? Our studies suggest that what actually obtains lies at the border of these two possibilities:  $V_{\text{eff}}$  is indeed stable with respect to *infinitesimal* increases in  $g_2$ , in the sense that

$$\left. \frac{\partial V_{\text{eff}}(g_1, g_2)}{\partial g_2} \right|_{g_2=0} = 0,$$

but, as a consequence, there are only two regions in the  $g_1$ - $g_2$  phase diagram: undressed and dressed. Except along the axes where either  $g_1$  or  $g_2$  vanish, there do *not* appear to exist separate “singly dressed” and “doubly dressed” regions. Thus, our results lend support to the idea<sup>19</sup> that carriers may be dressed by strong interactions with phonons of one mode while being merely scattered by another, provided that the coupling constant associated with the scattering mode is sufficiently small to be treated perturbatively. The variational treatment that we employ to explore these issues is intended to provide a qualitative indication of the crossover behavior that occurs, and of the different regimes that can exist in the model. Sophisticated, numerically intensive treatments such as those of Refs. 4 and 5 can always be used for obtaining details and quantitative predictions. The simpler treatment that we present here provides clearer insight and allows for a straightforward investigation of *temperature* dependent properties of the polaronic band narrowing that have not, as of yet, been accessible through zero temperature calculations of polaron eigenfunctions.

## II. VARIATIONAL TREATMENT FOR MULTIPLE BRANCHES OF EINSTEIN OSCILLATORS

The standard electron-phonon Hamiltonian  $H = H_{\text{el}} + H_{\text{ph}} + H_{\text{el-ph}}$  describes an electron moving among the sites of a lattice of  $N$  sites. Here

$$H_{\text{el}} = \sum_{\langle m,n \rangle} V_{mn} a_m^\dagger a_n,$$

describes the bare electron transport, while

$$H_{\text{ph}} = \sum_{q,\alpha} \omega_{q,\alpha} b_{q,\alpha}^\dagger b_{q,\alpha}, \quad (2)$$

$$H_{\text{el-ph}} = N^{-1/2} \sum_{m,q,\alpha} g_{q,\alpha} \omega_{q,\alpha} e^{iqm} a_m^\dagger a_m (b_{q,\alpha} + b_{-q,\alpha}^\dagger) \quad (3)$$

describe the multiple phonon branches with which the charge carrier interacts. In these expressions,  $a_m^\dagger$  creates a carrier at

crystal site  $m$ ,  $b_{q,\alpha}^\dagger$  creates a phonon of wave vector  $q$  and frequency  $\omega_{q,\alpha}$  in branch  $\alpha$ , the  $m$  sum is over nearest neighbors (for simplicity), and translational invariance requires the coupling constants to satisfy the condition  $g_{q,\alpha} = g_{-q,\alpha}^*$ . We ignore spin and work in the subspace containing one particle (carrier).

Following the basic procedure of Yarkony and Silbey,<sup>2</sup> we apply to  $H$  a *partial* polaron dressing transformation

$$U = \exp \left[ -N^{-1/2} \sum_{\alpha,q,m} f_{q,\alpha} \omega_{q,\alpha} e^{iqm} N_m (b_{q,\alpha} - b_{-q,\alpha}^\dagger) \right] \quad (4)$$

involving a set of phonon displacement parameters  $f_{q,\alpha} = f_{-q,\alpha}^*$ , leaving the transformed Hamiltonian

$$\begin{aligned} \tilde{H} = & H_{\text{ph}} + \sum_{\langle m,n \rangle} V_{mn} \theta_m^\dagger \theta_n a_m^\dagger a_n + N^{-1} \sum_q \omega_{q,\alpha} (f_{q,\alpha} - 2g_{q,\alpha}) f_{-q,\alpha} \\ & + N^{-1/2} \sum_q \omega_{q,\alpha} N_m (g_{q,\alpha} - f_{q,\alpha}) e^{iqm} (b_{q,\alpha} - b_{-q,\alpha}^\dagger) \end{aligned} \quad (5)$$

expressed in terms of the original electronic and oscillator operators, with  $H_{\text{ph}}$  as given in Eq. (2). In this last equation, the operators

$$\theta_m = \exp \left[ N^{-1/2} \sum_{\alpha,q} f_{q,\alpha} e^{iqm} (b_{q,\alpha} - b_{-q,\alpha}^\dagger) \right] \quad (6)$$

take into account the motion of the phonon cloud that moves along with the carrier. The goal of the variational calculation is to optimize the parameters  $f_{q,\alpha}$ , in order to find the best zeroth order description of the system. This is done by minimizing the Bogulubov bound  $A_B = -\beta^{-1} \ln \text{Tr}[e^{-\beta \tilde{H}_0}] > A = -\beta^{-1} \ln \text{Tr}[e^{-\beta \hat{H}}]$  for the free energy  $A$  of the system evaluated at temperature  $T = (k_B \beta)^{-1}$ , in which  $k_B$  is Boltzmann's constant, and  $H_0 = \langle \hat{H} \rangle = Z_{\text{ph}}^{-1} \text{Tr}[\hat{H} e^{-\beta H_{\text{ph}}}]$  is the thermal average of  $\hat{H} = \langle \hat{H} \rangle + (\hat{H} - \langle \hat{H} \rangle)$  taken with respect to the phonon part of the Hamiltonian. Our generalization of this procedure to treat the case of multiple phonon branches and a three-dimensional isotropic electronic band interacting locally ( $g_{q,\alpha} = g_\alpha$ ) with dispersionless oscillators ( $\omega_{q,\alpha} = \omega_\alpha$ ), results in

$$f_{q,\alpha} = g_\alpha \left\{ 1 + \frac{1}{2} \left[ \frac{2\beta |\tilde{V}| I_1(2\beta |\tilde{V}|)}{I_0(2\beta |\tilde{V}|)} \right] \left[ \frac{\coth(\beta \omega_\alpha / 2)}{\beta \omega_\alpha / 2} \right] \Sigma(q) \right\}^{-1} \quad (7)$$

$$= g_\alpha \left[ 1 + \frac{1}{2} \lambda(\tilde{v}) \mu(\tilde{\omega}_\alpha) \Sigma(q) \right]^{-1}. \quad (8)$$

This condition<sup>2</sup> allows us to determine the values of the variational parameters  $f_{q,\alpha}$  for which  $A_B$  is a local extremum. Here  $I_n(x)$  is the modified Bessel function of order  $n$ ,

$$\tilde{V} = V \exp \left[ -\frac{1}{3N} \sum_{\alpha,q} |f_{q,\alpha}|^2 \coth(\beta \omega_\alpha / 2) \Sigma(q) \right] \quad (9)$$

is the thermally averaged matrix element for motion associated with the unitary transformation (4),  $\Sigma(q) = \sum_{\gamma=1}^3 (1 - \cos q_\gamma)$  is a structure factor associated with the nearest-neighbor lattice, and  $q_\gamma$  is the component of the three-dimensional wave vector  $q$  along crystal axis  $\gamma$ . In Eq. (8)

we have introduced the dimensionless quantities

$$\tilde{v} = \beta\tilde{V}, \quad \tilde{\omega}_\alpha = \beta\omega_\alpha \quad (10)$$

and the functions  $\lambda(x) = 2xI_1(2x)/I_0(2x)$ , and  $\mu(x) = 2 \coth(x/2)/x$ . In our analysis, we do not assume in advance that the *variational parameters*  $f_{q,\alpha}$  are independent of  $q$ . Equation (8) is only an implicit equation for determining the  $f_{q,\alpha}$ , since the right hand side depends on the quantity  $\tilde{v}$ , which itself depends upon the values of *all* of the  $f_{q,\alpha}$  through Eqs. (10) and (9). Introducing  $v_0 = \beta V_0$ , however, we can use these equations to combine all of the Eq. (7) into a single implicit equation for the reduced matrix element

$$\begin{aligned} \tilde{v} &= \beta V_0 \exp \left[ -\frac{1}{3N} \sum_{\alpha,q} |f_{q,\alpha}|^2 \coth(\beta\omega_\alpha/2) \Sigma(q) \right] \\ &= v_0 \exp \left[ -\sum_{\alpha} g_\alpha^2 \coth(\beta\omega_\alpha/2) S_\alpha(\tilde{v}) \right], \end{aligned} \quad (11)$$

where

$$\begin{aligned} S_\alpha(\tilde{v}) &= \frac{1}{3N} \sum_q |f_{q,\alpha}/g_\alpha|^2 \Sigma(q) \\ &= \frac{1}{3} \int \frac{d^3q}{(2\pi)^3} \frac{\Sigma(q)}{\left[ 1 + \frac{1}{2} \lambda(\tilde{v}) \mu(\tilde{\omega}_\alpha) \Sigma(q) \right]^2}. \end{aligned} \quad (12)$$

In the last term of Eq. (12), we have taken the continuum limit in  $q$  space, and used the formal expression for  $f_{q,\alpha}$  from Eq. (8). When Eq. (12) is inserted into Eq. (11), the latter becomes a closed expression for determining the stationary value  $\tilde{v}$ . In practice, using numerical integration to evaluate Eq. (12), it is straightforward to search numerically for the value of  $\tilde{v}$  between  $v_0$ , and  $\tilde{v}_{\text{full}}$  given by

$$\tilde{v}_{\text{full}} = v_0 \exp \left[ -\sum_{\alpha} g_\alpha^2 \coth(\beta\omega_\alpha/2) \right]. \quad (13)$$

Equation (11) determines the values of  $\tilde{v}$  for which the free energy bound is stationary, not necessarily a minimum. Accordingly, once the value  $\tilde{v}$  satisfying Eq. (11) is found for a given set of parameters  $\{g_\alpha, \omega_\alpha, V_0, T\}$ , the relevant parts of its free energy bound<sup>2</sup>

$$\begin{aligned} \beta A_B^{(e\text{-ph})} &= -3 \ln I_0(2\tilde{v}) + N^{-1} \sum_{\alpha,q} \beta \omega_\alpha |f_{q,\alpha}|^2 \\ &\quad - 2N^{-1} \sum_{\alpha,q} \beta \omega_\alpha g_{q,\alpha} f_{-q,\alpha} \end{aligned} \quad (14)$$

must be compared with the corresponding expressions

$$\beta A_B^{(0)} = -3 \ln I_0(2v_0) \quad (15)$$

and

$$\beta A_B^{(\text{full})} = -3 \ln I_0(2\tilde{v}) - \sum_{\alpha} g_\alpha^2 \omega_\alpha \quad (16)$$

for the ‘‘end points,’’ corresponding in Eq. (15) to the uncoupled system ( $f_{q,\alpha} = 0, \tilde{v} = v_0$ ), and in Eq. (16) to the fully coupled system ( $f_{q,\alpha} = g_\alpha, \tilde{v} = \tilde{v}_{\text{full}}$ ). Of these three possibilities, the one with the lowest value for the free-energy bound

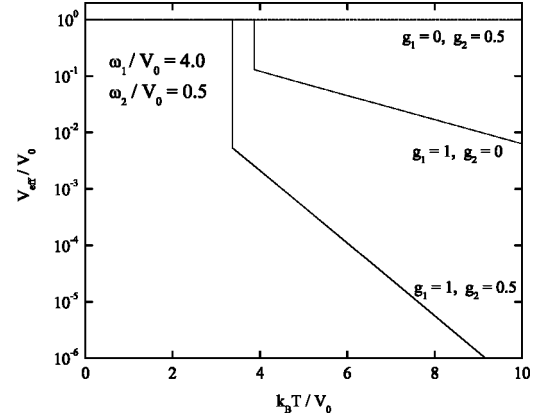


FIG. 1. Plot of  $V_{\text{eff}}/V_0$ , the effective carrier bandwidth relative to its bare value, as a function of the temperature  $T$ , measured in units of  $V_0/k_B$ . The strongly coupled high-frequency branch has  $\omega_1 = 4V_0$  and  $g_1 = 2$ . The weakly coupled low-frequency branch has  $\omega_2 = V_0/5$  and  $g_2 = 0.5$ . We show the bandwidth reduction that occurs when each branch is coupled alone to the carrier, as well as in combination.

is identified with the effective matrix element  $V_{\text{eff}} = \tilde{v} k_B T$ .

Substituting from Eq. (8) into Eq. (14), for the parameters  $f_{q,\alpha}$  satisfying the extremum condition, the relevant part of the free energy bound reduces to the expression

$$\beta A_B^{(e\text{-ph})} = -3 \ln I_0(2\tilde{v}) + \sum_{\alpha} [B_\alpha(\tilde{v}) - 2C_\alpha(\tilde{v})]. \quad (17)$$

Here

$$B_\alpha(\tilde{v}) = \int \frac{d^3q}{(2\pi)^3} \frac{g_\alpha^2 \tilde{\omega}_\alpha}{\left[ 1 + \frac{1}{2} \lambda(\tilde{v}) \mu(\tilde{\omega}_\alpha) \Sigma(q) \right]^2}, \quad (18)$$

$$C_\alpha(\tilde{v}) = \int \frac{d^3q}{(2\pi)^3} \frac{g_\alpha^2 \tilde{\omega}_\alpha}{\left[ 1 + \frac{1}{2} \lambda(\tilde{v}) \mu(\tilde{\omega}_\alpha) \Sigma(q) \right]} \quad (19)$$

are integrals that must also be performed numerically for each value of  $\tilde{v}$  satisfying Eq. (11). Note that Eq. (14) for the free energy bound clearly reduces to Eq. (15) for the undressed system ( $f_{q,\alpha} = 0$ ), and to Eq. (16) for the fully dressed system ( $f_{q,\alpha} = g_\alpha$ ), facilitating the comparison that must be made for each value of  $\tilde{v}$ .

### III. NUMERICAL RESULTS

We have implemented the above variational procedure numerically for a system with only two phonon branches, and explored a considerable range of parameter space associated with  $g_1, g_2, \omega_1, \omega_2, V_0$ , and  $T$ . Typical results are displayed in Fig. 1. The effective carrier bandwidth is plotted relative to its bare value as a function of  $T$ , measured in units of  $V_0/k_B$ . The strongly coupled branch has a high frequency  $\omega_1 = 4V_0$  (corresponding to  $1/3$  of the bare carrier bandwidth  $12V_0$ ) and large coupling constant  $g_1 = 2$ . The weaker coupling is to the lower frequency branch  $\omega_2 = V_0/5$ , with cou-

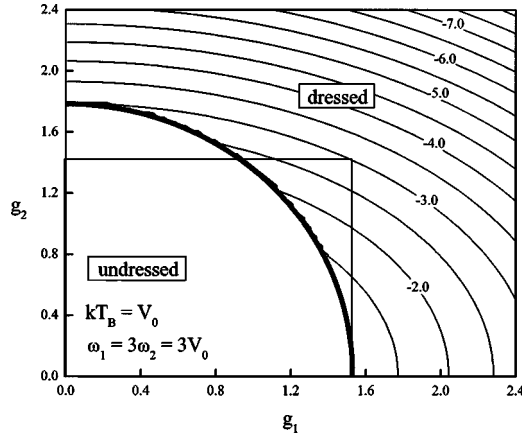


FIG. 2. Contour plot of  $V_{\text{eff}}/V_0$ , the effective carrier bandwidth for a two-branch system, as a function of the coupling strengths  $g_1$  and  $g_2$ , with optical frequencies  $\omega_1 = 3V_0 = 3\omega_2$ , and  $V_0 = k_B T$ . Thick curved line indicates the phase boundary between the undressed and dressed phases, as labeled. Thinner curved lines in the dressed phase are contours of constant  $V_{\text{eff}}$ , with attached labels indicating associated values of  $\log_{10}(V_{\text{eff}}/V_0)$ .

pling constant  $g_2 = 0.5$ . For contrast we show on the same plot the bandwidth reduction that would obtain if each were coupled alone to the carrier. One can observe that the lower frequency branch does not result in a bandwidth reduction until temperatures become much higher than those occurring in Fig. 1, and so corresponds to the horizontal line  $V_{\text{eff}}/V_0 = 1$ . As in earlier treatments that considered coupling to a single branch, the existence of a low  $T$  region where the band is not narrowed, and a collapse at higher temperatures to a reduced  $T$ -dependent bandwidth are evident here. As might be expected, the inclusion of an additional branch  $\omega_2$  to the already strongly coupled high frequency branch  $\omega_1$  causes a shift of the transition point to lower  $T$ , and an increased reduction of the bandwidth, due to the combined coupling of the two branches.

Systematical exploration of the phase space produces contour plots of the bandwidth reduction for a two-mode system. Such a plot is displayed in Fig. 2 for  $k_B T = V_0$ . In these plots we have taken oscillator modes with frequencies  $\omega_1 = 3V_0 = 3\omega_2$ , the thinner curved lines in the diagram are contours of constant  $V_{\text{eff}}$ , and the attached labels indicate the associated values of  $\log_{10}(V_{\text{eff}}/V_0)$ .

In Fig. 2 we see that, when both coupling constants are sufficiently small, there is a region where the effective matrix element is equal to its undressed value. As one moves along either axis there comes a critical value of the associated coupling constant where the effective matrix element collapses to a reduced value, narrowed by the single phonon branch appropriate to that axis. The thick black line is the phase boundary between the undressed phase near the origin, and the dressed phase, in which a  $T$ -dependent, reduced bandwidth would obtain. The region lying outside of the phase boundary, but within the rectangle shown, denotes a region of parameter space where the coupling to each individual oscillator is not strong enough to reduce the band on its own. Reduction in this region occurs as a result of the combined action of the oscillators on the carrier.

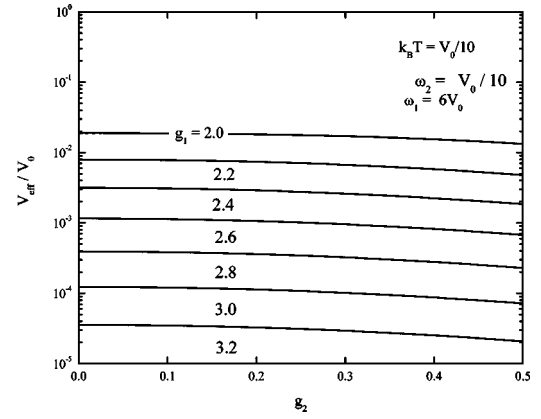


FIG. 3. Effective carrier bandwidth  $V_{\text{eff}}/V_0$  with  $V_0 = 10k_B T$ ,  $\omega_1 = 6V_0$ , and  $\omega_2 = V_0/10$ , as a function of the coupling strength  $g_2$  of the lower-frequency branch, for different values of the strength  $g_1$  of the high-frequency branch, showing the relative insensitivity of  $V_{\text{eff}}$  to the additional coupling for small to intermediate values of  $g_2$ .

We note three additional interesting features associated with this phase diagram. First, the value of the reduced bandwidth just outside the phase boundary is not constant along the boundary, insofar as it intersects contour lines associated with different values of  $V_{\text{eff}}$ . This is perhaps not surprising, since the reduction has to agree with the values that occur when each oscillator is coupled alone, i.e., along the different axes. Second, the contour lines intersect the  $g_1$  and  $g_2$  axes at right angles. This implies the condition

$$\left. \frac{\partial V_{\text{eff}}(g_1, g_2)}{\partial g_2} \right|_{g_2=0} = 0, \quad (20)$$

mentioned in Sec. I, and points out the fact that the bandwidth reduction produced by one branch is stable with respect to the addition of an infinitesimal component associated with other branches. In the limit in which the collapse occurs to a fully dressed band, this follows directly from Eq. (13), which implies that

$$\frac{\partial V_{\text{eff}}(g_1, g_2)}{\partial g_2} = -g_2 \coth(\beta\omega_2) V_{\text{eff}} \rightarrow 0 \quad \text{as } g_2 \rightarrow 0. \quad (21)$$

In the oligoacenes, recent electronic structure calculations<sup>22</sup> suggest a room temperature bare bandwidth of order 600 meV or larger. Such a value is more than 20 times  $k_B T$ . Thus, to investigate the issue of the stability of the *reduced* bandwidth with respect to finite but small changes in the amount of additional coupling  $g_2$ , we present Fig. 3. We plot here the effective matrix element  $V_{\text{eff}}/V_0$  for a system in which the bare matrix element  $V_0 = 10k_B T$ , as a function of the strength  $g_2$ , which is the more weakly coupled mode. The plot is parametric in the coupling constant  $g_1$  of the more strongly coupled mode. We have assumed  $\omega_1/V_0 = 6$ , and  $\omega_2/V_0 = 1/10$ , and have taken the values of  $g_2$  out from zero to intermediate values  $g_2 = 0.5$ . Thus, in the absence of the high-frequency mode, the coupling would be associated with significant scattering, but not significant dressing of the car-

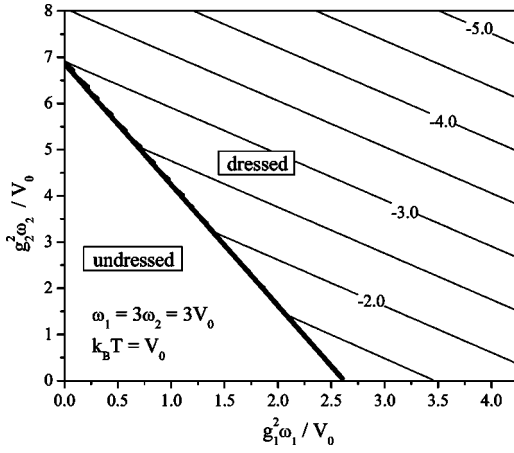


FIG. 4. Contour plot of  $V_{\text{eff}}/V_0$  as a function of the *square of the coupling constants*, specifically as a function of  $g_1^2\omega_1/V_0$  and  $g_2^2\omega_2/V_0$ , for the same parameters as in Fig. 2. As can be observed, in terms of these new variables the phase boundaries and contours of constant  $V_{\text{eff}}/V_0$  reduce to straight lines.

rier. The plot shows that the value of  $V_{\text{eff}}$  remains nearly constant with respect to increases in  $g_2$  in this range. We also note that for the parameters shown,  $V_{\text{eff}}/k_B T$  is actually less than or of the order of unity.

The third feature to be noticed in the phase diagram that we have obtained in Fig. 2 is the elliptical shape of the structures, i.e., the contour lines and phase boundary itself. The shape suggests that more appropriate variables for characterizing the behavior of the system are not the coupling constants  $g_1$  and  $g_2$ , but the contributions to the polaron binding energy

$$2E_b = \sum_{\alpha} g_{\alpha}^2 \omega_{\alpha} = g_1^2 \omega_1 + g_2^2 \omega_2 = \lambda_1 + \lambda_2 \quad (22)$$

associated with the fully dressed phase, i.e., the coordinates  $\lambda_{\alpha} = g_{\alpha}^2 \omega_{\alpha}$ . Therefore, we reexpress the phase diagram of Fig. 2 as a plot in the  $\lambda_1 - \lambda_2$  plane (see Fig. 4). In terms of these new coordinates, the phase boundary now appears as a dark straight line, and the contours as lighter straight lines. The contours are separated by fixed amounts equally spaced on the plane. This indicates that if the quantity  $\log_{10} \tilde{V}_{\text{eff}}(\lambda_1, \lambda_2)/V_0$  is plotted as a three-dimensional surface above the  $\lambda_1 - \lambda_2$  plane, it would appear as a triangular mesa near the origin, which falls off onto a tilted plane outside the phase boundary. This planar structure obtains, strictly speaking, only in the fully coupled regime. However, our numerical studies indicate that, even when  $v_{\text{eff}}$  arises from partial-polaron clothing, the bandwidth reduction does not differ by more than a few percent from that of the fully dressed system.

Hence, to reconstruct the phase plot for any combination of  $\omega_1, \omega_2$ , at fixed  $T$ , it is only necessary to find *for each mode independently* the critical values  $\lambda_{\alpha}^{(c)} = g_c^2 \omega$  where the collapse first occurs with increasing  $g$ , and the value  $\tilde{v}_c$  of the bandwidth reduction at the point of collapse for that mode. These values uniquely determine the phase boundary [which lies along the line  $\lambda_2 = \lambda_2^{(c)} + \lambda_1^{(c)} \lambda_1 / \lambda_2^{(c)}$ ]. The corre-

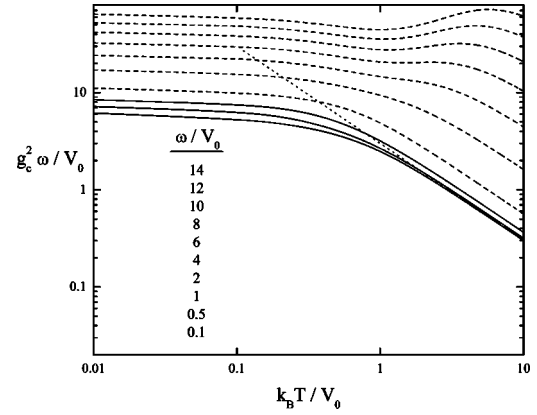


FIG. 5. Critical value of the square of the coupling  $g_c^2\omega^2/V_0$  at which bandwidth reduction first occurs for a single branch system as a function of temperature  $T$ , measured in units of  $V_0/k_B$ .

sponding planes then follow from the form of the reduced bandwidth for the fully dressed system. To facilitate construction of the phase diagram for this two-mode model, we present in Fig. 5 the critical values  $\lambda_{\alpha}^{(c)} = g_c^2 \omega$  as a function of  $k_B T/V_0$  for a wide range of  $\omega_{\alpha}$  associated with a single optical mode coupled to the carrier. In Fig. 5, we indicate with solid (dashed) lines those systems which collapse to a fully (partially) dressed polaron band. We see that higher-frequency modes generally have a higher critical value of  $\lambda^{(c)}$ , (although not necessarily a higher value of  $g_c$ , which is a non-monotonic function of  $\omega$  at fixed  $T$ ). We also note that the curves seem to approach a limiting curve for small  $\omega/V_0$ , and that all curves appear to approach a high- $T$  form that decreases as  $1/T$  at higher temperatures.

The high temperature behavior can be understood from a relatively simple argument. For the fully dressed one-mode system, we see from Eq. (13) that the reduced matrix element takes the form

$$\tilde{v}_{\text{full}} = v_0 \exp[-g_0^2 \coth(\beta\omega/2)] \quad (23)$$

and, through Eq. (16) is associated with a free energy

$$\beta A_B^{(\text{full})} = -3 \ln I_0(2\tilde{v}_{\text{full}}) - g_0^2 \beta \omega. \quad (24)$$

At high temperatures,  $v_0, \tilde{v}_{\text{full}} \rightarrow 0$ . In this limit we can replace the Bessel function by its series expansion  $I_0(x) \sim 1 + x^2/4$ , giving

$$\beta A_B^{(\text{full})} \sim -3 \ln(1 + \tilde{v}^2) - g_0^2 \beta \omega \sim -3\tilde{v}^2 - g_0^2 \beta \omega \quad (25)$$

which is to be compared to the bare free energy bound

$$\beta A_B^{(0)} = \sim 3 \ln I_0(2v_0) \sim -3v_0^2. \quad (26)$$

But in this limit  $\tilde{v}^2$  is small compared to  $v_0^2$ , and so the value of  $g_0$  for which the fully coupled and the bare system have equivalent free energy bounds is given to a good approximation by the condition  $3v_0^2 = g_0^2 \beta \omega$ , or

$$g_c^2 \frac{\omega}{V_0} \sim \frac{3V_0}{k_B T}. \quad (27)$$

This shows clearly the  $1/T$  decrease. In Fig. 5, the straight dashed line on the right corresponds to the Eq. (27). Al-

though the functional dependence on  $T$  can be expected for all curves at high enough temperatures, the numerical prefactors in Eq. (27) should be strictly valid only for temperatures such that  $g_c^2\omega/k_B T$  is small (since we are setting it equal to  $v_0=V_0/k_B T$  which has already been assumed small), and thus is expected to be satisfied best for small  $\omega/V_0$ . Indeed for small  $\omega$ , the critical value of  $g_c^2\omega/k_B T$  will be independent of  $\omega$ , which is the behavior that we see in the high temperature regime for  $\omega/V_0 < 1$ .

#### IV. DISCUSSION

In summary, we have investigated properties of a carrier moving through a three-dimensional isotropic band in interaction with two separate branches of optical phonons. The procedure we have used for the investigation is a generalization of a variational approach<sup>2</sup> originally employed for excitons in molecular crystals and subsequently extended in various contexts<sup>3</sup>. Using our procedure, we have produced phase diagrams showing regions of parameter space where cou-

pling to both phonon branches leads to significant dressing of the carrier. In the parameter regimes that we have explored, we have noted the absence of a sharp transition between a singly dressed and doubly dressed polaronic phase. Our investigations indicate that, when one high frequency branch is coupled to the carrier with an intermediate to strong coupling strength  $g_1$ , the effective bandwidth, already reduced by this coupling, is stable with respect to small to intermediate values of the coupling  $g_2$  associated with additional low frequency optical phonon branches. Thus, our present study lends support to the basic picture of a carrier moving through a narrowed polaron band being scattered by its interaction with additional weakly coupled phonon branches, that underlies our recent calculations<sup>19</sup> of the temperature dependence of injected charge carrier transport in the oligoacenes.

#### ACKNOWLEDGMENTS

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