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Small-Polaron Propagators

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The diagrammatic expansion in the real-time domain of the one-electron and electron-hole propagators for the small-polaron problem is presented. For this purpose, special graphs consisting of fermion lines, multiphonon interaction lines, and migration vertices are used. The spectral function of the small-polaron propagator is calculated for two cases. First, the interaction with a narrow band of optical modes, and second, the interaction with longitudinal acoustic modes, is considered. The expressions for the small-polaron mobility in the hopping region are also derived for both models.

I. INTRODUCTION

Since the publication in 1959 of Holstein's fundamental paper[1] on small polarons, the problem of the very low electron mobility in the case of strong electron-phonon interaction has been the subject of several theoretical investigations.[2–7] In this paper the field-theoretic techniques are applied to the small-polaron problem. Propagators for small polarons are introduced and their properties are investigated. The theory presented leads to some new results concerning the small-polaron mobility. One-electron propagators have been studied in some detail already in the previous paper by the author and Choi.[8]

Small-polaron theory deals with the motion of electrons in narrow bands. Therefore in calculations we use the tight-binding approach and the corresponding Wannier representation. In this representation the complete set of states for the particular band is given by the localized states $|i\rangle$ at the individual cells i of the crystal. The small-polaron Hamiltonian may be written as

$$H=\epsilon_0\sum_i c_i^\dagger c_i+\sum_{i,j} w_{ij}c_i^\dagger c_j+\sum_\lambda \omega_\lambda a_\lambda^\dagger a_\lambda - N^{-1/2}\sum_{i,\lambda}\omega_\lambda \eta^{1/2} e^{i\vec{q}\cdot\vec{R}_i}\, c_i^\dagger c_i(a_\lambda+a_{-\lambda}^\dagger),\quad \hbar=1 \qquad (1)$$

where $c_i^\dagger$ and c_i are, respectively, the creation and annihilation operators for electrons in the localized states $|i\rangle$, and where ϵ_0 is the local electron energy and w_{ij} the intercell transfer or resonance integral. $a_\lambda^\dagger$ and a_λ denote the creation and annihilation operators, respectively, for a phonon in the phonon mode λ. The parameter λ includes the wave vector $\vec{q}$ and the branch p of the phonon spectrum. The normal modes λ and $-\lambda$ belong to the same branch, the corresponding wave vectors being $\vec{q}$ and $-\vec{q}$, respectively. ω_λ is the phonon frequency and η_λ the electron-phonon coupling constant. N is the number of cells in the crystal and $\vec{R}_i$ the lattice vector of the ith cell. Additionally, w_{ij} and η_λ are real, and $w_{ij}=w_{ji}$.

The electron-phonon interaction is assumed to be linear in phonon operators and diagonal with respect to the localized states $|i\rangle$. If the phonon frequency is greater than the width of the electron band, only the diagonal coupling terms are important. This fact justifies the use of (1) in the case of narrow bands. In the small-polaron theory, the transfer integrals w_{ij} are considered as a small perturbation.

In Sec. II one-electron propagators are introduced and their properties are studied. Section III deals with the electron-hole propagators. Small-polaron mobility is calculated in Sec. IV.

II. ONE-ELECTRON PROPAGATORS

We would like to formulate the theory of propagators for a single polaron. We define the propagator for the small polaron by

$$g_{ij}(t)=-i\langle T\underline{c}_i(t)\underline{c}_j^\dagger(0)\rangle, \qquad (2)$$

where T is a time-ordering operator and $\langle\ \rangle$ denotes the canonical ensemble average over the states of the crystal with no electrons. The underlined operators are Heisenberg operators. It is easy to realize that the diagrammatic expansion of $g_{ij}(t)$ in the real-time domain is possible. We consider the second and also the last term of (1) as the perturbation. The effect of the electron-phonon interaction can be taken into account by introducing a retarded interaction of the electron with itself, as shown by Puff and Whitfield.[9] This interaction is temperature dependent. In the present problem only the electron migration term is small. Therefore the procedure of the perturbation expansion will not be completely standard.

First we shall consider the propagator $g_{ii}(t)$ in the case of the complete electron localization, i.e., if $w_{ij}=0$. This propagator does not depend on i and will be denoted by $g(t)$. In the perturbation expansion of $g(t)$ all contractions between fermion operators must be such that the creation operator is to the right of the annihilation operator in order to get a nonzero contribution. For each sequence of the intermediate times there is only one way to do this. Hence, the contractions of the fermion operators give a time factor $e^{-i\epsilon_0 t}$. The result does not depend on the intermediate times. Because of this fact, the multiple time integrals which appear in the individual terms of the perturbation expansion can be split into a product of the double integrals of the individual contractions between boson operators. The value of such a double integral is

$$\begin{aligned} &N^{-1}\omega_\lambda^2\eta_\lambda \int_0^t\int_0^t dt_1\, dt_2 \langle T[a_\lambda(t_1)+a_{-\lambda}^\dagger(t_1)]\,[a_{-\lambda}(t_2)+a_\lambda^\dagger(t_2)]\rangle \\ &\quad = 2N^{-1}\eta_\lambda[(2\overline{n}_\lambda+1)-i\omega_\lambda t-\overline{n}_\lambda e^{i\omega_\lambda t}-(\overline{n}_\lambda+1)\,e^{-i\omega_\lambda t}] \\ &\quad = 2N^{-1}v_\lambda(t), \end{aligned} \tag{3}$$

where $\overline{n}_\lambda$ is the thermal equilibrium number of phonons in the mode λ. The operators in (3) are now expressed in the interaction representation. In the $2n$th term of the perturbation expansion there are $(2n)!/2^n n!$ different contractions between boson operators. The contribution of the $2n$th term to $g(t)$ is therefore

$$-i\,e^{-i\epsilon_0 t}(n!)^{-1}[-N^{-1}\textstyle\sum_\lambda v_\lambda(t)]^n . \tag{4}$$

Hence, we have

$$g(t)=-i\,e^{-S}\,\Theta(t)\,e^{-i\epsilon t}h(t), \tag{5}$$

where $\Theta(t)$ is a step function, $\Theta(t)=1$ and 0 for $t>0$ and $t<0$, respectively, and

$$\begin{aligned} S&=N^{-1}\textstyle\sum_\lambda \eta_\lambda(2\overline{n}_\lambda+1), \\ \epsilon&=\epsilon_0-N^{-1}\textstyle\sum_\lambda \omega_\lambda\eta_\lambda, \\ h(t)&=\exp\{N^{-1}\textstyle\sum_\lambda \eta_\lambda[\overline{n}_\lambda e^{i\omega_\lambda t}+(\overline{n}_\lambda+1)\,e^{-\omega_\lambda t}]\}. \end{aligned} \tag{6}$$

Note that $N^{-1}\sum_\lambda \omega_\lambda\eta_\lambda$ is a small-polaron binding energy.

It is convenient to deal with the Fourier transform

$$g(z)=\int_{-\infty}^{\infty} g(t)\,e^{izt}\,dt, \quad \mathrm{Im}\,z>0. \tag{7}$$

Further we introduce the spectral function $A(E)$ which is defined by

$$g(z)=\int_{-\infty}^{\infty}\frac{A(E)}{z-E-\epsilon}\,dE. \tag{8}$$

In the following we present the calculation of $A(E)$ for two cases. First, the interaction of the electron with the optical modes in a narrow frequency band will be considered. Second, the interaction with the longitudinal acoustic modes, having the Debye spectrum, will be studied.

Optical Branch

The Gaussian function will be used for the density of phonon modes. The number of modes in the frequency interval $(\omega, \omega+d\omega)$ is therefore $ND(\omega)d\omega$ with

$$D(\omega)=\frac{1}{(2\pi)^{1/2}\omega_1}\exp\left(-\frac{(\omega-\omega_0)^2}{2\omega_1^2}\right), \tag{9}$$

where ω_0 is the mean phonon frequency and ω_1 measures the dispersion of the spectrum. We shall consider only narrow bands with $\omega_1 \ll \omega_0$ and the interval of temperatures for which $\beta\omega_1$ is less than or of the order 1 ($\beta=1/k_BT$). At very low temperatures, the approximation (9) for the density function is not good because only the modes in the lower tail of the spectrum are occupied. In this region the Gaussian distribution cannot correspond well enough to reality. Keeping in mind the narrowness of the optical spectrum, it is reasonable to assume that all η_λ are equal, $\eta_\lambda=\eta$. Further, we could approximate $\overline{n}_\lambda$ by the occupation number $\overline{n}$ for the central mode with the frequency ω_0. Actually, we shall use a better approximation:

$$\overline{n}_\lambda(\overline{n}_\lambda+1)\approx \overline{n}(\overline{n}+1)\,e^{-\beta(\omega_\lambda-\omega_0)}. \tag{10}$$

The direct evaluation of the function $h(t)$ is now possible. We obtain

$$\begin{aligned} h(t)&=e^{f(t+i\beta/2)}, \\ f(s)&=2u\,e^{-\omega_1^2 s^2/2}\cos(\overline{\omega}_0 s), \\ u&=\eta\,[\overline{n}(\overline{n}+1)]^{1/2}\,e^{\beta^2\omega_1^2/8}, \end{aligned} \tag{11}$$

where $\overline{\omega}_0=\omega_0-\frac{1}{2}\beta\omega_1^2$.

If the exponential function $h(t)$ is expanded into a power series and its Fourier transform is calculated term by term, we get the following expression for $A(E)$:

$$\begin{aligned} A(E)&=e^{-S}\,\delta(E)+B(E), \\ B(E)&=e^{-S}\,e^{\beta E/2}\sum_{l=1}^{\infty}\sum_{m=0}^{l}\frac{u^l}{m!\,(l-m)!} \end{aligned} \tag{12}$$

$$\times \frac{1}{(2l\pi)^{1/2}\omega_1} \exp\left(-\frac{[E+(l-2m)\overline{\omega}_0]^2}{2l\omega_1^2}\right).$$

The spectral function $A(E)$ has a sharp δ-function peak of the integrated intensity e^{-S} and the continuous background $B(E)$. The intensity e^{-S} has the same mathematical origin as the Debye-Waller factor in the scattering problems. The background function is quite complicated. It depends on the strength of the electron-phonon coupling, the phonon dispersion, and the temperature. If the coupling is weak and the temperature low, only the processes of the emission and absorption of a small number of phonons are important. One considers therefore the low-order terms in the expansion of $h(t)$. These terms contribute to $B(E)$ in the energy interval of few multiples of ω_0. Outside of this interval $B(E)$ is practically zero. In the small-polaron theory we are actually interested in the strong-coupling case and the many-phonon processes. This means $u \gg 1$. Here the background function $B(E)$ becomes relatively simple only if the variance ω_1 is small enough as compared with ω_0. Then we can neglect the overlap in (12) of the Gaussian functions which have different centers. $B(E)$ has now approximately separated peaks with centers at $n\overline{\omega}_0$, where n is an integer. For instance, the shape of the peak $n=0$ is obtained by considering only the terms with $2m=l$ in series (12). The most important of these terms are those with $m \approx u$. The variance of the Gaussian functions in these terms is about $(2u)^{1/2}\omega_1$. In order to avoid the overlap with the peaks $n=\pm 1$, the condition

$$\omega_1 < \tfrac{1}{2}(2u)^{-1/2}\omega_0 \approx \tfrac{1}{2}(\eta^{-1}\sinh\tfrac{1}{2}\beta\omega_0)^{1/2}\omega_0 \tag{13}$$

must be satisfied.

The integrated intensity α_n of the nth peak of $B(E)$ is

$$\alpha_n = e^{-S}\, e^{n\beta\overline{\omega}_0/2}[I_n(2u\, e^{\beta^2\omega_1^2/8}) - \delta_{n0}], \tag{14}$$

where $I_n(x)$ is a modified Bessel function.

Acoustic Branch

Only the interaction of the electron with the longitudinal lattice vibrations will be considered. In the long-wavelength limit such an interaction is usually of the simple deformation-potential type, i.e., $\eta_\lambda = \mathcal{E}/\omega_\lambda$, where the coupling parameter $\mathcal{E}$ has the dimension of the energy. It is reasonable to assume that at higher frequencies the coupling constant η_λ decreases faster than $\mathcal{E}/\omega_\lambda$. In the following calculations we use a phenomenological coupling constant

$$\eta_\lambda = (\mathcal{E}/\omega_\lambda)\, e^{-\alpha\omega_\lambda}, \tag{15}$$

where α is a new parameter. If $\alpha\omega_D \gg 1$ and $k_B T \gg \omega_D$, where ω_D is the Debye angular frequency, then the calculation of $h(t)$ and S is easy. By using the Debye density of phonon modes $D(\omega) = 3N\omega^2/\omega_D^3$ we obtain approximately

$$h(t) = \exp\left(\frac{T}{T_0}\frac{\alpha^2}{\alpha^2+t^2}\right), \quad S = \frac{T}{T_0}, \tag{16}$$

where T_0 is a characteristic temperature

$$T_0 = \alpha\omega_D^3/6\mathcal{E}\, k_B\ . \tag{17}$$

In the calculation of (16) the integration has been performed over the interval $(0,\infty)$ and $\overline{n}_\lambda$ or $\overline{n}_\lambda + 1$ have been approximated by $k_B T/\omega_\lambda$.

The spectral function $A(E)$ has a δ peak of the integrated intensity e^{-S} at $E=0$ and a continuous background $B(E)$

$$B(E) = 2\alpha\, e^{-S} e^{-\alpha E}\sum_{n=1}^{\infty}\left(\frac{T}{4T_0}\right)^n \frac{1}{(n-1)!\,n!}$$

$$\times \sum_{k=0}^{n-1}\frac{(2n-k-2)!}{k!\,(n-k-1)!}(2\alpha E)^k . \tag{18}$$

Thus far we have investigated the properties of the localized electron. In the next step we derive an approximate expression for $g_{ij}(z)$ with $j \neq i$ by taking account of the electron migration terms in the Hamiltonian.

Consider a particular graph in Fig. 1. The full and wavy lines represent, respectively, the zero-order electron and phonon propagators. The migration vertex is denoted by a cross. Time integrations over t_2 and t_4 in the perturbation expansion can be performed easily. By noting that the integration interval is (t_1, t_3) for t_2 and (t_3, t_5) for t_4 we derive the following contribution of the phonon line:

$$f_{\lambda,ij}(t_5-t_1) + f_{\lambda,ij}(0) - f_{\lambda,ij}(t_3-t_1) - f_{\lambda,ij}(t_5-t_3), \tag{19}$$

where

$$f_{\lambda,ij}(t) = N^{-1}\eta_\lambda\, e^{i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)}[\overline{n}_\lambda\, e^{i\omega_\lambda t} + (\overline{n}_\lambda+1)\, e^{-i\omega_\lambda t}]. \tag{20}$$

By using the same approach as in the calculation of the localized particle propagators one realizes

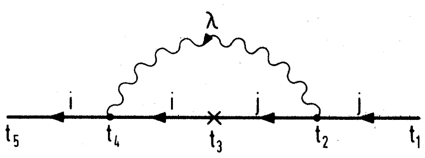

FIG. 1. Migration of the electron accompanied by the exchange of a phonon.

that it is possible to sum the contributions of all graphs with one migration vertex as in Fig. 1, but with an arbitrary number of phonon lines. The phonon lines either do or do not bridge the migration vertex. The result of such a summation is

$$-w_{ij}\, e^{-2S}\, e^{-i\epsilon(t_5-t_1)} h_{ij}(0) h_{ij}(t_5-t_1) \times \int_{t_1}^{t_5} dt_3\, h(t_3-t_1) h(t_5-t_3) h_{ij}^{-1}(t_3-t_1) h_{ij}^{-1}(t_5-t_3)\,, \tag{21}$$

where

$$h_{ij}(t) = \exp\left[\textstyle\sum_\lambda f_{\lambda,ij}(t)\right]. \tag{22}$$

Note that $h_{ii}(t) \equiv h(t)$.

On the basis of this example one can easily derive a general rule for the calculation of graphs with an arbitrary number of migration vertices. For this purpose a new kind of graph is introduced. First draw the fermion lines and migration vertices, then connect the initial and final points of the fermion lines in all possible ways by dashed lines with arrows in the positive time direction. This is shown in Fig. 2 for the preceding example. Each fermion line now contributes a factor

$$-i\, e^{-S} \Theta(t)\, e^{-i\epsilon t},$$

where t is the time difference between the final and initial points of the line. Further, each of the dashed lines gives a factor $h_{ij}^{\pm 1}(t)$, where i and j are the corresponding position indices of the localized particle and t is the time difference. The sign + stands for the lines which connect one initial and one final point of the particle lines. Otherwise the sign is −. The product of the line contributions and the vertex factors w_{ij} has to be finally integrated over the intermediate times. The integration domain is restricted to the region where all time differences t are positive.

Among the factors $h_{ij}(t)$ there are those for which $t = 0$. See for instance the dashed line a in Fig. 2. These factors can be fused together with the corresponding migration matrix elements in order to get an effective or renormalized migration matrix element $\tilde{w}_{ij}$:

$$\tilde{w}_{ij} = w_{ij} h_{ij}(0)\,. \tag{23}$$

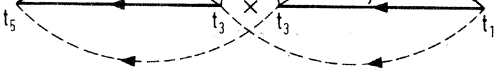

FIG. 2. Graph with one migration vertex and multiphonon interaction lines.

Calculation of the contributions of the graphs with migration vertices leads to complicated integrations which usually cannot be performed analytically. In the theory of small polarons, the migration vertices are assumed to be small. This assumption allows considerable simplification of the calculations.

Consider the time behavior of a localized electron propagator $g(t)$, given by formula (5). The function $h(t)$ decays in a complicated way from the initial value e^S towards 1 as t increases from 0 to infinity. The characteristic decay time τ_c is determined by the width of the central peak of the background spectral function $B(E)$. In the case of electron interaction with optical phonons we have $\tau_c \approx (2u)^{-1/2}\omega_1^{-1}$. Similarly, we have $\tau_c \approx \alpha(T_0/T)^{1/2}$ for interaction with acoustic phonons. The characteristic time is a measure of the time required for formation of lattice distortion around the electron. If the migration velocity of the polaron is sufficiently slow that $w_{ij}\tau_c \ll 1$, then the background spectrum $B(E)$ is not significantly affected by taking into account graphs containing migration vertices. We can neglect such corrections.

The situation is completely different if one investigates the effect of electron migration on the central δ-function peak of $A(E)$. This peak, with an intensity e^{-S}, describes the undamped propagation of the electron. Because of the possibility of migration, new electron energy eigenstates are Bloch band states and therefore the δ-function peak spreads. In the first approximation in calculating the graph contribution we replace the factors for the dashed lines by 1, except if the corresponding time difference t is 0. Consider an arbitrary graph which describes the indirect transition of the electron from the molecule j to the molecule i. The transition takes place through the localized states $|s\rangle, \ldots, |l\rangle, |m\rangle$ at intermediate molecules. It is convenient to deal here with the Fourier transforms of the propagators. Each electron line gives a factor $g_0(z) = e^{-S}/(z-\epsilon)$ and each vertex a factor $\tilde{w}_{mn}$. The contribution of such a graph is

$$g_0(z)\tilde{w}_{im} g_0(z) \tilde{w}_{ml} g_0(z) \cdots g_0(z) \tilde{w}_{sj} g_0(z)\,. \tag{24}$$

The intermediate molecules are arbitrary with the exception $m = i, l = m, \ldots, s = j$. To avoid this restriction, we put $\tilde{w}_{ii} = 0$. We would like to sum up the contributions (24) of all possible intermediate states. To this aim we introduce the Fourier transform $\tilde{\epsilon}(\vec{k})$ of $\tilde{w}_{ml}$, defined by

$$\tilde{w}_{ml} = N^{-1} \textstyle\sum_{\vec{k}} \tilde{\epsilon}(\vec{k})\, e^{i\vec{k}\cdot(\vec{R}_m - \vec{R}_l)}, \tag{25}$$

where $\vec{k}$ is the wave vector in the first Brillouin zone. By substituting (25) in (24) and summing up over all intermediate states we easily derive the total contribution

$$g_0^{n+1}(z) N^{-1} \sum_{\vec{k}} \tilde{\epsilon}^{\,n}(\vec{k})\, e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)}, \tag{26}$$

where $n-1$ is the number of intermediate steps.

By adding up the contributions of the graphs with $n=1, 2, \ldots,$ we finally obtain

$$g_{ij}(z) = e^{-S} N^{-1} \sum_{\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)}}{z-\epsilon-\epsilon(\vec{k})}, \tag{27}$$

with

$$\epsilon(\vec{k}) = e^{-S}\tilde{\epsilon}(\vec{k}). \tag{28}$$

This formula is correct also for $j=i$ and reflects the translational symmetry of the system. Expression (27) represents a familiar result for motion in the energy band, except for the factor e^{-S} in front of the formula. In the small-polaron case the propagator amplitude is reduced by the factor e^{-S} because only the δ-function peak of the spectral function for the localized electron participates in the formation of the band. The temperature dependence of the small-polaron band energy (28) is a well-known phenomenon.[1] In the present approximation the Bloch states have an infinite lifetime.

Next we shall investigate the graphs which produce the damping of the Bloch states. These are the graphs in which the dashed lines with $t\neq 0$ are not discarded completely. Consider for instance the graph in Fig. 3 which corresponds to an indirect transition from the localized state $|j\rangle$ to the state $|i\rangle$. The intermediate molecule is denoted by l. Such graphs give the simplest vertex correction for the migration matrix element $\tilde{w}_{ij}$. The vertex correction $\Delta\tilde{w}_{ij}(t)$ is obtained by summing the contributions of all graphs of a kind shown in Fig. 3, with two external lines removed:

$$\Delta\tilde{w}_{ij}(t) = -i\, e^{-S}\Theta(t)\, e^{-i\epsilon t} \times \sum_l \tilde{w}_{il}\tilde{w}_{lj}\left[h(t)h_{ij}(t)h_{il}^{-1}(t)h_{lj}^{-1}(t)-1\right]. \tag{29}$$

By adding the term -1 in the square brackets of (29) we avoid the double counting of the contributions with $h_{ij}(t)=1$.

Now we must substitute in the propagator formula (27) a new band energy $\epsilon(\vec{k})+\Delta\epsilon(\vec{k}, z)$, where

$$\Delta\epsilon(\vec{k}, z) = e^{-S}\sum_i e^{-i\vec{k}\cdot(\vec{R}_i-\vec{R}_i)} \times \int_0^\infty \Delta\tilde{w}_{ij}(t)\, e^{izt}\, dt. \tag{30}$$

The real part of $\Delta\epsilon(\vec{k}, z)$ at the pole $z=\epsilon+\epsilon(\vec{k})+i\delta$, where δ is positive and very small, gives the shift of the Bloch energy, and the imaginary part the corresponding damping. In view of the smallness of w_{ij}, we restrict our attention only to the calculation of the damping. For the same reason, we are allowed to move the pole to $z=\epsilon+i\delta$. The damping $\Gamma(\vec{k})$ is therefore equal to

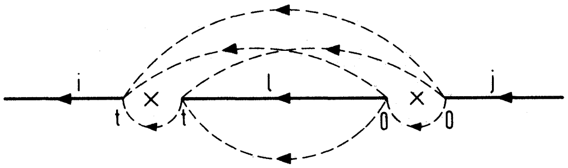

FIG. 3. Graph for an indirect transition from $|j\rangle$ to $|i\rangle$.

$$\Gamma(\vec{k}) = e^{-2S}\,\mathrm{Re}\Big(\sum_i e^{-i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)}\sum_l \tilde{w}_{il}\tilde{w}_{lj} \times \int_0^\infty \left[h(t)h_{ij}(t)h_{il}^{-1}(t)h_{lj}^{-1}(t)-1\right]dt\Big\}. \tag{31}$$

The most important terms in the series (31) are those with $i=j$. In fact, the contribution of the processes in the case with emission of the phonon at one molecule and absorption at another is smaller than when both events take place at the same molecule. This is a consequence of the destructive interference effects in the exponent of $h_{ij}(t)$, where the phase differences of the lattice waves at two molecules i and j are added over the entire phonon spectrum. Actually, $h_{ij}(t)-1$ with $i\neq j$ is identically zero for the Einstein model of the phonon spectrum. By taking into account only the terms $i=j$ we get

$$\Gamma(\vec{k}) = \Gamma = e^{-2S}\sum_l \tilde{w}_{il}^2\,\mathrm{Re}\int_0^\infty \left[h^2(t)h_{il}^{-2}(t)-1\right]dt. \tag{32}$$

In this approximation $\Gamma(\vec{k})$ has the same value Γ for all states of the band. We shall not carry on the integration in (32) at this point as the same integral happens to appear later in the calculation of the small-polaron mobility.

Thus far we have investigated only the behavior of the central peak of the spectral function of the propagator $g_{ij}(z)$ with $i\neq j$. The corresponding background function is proportional to some power of the typical w_{ml} and can be neglected in our calculations of the mobility.

III. ELECTRON-HOLE PROPAGATORS

Transport coefficients can be expressed in terms of the Fourier transforms of the electron-hole Green's functions. First, we introduce the temperature-dependent Green's function

$$g_{ijkl}(\tau) = -\langle\langle T_\tau \underline{c}_i^\dagger(\tau)\underline{c}_j(\tau)\underline{c}_k^\dagger(0)\underline{c}_l(0)\rangle\rangle, \quad -\beta\leq\tau\leq\beta \tag{33}$$

which is most convenient for the calculation of the electrical conductivity. Here the symbol $\langle\langle\rangle\rangle$ denotes the grand canonical ensemble average, and

$$\underline{c}_i(\tau) = e^{(H-\mu N)\tau} c_i\, e^{-(H-\mu N)\tau}, \tag{34}$$

where μ is a chemical potential and N the number operator of small polarons. Further, T_τ is the ordering operator with respect to τ.

Note the identity

$$g_{ijkl}(\tau > 0) = -\langle\langle \underline{c}_l(\beta)\underline{c}_i^\dagger(\tau)\underline{c}_j(\tau)\underline{c}_k^\dagger(0)\rangle\rangle \,. \tag{35}$$

This leads us to consider the two-time temperature-dependent Green's function

$$g_{ijkl}(\tau_1, \tau) = \langle\langle T_\tau \underline{c}_l(\tau_1)\underline{c}_i^\dagger(\tau)\underline{c}_j(\tau)\underline{c}_k^\dagger(0)\rangle\rangle \tag{36}$$

defined for $\beta \geqslant \tau_1 \geqslant 0$ and $\beta \geqslant \tau \geqslant 0$. By substituting the value β for τ_1 we obtain $-g_{ijkl}(\tau > 0)$. In the following we shall omit the subscript *ijkl* when it proves convenient. It is useful to extend the definition [Eq. (36)] of $g(\tau_1, \tau)$ to the negative τ_1 and τ regions $-\beta \leqslant \tau_1 \leqslant 0$ and $-\beta \leqslant \tau \leqslant 0$ by the prescription

$$\begin{aligned} g(\tau_1 < 0, \tau) &= -g(\tau_1 + \beta, \tau)\,, \\ g(\tau_1, \tau < 0) &= g(\tau_1, \tau + \beta). \end{aligned} \tag{37}$$

$g(\tau_1, \tau)$ shows therefore a fermionlike behavior with respect to τ_1 and a bosonlike behavior with respect to τ.

The double Fourier transform of (36) reads

$$\begin{aligned} g(z_1, z) = \Big(\sum_m e^{-\beta\omega_m}\Big)^{-1} \sum_{m,n,p} \Bigg[&\langle p| c_k^\dagger | m\rangle \frac{e^{-\beta\omega_m} + e^{-\beta\omega_p}}{z_1 + z + \omega_{mp}} \left(\frac{\langle m| c_l | n\rangle\langle n| c_i^\dagger c_j | p\rangle}{z_1 + \omega_{mn}} - \frac{\langle m| c_i^\dagger c_j | n\rangle\langle n| c_l | p\rangle}{z_1 + \omega_{np}} \right) \\ &+ \langle n| c_i^\dagger c_j | p\rangle \frac{e^{-\beta\omega_n} - e^{-\beta\omega_p}}{z + \omega_{np}} \left(\frac{\langle p| c_k^\dagger | m\rangle\langle m| c_l | n\rangle}{z_1 + \omega_{mn}} + \frac{\langle p| c_l | m\rangle\langle m| c_k^\dagger | n\rangle}{z_1 + \omega_{pm}} \right) \Bigg] \,, \end{aligned} \tag{38}$$

with $z_1 = i(2m' + 1)\pi/\beta$ and $z = i2n'\pi/\beta$, where m' and n' are integers. At the calculation of (38) a complete set of eigenstates $|m\rangle$ of $H - \mu N$ has been inserted between the operators. ω_m are the corresponding eigenvalues and $\omega_{mn} = \omega_m - \omega_n$. We are interested in the properties of the dilute system of polarons with no mutual interactions. This means that $\mu \to -\infty$ and ω_m are very large and positive except for the states with no electrons. As $\mu \to -\infty$ the Fourier transform (38) goes to

$$g(z_1, z) = \Big(\sum_m e^{-\beta E_m}\Big)^{-1} \sum_{m,n,p} e^{-\beta E_m} \times \frac{\langle m| c_l | n\rangle\langle n| c_i^\dagger c_j | p\rangle\langle p| c_k^\dagger | m\rangle}{(z_1 + z + E_m - E_p + \mu)(z_1 + E_m - E_n + \mu)}\,, \tag{39}$$

where the summation now runs over the states $|m\rangle$ with no electrons and states $|n\rangle$ and $|p\rangle$ with one electron. E_m, E_n, and E_p are the energies of these states.

Next consider the time-dependent Green's function

$$g(t_1, t) = -\langle T \underline{c}_l(t_1)\, \underline{c}_i^\dagger(t)\, \underline{c}_j(t)\, \underline{c}_k^\dagger(0)\rangle \tag{40}$$

defined in the real-time domain $(-\infty, \infty)$ for t_1 and t. The double Fourier transform of $g(t_1, t)$ reads

$$g(z_1, z) = \Big(\sum_m e^{-\beta E_m}\Big)^{-1} \sum_{m,n,p} e^{-\beta E_m} \times \frac{\langle m| c_l | n\rangle\langle n| c_i^\dagger c_j | p\rangle\langle p| c_k^\dagger | m\rangle}{(z_1 + z + E_m - E_p + i\delta)(z_1 + E_m - E_n + i\delta)}\,, \tag{41}$$

where z_1 and z are now real frequencies. By comparing (41) with (39) we see that the Fourier transform of the temperature-dependent Green's function $g(\tau_1, \tau)$ can be obtained by the analytical continuation into the upper half of the complex plane of the Fourier transform (41) of the time-dependent function $g(t_1, t)$. This is an important result because now we can do all calculations of the electron-hole propagators in the real-time domain.

As an example we present in Fig. 4 the simplest graph for $g(t_1, t)$, in the case $l = i$ and $k = j$, which has a similar structure to the graph in Fig. 2. The contribution of this graph is

$$h_{ij}(0)\, h_{ij}(t_1)\, s_{ij}(t)\, s_{ij}(t_1 - t) \quad , \tag{42}$$

with

$$s_{ij}(t) = -ie^{-S}\Theta(t)e^{-i\epsilon t}\, h(t)\, h_{ij}^{-1}(t) \quad . \tag{43}$$

The factor $h_{ij}(t_1)$ in (42) can now be analytically continued toward $h_{ij}(-i\beta) = h_{ij}(0)$ without any intermediate steps. On the other hand, the product $s_{ij}(t)\, s_{ij}(t_1 - t)$ should first be Fourier transformed.

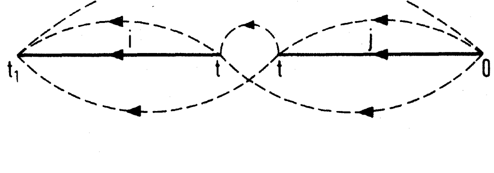

FIG. 4. Lowest-order graph for $g(t_1, t)$ [Eq. (40)] in the case $l = i$ and $k = j$.

Its double Fourier transform is

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dE_1\, dE_2\, \frac{S_{ij}(E_1)\, S_{ij}(E_2)}{(z_1+z-E_1-\epsilon+i\delta)(z_1-E_2-\epsilon+i\delta)}\,, \tag{44}$$

where $S_{ij}(E)$ is a spectral function of $s_{ij}(t)$ defined by an equation of type (8). Next we perform the analytical continuation. The final result for the contribution of the graph in Fig. 4 to the Fourier transform of $g_{ijji}(\tau)$ is therefore

$$\begin{aligned} g_{ijji}(z) &= h_{ij}^2(0)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dE_1\, dE_2\, S_{ij}(E_1)\, S_{ij}(E_2)\, \beta^{-1}\sum_{z_1}\frac{1}{(z_1+z-E_1-\epsilon+\mu)(z_1-E_2-\epsilon+\mu)} \\ &= h_{ij}^2(0)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dE\, d\omega\, S_{ij}(E)\, S_{ij}(E+\omega)\, e^{-\beta(E+\epsilon-\mu)}\,\frac{1-e^{-\beta\omega}}{z-\omega}\,. \end{aligned} \tag{45}$$

This expression will be used in Sec. IV in the calculation of the small-polaron mobility.

IV. SMALL-POLARON MOBILITY

The mobility problem leads to the study of the current-density correlation function. First we introduce the current-density operator

$$\vec{\mathrm{j}} = -i\,\frac{e}{V}\sum_{ij}(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_j)\, w_{ij}c_i^\dagger c_j\,, \tag{46}$$

where e is the electron charge and V the volume of the crystal, and the spectral weight function $\overleftrightarrow{\mathrm{J}}(E)$ of the current correlation function

$$\langle\langle \vec{\mathrm{j}}(t)\,\vec{\mathrm{j}}(0)\rangle\rangle = \int_{-\infty}^{\infty}\overleftrightarrow{\mathrm{J}}(E)e^{-iEt}\,dE\,. \tag{47}$$

The real part $\overleftrightarrow{\sigma}(\omega)$ of the conductivity tensor now can be written, according to Kubo formula,[10] as

$$\overleftrightarrow{\sigma}(\omega) = \pi V\omega^{-1}(1-e^{-\beta\omega})\,\overleftrightarrow{\mathrm{J}}(\omega)\,, \tag{48}$$

where ω is the frequency of the applied electric field. Another useful relation is

$$\overleftrightarrow{\mathrm{J}}(E)(1-e^{-\beta E}) = (i/2\pi)\,[\overleftrightarrow{\mathrm{g}}(E+i\delta)-\overleftrightarrow{\mathrm{g}}(E-i\delta)]\,, \tag{49}$$

where $\overleftrightarrow{\mathrm{g}}(z)$ is the Fourier transform of the temperature-dependent Green's function

$$\overleftrightarrow{\mathrm{g}}(\tau) = -\langle\langle T_\tau\,\vec{\mathrm{j}}(\tau)\,\vec{\mathrm{j}}(0)\rangle\rangle\,. \tag{50}$$

By substituting (46) in (50) the function $\overleftrightarrow{\mathrm{g}}(\tau)$ gets expressed interms of the electron-hole propagators (33).

In the present paper we shall discuss in detail only the dc conductivity at high temperatures where the hopping type of the polaron motion prevails. In the high-temperature region the electron-hole propagators $g_{ijji}(\tau)$ give the largest contribution to the current. In the case of small w_{ij} such a propagator can be approximated by the graph shown in Fig. 4. In this approximation we derive the following expression for the dc conductivity:

$$\overleftrightarrow{\sigma}(0) = \pi e^2\beta V^{-1}\sum_{ij}(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_j)(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_j)\tilde{w}_{ij}^2 \times\int_{-\infty}^{\infty}S_{ij}^2(E)e^{-(E+\epsilon-\mu)}\,dE\,. \tag{51}$$

Actually the integral in (51) diverges. The divergence is due to the δ peak of the integrated intensity e^{-S} in $S_{ij}(E)$ at $E=0$. This peak corresponds to the band-type motion of the small polaron. Higher-order graphs for $g_{ijji}(\tau)$ would produce spreading of the peak. For instance, we could replace the zero-order electron propagators in Fig. 4 by the band propagators $g_{ii}(z)$ as given by formula (27). Now the width of the peak at $E=0$ in $S_{ij}(E)$ spreads for an amount of the order of the small-polaron bandwidth. By using the spectral function $S_{ij}(E)$, corrected in this way, the divergence of (51) disappears. The hopping region of the small-polaron motion is characterized by the fact that the main contribution to the conductivity comes from the background of $S_{ij}(E)$. Therefore, we do not calculate the spreading of the central peak explicitly, but instead we simply subtract the divergent term from (51).

In order to calculate the mobility one must know the concentration n of carriers. The concentration can be derived from the temperature-dependent one-electron propagator

$$\overleftrightarrow{\mathrm{g}}(\tau) = -\langle\langle\, T_\tau\,\underline{c}_i(\tau)\,\underline{c}_i^\dagger(0)\,\rangle\rangle\,. \tag{52}$$

If the system of polarons is dilute and the migration term in (1) represents a small perturbation, one easily shows that

$$n = \frac{N}{V}\int_{-\infty}^{\infty}A(E)\,e^{-\beta(E+\epsilon-\mu)}\,dE = \frac{N}{V}\;e^{-\beta(\epsilon-\mu)}. \tag{53}$$

The expression for the mobility therefore reads

$$\overleftrightarrow{\mu} = \pi e\beta\sum\nolimits_i(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_j)(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_j)\,\tilde{w}_{ij}^2\int_{-\infty}^{\infty}S_{ij}^2(E)\,e^{-\beta E}dE. \tag{54}$$

Formula (54) can be put in another sometimes useful form. Note that $S_{ij}(-E) = S_{ij}(E)\, e^{-\beta E}$. By using the convolution property of Fourier transforms we easily find

$$\overleftrightarrow{\mu} = e\beta \textstyle\sum_i (\vec{\mathrm{R}}_i - \vec{\mathrm{R}}_j)(\vec{\mathrm{R}}_i - \vec{\mathrm{R}}_j)\, \tilde{w}_{ij}^2\, e^{-2S}$$

$$\times \operatorname{Re} \int_0^\infty [h^2(t)\, h_{ij}^{-2}(t) - 1]\, dt. \qquad (55)$$

We have added − 1 in the square brackets in order to avoid the divergence. The integral in (55) is the same as in formula (32) for the damping Γ of the small-polaron band states.

As an example we apply the theory to the case of a one-dimensional crystal and a possibility of electron transfer only between nearest neighbors. The corresponding migration matrix element is w. The electron strongly interacts with the optical phonons in the narrow frequency band which satisfies condition (13). Because of the small-phonon dispersion we shall approximate $h_{ij}(t)$ with $j \neq i$ by 1 in the following. In this model we obtain from (54) or (55) the following approximate expression for the mobility:

$$\mu = \pi^{1/2}\, e\beta a^2 w^2 \omega_1^{-1} e^{-2S} I(4u), \qquad (56)$$

where a is the lattice constant and

$$I(x) = \sum_{n=1}^{\infty} n^{-1/2} \frac{(\frac{1}{2}x)^{2n}}{(n!)^2}. \qquad (57)$$

Many-phonon processes correspond to $u > 1$. In the asymptotic region $x \gg 1$

$$I(x) \approx \pi^{-1/2} x^{-1} e^x. \qquad (58)$$

Therefore we have approximately

$$\mu = \frac{e\beta a^2 w^2 \sinh(\frac{1}{2}\beta\omega_0)}{2\omega_1 \eta}\, e^{-2\eta \tanh(\beta\omega_0/4)}. \qquad (59)$$

This formula should be compared with Holstein's result[1] for the hopping motion mobility

$$\mu = \frac{\pi^{1/2} e\beta a^2 w^2 \sinh^{1/2}(\frac{1}{2}\beta\omega_0)}{\omega_0\, \eta^{1/2}}\, e^{-2\eta \tanh(\beta\omega_0/4)}. \qquad (60)$$

Our expression (59) for the mobility is very sensitive to the width ω_1 of the phonon spectrum, whereas Holstein's formula does not depend explicitely on ω_1 at all. This is the most important difference. The physical background of our result is the following: The density of final states in the hopping process is inversely proportional to the dispension of the phonon frequencies and therefore decreases with increasing ω_1. For the derivation of (60) a sufficient dispersion is required. By substituting for ω_1 in (59) the right-hand side of the inequality (13), one obtains Holstein's formula except for the numerical factor $\pi^{1/2}$.

Next we shall consider the case when the electron is interacting with the acoustic modes. Again, the electron will be restricted to one-dimensional motion. However, the phonon modes will be described by the three-dimensional Debye spectrum. In this case the function $h_{ij}(t)$ with $j \neq i$ cannot be approximated by 1. Actually, we get for the nearest neighbors approximately

$$h(t)\, h_{ij}^{-1}(t) = \exp\left[\frac{T}{3T_0 \nu^2 \alpha^2} \left(\frac{\alpha^2}{\alpha^2 + t^2}\right)^3 \left(1 - 3\, \frac{t^2}{\alpha^2}\right)\right], \qquad (61)$$

where $\nu = s/a$ and s the sound velocity. Note that ν is of the order of magnitude of the Debye frequency. In the calculation of (61) the same assumptions and approximations have been used as before in deriving formula (16) for $h(t)$. Further, the exponential function $e^{i\vec{q}\cdot(\vec{\mathrm{R}}_i - \vec{\mathrm{R}}_j)}$ in $h_{ij}(t)$ has been expanded into a power series and only the first three terms have been taken into account. This can be justified as $\nu\alpha > 1$. By substituting (61) in (55) we find

$$\mu = \pi e\beta a^2 w^2 \alpha\, e^{-z} \sum_{n=1}^{\infty} (4z)^n \sum_{k=0}^{n} (-1)^k (\tfrac{3}{4})^k$$

$$\times \frac{(6n - 2k - 3)!!}{k!\,(n-k)!\,(6n - 2k - 2)!!}, \qquad (62)$$

with $z = 2T/3T_0 \nu^2 \alpha^2$. This result has been obtained by expanding the exponential function in the integrand into a power series and by integrating term by term. It is interesting that in the strong-coupling limit $z \gg 1$ the small-polaron mobility does not show here an exponential temperature dependence, characteristic of an activation process.

We could now also easily calculate the band polaron mobility because the total site-jump probability which can be derived from (55) and the inverse lifetime of the polaron-band states, given by (32), are equal. This agrees with Holstein.[1]

The presented theory shows the usefulness of the propagator approach to the small-polaron problem. The perturbation expansion of the one-electron and electron-hole propagators in terms of special graphs in the real-time domain allows a better insight in the time development of the individual processes. Selection of approximations is therefore easier.

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Theory of the Effect of Finite Crystal Size on the Frequencies and Intensities of Impurity Absorption Lines in Semiconductors*

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It is demonstrated that when the dimensions of a semiconducting crystal are decreased to sizes of the order of the bulk impurity-electron Bohr radius a_0, the impurity absorption edge abruptly shifts to higher energies, while the absorption intensity decreases abruptly (both within a few a_0). The larger the dielectric constant, the larger the dimensions at which the transitional behavior occurs. Various computed results are presented for an idealized model of a shallow impurity embedded at the center of various simple finite geometries.

INTRODUCTION

In semiconducting crystals, the impurity-electron[1] Bohr radius a_0 may exceed the interlattice spacing by as much as a few orders of magnitude,[2] depending on the values of the effective mass m^* and the dielectric constant ϵ ($a_0/a_H = \epsilon m_e/m^*$, where m_e is the electronic mass, and $a_H \sim 0.53$ Å, the free-hydrogen Bohr radius). So, although a thin semiconducting crystal may contain a large enough number of atomic layers to be described, at least approximately, in terms of bulk (infinite-crystal) properties, it may nevertheless be small enough to substantially alter the motion of impurity electrons. With recent progress in thin-film technology, and in view of the desirability of performing light-absorption experiments in such crystals,[3] finite-size considerations should be of central importance in the interpretation of thin-film data, and, specifically, in deducing bulk properties from such data.

In the present paper we consider a very highly simplified model, where a single impurity is assumed fixed in the center of three specific geometries, illustrating cases where three, two, or one of the crystal dimensions are (is) finite, respectively: (a) sphere of radius R, (b) cylinder of radius R, and (c) thin film of half-width R. We employ an isotropic effective mass m^* and assume[1] a Coulomb interaction between electron and impurity. The purpose of the various simplifications is to allow the principal physical effects in such systems to emerge most clearly and directly, unhampered by unessential complications. The extension to generalizations such as nonisotropic mass, non-Coulomb interactions, or distributions of impurities should be evident from the development.

For purposes of definiteness let us from this point on speak in terms of a shallow acceptor[1] with binding energy $E_A = E_0$ in the bulk, bearing in mind that a parallel discussion follows as well for the donor case. Neglecting various broadening effects, impurity (assisted) absorption of light[4] onsets when the photon energy ω satisfies $\omega = E_g - E_0$, where E_g is the energy gap. As $\omega \to E_g$ the absorption rate increases, undergoing a new onset (edge) at $\omega = E_g$ for unassisted absorption. As detailed in various places,[5] this simplified picture can be directly generalized to include a series of impurity-electron states, as well as exciton effects. In our development we will not, for the most part, consider such effects: rather, we emphasize the impurity-electron ground state (gs) and its energy E relative to the gap E_g. For example, E_0 is the absolute value of E in the infinite crystal (binding energy or ionization energy). Note that in a finite crystal the term "binding energy" is misleading, as the gs energy E as defined here will now take on positive values; also, one does not have a continuum for energies above E_g as in the infinite crystal.

We are now in a position to point out two principle ways in which the impurity absorption is effected for $R \sim a_0$. First, the gs energy E is changed, so that the frequency at which absorp-