i.e., if it were wavelength-dependent. Thus the three shell-model force constants are equivalent to one wavelength-dependent rigid-ion model force "constant"; this wavelength dependence is negligible for nondispersive modes. Equation (A3) can be written, for small κ,

$$M\omega^2=(k+k_2)\kappa^2a^2-\left[\frac{2(k+k_2)}{4!}-k_2^2/k_1\right]\kappa^4a^4+O(\kappa^6).$$

The concept of elasticity is useful only for slowly varying deformations, i.e., when terms in κ^3a^3 and higher are small compared with the term in κ^2a^2. Thus the three shell-model force constants are equivalent to one wavelength-independent rigid-ion constant $k'\equiv(k+k_2)$ as long as we are concerned only with elasticity data. The modifications due to the use of the shell model appear only at shorter wavelengths.

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Adiabatic Theory of Nearly Small Polarons*

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An adiabatic theory of polarons is developed under conditions when the polarons are "nearly small," that is, when their binding energy is greater than or of the order of half the rigid-lattice bandwidth, but is not so great that small-polaron theory is applicable. In such an adiabatic theory there are a set of minimum-energy nuclear configurations, each of which has associated electronic wave-functions concentrated mainly on one positive ion, but spreading slightly to its neighbors. At and near these configurations trial electronic wave functions are taken in the form of linear combinations of single-ion functions for a particular ion and its nearest neighbors, with coefficients determined by minimizing the energy. Conditions for localized normal modes to be associated with any minimum are examined. Properties of wave functions describing the nuclear motion are studied within the framework of a generalized tight-binding approach. It is shown that, if localized modes are not formed, then bandwidths will decrease with increasing temperature as in small-polaron theory, but that when localized modes are present, then at nonzero temperatures, a discrete distribution of bandwidths will occur, and the thermal average of these widths may increase with increasing temperature. Optical absorption due to transitions between a wide valence band for which electron-phonon coupling is neglected and an adiabatic nearly-small-polaron conduction band with localized modes is considered. Results for absorption at absolute zero are similar to those obtained previously for a small-polaron conduction band without localized modes, but the temperature dependence of the absorption obtained here shows some new features. Parameters occurring in the theory are estimated using a continuum-polarization model for electron-phonon interactions, and numerical values are found for a simplified model of a possible conduction band in $SrTiO_3$. The calculations indicate that electronic states may exist from which both adiabatic nearly small polarons and weak-coupling large polarons can be formed, and that the lowest energy polaron state may suddenly change from one type to the other as electronic overlap integrals or electron-phonon interactions are altered in magnitude.

I. INTRODUCTION

AN excess electron in an ionic crystal produces a polarization of the lattice around it by Coulomb interaction with the surrounding ions. The complex of electron plus its surrounding lattice polarization is usually called a polaron, and the study of polarons is thus equivalent to the study of electrons interacting with a phonon field. Different methods of approach to the polaron problem are suitable according to the strength of the electron-phonon coupling[1–2]—for weak coupling it is a fair approximation to assume that the ionic displacements follow the motion of the electron, while for strong coupling the opposite approximation that the electron adjusts to the ionic motion adiabatically is generally more suitable.

If one looks at the polarization as a function of distance from the center of the polaron, which may be the instantaneous position of the electron (for weak coupling), or its averaged position over motion in its self-induced potential well (for strong coupling), then at large distances the polarization is just that which would be induced by a fixed point charge at the polaron center, while at short distances from the center the polarization potential flattens off.[1] The distance below which this potential flattens off may be said to define a polaron radius.

If the radius is appreciably greater than a lattice constant, a fair description of the system of one electron plus optical phonons is given by a Hamiltonian

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introduced by Fröhlich,[1] which was derived under three main assumptions: (1) the total effect of the one-electron periodic potential of the rigid lattice is assumed to be taken into account by giving the electron an effective mass which may differ from the free-electron mass; (2) a continuum-polarization model is used to calculate the strength of the electron-phonon interaction; (3) only a single-mode frequency occurs, that of the long-wavelength longitudinal optical phonons.

When the polaron radius is smaller than a lattice constant, the above assumptions will not be valid, but different approximations, depending on the smallness of the overlap between electron wave functions on neighboring sites may be made.[3–14] In this case of "small" polaron theory,[8] states of the system of one electron plus phonons are built up from basic localized states, each of which consists of a product of an electron state localized on a single lattice site and a set of displaced lattice oscillator states, with displacements depending on the site of the electron. Matrix elements of the Hamiltonian between localized states are divided into two types, diagonal and nondiagonal, according to whether the set of oscillator occupation numbers remains the same or changes between one state and the other. The diagonal matrix elements give rise to an energy band structure, with a bandwidth drastically altered from that of the rigid lattice by the smallness of the overlap integrals between the displaced oscillator wave functions associated with one site and the next, and this width decreases further as the temperature rises. The nondiagonal matrix elements give rise to scattering at low temperatures, while at high temperatures band theory breaks down, and they act in a different way to give a hopping motion from site to site.

A necessary condition for the polaron radius to be small is that half the rigid lattice bandwidth W_r, which equals twice the absolute value J of the electronic-energy overlap integral between electronic functions on neighboring sites in the one-dimensional tight-binding model of Holstein,[8] should be much less than the value of the modulus of the polaron self-energy, or polaron binding energy E_b which would exist if the rigid-lattice bandwidth were zero, i.e., we require for this one-dimensional model that

$$2J=\tfrac{1}{2}W_r\ll E_b. \tag{1.1}$$

In order for the perturbation approach to intersite transitions to be valid further conditions on the smallness of J have to be satisfied, viz.

$$2J<E_b^{1/2}(\hbar\omega)^{1/2},\quad T<T_t \tag{1.2}$$

or

$$J<\pi^{-3/4}(E_b)^{1/4}(kT)^{1/4}(\hbar\omega)^{1/2},\quad T>T_t, \tag{1.3}$$

where ω is the phonon frequency for the problem, and T_t is the transition temperature between the band and hopping regimes.

Small-polaron theory is adiabatic as far as single-site motion is concerned, in the sense that the lattice only responds to the averaged motion of the electron over the single-site region, but the treatment of transitions from site to site by perturbation theory is nonadiabatic. For values of overlaps J somewhat larger than those given by inequalities (1.1) to (1.3) a full adiabatic approach at the polaron problem may be more suitable. Such no approach has been used by several authors in studies of large polarons.[15,16] In this paper an adiabatic theory is developed under the conditions shown below in Eqs. (1.4) to (1.6), i.e.,

$$\{(1/z)(\tfrac{1}{2}W_r/E_b)^2\}\ll 1, \tag{1.4}$$

$$2J>\hbar\bar{\omega}, \tag{1.5}$$

and

$$W\ll\hbar\bar{\omega}. \tag{1.6}$$

In these equations, z represents the number of nearest-neighbor lattice sites to any given site, $\bar{\omega}$ is an average phonon frequency, J is an electron overlap energy, W_r is the rigid lattice bandwidth, and W is the polaron bandwidth. In general, for a tight-binding model,

$$W_r=qJ, \tag{1.7}$$

where q is a number whose order of magnitude is given by

$$q\sim 2z. \tag{1.8}$$

The exact relation of q to z depends on the lattice structure.

In the adiabatic polaron theory developed here under conditions (1.4) to (1.6), there is a set of minimum energy nuclear configurations each of which has associated electronic wave functions concentrated mainly

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on one ion, but spreading slightly to its nearest neighbors. In Sec. II a small quantity ϵ_1, whose order of magnitude is given by the left-hand side of (1.4), is introduced together with two other small quantities ϵ_2 and ϵ_3, describing the part of the electron-phonon interaction of second order in the normal coordinates and of anharmonic terms in the ordinary lattice potential, respectively. An adiabatic potential at and near minimum energy configurations is found to first order in the ϵ's by use of a variational method, with trial electronic wave functions concentrated on one positive ion but containing slight admixtures of neighboring ion functions. Because of the slight admixture of neighboring ion functions we call the polarons in the theory "nearly small." In small-polaron theory, energies and wave functions at minimum configurations are calculated to zeroth order in ϵ_1 only, and in the usual treatment terms involving ϵ_2 and ϵ_3 are not introduced either. Although for large-polaron theory it is probably a good approximation to neglect interactions quadratic in the normal coordinates and anharmonic terms in the lattice potential energy, because the actual lattice displacements around a polaron in this case are very small, for small polarons these displacements can be comparatively large (of the order of a tenth of a nearest-neighbor distance), and so such terms can be more significant. The terms proportional to the ϵ's in the potential energy expansion about a minimum represent local force constant changes, and thus tend to produce localized-normal modes for motion about this minimum. Conditions for such modes to exist are discussed qualitatively. The inequality (1.5) comes in as a necessary condition for an adiabatic theory to be valid.

In Sec. III properties of wave functions describing the ionic motion are considered within the framework of a generalized tight-binding model, and effective masses are calculated in this model for two cases with (i) no localized modes and (ii) only one localized mode per minimum and no displacements associated with the nonlocalized modes. The inequality (1.6) gives a condition for a generalized tight-binding approach to be suitable.

In Sec. IV, optical absorption due to transitions from a wide valence band for which electron-phonon coupling is neglected, to an adiabatic nearly-small-polaron conduction band with one localized mode per minimum as for case (ii) above, is calculated (to lowest order in the ϵ's) by finding transition probabilities between approximate stationary states of the electron-phonon system by perturbation theory, with the electron-radiation interaction as a perturbation. This section may be regarded as an extension of the work of Ref. 3 on absorption due to transitions between a wide band and a small-polaron band.

In Sec. V most of the parameters occurring in the theory of Secs. II to IV are evaluated by use of a continuum-polarization model of electron-phonon interactions, and as an illustration numerical values of the parameters are obtained for a simplified model of a possible conduction band in $SrTiO_3$. A brief discussion is given of the possibility that the lowest energy polaron states may suddenly change from those of the type considered here to those of a large-polaron, weak-coupling model as the electronic overlap integrals are allowed to increase, and some remarks about effects connected with localized modes around polarons are made.

II. ADIABATIC POTENTIAL AT AND NEAR MINIMUM-ENERGY CONFIGURATIONS

A. General

Suppose we have an excess electron in an ionic crystal in interaction with phonons, and we consider the adiabatic potential associated with such an electron for various fixed positions of the ions. Then, provided the electron-phonon coupling is sufficiently strong, the lowest energy ionic configurations will be those which tend to localize the electron within a region centered about some lattice point. In this section we study the adiabatic potential at and near the lowest energy configurations under conditions when it is possible to use a variational method in which trial electronic wave functions are taken which are concentrated mainly on one positive ion, but which spread slightly to neighboring ions of the same type.

We first split up the Hamiltonian H for one electron plus phonons into two parts by writing

$$H = H_0 + T_p. \tag{2.1}$$

Here T_p is the lattice kinetic energy, and

$$H_0 = T_e + V_{e\text{-}i} + V_p, \tag{2.2}$$

where T_e is the electron kinetic energy, $V_{e\text{-}i}$ is the electron-ion interaction energy and V_p is the lattice potential energy. Expanding V_p in terms of dimensionless real normal coordinates q_λ, and ignoring terms of higher order than the third in the q's we have

$$V_p = \tfrac{1}{2} \sum_{\lambda} q_\lambda^2 \hbar\omega_\lambda + \tfrac{1}{6} \sum_{\lambda\lambda'\lambda''} V_{\lambda\lambda'\lambda''}{}^{(3)} q_\lambda q_{\lambda'} q_{\lambda''}, \tag{2.3}$$

where the summations are over all the λ's, ω_λ is the angular frequency of the mode λ, and $V_{\lambda\lambda'\lambda''}{}^{(3)}$ is a symmetric tensor. In terms of the creation and annihilation operators $b_\lambda{}^\dagger$ and b_λ for the mode λ, the coordinate q_λ and its conjugate momentum p_λ may be written

$$q_\lambda = (1/\sqrt{2})(b_\lambda{}^\dagger + b_\lambda), \tag{2.4}$$

$$p_\lambda = (i/\sqrt{2})(b_\lambda{}^\dagger - b_\lambda). \tag{2.5}$$

To develop an adiabatic theory we have two problems to solve, first to find the stationary states of H_0 for the ionic configurations of interest, and then to study the ionic motion with the eigenvalues of H_0

coming in as a potential. The second part of the problem is discussed in Sec. III within the framework of a generalized tight-binding model, whereas the first part of the problem is studied in this section by a variational method as follows. Let us consider a set of real orthogonalized electronic wavefunctions $\phi_{\mathbf{R}}(\mathbf{r},q)$, which are concentrated on and moving with ions originally at lattice points $\mathbf{R}$, and which depend on electron coordinates $\mathbf{r}$ and on the set of all lattice coordinates, denoted by q. Suppose that we expand single site and overlap electronic energies associated with these functions in powers of the q's up to the second, and ignore higher order terms; i.e., we put

$$E_0(\mathbf{R},q)\equiv-\int\phi_{\mathbf{R}}(\mathbf{r},q)(T_e+V_{e-i})\phi_{\mathbf{R}}(\mathbf{r},q)d^3r$$
$$=E_{00}+E_{01}+E_{02},\quad(2.6)$$

and

$$J(\mathbf{R},\mathbf{G},q)\equiv-\int\phi_{\mathbf{R}}(\mathbf{r},q)(T_e+V_{e-i})\phi_{\mathbf{R}+\mathbf{G}}(\mathbf{r},q)d^3r$$
$$=J_0+J_1+J_2,\quad(2.7)$$

where in (2.6)

$$E_{01}=\sum_\lambda E_\lambda{}^{(1)}(\mathbf{R})q_\lambda,\quad(2.8)$$

$$E_{02}=\tfrac{1}{2}\sum_{\lambda\lambda'}E_{\lambda\lambda'}{}^{(2)}(\mathbf{R})q_\lambda q_{\lambda'},\quad(2.9)$$

while in (2.7)

$$J_1=\sum_\lambda J_\lambda{}^{(1)}(\mathbf{R},\mathbf{G})q_\lambda\quad(2.10)$$

and

$$J_2=\tfrac{1}{2}\sum_{\lambda\lambda'}J_{\lambda\lambda'}{}^{(2)}(\mathbf{R},\mathbf{G})q_\lambda q_{\lambda'}.\quad(2.11)$$

The tensors $E_{\lambda\lambda'}{}^{(2)}$ and $J_{\lambda\lambda'}{}^{(2)}$ in (2.9) and (2.11) are chosen to be symmetric.

The electron-ion interaction V_{e-i} is often split up into two parts, the periodic potential for the rigid lattice and the electron-phonon interaction, but since we are dealing with matrix elements of this potential between wave functions which themselves depend on normal coordinates q_λ, such a splitting is not useful for our problem at this stage.

Let us now suppose that the relative magnitudes of E_{01} and J are such that a fair approximation to the lowest electronic eigenvalue for q's near a minimum energy configuration may be obtained by taking trial electronic wave functions ψ of the form

$$\psi=a(q)\phi_{\mathbf{R}}(\mathbf{r},q)+\sum_{\mathbf{G}}b_{\mathbf{G}}(q)\phi_{\mathbf{R}+\mathbf{G}}(\mathbf{r},q),\quad(2.12)$$

where the sum over $\mathbf{G}$ extends over all nearest-neighbor lattice vectors, and the a's and b's are real variational coefficients satisfying

$$a^2+\sum_{\mathbf{G}}b_{\mathbf{G}}{}^2=1,\quad(2.13)$$

and are to be determined by minimizing the expectation value of H_0.

We next introduce three parameters ϵ_1, ϵ_2, and ϵ_3, defined by

$$\epsilon_1=z(2J/E_{01}),^2\quad\epsilon_2=(2E_{02}/E_{01}),\quad\epsilon_3=(2V_3/E_{01}),\quad(2.14)$$

where z is the number of nearest-neighbor lattice sites, V_3 is the anharmonic term in the lattice potential energy given by

$$V_3=\tfrac{1}{6}\sum_{\lambda\lambda'\lambda''}V_{\lambda\lambda'\lambda''}{}^{(3)}q_\lambda q_{\lambda'}q_{\lambda''},\quad(2.15)$$

and it is to be understood that the quantities occurring in (2.14) are to be taken at a minimum energy ionic configuration. We now define a quantity ϵ by

$$\epsilon=\max(\epsilon_1,\epsilon_2,\epsilon_3,b^2),\quad(2.16)$$

and assume that ϵ is small. We shall later show that

$$\sum_{\mathbf{G}}b_{\mathbf{G}}{}^2\sim\epsilon_1.\quad(2.17)$$

Then, from (2.6) to (2.11), (2.2) and (2.3), by expanding in powers of ϵ we find that the expectation value of H_0 satisfies

$$\langle H_0\rangle=-E_{00}-\sum_\lambda q_\lambda E_\lambda{}^{(1)}(\mathbf{R})+\tfrac{1}{2}\sum_\lambda q_\lambda{}^2\hbar\omega_\lambda-2\sum_{\mathbf{G}}b_{\mathbf{G}}J_0$$
$$+\sum_\lambda q_\lambda[\sum_{\mathbf{G}}b_{\mathbf{G}}{}^2\{E_\lambda{}^{(1)}(\mathbf{R})-E_\lambda{}^{(1)}(\mathbf{R}+\mathbf{G})\}$$
$$-2\sum_{\mathbf{G}}b_{\mathbf{G}}J_\lambda{}^{(1)}(\mathbf{R},\mathbf{G})]-\tfrac{1}{2}\sum_{\lambda\lambda'}q_\lambda q_{\lambda'}$$
$$\times\{E_{\lambda\lambda'}{}^{(2)}(\mathbf{R})+2\sum_{\mathbf{G}}b_{\mathbf{G}}J_{\lambda\lambda'}{}^{(2)}(\mathbf{R},\mathbf{G})\}$$
$$+\tfrac{1}{6}\sum_{\lambda\lambda'\lambda''}V_{\lambda\lambda'\lambda''}{}^{(3)}q_\lambda q_{\lambda'}q_{\lambda''}+O(\epsilon^2).\quad(2.18)$$

We should remember that

$$E_{\lambda'\lambda}{}^{(2)}=E_{\lambda\lambda'}{}^{(2)},\quad(2.19)$$

$$J_{\lambda'\lambda}{}^{(2)}=J_{\lambda\lambda'}{}^{(2)},\quad(2.20)$$

and

$$V_{P(\lambda\lambda'\lambda'')}{}^{(3)}=V_{\lambda\lambda'\lambda''}{}^{(3)},\quad(2.21)$$

where $P(\lambda\lambda'\lambda'')$ denotes any permutation of $(\lambda\lambda'\lambda'')$.

B. Minimum-Energy Configurations

It is now straightforward to find expectation values of H_0 at a minimum energy configuration by minimizing the right-hand side of (2.18) with respect to the q's for fixed a and b, and then minimizing the resulting energy with respect to a and b, subject to (2.13).

First, we expand the lowest energy q's for fixed a and b in powers of ϵ, i.e., we put

$$q_\lambda=q_\lambda{}^{(0)}+q_\lambda{}^{(1)}+\cdots,\quad(2.22)$$

where the superscripts refer to the powers of ϵ involved. Differentiating $\langle H_0\rangle$ of (2.18) with respect to q_λ, equating the result to zero, and ignoring terms of order ϵ gives immediately

$$q_\lambda{}^{(0)}=\{E_\lambda{}^{(1)}(\mathbf{R})/\hbar\omega_\lambda\}.\quad(2.23)$$

Putting this value of q_λ into the terms of order ϵ in

$\{\partial\langle H_0\rangle/\partial q_\lambda\}$ we deduce

$$q_\lambda^{(1)}=(\hbar\omega_\lambda)^{-1}\Bigg[\sum_{\mathbf{G}} b_{\mathbf{G}}^2\{E_\lambda^{(1)}(\mathbf{R}+\mathbf{G})-E_\lambda^{(1)}(\mathbf{R})\}$$
$$+2\sum_{\mathbf{G}} b_{\mathbf{G}}\left\{J_\lambda^{(1)}(\mathbf{R},\mathbf{G})+\sum_{\lambda'}\frac{E_{\lambda'}^{(1)}(\mathbf{R})}{\hbar\omega_{\lambda'}}J_{\lambda\lambda'}^{(2)}(\mathbf{R},\mathbf{G})\right\}$$
$$+\sum_{\lambda'}\frac{E_{\lambda'}^{(1)}(\mathbf{R})}{\hbar\omega_{\lambda'}}E_{\lambda\lambda'}^{(2)}(\mathbf{R})$$
$$-\tfrac{1}{2}\sum_{\lambda'\lambda''}V_{\lambda\lambda'\lambda''}^{(3)}\frac{E_{\lambda'}^{(1)}(\mathbf{R})E_{\lambda''}^{(1)}(\mathbf{R})}{\hbar\omega_{\lambda'}\hbar\omega_{\lambda''}}\Bigg]. \qquad (2.24)$$

Hence, substituting from (2.22) to (2.24) into (2.18), we obtain, to first order in ϵ,

$$\langle H_0\rangle=-E_{00}-B_0-2\sum_{\mathbf{G}} b_{\mathbf{G}}J_m+2\sum_{\mathbf{G}} b_{\mathbf{G}}^2(B_0-C_0)-B_2+V_{3m}, \qquad (2.25)$$

where

$$B_0=\tfrac{1}{2}\sum_\lambda(\{E_\lambda^{(1)}(\mathbf{R})\}^2/\hbar\omega_\lambda), \qquad (2.26)$$

$$J_m=J(\mathbf{R},\mathbf{G},q)_{q_\lambda=q_\lambda^{(0)}}, \qquad (2.27)$$

$$C_0=\tfrac{1}{2}\sum_\lambda(E_\lambda^{(1)}(\mathbf{R})E_\lambda^{(1)}(\mathbf{R}+\mathbf{G})/\hbar\omega_\lambda) \qquad (2.28)$$

$$B_2=\tfrac{1}{2}\sum_{\lambda\lambda'}(E_\lambda^{(1)}(\mathbf{R})E_{\lambda'}^{(1)}(\mathbf{R})E_{\lambda\lambda'}^{(2)}(\mathbf{R})/\hbar\omega_\lambda\hbar\omega_{\lambda'}) \qquad (2.29)$$

and

$$V_{3m}=V_3(q)_{q_\lambda=q_\lambda^{(0)}}. \qquad (2.30)$$

Minimizing (2.25) with respect to $b_{\mathbf{G}}^2$, we find that (to first order in ϵ) $b_{\mathbf{G}}$, a, and the energy at the minimum $E_{\min}$ satisfy

$$b_{\mathbf{G}}=J_m/F, \qquad (2.31)$$

$$a=\{1-z(J_m/F)^2\}^{1/2}\simeq\{1-\tfrac{1}{2}z(J_m/F)^2\}, \qquad (2.32)$$

and

$$E_{\min}=-E_{00}-B_0-(zJ_m^2/F)-B_2+V_{3m}, \qquad (2.33)$$

where we have introduced the notation

$$F=2(B_0-C_0). \qquad (2.34)$$

In (2.26), (2.29), and (2.34), B_0 is the polaron binding energy that would exist if all ϵ's were zero, B_2 is the change of polaron binding energy due to terms in single site energies of second order in the normal coordinates, and F may be understood by noting that $\frac{1}{4}F$ represents the difference in energy on the adiabatic potential curve that would exist between a minimum and a saddle point between two minima if all ϵ's were zero.

C. Configurations near Minimum

For general q's, a and b may be determined in our variational method by minimizing the expression (2.18) for the energy with respect to the b's. Differentiating the right-hand side of (2.18) with respect to $b_{\mathbf{G}}$, and equating the result to zero, we find that

$$b_{\mathbf{G}}=\frac{J_0+\sum_\lambda q_\lambda J_\lambda^{(1)}(\mathbf{R},\mathbf{G})+\frac{1}{2}\sum_{\lambda\lambda'}q_\lambda q_{\lambda'}J_{\lambda\lambda'}^{(2)}(\mathbf{R},\mathbf{G})}{\sum_\lambda q_\lambda\{E_\lambda^{(1)}(\mathbf{R})-E_\lambda^{(1)}(\mathbf{R}+\mathbf{G})\}}. \qquad (2.35)$$

To determine the $b_{\mathbf{G}}$'s for small departures of the normal coordinates q from their values $q_{\lambda m}$ (say) at a minimum configuration, we put

$$q_\lambda=q_{\lambda m}+\theta_\lambda, \qquad (2.36)$$

and expand $b_{\mathbf{G}}$ in powers of θ_λ. Thus we write

$$b_{\mathbf{G}}=b_0+b_{1\mathbf{G}}+b_{2\mathbf{G}}+\cdots, \qquad (2.37)$$

where the numerical subscripts refer to the powers of the θ's involved. Then, from (2.35) and (2.36), making use of (2.26), (2.28), (2.34), (2.22), and (2.23), we find, to the first order in ϵ, that

$$b_0=(J_m/F), \qquad (2.38)$$

$$b_{1\mathbf{G}}=(J_m/F)\sum_\lambda\theta_\lambda\{P_\lambda(\mathbf{R},\mathbf{G})+Q_\lambda(\mathbf{R},\mathbf{G})\}, \qquad (2.39)$$

and

$$b_{2\mathbf{G}}=(J_m/F)\sum_{\lambda\lambda'}\theta_\lambda\theta_{\lambda'}[\{P_\lambda(\mathbf{R},\mathbf{G})+Q_\lambda(\mathbf{R},\mathbf{G})\}\times Q_{\lambda'}(\mathbf{R},\mathbf{G})+S_{\lambda\lambda'}(\mathbf{R},\mathbf{G})], \qquad (2.40)$$

where, as in (2.27), J_m is the overlap energy at the minimum, and P_λ, Q_λ, and $S_{\lambda\lambda'}$ are defined by

$$P_\lambda(\mathbf{R},\mathbf{G})=(1/J_m)\{J_\lambda^{(1)}(\mathbf{R},\mathbf{G})+\sum_{\lambda'}(E_{\lambda'}^{(1)}(\mathbf{R})/\hbar\omega_{\lambda'})J_{\lambda\lambda'}^{(2)}(\mathbf{R},\mathbf{G})\}, \qquad (2.41)$$

$$Q_\lambda(\mathbf{R},\mathbf{G})=(1/F)\{E_\lambda^{(1)}(\mathbf{R}+\mathbf{G})-E_\lambda^{(1)}(\mathbf{R})\}, \qquad (2.42)$$

and

$$S_{\lambda\lambda'}(\mathbf{R},\mathbf{G})=\{\tfrac{1}{2}J_{\lambda\lambda'}^{(2)}(\mathbf{R},\mathbf{G})/J_m\}. \qquad (2.43)$$

The quantities $P_\lambda\theta_\lambda$ and $Q_\lambda\theta_\lambda$ in (2.39) and (2.40) represent, respectively, the fractional change, due to change of q_λ from $q_{\lambda m}$ to $(q_{\lambda m}+\theta_\lambda)$, of overlap J and of the energy difference, to zeroth order in ϵ, between the point q_λ and a saddle point on the adiabatic potential-energy surface.

Substituting from (2.36) to (2.40) into (2.18), using (2.41) to (2.43), and consistently ignoring terms in ϵ^2, we find, after some algebra, that to first order in ϵ and second order in the θ's the energy near a minimum satisfies

$$E=E_{\min}+\sum_{\lambda\lambda'}U_{\lambda\lambda'}\theta_\lambda\theta_{\lambda'}, \qquad (2.44)$$

where

$$U_{\lambda\lambda'}=\tfrac{1}{2}\delta_{\lambda\lambda'}\hbar\omega_\lambda-\sum_{\mathbf{G}}[(J_m^2/F)\times\{(P_\lambda+Q_\lambda)(P_{\lambda'}+Q_{\lambda'})+2S_{\lambda\lambda'}\}]-\tfrac{1}{2}E_{\lambda\lambda'}^{(2)}+\tfrac{1}{2}\sum_{\lambda''}V_{\lambda\lambda'\lambda''}^{(3)}\{E_{\lambda''}^{(1)}(\mathbf{R})/\hbar\omega_{\lambda''}\}. \qquad (2.45)$$

From (2.44) and (2.45) we see that, to zeroth order in ϵ, phonon frequencies are unchanged by the presence of the polaron. Hence, using (2.23), the polaron-binding energy E_b for zero J satisfies $E_b \simeq B_0$. Further, from (2.8), (2.23), and (2.26), $B_0 \simeq \frac{1}{2}E_{01}$. Thus, since the rigid lattice bandwidth W_r satisfies $W_r \sim 2zJ$, the condition that ϵ_1 of (2.14) be small may be rewritten in the form (1.4).

D. Possibility of Localized Modes

The last three terms in (2.45) only contain contributions from ions within a limited region of the solid. Let us diagonalize these terms separately, i.e., we put

$$E = E_{\min} + \sum_\lambda \tfrac{1}{2}\hbar\omega_\lambda\theta_\lambda^2 + \sum_s \tfrac{1}{2}C_s\xi_s^2\hbar\bar{\omega}, \qquad (2.46)$$

where the ξ_s's are obtained by a unitary transformation from the θ_λ's, $\bar{\omega}$ is a mean-phonon frequency (for definiteness let it be the unweighted arithmetic mean), and we choose C_s so that

$$C_s = \pm A_s, \qquad (2.47)$$

where A_s is positive and

$$A_1 \geqslant A_2 \geqslant \cdots \geqslant A_i \geqslant A_{i+1} \geqslant \cdots. \qquad (2.48)$$

Because the last term in (2.46) represents appreciable ionic displacements only within a small region, we know that only a limited number of A_i's are significantly different from zero. Each of the ξ_i's associated with these A_i's will be composed of displacements of ions within a limited distance of the polaron, and in particular the first few ξ_i's will contain an appreciable fraction of nearest-neighbor displacements.

Now, as discussed above in subsection C, at a minimum energy configuration the magnitude of the first-order term in the single site energy E_{01} satisfies $E_{01} \simeq 2B_0$, to zeroth order in ϵ, and so, from the definitions (2.14) of the ϵ's, and use of (2.41), (2.42), (2.43), (2.23), (2.26), (2.28), (2.34), (2.7), (2.10), (2.11) and the fact that we expect $F \sim B_0$ (see Sec. V), we deduce that the contribution to the energy expression $(\sum_{\lambda\lambda'} U_{\lambda\lambda'}q_{\lambda m}q_{\lambda' m})$ from the last three terms of (2.45) is of order $B_0\epsilon$. Thus, if we introduce quantities v_s which are related to the q's in the same way as the quantities ξ_s are to the θ_λ's (i.e., if $\boldsymbol{\xi} = U\boldsymbol{\theta}$, then $\mathbf{v} = U\mathbf{q}$, where U is a unitary matrix and $\boldsymbol{\xi}, \boldsymbol{\theta}$, $\mathbf{v}$, and $\mathbf{q}$ denote vectors with components ξ_λ, θ_λ, v_λ, and q_λ), then we expect, for a minimum q configuration, that

$$\left|\sum_s \tfrac{1}{2}C_s v_s^2\right| \sim (B_0/\hbar\bar{\omega})\epsilon. \qquad (2.49)$$

Further, if we let $\hat{\zeta}$ be a unit vector in q space in the direction from the origin to the minimum configuration being considered, and let $\hat{v}_s$ be a unit vector in the direction corresponding to v_s, then, since, from (2.33), to lowest order in ϵ the energy $E_{\min}$ at the minimum satisfies

$$E_{\min} \simeq -E_{00} - B_0, \qquad (2.50)$$

then the displacement ζ_m at the minimum in the direction of $\hat{\zeta}$ is given by

$$\zeta_m \simeq (2B_0/\hbar\bar{\omega}_\zeta)^{1/2}, \qquad (2.51)$$

where $\bar{\omega}_\zeta$ is a mean phonon frequency weighted by the factors $q_{\lambda m}{}^{(0)}$. Thus values of v_s at the minimum satisfy

$$v_s = (\hat{\zeta}\cdot\hat{v}_s)(2B_0/\hbar\bar{\omega}_\zeta)^{1/2}. \qquad (2.52)$$

Hence from (2.49) to (2.52) we deduce

$$\left|\sum_s C_s(\hat{\zeta}\cdot\hat{v}_s)^2\right| \sim \epsilon. \qquad (2.53)$$

If the C_s's of significance are all of the same sign we may deduce from (2.53) and (2.47) that

$$|C_1| = A_1 \lesssim \epsilon. \qquad (2.54)$$

For further discussion of the magnitude of A_1 it is helpful to distinguish between cases where the second, third or fourth term of $U_{\lambda\lambda'}$ of (2.45) is the largest. If we consider the expression $(\sum_{\lambda\lambda'} U_{\lambda\lambda'}q_{\lambda m}q_{\lambda' m})$ then we can show, by use of equations mentioned in the argument leading to (2.49), that the contributions of the second, third, and fourth terms of (2.45) to the energy are in the ratio $\epsilon_1{:}\epsilon_2{:}\epsilon_3$. Hence it is probable that the ratio of the contributions of the second, third, and fourth terms of (2.45) in the expression $(\sum_{\lambda\lambda'} U_{\lambda\lambda'}\theta_\lambda\theta_{\lambda'})$ are also in the ratio $\epsilon_1{:}\epsilon_2{:}\epsilon_3$. Thus the term dominates which corresponds to the largest ϵ_i. The terms involving $E_{\lambda\lambda'}{}^{(2)}$ and $V_{\lambda\lambda'\lambda''}{}^{(3)}$ could exist for small polarons as well as for nearly small ones, and to make a study of these terms would require the introduction of a particular force-constant model. However, the term proportional to $(J_m{}^2/F)$ in (2.45), being dependent on wave-function spreading, is peculiar to nearly small polarons, and can be examined without too many further hypotheses.

We here make a study of the *special case* arising when

$$\epsilon_1 \gg \epsilon_2, \epsilon_3;\; Q_\lambda \gg P_\lambda;\; Q_\lambda Q_{\lambda'} \gg S_{\lambda\lambda'}. \qquad (2.55)$$

The first two inequalities in (2.55) mean that effects of wave-function spreading are of more importance than those of electron-phonon interactions quadratic in the normal coordinates or of anharmonic terms in the lattice potential energy. The last two inequalities imply that terms in the energy arising from a dependence of the amount of wave-function spreading on lattice coordinates are larger than those arising from dependence of the magnitude of overlap integrals on ionic displacements.

Now, using the definitions (2.42), (2.34), (2.26), and (2.28) of Q_λ, F, B_0, and C_0, we find that

$$\sum_\lambda (Q_\lambda{}^2/\hbar\omega_\lambda) = 2/F. \qquad (2.56)$$

We rewrite (2.56) as

$$\sum_\lambda Q_\lambda{}^2 = (2\hbar\bar{\omega}_Q/F), \qquad (2.57)$$

where (2.57) defines a weighted average-phonon frequency $\bar{\omega}_Q$. Under the assumptions (2.55), using (2.45), and taking into account the remarks of the previous paragraph, the energy expression (2.44) becomes

$$E \simeq E_{\mathrm{min}} + \sum_\lambda \tfrac{1}{2}\hbar\omega_\lambda \theta_\lambda{}^2 - \tfrac{1}{2}(2J_m/F)^2 \hbar\bar{\omega}_Q \sum_{\mathbf{G}} \eta_{\mathbf{G}}{}^2 , \tag{2.58}$$

where

$$\eta_{\mathbf{G}} = \sum_\lambda Q_\lambda \theta_\lambda (F/2\hbar\bar{\omega}_Q)^{1/2} . \tag{2.59}$$

Using (2.57) we see that the sum of squares of coefficients of θ_λ in the expansion of $\eta_{\mathbf{G}}$ is unity. However, the $\eta_{\mathbf{G}}$'s are not necessarily orthogonal. Taking suitable orthogonal linear combinations ξ_s of the $\eta_{\mathbf{G}}$'s ($s=1$ to z, where z is the number of nearest-neighbor lattice sites), and completing an orthonormal set with any suitable expressions ξ_s ($s>z$), we obtain an expression for the energy of the form (2.46) (with $C_s=0$ for $s>z$), and so by considering the extreme cases where all the $\eta_{\mathbf{G}}$'s are the same, or where they are all mutually perpendicular, we find that

$$z(2J_m/F)^2 \geqslant A_1 \geqslant (2J_m/F)^2 . \tag{2.60}$$

Now let us return to the general expression (2.46) and examine conditions for the term $(\sum_s \frac{1}{2} C_s \xi_s{}^2 \hbar\bar{\omega})$ in the energy to produce localized modes. Each term $(\frac{1}{2} C_s \xi_s{}^2 \hbar\bar{\omega})$ represents an addition to the potential energy within a certain limited region of the crystal, i.e., it represents local force constant changes. Most theoretical work on localized-mode formation[17] has been done for mass defects without force-constant changes; such defects introduce extra terms in the kinetic energy over a limited region instead of in the potential energy as for the force-constant case. In one and two dimensions any mass defect will produce a localized mode, while in three dimensions the difference in mass of the impurity from that of the host atoms must exceed a certain minimum value for localized modes to be formed. If m' is the mass of a defect and m the mass of the atoms of a host crystal with one atom per unit cell, and we write $(m'-m)/m=\epsilon'$, the condition on ϵ' for localized modes to exist was discovered by Lifshitz[18] many years ago. In our case $(\frac{1}{2} A_1 \xi_1{}^2 \hbar\bar{\omega})$ represents a term in the potential energy analogous to the mass-defect term in the kinetic energy with A_1 replacing ϵ' above. If further, we suppose that ξ_1 is composed mainly of coordinates of modes of one branch of the phonon spectrum (which is likely, at least for our special case (2.55) above, because then ξ_1 contains the largest contributions from modes with the biggest displacements, which in an ionic crystal are probably the longitudinal-optical modes) then we might suppose that a formula analogous to the condition of Lifshitz holds as a condition for the term $(\frac{1}{2} A_1 \xi_1{}^2 \hbar\bar{\omega})$ to produce localized modes. Making this assumption, by use of Eq. (13) of Ref. 18, we deduce that if

$$A_1 > \epsilon_0 \tag{2.61}$$

localized modes occur, but if

$$A_1 < \epsilon_0 \tag{2.62}$$

localized modes do not occur, where ϵ_0 is defined by

$$\epsilon_0 \equiv 8\pi^3 \Big/ V_c \omega_0{}^2 \int \frac{d^3\mathbf{w}}{[\omega_0{}^2 - \omega^2(\mathbf{w})]} \sim \frac{\Delta\omega}{\bar{\omega}} . \tag{2.63}$$

In (2.63) V_c is the volume of a unit cell of the crystal, ω_0 represents an extreme frequency of the optical modes, $\bar{\omega}$ is a mean frequency, $\Delta\omega$ is a spread of frequencies, $\omega(\mathbf{w})$ is the frequency of the mode of wave vector $\mathbf{w}$ for the branch of the phonon spectrum being considered, and the integration is over all phonon wave vectors $\mathbf{w}$. The right-hand side of (2.63) follows if we assume $\bar{\omega} \gg \Delta\omega$, and that the average value of $1/[\omega_0 - \omega(\mathbf{w})]$ is of order $(2/\Delta\omega)$.

Thus, if $A_1 \sim \epsilon$, we have in (2.61) to (2.63) conditions on ϵ for the existence of localized modes. Since each term in $\xi_s{}^2$ in (2.46) gives a tendency to change the frequency associated with ξ_s by a factor of about $(1 \pm \frac{1}{2} A_s)$ for small A_s, using (2.63) we see that (2.61) states the condition that this potential change of frequency should be greater than half the phonon band width.

E. Potential along Lines Joining Minima

So much for the values of H_0 for the lowest energy electronic states of the form of our trial functions of (2.12) for ionic configurations at and near those which give the lowest energy. The lowest eigenvalues of H_0 for large displacements from the minimum energy configuration, and the form of the energy curves for excited-electronic states are not known in detail, but, from the work of Yamashita and Kurosowa,[9] we expect the general form along lines joining two minima to be as indicated in Fig. 1, with the minimum separation between the ground and excited states equal to $2J$ to lowest order in ϵ. We thus expect that a necessary condition for an adiabatic theory to hold is that this separation should be greater than a mean phonon frequency, i.e., we require

$$2J > \hbar\bar{\omega} . \tag{2.64}$$

In the figure the dotted lines indicate that if J were zero the potential energy curves would continue to rise quadratically. Thus, at a minimum point on the lower curve, from (2.23), (2.36), (2.44), and (2.45), to lowest order in ϵ we find that the energy separation E_s satisfies

$$E_s \simeq \tfrac{1}{2} \sum_\lambda \left\{ \frac{E_\lambda{}^{(1)}(\mathbf{R}+\mathbf{G}) - E_\lambda{}^{(1)}(\mathbf{R})}{\hbar\omega_\lambda} \right\}^2 \hbar\omega_\lambda = F , \tag{2.65}$$

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[17] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and G. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

[18] I. M. Lifshitz, Nuovo Cimento Suppl. 3, 716 (1956).

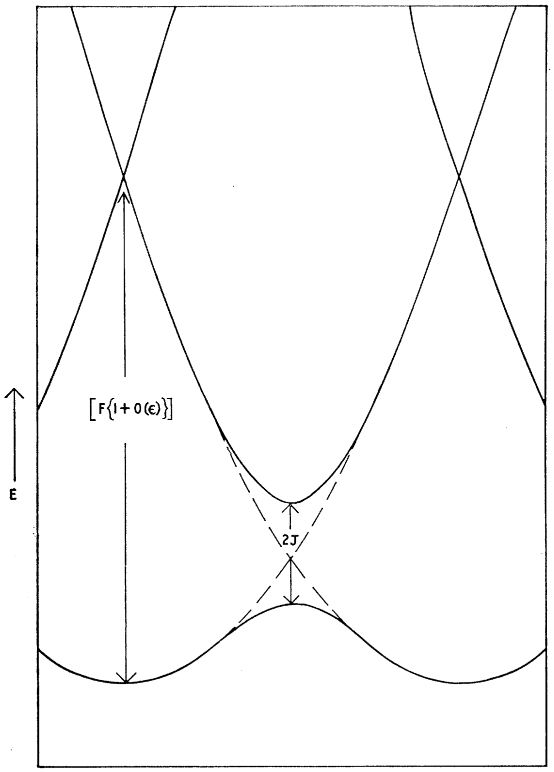

FIG. 1. Sketch of expected form of lowest and first excited-state adiabatic potential energy E along a line joining two points of minimum potential on the lower energy surface in q space.

where to obtain the right-hand equality to make use of the definitions (2.26), (2.28), and (2.34).

III. WAVE FUNCTIONS DESCRIBING IONIC MOTION

A. Generalized Tight-Binding Method

The first part of the adiabatic problem, that of finding the eigenfunctions and eigenvalues of the part H_0 of the Hamiltonian H of (2.1) was treated in Sec. II for low-energy ionic configurations by use of a variational method, with trial functions of the form shown in (2.12). The second part of the problem, the investigation of the wave functions describing the ionic motion with the eigenvalues of H_0 coming in as a potential, would in general, be very difficult. However, if the potential wells at the minima in the potential are sufficiently deep, then a generalized tight-binding method should be of use, and in this section we study the wave functions describing the ionic motion by such a method, concentrating on two cases when (i) no localized modes are formed around the polaron or (ii) there exists one localized mode associated with each minimum and there are no mode displacements associated with the nonlocalized modes.

If we denote the creation and annihilation operators for the ith normal mode for the minimum in the adiabatic potential associated with $\mathbf{R}$ by $b_i^\dagger(\mathbf{R})$ and $b_i(\mathbf{R})$, then the eigenstates $|\chi_{n\mathbf{R}}\rangle$ of the Hamiltonian $\{\langle H_0\rangle + T_p\}$ describing the ionic motion that would exist if $\langle H_0\rangle$ continued to be harmonic at all distances from the minimum, may be written as

$$|\chi_{n\mathbf{R}}\rangle = \prod_i (\{b_i^\dagger(\mathbf{R})\}^{n_i}/(n_i!)^{1/2}) |0_\mathbf{R}\rangle, \qquad (3.1)$$

where the product is over all modes i, and $|0_\mathbf{R}\rangle$ denotes the vacuum state for the set of modes associated with $\mathbf{R}$. Having chosen the labeling i for the set of modes associated with one minimum, we can choose the labeling for those associated with the other minima in such a way that the translation operator which changes $\mathbf{R}$ into $\mathbf{R}'$ transforms the annihilation operator $b_i(\mathbf{R})$ into $b_i(\mathbf{R}')$, and similarly for creation operators. Thus, it is meaningful to divide matrix elements between states as given by (3.1) into two types, diagonal and nondiagonal, according to whether or not the set of mode occupation numbers n_i is identical for both states or not.

Now, if the potential wells associated with minima are sufficiently deep relative to the hills in between them, the overlap between different functions with the same set of occupation numbers n_i will be small, i.e., we have

$$\langle \chi_{n\mathbf{R}} | \chi_{n\mathbf{R}'} \rangle \ll 1 . \qquad (3.2)$$

Hence, if following Sewell[6] and Holstein's[8] approach for small-polaron theory, we suppose that the polaron band structure is associated with the diagonal matrix elements of the Hamiltonian between states for different minima,[19] while the nondiagonal matrix elements just give scattering at low temperatures, then we may study the band structure by use of a generalized tight-binding model, in which the band states are built up as Bloch-type linear combinations $|\chi_{n\mathbf{k}}\rangle$ of a set of orthogonalized states $|\chi'_{n\mathbf{R}}\rangle$ obtained from the set $|\chi_{n\mathbf{R}}\rangle$ for a fixed set of occupation numbers. Thus we take band states of the form

$$|\chi_{n\mathbf{k}}\rangle = \frac{1}{N^{1/2}} \sum_\mathbf{R} \exp(i\mathbf{k}\cdot\mathbf{R}) |\chi'_{n\mathbf{R}}\rangle, \qquad (3.3)$$

where N is the number of cells in the crystal. However, the actual method of forming the orthogonalized set of states $|\chi'_{n\mathbf{R}}\rangle$ from the set $|\chi_{n\mathbf{R}}\rangle$ is not obvious, since the overlap between states $|\chi_{n\mathbf{R}}\rangle$ and $|\chi_{n\mathbf{R}'}\rangle$ does not become small as $(\mathbf{R}-\mathbf{R}')$ becomes large, and in fact, it is shown in Appendix A, for the case where all the ϵ's of Sec. II are neglected, if a continuum polarization model for the electron-phonon interaction is used and there is no dispersion of phonon frequencies, that

$$\langle \chi_{n\mathbf{R}} | \chi_{n\mathbf{R}'} \rangle = K + O(C/|\mathbf{R}-\mathbf{R}'|), \qquad (3.4)$$

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[19] This approach is only applicable if the dispersion of phonon frequencies is greater than some minimum value, probably of the order of ΔE, where ΔE is the uncertainty in energy of electron states due to scattering. For dispersion smaller than this value but still under conditions when localized modes are not formed, then an approach due to Nagaev may be more suitable (Ref. 20).

for large $(\mathbf{R}-\mathbf{R}')$, where K and C are constants. Notwithstanding this fact, provided that the actual value of the individual overlaps between the states $|\chi_{n\mathbf{R}}\rangle$ is small, then it is probable that we can form the orthogonalized set $|\chi'_{n\mathbf{R}}\rangle$ in such a way that

$$\big|\,|\chi'_{n\mathbf{R}}\rangle-|\chi_{n\mathbf{R}}\rangle\big|\ll 1\,, \qquad (3.5)$$

for all $\mathbf{R}$. This is shown to be possible in Appendix B if all overlaps are constant (independent of $|\mathbf{R}-\mathbf{R}'|$), or if all overlaps are zero except in a small region, or for a combination of these two factors. With a term of order $\{C/|\mathbf{R}-\mathbf{R}'|\}$ occurring in the overlap a proof that an orthogonal set can be formed to satisfy the relation (3.5) has not been found. However, as overlaps proportional to $(1/r)$ are in some sense intermediate between overlaps independent of r and those of short range, it would be surprising if such an orthogonal set did not exist.

If we assume (3.5), it is then straightforward to show that the matrix elements between states of the Hamiltonian between orthogonalized functions satisfy

$$\langle\chi'_{n\mathbf{R}}|H_g|\chi'_{n\mathbf{R}'}\rangle\simeq\langle\chi_{n\mathbf{R}}|(H_g-H_{\mathbf{R}'})|\chi_{n\mathbf{R}'}\rangle\,, \qquad (3.6)$$

where $H_g=\{\langle H_0\rangle+T_p\}$, and $H_{\mathbf{R}'}$ is the Hamiltonian of which $|\chi_{n\mathbf{R}'}\rangle$ is an eigenfunction. Hence, choosing our origin of energy suitably, we obtain that the energy $E_{\mathbf{k}}$ associated with a Bloch-type function is given by

$$E_{\mathbf{k}}\simeq\sum_{\mathbf{R}'\neq\mathbf{R}}\exp\{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})\}\langle\chi_{n\mathbf{R}}|(H_g-H_{\mathbf{R}'})|\chi_{n\mathbf{R}'}\rangle\,. \qquad (3.7)$$

Now, at the point of maximum overlap of $|\chi_{n\mathbf{R}}\rangle$ and $|\chi_{n\mathbf{R}'}\rangle$, which will occur at the saddle point in the potential energy function lying on the line joining the minima associated with $\mathbf{R}$ and $\mathbf{R}'$, the difference in energy $(H_g-H_{\mathbf{R}'})$ will be equal, to lowest order in ϵ, to the energy overlap integral between electronic states associated with ions originally at $\mathbf{R}$ and $\mathbf{R}'$, since to this order in ϵ it is only these overlaps which change the potential energy curve from the simple harmonic form. Since these overlaps have been assumed small even for nearest neighbors, they will be negligible for any more distant neighbors. Thus, the bandwidth just depends on matrix elements as given by (3.6) for $\mathbf{R}'=\mathbf{R}+\mathbf{G}$, where $\mathbf{G}$ is a nearest-neighbor lattice vector. Now, provided that the energy $(H_g-H_{\mathbf{R}+\mathbf{G}})$ only changes slightly in the region of significant overlap of $|\chi_{n\mathbf{R}}\rangle$ and $|\chi_{n,\mathbf{R}+\mathbf{G}}\rangle$, then we may put $(H_g-H_{\mathbf{R}+\mathbf{G}})$ equal to the value J_s in the matrix element, where J_s is the electronic energy overlap integral at the saddle point. Hence in our generalized tight-binding approximation we find, using (3.7) and the remarks above, that the bandwidth W satisfies

$$\begin{aligned}W&\simeq q\langle\chi_{n\mathbf{R}}|(H_g-H_{\mathbf{R}+\mathbf{G}})|\chi_{n,\mathbf{R}+\mathbf{G}}\rangle\\&\simeq qJ_s\langle\chi_{n\mathbf{R}}|\chi_{n,\mathbf{R}+\mathbf{G}}\rangle\,,\end{aligned} \qquad (3.8)$$

where q is the quantity, of the order of twice the number of nearest neighbors z, which relates bandwidth to overlap integrals in a tight-binding calculation. (For a simple cubic lattice $q=12$ and $z=6$, while for the NaCl structure $q=16$ and $z=12$.) The condition for the right-hand equality of (3.8) to hold may be seen by considering the case of no dispersion of the normal-mode frequencies, when the coordinate η (say) which describes motion from one minimum to the next may be considered as a normal coordinate if terms proportional to ϵ in the potential energy are ignored. Now the separation of the harmonic curve from the adiabatic potential curve is of order J_s over a region where the potential energy $(\frac{1}{2}\eta^2\hbar\omega)$ changes by an amount of order J_s, and over this region the lattice wave function changes by a factor $\exp(-J_s/\hbar\omega)$. Thus, the criterion for the applicability of the right-hand equation of (3.8) is that

$$\exp(2J_s/\hbar\omega)\gg 1\,, \qquad (3.9)$$

which is roughly equivalent to the previous criterion (1.5) for the adiabatic theory to apply, but slightly stronger. Since it is necessary that the system stay near one minimum for a time long compared with a mean reciprocal frequency of the lattice $(1/\bar{\omega})$ for the tight-binding approximation to be suitable, another necessary condition for the validity of our approximations is that the bandwidth W should satisfy

$$W\ll\hbar\bar{\omega}\,. \qquad (1.6)$$

We should note that in the perturbation approach to small-polaron theory, valid for small overlaps J, a tight-binding method is used for the total-wave function of the system instead of just for the part of the wave function describing the ionic motion as discussed here, and the result obtained for the bandwidth is just of the form (3.8). Thus it seems that the conditions (1.5) and (3.9) may not be of significance for our problem, and that (3.8) is valid for all J sufficiently small for (1.6) to hold.

Having obtained (3.8), our next task is to put the creation and annihilation operators associated with one minimum in terms of those associated with the next, or more conveniently to put them both in terms of some sets β_i and $\beta_i^\dagger$, which we choose so that

$$b_i(\mathbf{R}+\mathbf{G})=\beta_i+X_i \qquad (3.10)$$

and

$$b_i(\mathbf{R})=\beta_i-\sum_j a_{ij}\beta_i-\sum_j c_{ij}\beta_j^\dagger\,, \qquad (3.11)$$

where X_i are mode displacements, and a_{ij} and c_{ij} are expansion coefficients, satisfying

$$|1-a_{ii}|^2+\sum_{j\neq i}|a_{ij}|^2-\sum_j|c_{ij}|^2=1\,. \qquad (3.12)$$

For a single oscillator with an added term in the potential energy of order ϵ times the original one, it is easy to show that the ratio (c/a) of the coefficients in the equation of the form (3.12) is of order ϵ. Thus, extrapolating to the case of many modes and additional potential energy terms of order ϵ times the contribution from the original terms in a localized region as in (2.44) and (2.45), we expect that the c_{ij}'s will be small, satisfying

$$(c_{ij}/a_{ij}) \lesssim \epsilon. \qquad (3.13)$$

We shall assume that the c_{ij}'s can be neglected for the remainder of this section. Making this approximation, and noting that the vacuum state associated with a displaced oscillator $(b+d)$ is related to the vacuum associated with b by

$$|O_d\rangle = \exp(-b^\dagger d)|0\rangle \exp\{-\tfrac{1}{2}|d|^2\}, \qquad (3.14)$$

we deduce from (3.1), (3.10), (3.13), and (3.14) that the diagonal overlap integrals Q_{nn} between states $|\chi_{n\mathbf{R}}\rangle$ and $|\chi_{n,\mathbf{R}+\mathbf{G}}\rangle$ satisfy

$$Q_{nn} \equiv \langle \chi_{n\mathbf{R}} | \chi_{n,\mathbf{R}+\mathbf{G}} \rangle \simeq \langle O_\beta | \textstyle\prod_i [\{(\beta_i - \sum_j a_{ij}\beta_j)^{n_i} \times (\beta_i^\dagger + X_i^*)^{n_i} | n_i!\} \exp(-\beta_i^\dagger X_i)] | 0_\beta \rangle \exp(-\tfrac{1}{2}S), \qquad (3.15)$$

where $|0_\beta\rangle$ denotes the vacuum state with respect to the β's, and S is the sum of squares of displacements defined by

$$S = \textstyle\sum_i |X_i|^2. \qquad (3.16)$$

The neglect of some terms of first order in ϵ in deriving (3.15) might seem to be inconsistent with inclusion of first-order terms previously. However there are two special features about the effects of the terms which were included before: (1) they can produce localized modes of lattice vibration, i.e., qualitative changes in the surroundings of the polaron; (2) they can produce changes in the quantity S in (3.15) of order ϵS, and since we expect $S \gtrsim 10$ (see Sec. V) the effects of these changes on the polaron bandwidth are not small. Neither of these special features is expected to arise in connection with the ignoring of the c_{ij}'s in deriving (3.15).

In order to make further progress we need to make assumptions about the normal modes associated with a particular minimum, and we consider first the special case of no localized modes.

B. No Localized Modes

In the case where the extra localized terms in the potential energy expressions (2.44) and (2.45) are sufficiently small that localized modes are not formed, then, if one expands $b_i(\mathbf{R})$ in terms of the annihilation operators for the original normal modes of the crystal without the extra electron, the coefficients will be concentrated about a certain λ, λ_i (say), and the spread of frequencies ω_λ for which the coefficients will be appreciable will be proportional to $(1/N)$, where N is the number of cells in the crystal. For large crystals we expect that negligible errors will be made by making the replacements

$$b_i(\mathbf{R}) = b_{\lambda_i} + d_{\lambda_i}(\mathbf{R}) = \beta_i \qquad (3.17)$$

and

$$b_i(\mathbf{R}+\mathbf{G}) = b_{\lambda_i} + d_{\lambda_i}(\mathbf{R}+\mathbf{G}) = \beta_i + X_i, \qquad (3.18)$$

where $d_{\lambda_i}(\mathbf{R})$ and $d_{\lambda_i}(\mathbf{R}+\mathbf{G})$ are mode displacements, and the right-hand sides of the equations define β_i and X_i. Thus we have

$$X_i = \{d_{\lambda_i}(\mathbf{R}+\mathbf{G}) - d_{\lambda_i}(\mathbf{R})\} = O(1/N^{1/2}). \qquad (3.19)$$

The right-hand side of (3.19) is a general result for displacements of nonlocalized modes due to localized perturbations.

Substituting from (3.17) and (3.18) into (3.15), and using $X_i = O(1/N^{1/2})$, we find that, to lowest order in $(1/N)$,

$$Q_{nn} = \exp(-\tfrac{1}{2}S) \textstyle\prod_i (1 - n_i X_i X_i^*) = \exp(-\tfrac{1}{2}S) \times \exp\{-\sum_i n_i |X_i|^2\}. \qquad (3.20)$$

Hence, from (3.8), (3.15), and (3.20) we deduce that the bandwidth W satisfies

$$W = qJ_s \exp\{-\tfrac{1}{2}S(2\bar{n}+1)\}, \qquad (3.21)$$

where $\bar{n}$ is a mean phonon occupation number defined by

$$\bar{n}S = \textstyle\sum_i n_i |X_i|^2. \qquad (3.22)$$

Thus the results are similar to those for small polarons, with the bandwidth decreasing with increasing temperature. However, the values of the displacements d_λ will have slight differences from the ordinary small-polaron values, due to additional contributions of the order of ϵ times these values. Using the relation (2.4) between the b's and the q's, and (3.16) and (3.19), we may write

$$S = \tfrac{1}{2} \textstyle\sum_\lambda \{q_{\lambda m}(\mathbf{R}) - q_{\lambda m}(\mathbf{R}+\mathbf{G})\}^2, \qquad (3.23)$$

where $q_{\lambda m}$ are the displacements of the q's at the minimum, given by (2.23) to lowest order in ϵ. Hence putting

$$S = S_0 + S_1, \qquad (3.24)$$

where the subscripts refer to the powers of ϵ involved, we find, using (3.23), (2.26), (2.28), (2.34), and (3.24), that for the special case of no dispersion of phonon frequencies,

$$S_0 = (F/\hbar\omega). \qquad (3.25)$$

Making use of (2.24) and (2.31), a complicated expression for S_1 could also be obtained. We shall not write this down in general, but note that its order of magnitude will satisfy

$$|S_1| \sim \epsilon S_0. \qquad (3.26)$$

Now a typical value of S_0 for an alkali halide crystal might be as high as 50, and in all materials for which our theory applies we expect $S_0 \gtrsim 10$, and so although we are assuming ϵ is small, the effect on the bandwidth of the factor $\exp(-\tfrac{1}{2}S_1)$, may be quite large.

For the special case of (2.55), where wave-function spreading is more important than electron-phonon interactions of second order in the normal coordinates or anharmonic terms in the ordinary lattice potential energy, then at the minimum configuration the expression (2.24) for $q_\lambda^{(1)}$ reduces to

$$q_\lambda^{(1)} \simeq (\hbar\omega_\lambda)^{-1} \sum_{\mathbf{G}} (J_m/F)^2 \times \{E_\lambda^{(1)}(\mathbf{R}+\mathbf{G}) - E_\lambda^{(1)}(\mathbf{R})\}. \quad (3.27)$$

Hence, neglecting phonon dispersion and using (3.23), (2.23), and (3.27), we deduce that

$$S_1 = -2z\left(\frac{J_m}{F}\right)^2 \left[\frac{2(B_0-C_0)-2(C_0-D_0)}{\hbar\omega}\right], \quad (3.28)$$

where B_0 and C_0 are given by (2.26) and (2.28), and D_0 is defined by

$$D_0 = \tfrac{1}{2}\mathrm{Av}_{\mathbf{G}'} \sum_\lambda \{E_\lambda^{(1)}(\mathbf{R}) E_\lambda^{(1)}(\mathbf{R}+\mathbf{G}+\mathbf{G}')/\hbar\omega\}. \quad (3.29)$$

Here $\mathrm{Av}_{\mathbf{G}'}$ denotes an average over all nearest-neighbor lattice vectors **G**.

We expect that S_1 of (3.28) will generally be negative, and so the bandwidth will be increased by wave-function spreading effects. We should note that similar additional terms in the bandwidth to those proportional to $\exp(-\frac{1}{2}S_1)$ with S_1 given by (3.28) were obtained by Holstein in a two-site adiabatic small-polaron model in Eq. (116) of Part II of Ref. 8.

C. One Localized Mode

If localized modes are formed around the polaron, the general problem of finding the bandwidth at all temperatures would be rather difficult. However, some insight into the effect of localized modes is obtained here by considering the special case when there is only one localized mode per minimum, and when there are no displacements associated with the nonlocalized modes. Thus we assume that mode $i=1$ is localized and

$$X_i = 0, \quad i>1. \quad (3.30)$$

We restrict our studies to low temperatures, that is to cases where the occupation numbers n_i of the nonlocalized modes $i>1$ satisfy

$$\begin{aligned} n_i &= 1, \quad i\in\{A\} \\ n_i &= 0, \quad i\notin\{A\}, \end{aligned} \quad (3.31)$$

where the set $\{A\}$ contains M members, and we assume that

$$M \ll N. \quad (3.32)$$

With these occupation numbers for the nonlocalized modes, we now have two types of overlap integrals Q_{nn} to consider at low temperatures, i.e., those in which the occupation number n_1 of the localized mode satisfies (a) $n_1=0$ or (b) $n_1=1$.

(a) If $n_1=0$ we find, by using (3.15), (3.16), (3.30) and (3.31), and inspecting the coefficient of

$$\{\prod_{i\in\{A\}} (\beta_i^\dagger \beta_i)\}$$

that, to first order in (M/N), the relevant overlap integral, which we call $Q_{nn}^{(0)}$, is given by

$$Q_{nn}^{(0)} \simeq \{1 - \sum_{i\in\{A\}} a_{ii}\} \exp(-\tfrac{1}{2}S), \quad (3.33)$$

where $S=X_1^2$. Hence, using (3.8), to first order in the thermal occupation number n_i of the nonlocalized modes, the bandwidth W_0 associated with zero-occupation number for the localized mode satisfies

$$W_0 \simeq qJ_s(1-\bar{n}\mu) \exp(-\tfrac{1}{2}S), \quad (3.34)$$

where μ is defined by

$$\mu = \sum_{i>1} a_{ii}, \quad (3.35)$$

and $\bar{n}$ is a weighted average of the occupation numbers $\bar{n}_i$, weighted by the factors a_{ii}.

(b) If $n_1=1$ then, denoting the relevant overlap integral by $Q_{nn}^{(1)}$, we may show in a similar manner that to first order in (M/N)

$$Q_{nn}^{(1)} \simeq \{1 - \sum_{i\in\{A\}} a_{ii}\}(1-S) \times \{1 - a_{11} + \sum_{j\in\{A\}} a_{1j}a_{j1}\} \exp(-\tfrac{1}{2}S). \quad (3.36)$$

Thus, to first order in $\bar{n}$, the bandwidth W_1 associated with $n=1$ is given by

$$W_1 \simeq qJ_s(1-\mu\bar{n})|S-1|(1-a_{11}+v\bar{n}_{aa}) \times \exp(-\tfrac{1}{2}S), \quad (3.37)$$

where v is defined by

$$v = \sum_{j>1} a_{1j}a_{j1}, \quad (3.38)$$

and $\bar{n}_{aa}$ is an average of the occupation numbers $\bar{n}_i$ weighted by the factors $(a_{1i}a_{i1})$. Hence from (3.34) and (3.37), to first order in $\bar{n}$, $\bar{n}_{aa}$ and $\bar{n}_1$, where $\bar{n}_1$ is the thermal occupation number of the localized modes, we deduce that the thermal average bandwidth $\bar{W}$ is given by

$$\bar{W} \simeq qJ_s\{(1-\bar{n}\mu-\bar{n}_1)+\bar{n}_1(1-a_{11})|S-1|\} \times \exp(-\tfrac{1}{2}S). \quad (3.39)$$

Now one expects that a_{ii}, which is nonzero because of the normalization required by the addition of operators β_j in the expansion (3.11) of $b_i(\mathbf{R})$, will satisfy $a_{ii} \lesssim (1/N)$, and hence that μ defined in (3.35) will satisfy

$$\mu \lesssim 1. \quad (3.40)$$

Thus we conclude that, if localized modes exist, a discrete distribution of bandwidths will occur at nonzero temperatures, and from (3.39) and (3.40) that if $(1-a_{11})|S-1|$ is sufficiently large, i.e., if the localized mode associated with one minimum is not orthogonal to that associated with the next, and the electron-phonon coupling giving rise to the mode displacement X_1 is strong enough, then the mean bandwidth will increase with increasing temperature.

Physically one might expect the mean bandwidth to increase with increasing temperature on a localized mode picture, since increase of temperature represents greater local vibrations and hence a higher probability of transfer to a different branch of the potential energy curve. Thus, the surprising result regarding effective masses is the increase of mass with increasing temperature obtained in the usual case without localized modes, rather than the decrease in the localized mode case.

We should note that, for small polarons and small dispersion of phonon frequencies, Nagaev predicted a distribution of bandwidths such that the mean-square width increases with increase of temperature.[20] He did not find the distribution of widths explicitly, but we can show that his results for the mean-square width at low temperatures would be the same as ours for the special case $\bar{n}_1=\bar{n}$, $a_{11}=0$, $\mu=0$. However, $a_{11}=0$ would imply that mode 1 were not localized, and so Nagaev's results are applicable to a case not considered in this paper, i.e., to the case in which localized modes are not formed, but the dispersion in phonon frequencies is less than some maximum value, probably of the order of $(1/\tau)$, where τ is the scattering time for the polarons.

IV. OPTICAL ABSORPTION DUE TO TRANSITIONS FROM A WIDE BAND TO A NEARLY-SMALL-POLARON BAND

A. General

In this section we study optical absorption due to transitions between a wide valence band for which electron-phonon coupling is neglected to an adiabatic nearly small-polaron conduction band. As in Ref. 3, where a small-polaron conduction band was treated, we use the straightforward method of finding transition probabilities between approximate stationary states of the electron-phonon system by perturbation theory, with the electron-radiation interaction, for a radiation field modified by the refractive index of the material, as a perturbation.[21] As far as the conduction band is concerned, we concentrate on the special case of Sec. IIIC, when there is just one localized mode associated with each minimum in the adiabatic potential, and mode displacements are zero for the nonlocalized modes. A wide valence band and a narrow conduction band were chosen in Ref. 3 in view of possible applications to the transition metal oxides, and we treat the case of a wide valence band and narrow conduction band here, rather than the reverse, in order to facilitate comparison with previous results. The importance of the effect of electron-phonon interactions is much greater for narrow than for wide bands, and hence the neglect of electron-phonon coupling for the valence band need not be inconsistent with strong effects of the coupling on the carriers in the conduction band.

We write the wave function $\Psi_{v\mathbf{k}n}(\mathbf{r},q)$ for an electron of wave vector $\mathbf{k}$ in the valence band plus phonons as

$$\Psi_{v\mathbf{k}n}(\mathbf{r},q)=N^{-1/2}u_{\mathbf{k}}(\mathbf{r},q)\exp(i\mathbf{k}\cdot\mathbf{r})\chi_n(q)\,, \qquad (4.1)$$

where $\mathbf{r}$ is the electron coordinate, q denotes the set of all lattice coordinates, $u_{\mathbf{k}}$ is a function which is invariant under the action of the translation operator through a lattice vector,[22] N is the number of cells in the crystal, and $\chi_n(q)$ is the wave function associated with a lattice state $|\chi_n\rangle$ defined by

$$|\chi_n\rangle=\prod_\lambda\{(b_\lambda^\dagger)^{n_\lambda}/(n_\lambda!)^{1/2}\}|0\rangle\,. \qquad (4.2)$$

Here $b_\lambda^\dagger$ is the creation operator associated with a normal mode λ, n_λ is a mode occupation number, $|0\rangle$ is the phonon vacuum state, and the product is over all modes λ.

For the wave function $\Psi_{c\mathbf{k}'n'}(\mathbf{r},q)$ describing a carrier of wave vector $\mathbf{k}'$ in the conduction band in interaction with the phonons, we take adiabatic tight-binding nearly-small-polaron functions as described in Secs. II and III of the form

$$\Psi_{c\mathbf{k}'n'}(\mathbf{r},q)=\psi(\mathbf{r},q)\chi_{c\mathbf{k}'n'}(q)\,, \qquad (4.3)$$

where, for q's at or near a minimum energy configuration, ψ is taken in the form of a linear combination of electronic wave functions on one positive ion and its neighbors as given by (2.12), and the lattice wave function $\chi_{c\mathbf{k}'n'}$ satisfies

$$\chi_{c\mathbf{k}'n'}(q)=N^{-1/2}\sum\nolimits_{\mathbf{R}}\exp(i\mathbf{k}'\cdot\mathbf{R})\chi'_{n'\mathbf{R}}(q)\,. \qquad (4.4)$$

Here the sum is over all lattice points $\mathbf{R}$, and $\chi'_{n'\mathbf{R}}(q)$ are a set of wave functions associated with a set of

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[20] E. L. Nagaev, Fiz. Tverd. Tela 4, 2201 (1962) [English transl.: Soviet Phys.—Solid State 4, 1611 (1963)].

[21] More sophisticated methods of studying optical properties associated with small polarons have been used by H. G. Reik, Phys. Letters 5, 236 (1963); G. M. Genkin, Fiz. Tverd. Tela 6, 1608 (1964) [English transl.: Soviet Phys.—Solid State 6, 1265 (1964)]; E. K. Kudinov and Yu. A. Firsov, Zh. Eksperim. i Teor. Fiz. 47, 601 (1964) [English transl.: Soviet Phys.—JETP 20, 400 (1965)]. Reik and Genkin treat high-frequency conductivity due to polarons in one small-polaron band at high temperatures, and obtain results which are qualitatively similar to those given in Ref. 3 for this case, but there seem to be some quantitative differences between the three sets of results. The calculations of Reik and Genkin were not given in sufficient detail for the present author to find the source of the discrepancies. Kudinov and Firsov study structure in the absorption coefficient and refractive index due to transitions from a deep atomic level to a small polaron band, and obtain results for absorption very similar to those of Ref. 3 for absorption due to transitions between two small-polaron bands.

[22] We have allowed the function u to depend on lattice coordinates q, and later in a discussion of a tight-binding model we shall assume that u is bulit up from electronic functions which move round with the ions as the ions move. Thus, we have not completely ignored electron-phonon interactions in one sense of this expression but, since we are assuming that the functions χ are just the free-phonon functions, then in another sense we are ignoring interactions.

states $\{|\chi'_{n\mathbf{R}}\rangle\}$, which is an orthogonalized set formed from the states $|\chi_{n'\mathbf{R}}\rangle$ defined as in (2.1) by

$$|\chi_{n'\mathbf{R}}\rangle=\prod_i \frac{\{b_i^\dagger(\mathbf{R})\}^{n_i'}}{(n_i'!)^{1/2}}|0_\mathbf{R}\rangle, \qquad (4.5)$$

where $b_i^\dagger(\mathbf{R})$ is the creation operator for the ith normal mode for the minimum associated with $\mathbf{R}$, n_i' are mode occupation numbers, and $|0_\mathbf{R}\rangle$ is the vacuum state for these normal modes.

Now, for radiation polarized in the x direction, the absorption coefficient due to transitions between states of the type described by (4.1) to (4.5) depends on matrix elements $M_{\mathbf{kk}'nn'}$ defined by

$$M_{\mathbf{kk}'nn'}\equiv\int \Psi_{v\mathbf{k}n}^*(\mathbf{r},q)\frac{\partial}{\partial x}\Psi_{c\mathbf{k}'n'}(\mathbf{r},q)d^3r\,d^nq$$

$$=\frac{1}{N}\sum_\mathbf{R}\exp(i\mathbf{k}'\cdot\mathbf{R})\int f_\mathbf{k}(q)\chi_n^*(q)\chi'_{n'\mathbf{R}}(q)d^nq, \qquad (4.6)$$

where $\int d^nq$ denotes an integration over all lattice normal coordinates, and

$$f_\mathbf{k}(q)\equiv\int u_\mathbf{k}^*(\mathbf{r},q)\exp(-i\mathbf{k}\cdot\mathbf{r})\frac{\partial}{\partial x}\psi(\mathbf{r},q)d^3r. \qquad (4.7)$$

The right-hand side of (4.6) follows directly from (4.1), (4.3), and (4.4).

If we use a tight-binding type of approximation for the valence-band wave functions, but allow the localized functions to follow the motion of the ions, and if we further suppose that the main contribution to the matrix element comes from functions localized on the same type of ions as those on which the conduction wave functions lie, then the difference of the quantity $f_\mathbf{k}(q)$ at a point q near the potential minimum associated with $\mathbf{R}$ from its value $f_{\mathbf{k}m}(\mathbf{R})$ at the minimum will arise from the change of a and b with q. Now from (2.13) and the fact that $b\ll a$, we deduce that b changes with q much more than a does. Hence, the fractional change of the quantities $f_\mathbf{k}$ due to displacements associated with zero-point vibration about a minimum is of the order of a sum of terms of magnitude of order Δb, where Δb is the difference in value of b at the point q from its value at the minimum. Since for general displacements there is no reason why the signs of the Δb's should be correlated, we deduce that

$$|\{[f_\mathbf{k}(q)/f_{\mathbf{k}m}(\mathbf{R})]-1\}|\sim z^{1/2}|\Delta b| \lesssim \epsilon_1^{1/2}(\hbar\bar{\omega}/B_0)^{1/2}, \qquad (4.8)$$

where z is the number of neighbors, ϵ_1 is defined in (3.14), and $\bar{\omega}$ is a typical phonon frequency. The right-hand inequality of (4.8) is obtained by the following argument. The energy associated with zero-point displacements of the q's along directions from the origin to a minimum energy configuration is of order $\hbar\bar{\omega}$, where $\bar{\omega}$ is a typical phonon frequency, while the energy associated with displacements from the equilibrium positions in a perfect lattice to the minimum is of order B_0. Hence, for displacements in the direction mentioned, the ratio of the typical change Δq of q associated with zero-point motion to the value of q at the minimum, which we call q_m, satisfies $(\Delta q/q_m)\sim(\hbar\bar{\omega}/B_0)^{1/2}$. Combining this fact with the assumption, related to that regarding the discarding of terms of higher order than the second in the expansion of electron overlap energies in (2.7), that b changes by a factor less than or of the order of its own magnitude, when the q's change by amounts $q_{\lambda m}$, we deduce that $(\Delta b/b)\lesssim(\hbar\bar{\omega}/B_0)^{1/2}$. Further, from (2.8), (2.14), (2.23), (2.26), and (2.31), supposing $F\sim B_0$ (see Sec. V), we may deduce that $b\sim(\epsilon_1/z)^{1/2}$, and so we find

$$z^{1/2}\Delta b=z^{1/2}b(\Delta b/b)\lesssim\epsilon_1^{1/2}(\hbar\bar{\omega}/B_0)^{1/2}.$$

Now, bearing in mind (4.8), we assume, for q's near the minimum associated with $\mathbf{R}$, that

$$f_\mathbf{k}(q)\simeq f_{\mathbf{k}m}(\mathbf{R}). \qquad (4.9)$$

Although this approximate equality has only been shown to be reasonable for the particular assumptions made about the form of the valence band wave functions and about the matrix elements as discussed in the last paragraph, it may, of course, be a more general result.

Because of the term $\exp(-i\mathbf{k}\cdot\mathbf{r})$ in the definition (4.7) of $f_\mathbf{k}(q)$ we may write

$$f_{\mathbf{k}m}(\mathbf{R})=f_{\mathbf{k}0}\exp(-i\mathbf{k}\cdot\mathbf{R}), \qquad (4.10)$$

where $f_{\mathbf{k}0}$ is independent of $\mathbf{R}$.

Thus, from (4.6), (4.9), and (4.10), using (3.5), we deduce that

$$M_{\mathbf{kk}'nn'}\simeq N^{-1}\sum\nolimits_\mathbf{R}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}]f_{\mathbf{k}0}G_{nn'}(\mathbf{R}), \qquad (4.11)$$

where $G_{nn'}(\mathbf{R})$ is defied by

$$G_{nn'}(\mathbf{R})\equiv\int\chi_n^*(q)\chi_{n'\mathbf{R}}(q)d^nq. \qquad (4.12)$$

In order to proceed further we need to obtain explicit expressions for $G_{nn'}(\mathbf{R})$. In general, we may expand the annihilation operators $b_i(\mathbf{R})$ in terms of the creation and annihilation operators $b_\lambda^\dagger$ and b_λ for the phonons for the perfect unexcited crystal in the form

$$b_i(\mathbf{R})=\sum\nolimits_\lambda k_{i\lambda}b_\lambda+\sum\nolimits_\lambda m_{i\lambda}b_\lambda^\dagger+d_i, \qquad (4.13)$$

where d_i are mode displacements, and $k_{i\lambda}$ and $m_{i\lambda}$ are expansion coefficients. As for the ratio (c_{ij}/a_{ij}) in the expansion (3.11), we expect that $(m_{i\lambda}/k_{i\lambda})\sim\epsilon$, and we shall ignore $m_{i\lambda}$ for the remainder of the section. As in Sec. III, we consider two special cases: (i) no localized modes; (ii) one localized mode per minimum, and no mode displacements associated with the nonlocalized modes.

B. No Localized Modes

In this case the expansion of the annihilation operators $b_i(\mathbf{R})$ for the normal modes for the minimum associated with $\mathbf{R}$ in terms of operators b_λ as in (4.13) will be concentrated at a particular energy, with a spread in energy decreasing with increasing size of the crystal. For large crystals we expect to make negligible errors by making the replacement $b_i(\mathbf{R}) \to \{b_{\lambda_i}+d_{\lambda_i}(\mathbf{R})\}$, where λ_i labels the mode about which the expansion for b_i is concentrated.

Thus the expression for the overlap integral $G_{nn'}(\mathbf{R})$ will be similar to that for the overlap integral $\prod_w \langle n_w | n_{w_1}' f_w(\mathbf{R}')\rangle$ occurring in Eq. (13) of Ref. 3, the expression (4.11) for $M_{\mathbf{kk}'nn'}$ will be similar to that of Eq. (18) of Ref. 3, and all results for the absorption coefficient obtained there should hold for the case considered here also. However, the actual values of the mode displacements can be different in the two cases, because in the present model these displacements will be altered by terms proportional to the parameter ϵ introduced in Sec. II.

C. One Localized Mode

As in Sec. III, we suppose that mode $i=1$ is localized, and that $d_i=0$ for $i>1$, where d_i are the mode displacements of (4.13). For convenience, we next rewrite the expansion (4.13) for the annihilation operator for the localized mode $b_1(\mathbf{R})$ as

$$b_1(\mathbf{R})=\sum_\lambda k_{1\lambda}(\mathbf{R})b_\lambda+d(\mathbf{R})\equiv\beta(\mathbf{R})+d(\mathbf{R}), \quad (4.14)$$

where we have put $m_{i\lambda}=0$ as discussed previously, and have made the replacement $d_1=d$. The right-hand side of the equation defines β. For $i>1$ we are assuming zero mode displacements, and so we have

$$b_i(\mathbf{R})=\sum_\lambda k_{i\lambda}(\mathbf{R})b_\lambda, \quad i>1, \quad (4.15)$$

where $k_{i\lambda}$ will be concentrated near a particular λ.

Now, inverting (4.14) and (4.15) we may write

$$b_\lambda=\alpha_\lambda(\mathbf{R})\beta(\mathbf{R})+\sum_i \mu_{\lambda_i}(\mathbf{R})b_i(\mathbf{R}), \quad (4.16)$$

where α_λ and μ_{λ_i} are expansion coefficients, μ_{λ_i} is concentrated near a particular i, $i(\lambda)$ say, and the extent in energy of the spread of appreciable coefficients decreases with increasing size of crystal. In calculating overlap integrals $G_{nn'}(\mathbf{R})$, we expect to introduce negligible errors by making the replacement

$$b_\lambda \to (1+\alpha_i\alpha_i^*)^{-1/2}\{b_i(\mathbf{R})+\alpha_i(\mathbf{R})\beta(\mathbf{R})\} \quad (4.17)$$

for b_λ whenever it occurs. Here we have written $\alpha_\lambda=\alpha_i$, where $i=i(\lambda)$ is the mode about which μ_{λ_i} is concentrated, and the term $(1+\alpha_i\alpha_i^*)^{-1/2}$ is a normalization factor.

The initial states may now be characterized by a set of occupation numbers $n_\lambda=n_i$, where $i=i(\lambda)$, and the final states by a set of occupation numbers n_i for the nonlocalized modes and an occupation number p for the localized mode. By use of (4.2), (4.5), (4.12), (4.14), and (4.17) we can show that the overlap integral $G_{(n_i)(p,n_i')}$ between such states satisfies

$$G_{(n_i)(p,n_i')}(\mathbf{R})=\frac{1}{(p!)^{1/2}}\prod_i\left\{\frac{(1+\alpha_i\alpha_i^*)^{-\frac{1}{2}n_i}}{(n_i!)^{1/2}(n_i'!)^{1/2}}\right\}$$
$$\times\langle 0_\mathbf{R}'|\prod_i\{(b_i+\alpha_i\beta)^{n_i}(b_i^\dagger)^{n_i'}\}(\beta^\dagger+d^*)^p$$
$$\times\exp(-\beta^\dagger d)|0_\mathbf{R}'\rangle\exp\{-\tfrac{1}{2}|d|^2\}, \quad (4.18)$$

where $|0_\mathbf{R}'\rangle$ is the vacuum state with respect to β and the β_i's, and is related to $|0_\mathbf{R}\rangle$ of (4.5) by

$$|0_\mathbf{R}\rangle=\exp(-\beta^\dagger d)|0_\mathbf{R}'\rangle\exp\{-\tfrac{1}{2}|d|^2\}. \quad (4.19)$$

By inspection of (4.18) we see that the right-hand side is zero unless $n_i'\leqslant n_i$, for all i. Further, the coefficients α_i satisfy $\alpha_i\sim(1/N^{1/2})$, and so the probability of a change of occupation number of any particular mode by more than one may be neglected. Hence we look at the case where

$$\begin{aligned} n_i'&=n_i-1 \quad i\in\{A\},\\ n_i'&=n_i \qquad\;\; i\notin\{A\}, \end{aligned} \quad (4.20)$$

where we suppose that the set $\{A\}$ contains r members.

Substituting from (4.20) into (4.18), and studying coefficients of $\prod_i\{(b_i)^{n_i'}(\beta^\dagger)^r\}$, we find that

$$G_{(n_i)(p,n_i')}(\mathbf{R})=(p!)^{-1/2}\prod_i(1+\alpha_i\alpha_i^*)^{-\frac{1}{2}n_i}$$
$$\times\prod_{i\in\{A\}}(n_i^{1/2}\alpha_i)(d^*)^p d^r H_{p,r}\exp(-\tfrac{1}{2}D), \quad (4.21)$$

where we have written

$$|d|^2=D, \quad (4.22)$$

and $H_{p,r}$ is defined by

$$H_{p,r}\equiv r!\sum_{t=0}^{t_m}\{(-1)^{r-t}({}^pC_t)/(r-t)!D^t\}, \quad (4.23)$$

with

$$t_m=\min(p,r). \quad (4.24)$$

If we characterize the mode λ by a branch number s and a wave vector $\mathbf{w}$, then, by symmetry arguments,

$$\alpha_\lambda(\mathbf{R})\equiv\alpha_{\mathbf{w}s}(\mathbf{R})=\alpha_{0\mathbf{w}s}\exp(-i\mathbf{w}\cdot\mathbf{R}), \quad (4.25)$$

where $\alpha_{0\mathbf{w}s}$ is independent of $\mathbf{R}$. We may then make this substitution for $\alpha_i\{i=i(\lambda)\}$ in (4.21).

Additional simplification of (4.21) is made possible by noting that, since in order to give correct commutation relations the transformation (4.16) must be unitary, we have

$$\sum_\lambda|\alpha_\lambda|^2=1. \quad (4.26)$$

Hence,

$$\sum_i|\alpha_i|^2=1+O(1/N), \quad (4.27)$$

and, to lowest order in $(1/N)$,

$$\prod_i(1+\alpha_i\alpha_i^*)^{-\frac{1}{2}n_i}=\exp(-\tfrac{1}{2}\bar{n}), \tag{4.28}$$

where $\bar{n}$ is an average phonon occupation number, weighted according to the factors $|\alpha_i|^2$.

Now, from standard absorption theory, for radiation-polarized in the x direction, the product of refractive index n, photon energy Ω, and absorption coefficient $K(\Omega)$ satisfies

$$n\Omega K(\Omega) = A\ \mathrm{Av}_n \textstyle\sum_{n'}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}|M_{\mathbf{k}\mathbf{k}'nn'}|^2\delta\ (\text{energy}). \tag{4.29}$$

Here, $M_{\mathbf{k}\mathbf{k}'nn'}$ is the matrix element introduced in (4.6), and A is a constant defined by

$$A=V^{-1}(4\pi e^2\hbar^3/m_e{}^2c), \tag{4.30}$$

where V is the volume of the crystal, e is an electronic charge, m_e the free electron mass, and c the velocity of light in vacuo.

If we integrate (4.29) over energy, the delta function is removed. Then using (4.11), (4.21), and (4.25), we see that the matrix element is zero unless wave vector is conserved, and so, for given initial wave vector $\mathbf{k}$ and phonon occupation numbers, summation over $\mathbf{k}'$ just selects that $\mathbf{k}'$ which conserves wave vector. Hence, if we now divide the absorption coefficient K into parts $K_{p,r}$ associated with emission of p-localized phonons and absorption of r-nonlocalized phonons, i.e., if we put

$$K(\Omega)=\sum_{p,r}K_{p,r}(\Omega), \tag{4.31}$$

then in the integrated form of (4.29) we may carry out the summation over sets $\{A\}$ of size r, and average over initial phonon occupation numbers to obtain, using (4.11), (4.21), (4.22), (4.25), and (4.28), that

$$\int n\Omega K_{p,r}(\Omega)d\Omega = A\textstyle\sum_{\mathbf{k}}|f_{\mathbf{k}0}|^2((\bar{n})^rD^{p+r}/p!r!)|H_{p,r}|^2 \times\exp\{-(D+\bar{n})\}. \tag{4.32}$$

To proceed further, we specialize to the case where both the width of the conduction band and the dispersion in frequency of the relevant nonlocalized modes is negligible. In this case, for initial states with the right energy, the summation over $\mathbf{k}'$ in (4.29) just selects the $\mathbf{k}'$ which conserves wave vector, and so the dependence of the partial absorption coefficient $K_{p,r}$ on energy is given by

$$K_{p,r}\propto F(\Omega-E_G-p\hbar\omega_1+r\hbar\omega), \tag{4.33}$$

where E_G is the energy gap, ω_1 and ω are the localized and nonlocalized mode frequencies, and $F(E)$ is defined by

$$F(E)=P^2(E)\rho_v(E), \tag{4.34}$$

where

$$P^2(E)=\mathrm{Av}_{\mathbf{k}}|f_{\mathbf{k}0}|^2, \tag{4.35}$$

the average being over all initial wave vectors $\mathbf{k}$ which conserve energy, and $\rho_v(E)$ is the density-of-states per unit energy for the valence band, with energy measured from the top of the band.

Hence, from (4.31), (4.32), and (4.33),

$$n\Omega K(\Omega)=A\sum_{p,r}F(\Omega-E_G-p\hbar\omega_1+r\hbar\omega) \times((\bar{n})^rD^{p+r}/p!r!)|H_{p,r}|^2\exp\{-(D+\bar{n})\}. \tag{4.36}$$

When we compare the results (4.32) and (4.36) with those obtained in Ref. 3 for a small polaron conduction band without localized modes, we see that at $T=0$ the expression for the absorption here has just the same form as obtained previously. However, the temperature dependence is different, as may be seen by considering the partial integrated absorption $\int n\Omega K_s(\Omega)d\Omega$ with net emission of s phonons in the two cases. For case 1 without localized modes, from Eq. (23) of Ref. 3, we have

$$\int n\Omega K_s(\Omega)d\Omega\propto R_s, \tag{4.37}$$

where

$$R_s=\sum_{r=r_1}^{\infty}(D^{2r+s}/(r+s)!r!)(\bar{n}+1)^{r+s}\bar{n}^r \times\exp\{-(2\bar{n}+1)D\}, \tag{4.38}$$

with $r_1=\max(0,-s)$. On the other hand, for case 2 with one localized mode, from (4.32) we may deduce that

$$\int n\Omega K_s(\Omega)d\Omega\propto L_s, \tag{4.39}$$

where

$$L_s=\sum_{r=r_1}^{\infty}(D^{2r+s}/(r+s)!r!)\bar{n}^r|H_{r+s,r}|^2 \times\exp\{-(D+\bar{n})\}, \tag{4.40}$$

with $r_1=\max(0,-s)$ as in (4.38), and H defined by (4.23).

At $T=0$ expressions (4.38) and (4.40) are identical, since $H_{n,0}=|H_{0,n}|=1$ for all integers $n\geqslant 0$. For general temperatures it is difficult to get simple results. However, for $s=-n$, where n is positive or zero, we can show that, to second order in $\bar{n}^2$, $(L_{-n}|R_{-n})$ satisfies

$$(L_{-n}/R_{-n})=1+n\bar{n}+[\{D^2/(n+1)\} -2D+\tfrac{1}{2}(n^2+n+1)]\bar{n}^2+\cdots. \tag{4.41}$$

Thus, for given D, the tail to the absorption at low temperatures is stronger in the presence of localized modes than in the absence of them, and so it may be possible to test for localized modes by looking at the temperature dependence of the absorption tail.

Another point to notice is that, although the total-integrated absorption in Ref. 3 is independent of $\bar{n}$, in the case here with localized modes this is only true to first order in $\bar{n}$, and to second order in $\bar{n}$ we have $\int n\Omega K(\Omega)d\Omega \propto (1+\frac{1}{2}\bar{n}^2)$.

V. DISCUSSION

A. Values of Parameters in a Continuum Polarization Model

The calculations of the previous three sections have been of a somewhat formal nature, and so we now try to give a clearer idea of the meaning of some of the parameters introduced by considering a special case in which electron-phonon interactions are treated within the framework of a continuum polarization model.

We first look at the expansion of the single site energy E_0 of (2.6) in order to estimate the values of the parameters $E_\lambda^{(1)}(\mathbf{R})$ of (2.8). For this purpose it is convenient to rewrite E_0 as

$$E_0 = -\int \phi_{\mathbf{R}}\{T_e + V_{\mathbf{R}}(\mathbf{r},q) + V'(\mathbf{r},q)\}\phi_{\mathbf{R}} d^3r, \tag{5.1}$$

where $V_{\mathbf{R}}$ denotes the potential due to the ion whose equilibrium position is at $\mathbf{R}$, and $V'(\mathbf{r},q)$ is the potential due to all the other ions. We next expand V' in powers of the q's, i.e., we write

$$V' = V_0' + V_1' + \cdots, \tag{5.2}$$

where the subscripts refer to the powers of the q's involved.

Now, except for small effects due to q dependence or orthogonality requirements for the ϕ's, the contribution from the first two terms in the brackets to the integral in (5.1) will not have any q dependence, since we are assuming that $\phi_{\mathbf{R}}$ follows the ion originally at $\mathbf{R}$. Further, for ions in a position with inversion symmetry, there is no contribution of first order in the q's to E_0 from the term V_0', and so in this case we find, using (2.8), (5.1), (5.2) and noting the remarks above, that to a good approximation

$$\sum_\lambda E_\lambda^{(1)}(\mathbf{R}) q_\lambda \simeq -\int \phi_{\mathbf{R}} V_1' \phi_{\mathbf{R}} d^3\mathbf{r} \simeq -V_1'(\mathbf{R},q). \tag{5.3}$$

The second approximate equality holds because $V_1'(\mathbf{r},q)$ will not vary much with $\mathbf{r}$ over the region of extent of the wave functions ϕ.

Our next assumption is to suppose that V_1' is the same as the electron-phonon interaction in a continuum-polarization model. It is convenient at this point to discard our previous convention of choosing real normal coordinates. We may then write

$$V_1'(\mathbf{r},q) = \sum\nolimits_{\mathbf{w}} V_{\mathbf{w}}(b_{-\mathbf{w}}^\dagger + b_{\mathbf{w}}) \exp(i\mathbf{w}\cdot\mathbf{r}), \tag{5.4}$$

where $b_{\mathbf{w}}^\dagger$ and $b_{\mathbf{w}}$ are creation and annihilation operators for polar-longitudinal phonons of wave vector $\mathbf{w}$ (it is assumed that there is only one branch of the phonon spectrum of this type), the sum is over all wave vectors $\mathbf{w}$, and $V_{\mathbf{w}}$ is given by[1]

$$V_{\mathbf{w}} = \pm\frac{ie}{w}\left[2\pi\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right)\frac{\hbar\omega}{V}\right]^{1/2}. \tag{5.5}$$

Here $w = |\mathbf{w}|$, ϵ_∞ and ϵ_s are the high-frequency and static dielectric constants of the material, ω is the phonon frequency, which is assumed to be independent of $\mathbf{w}$, V is the volume of the crystal, and the plus or minus sign is chosen according to the direction of $\mathbf{w}$. Hence, putting

$$q_{\mathbf{w}} = (1/\sqrt{2})(b_{-\mathbf{w}}^\dagger + b_{\mathbf{w}}), \tag{5.6}$$

from (5.3) and (5.4) we have

$$E_{\mathbf{w}}^{(1)}(\mathbf{R}) = -\sqrt{2} V_{\mathbf{w}} \exp(i\mathbf{w}\cdot\mathbf{R}). \tag{5.7}$$

Now, with running wave coordinates $q_{\mathbf{w}}$, the coefficients $E_{\mathbf{w}}^{(1)}$ and $E_{-\mathbf{w}}^{(1)}$ may be related to a pair of coefficients $E_\lambda^{(1)}$ and $E_{\lambda'}^{(1)}$ in the expansion in terms of real coordinates by

$$\begin{gathered}(1/\sqrt{2})(E_{\mathbf{w}}^{(1)} + E_{-\mathbf{w}}^{(1)}) = E_\lambda^{(1)},\\ (i/\sqrt{2})(E_{\mathbf{w}}^{(1)} - E_{-\mathbf{w}}^{(1)}) = E_{\lambda'}^{(1)},\end{gathered} \tag{5.8}$$

and, because the energy is real we have

$$E_{-\mathbf{w}}^{(1)} = E_{\mathbf{w}}^{(1)*}. \tag{5.9}$$

Thus, expressions (2.26), (2.28), and (3.29) for B_0, C_0, and D_0 can be put in terms of the $E_{\mathbf{w}}^{(1)}$'s without difficulty.

If we make the simplication of replacing the first Brillouin zone by a sphere of radius w_0 defined by

$$\tfrac{4}{3}\pi(w_0/2\pi)^3 = (1/V_c), \tag{5.10}$$

where V_c is the volume of a unit cell, and transform from a summation to an integration in the usual manner, we find, using (5.5) and (5.7), that in our model B_0 is given by

$$B_0 = \tfrac{1}{2}\sum_{\mathbf{w}} \frac{|E_{\mathbf{w}}^{(1)}(\mathbf{R})|^2}{\hbar\omega} = \frac{e^2 w_0}{\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right), \tag{5.11}$$

while C_0 and D_0 may be obtained by noting that the quantity $E_{\mathbf{RR}'}$ defined below satisfies

$$\begin{aligned} E_{\mathbf{RR}'} &\equiv \tfrac{1}{2}\sum_\lambda \frac{E_\lambda^{(1)}(\mathbf{R}) E_\lambda^{(1)}(\mathbf{R}')}{\hbar\omega} = \tfrac{1}{2}\sum_{\mathbf{w}} \frac{E_{\mathbf{w}}^{(1)}(\mathbf{R}) E_{\mathbf{w}}^{(1)*}(\mathbf{R}')}{\hbar\omega_{\mathbf{w}}} \\ &= \tfrac{1}{2}\sum_{\mathbf{w}} [|E_{\mathbf{w}}^{(1)}(\mathbf{R})|^2 \exp\{-i\mathbf{w}\cdot(\mathbf{R}'-\mathbf{R})\}/\hbar\omega] \\ &= B_0\left\{\frac{\mathrm{Si}(w_0 r)}{w_0 r}\right\}, \end{aligned} \tag{5.12}$$

where $r = |\mathbf{R}' - \mathbf{R}|$, and

$$\mathrm{Si}(x) \equiv \int_0^x \sin t/t dt. \tag{5.13}$$

Another quantity of interest to calculate is the polaron binding energy E_p. Assuming that the parameters J_0 and J_m are positive, and that effects due to changes of phonon frequencies (which result from the presence of the polaron) are negligible, we find using (2.33) and (3.21) that, to lowest order in ϵ_2 and ϵ_3, for a carrier at the bottom of the band, E_p satisfies

$$E_p = B_0 + (zJ_m{}^2/F) - zJ_0 + zJ_s \times \exp\{-\tfrac{1}{2}S(2\bar{n}+1)\}, \quad (5.14)$$

since in a simple tight-binding calculation the energy at the bottom of the band lies at a level (zJ_{eff}) below the single site level, where J_{eff} is an effective overlap energy.

We now discuss the magnitude of the polaron radius r_p. The precise definition of this is somewhat arbitrary, but one possible choice is to use the defining relation

$$\exp(-G/r_p) \equiv b/a \simeq J_m/F, \quad (5.15)$$

where the values of a and b are taken at a minimum configuration, and the second approximate equality follows from (2.31) and (2.32), to lowest order in ϵ. Since we are assuming that b^2 is small, r_p will be smaller than the lattice distance G; hence, our use of the word "small" in the title. "Nearly" is included so that we can reserve the term "small polaron" for cases in which wave function spreading to neighboring sites is completely negligible.

Next, we show how to estimate the order of magnitude of ionic displacements in our model, in order to be able to ascertain the validity of the approximation of neglecting terms of higher order than the second in the q's in the expression (2.7) for the electronic energy overlap integral. Let us define a localized-dimensionless displacement $q(\mathbf{R}')$ at $\mathbf{R}'$ associated with the branch of the phonon spectrum being considered by

$$q(\mathbf{R}') \equiv N^{-1/2} \textstyle\sum_{\mathbf{w}} q_{\mathbf{w}} \exp(i\mathbf{w}\cdot\mathbf{R}'). \quad (5.16)$$

Now, using (5.7), (5.5), (5.16) and the generalization of (2.23) to nonreal normal coordinates, viz.

$$q_{\mathbf{w}}{}^{(0)} = E_{\mathbf{w}}{}^{(1)*}(\mathbf{R})/\hbar\omega_{\mathbf{w}}, \quad (5.17)$$

and replacing the summation over all wave vectors by an integration over a sphere of radius w_0 given by (5.10), we obtain, for a polaron at the origin, that

$$|q(\mathbf{R}')| = \left\{\frac{3}{2\pi}\frac{e^2 w_0}{\hbar\omega}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right)\right\}^{1/2} \left\{\frac{1-\cos(w_0 R')}{\frac{1}{2}(w_0 R')^2}\right\}. \quad (5.18)$$

In order to deduce the actual ionic displacements from (5.18) we would need to know the form of the motion of the ions associated with the coordinates $q_{\mathbf{w}}$. However, without knowing this motion in detail, it is safe to say that for a crystal with two atoms per unit cell, the order of magnitude of the displacements Δ_- of the negative ions nearest to the polaron satisfy

$$\Delta_- \sim (\hbar/M_-\omega)^{1/2} |q(0)|, \quad (5.19)$$

where M_- is the mass of the ions. Similarly, for the displacements associated with nearest-neighbor positive ions, we have

$$\Delta_+ \sim (\hbar/M_+\omega)^{1/2} |q(\mathbf{G})|, \quad (5.20)$$

where $\mathbf{G}$ is a nearest-neighbor lattice vector, and M_+ is the positive ion mass.

If we are concerned with simple overlaps between positive ion wave functions, then, judging from the estimates made by Fröhlich *et al.*,[11] using Gaussian electronic wave functions, the condition that terms of higher order than the second in the q's in expression (2.7) for the electronic overlap energy can be neglected is

$$\{\exp(G\Delta_+/2r_0{}^2) - 1\} \ll 1, \quad (5.21)$$

where $G = |\mathbf{G}|$, Δ_+ is given by (5.20), and r_0 is the radius of the electronic wave functions on the ions.

Finally, we calculate the angles made by the vectors associated with the coordinates $\eta_{\mathbf{G}}$ introduced in (2.59) with each other, and with the vector from the origin in q space to the minimum associated with $\mathbf{R}$. Denoting by $\hat{\eta}_{\mathbf{G}}$ a unit vector in the direction associated with $\eta_{\mathbf{G}}$, and by $\hat{\zeta}$ a unit vector in the direction from the origin to the minimum associated with $\mathbf{R}$, we find, using (2.59), (2.42), (2.26), (2.28), (2.34), and (5.12), that

$$\hat{\eta}_{\mathbf{G}} \cdot \hat{\eta}_{\mathbf{G}'} = \tfrac{1}{2}\{1 - (C_0 - E_{\mathbf{R}+\mathbf{G},\mathbf{R}+\mathbf{G}'})/(B_0 - C_0)\}, \quad (5.22)$$

and

$$|\hat{\eta}_{\mathbf{G}} \cdot \hat{\zeta}| = \tfrac{1}{2}(F/B_0)^{1/2}. \quad (5.23)$$

These expressions can be easily evaluated for the model being used in this section by use of (5.11) and (5.12).

We have now shown how to estimate a large proportion of the quantities appearing in the theory of Secs. II to IV by use of a continuum-polarization model of electron-phonon interactions. Estimates of the magnitude of the terms of second order in q in the expansion of the single site energies or of the size of the contribution to the energy of the ordinary anharmonic terms in the electron-phonon interaction would require knowledge of changes of ionic polarizabilities due to the presence of extra electrons, or information regarding third-order elastic constants, and such estimates will not be made here. However, provided that these effects are neglected, we are in a position to find values for all polaron parameters, given only the lattice and dielectric constants of the material, and an estimate of the electronic energy overlap integrals for a rigid lattice.

B. Application to $SrTiO_3$

We continue our discussion by putting in figures for polarons in a simple model for a possible conduction band in $SrTiO_3$. This substance has the cubic perovskite structure[23] above 108°K, i.e., it consists of five simple cubic sublattices, one each of Ti and Sr and three of 0. The unit cell is a cube of dimension 3.92 Å, with a

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[23] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).

titanium ion at the center, oxygens at the centers of the faces and strontiums at the corners. The first-Brillouin zone is also a simple cube of dimension $2w_m$, with $w_m = 0.80\times 10^8$ cm^{-1}. Replacing this zone by a sphere of radius w_0 of the same volume we find $w_0 = 0.99\times 10^8$ cm^{-1}.

The results of a study of the fitting of the observed lattice vibration frequency spectrum with the use of theoretical-shell models[24] indicate that the material is strongly ionic. The high frequency and static dielectric constants at room temperature are $\epsilon_\infty = 5.2$ and $\epsilon_s = 310$, respectively.[25,26] There are three longitudinal polar branches of the phonon spectrum, whose phonon energies at zero wave vector are 0.022, 0.058, and 0.099 eV. However, it has been shown that in a continuum-polarization model most of the electron-phonon coupling is between electrons and the highest frequency branch,[27] and we shall assume that this is the only branch of interest, and shall neglect dispersion of frequencies within it.

Band structure calculations using a tight-binding model[28] give valence and conduction band wave functions composed of mixtures of titanium $3d$ and oxygen ion $2p$ functions, with the valence band consisting mainly of oxygen functions and the conduction band mainly of titanium functions. Judging from a graphical presentation of the results, the width of the lowest conduction band in these calculations is somewhat greater than 1 eV, although the band is nearly flat along the [100] directions. In order to make a comparison with our theory we have to make the rather drastic simplifications of neglecting degeneracy, and assuming that the bandwidth is determined by direct Ti-Ti overlap instead of by indirect overlaps via the oxygens. On this assumption the quantity q relating bandwidth to overlap integrals in (1.7) is given by $q = 12$. The number z of nearest-neighbor lattice vectors satisfies $z = 6$. We shall, for our calculations, suppose that the electronic energy overlap J_0 is given by $J_0 = 0.1$ eV, which implies a rigid-lattice bandwidth $W_r = 1.2$ eV.

Now, from (5.14), the polaron-binding energy E_b which would exist if electronic overlap integrals were zero satisfies $E_b \simeq B_0$, to lowest order in ϵ_2 and ϵ_3, and using (5.11) and the figures for w_0, ϵ_∞ and ϵ_s quoted above, we find, for a continuum-polarization model, that $B_0 = 0.86$ eV. Hence, with $W_r = 1.2$ eV, condition (1.4) becomes $0.08 \ll 1$, and so is satisfied, while, with $J = 0.1$ eV and $\hbar\bar{\omega} = 0.099$ eV, condition (1.5) also holds. Thus it appears that, provided the final bandwidth satisfies (1.6), our adiabatic nearly-small-polaron theory should be applicable, and so we set out to calculate the parameters of this theory within a continuum-polarization model, assuming for bandwidth calculations that localized modes are not formed around the polaron. Putting $\epsilon_\infty = 5.2$, $\epsilon_s = 310$, $w_0 = 0.99\times 10^8$ cm^{-1} and $\hbar\omega = 0.099$ eV, from (5.12), (5.13), (2.28), (2.34), (3.25), and (3.29) we find $C_0 = 0.45B_0 = 0.39$ eV, $F = 0.95$ eV, $S_0 = 9.6$, and

$$D_0 = B_0 \times \frac{1}{6}\left\{1 + \frac{4\mathrm{Si}(w_0 G\sqrt{2})}{w_0 G\sqrt{2}} + \frac{\mathrm{Si}(2w_0 G)}{2w_0 G}\right\} = 0.38B_0 = 0.33 \text{ eV}, \quad (5.24)$$

where the lattice constant $G = 3.92$ Å.

Further, from (5.18), $q(0) = 3.6$ and $q(\mathbf{G}) = 0.8$, and so, assuming that the relevant modes are mainly composed of titanium ions vibrating relative to all the oxygens,[24] and that (5.19) and (5.20) apply, with $M_+ = 48$ amu and $M_- = 3\times 16 = 48$ amu, we obtain $\Delta_+ \sim 2\times 10^{-10}$ cm and $\Delta_- \sim 1.1\times 10^{-9}$ cm. In order to obtain an energy overlap of the order of 0.1 eV we probably require a wave function overlap of the order of $10^{-2} = \exp(-4.6)$, and hence an electronic radius r_0 for the ion satisfying $r_0 \sim 0.9$ Å. Thus we find that $(G\Delta_+/r_0^2) \sim (0.1)$. As the actual overlaps are indirect via oxygens we should, perhaps, note that for $r_0 \sim 1$ Å, $\{\frac{1}{2}G\Delta_-/r_0^2\} \sim 0.2$. A similar equation to (5.21) will probably give the condition for corrections to Ti—O overlaps due to ionic motion to be unimportant. Thus for direct or indirect overlaps we expect that corrections due to ionic displacements will be small. We shall ignore any such corrections, and so put $J_s = J_m = J_0 = 0.1$ eV.

Now with $J_m = 0.1$ eV, using the values of B_0, C_0, D_0, and F obtained above, and assuming electron-phonon interactions quadratic in the normal coordinates and anharmonic terms in the ordinary lattice potential energy are negligible, from (3.28) we find $S_1 = -1.1$. Hence, $S = (S_0 + S_1) = 8.5$, and the bandwidth reduction factor is $\exp(-4.25) = 0.014$. Thus, the polaron band width $W = 0.016$ eV, and, with $\hbar\omega = 0.099$ eV, the condition (1.6) is just about satisfied. The bare mass m_b in our simple model satisfies $m_b = (\hbar^2/2J_0 G^2)$. With $J_0 = 0.1$ eV, this gives $m_b = 2.48m_e$, where m_e is the free-electron mass, and so the polaron mass m_p is given by $m_p = m_b \exp(\frac{1}{2}S) = 1.7\times 10^2 m_e$.

From (5.14), putting in figures for B_0, S, J_0, and J_m, we find that the polaron binding energy E_p satisfies

$$E_p = (0.86 + 0.06 - 0.60 + 0.01) \text{ eV} = 0.33 \text{ eV}. \quad (5.25)$$

Finally, from (5.15) the polaron radius r_p may be calculated to satisfy $r_p = 1.7$ Å.

We have shown that for a simplified model of a possible conduction band in SrTiO$_3$ the necessary conditions for the applicability of our adiabatic theory of nearly small polarons seem to hold. For the values of

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[24] R. A. Cowley, Phys. Rev. **134**, A981 (1964).

[25] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).

[26] A. Linz, Jr., Phys. Rev. **91**, 753 (1953).

[27] D. M. Eagles, J. Phys. Chem. Solids **25**, 1243 (1964) and **26**, 672 (1965). There is an error in the second of these references. The coupling constant with the lowest frequency longitudinal modes in SrTiO$_3$ should have been given by $\alpha_1(m_e/m)^{1/2} \simeq 0.01$ (not 0.001 as stated there).

[28] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

electronic overlap integrals chosen, corrections due to wave-function spreading to polaron masses bring about appreciable reductions in these masses, but nevertheless they are still made enormously large by polaron effects.

It is now of interest to compare our results with those which would be obtained by the use of large-polaron theory.

The bare mass m_b for $J_0=0.1$ eV is $m_b=2.48m_e$, and so, using an extension of a calculation of the continuum-polarization model of electron-phonon interactions to materials with several types of polar modes[27] as applied to $SrTiO_3$, we find that the coupling constants α_1, α_2, and α_3 with the modes of phonon energies $\hbar\omega_1=0.022$ eV, $\hbar\omega_2=0.058$ eV, and $\hbar\omega_3=0.099$ eV are $\alpha_1=0.01(m_b/m_e)^{1/2}=0.02$, $\alpha_2=0.05(m_b/m_e)^{1/2}=0.79$, and $\alpha_3=1.83(m_b/m_e)^{1/2}=2.88$. Hence, a weak coupling-type of model should be fairly good, and so the polaron binding energy E_p' will satisfy

$$E_p'=\sum_{i=1}^{3}\alpha_i\hbar\omega_i=0.33\text{ eV}, \tag{5.26}$$

while the ratio of the polaron mass m_p' to the bare mass m_b will be given by

$$(m_p'/m_b)=1+\tfrac{1}{6}\sum_i\alpha_i=1.6. \tag{5.27}$$

i.e., we find $m_p=4.0m_e$. If we consider the highest frequency modes only, then[27] the polaron radius is $6.2(m_e/m_b)^{1/2}=3.9$ Å, i.e., the radius is about equal to a lattice constant, and so the effective-mass approximation made in large-polaron theory may not be very good. However, if corrections to the theory were made, but still within the framework of an approximation where the lattice displacements follow the instantaneous position of the electron, it would be surprising if the effective-mass ratio were changed drastically from the values noted in (5.27). Thus, it seems that for $J=0.1$ eV two types of solution to the polaron problem may exist, both with about the same polaron-binding energies, but with very different masses. For $J>J_c$, where J_c is some critical value of J, a weak-coupling large-polaron theory should given the lowest polaron energy, while for $J<J_c$ the adiabatic nearly small polarons discussed in this paper should be energetically more favorable. The transition to weak-coupling large-polaron theory with increasing J is somewhat surprising, and presumably need not be expected for all cases. Thus, if the polaron binding energy were sufficiently large relative to $\hbar\omega$, one would expect that the transition to large-polaron theory with increase of J would occur in a region where the strong-coupling, adiabatic large-polaron theory were valid, and so in this case a smooth transition would be expected.

We should note that the observed masses in $SrTiO_3$ as deduced from thermoelectric power measurements[29] are about $6m_e$ at 78°K, and around $16m_e$ at room temperature. Thus, the observed masses are more consistent with those expected for a weak-coupling, large-polaron theory than with those of our theory. However, we might postulate that the increased mass observed at room temperature could be connected with a much narrower band of our type starting at an energy a few hundredths of an electron volt above the bottom of the lowest band. This is very speculative, and we should emphasize that both polaron theories discussed are based on over-simplified models of the conduction band, and that the actual rigid lattice band structure calculations indicate a minimum energy in the [100] direction for the lowest conduction band, and bare masses which are very anisotropic, being much larger in one direction than the other two.

We conclude this section by making some comments on the possibility of localized-mode formation in $SrTiO_3$, assuming that nearly small polarons with parameters used above are produced.

From (5.22) and (5.23) we find that the cosines of the angles between the vectors $\hat{\eta}_{\mathbf{G}}$ associated with the coordinates $\eta_{\mathbf{G}}$ of (2.59), and those between these vectors and the vector $\hat{\xi}$ in the direction from the origin in q space to the minimum associated with $\mathbf{R}$, satisfy

$$\begin{aligned}\hat{\eta}_{\mathbf{G}}\cdot\hat{\eta}_{\mathbf{G}'}&=0.34, \quad |\mathbf{G}-\mathbf{G}'|=G\sqrt{2}\\ &=0.27, \quad |\mathbf{G}-\mathbf{G}'|=2G,\end{aligned} \tag{5.28}$$

and

$$|\hat{\eta}_{\mathbf{G}}\cdot\hat{\xi}|=0.52. \tag{5.29}$$

With $J_m=0.1$ eV and $F=0.95$ eV the inequalities (2.60) satisfied by the coefficient A_1 in the expansion of the potential energy about a minimum as given by (2.46) to (2.48) become

$$0.26\geqslant A_1\geqslant 0.04. \tag{5.30}$$

Further, if the coordinate ξ_1 of (2.46) satisfies

$$\xi_1\propto\sum\nolimits_{\mathbf{G}}\eta_{\mathbf{G}}, \tag{5.31}$$

we expect that

$$A_1=6(\hat{\eta}_{\mathbf{G}}\cdot\hat{\xi})^2(2J_m/F)^2=0.07. \tag{5.32}$$

Now, judging from the phonon-dispersion curves obtained from model IV of Cowley's work,[24] it seems that for the highest frequency longitudinal branch of the phonon spectrum $(\Delta\omega/\omega)\simeq 0.1$. Hence, using the value of A_1 given by (5.32), from (2.61) to (2.63) we see that we are about on the borderline for the production of localized modes. However, since $0.07<0.1$, and also because the fact that $\hat{\eta}_{\mathbf{G}}$ and $\hat{\xi}$ will contain some contributions from other branches of the phonon spectrum will tend to reduce A_1 from the value of (5.32), it appears probable that localized modes will not be formed. The value of 0.1 eV chosen for electronic energy overlap integrals is approaching the maximum for which it is possible to use our tight-binding approach to nearly small-polaron theory, since (i) inequality (1.6)

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[29] H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Phys. Rev. **134**, A442 (1964).

will not be satisfied for larger value of J and (ii) in any case large-polaron theory seems to give lower polaron energies when $J>0.1$ eV.

C. Comments

From a study of a simplified model for a conduction band in $SrTiO_3$ it appears that it is possible to find materials such that the necessary conditions for applicability of our adiabatic nearly small-polaron theory hold, while at the same time large polarons in a weak-coupling theory can exist. As the overlap integral increases through a critical value, the type of polaron with the lowest energy changes from that discussed in this paper to that of large-polaron theory. The effective masses in the two types of theory are drastically different, and so presumably are some other polaron properties such as mobility. Thus, it seems that, as a function of rigid lattice bandwidth, or alternatively as a function of strength of electron-phonon coupling, which strength depends on static- and high-frequency dielectric constants and lattice constants, there may be a sudden change of observable quantities connected with the polaron. It might be possible to see such changes by studying a suitable material in its dependence on temperature or pressure.

We should note that such a sharp transition from one type of solution to another was predicted by Toyozawa[30] for electrons in interaction with acoustical phonons but, because of the work of Feynman[31] on large polarons where a continuous variation of polaron energy and effective mass is predicted as a function of coupling constant, it is generally thought that for optical phonons no sharp transition should be expected. Our result appears to indicate that taking into account the structure of the lattice explicitly instead of making use of the effective-mass approximation can change a gradual transition into a sudden one. However, more work is perhaps required on a study of whether the necessary conditions (1.4), (1.5) and (1.6) for our theory to apply are also sufficient, and also on the corrections to an effective-mass approximation in a weak-coupling type of theory for polarons of radii of the order of a lattice constant, before we can be sure that a sudden transition really occurs.

The most striking prediction within our theory, that of a discrete distribution of effective masses when localized modes are formed, might be difficult to observe experimentally, since the predicted masses are probably too large to be observable by cyclotron resonance. Thus it would be desirable to develop a theory of mobility under conditions when localized modes are formed.

An observable effect of localized-mode formation on the temperature dependence of wide-band to narrow-band optical absorption is predicted in Sec. IV in that the expressions for the absorption coefficient obtained there are not the same as predicted for a similar absorption when there are no localized modes connected with carriers in the narrow band. However, since the absorption in both cases depends on the density-of-states function for the wide band, which may not be known, it may be difficult to isolate effects due to localized-mode formation. If a theory of absorption due to transitions within and between nearly small polaron bands were developed, which would require some knowledge of wave functions associated with the excited-state potential curves shown in Fig. 1, then it is likely that, as for wide-to-narrow band absorption, results would be similar to those for small polarons, but in this case any differences due to the presence of localized modes around the polaron might be easier to detect than in the wide-to-narrow band case, especially if the dispersion in frequencies of the nonlocalized modes were sufficiently small for sharp absorption lines to be seen.

The conditions for the existence of localized modes, given by (2.61) and (2.63), required that a small quantity A_1 be greater than the fractional dispersion of phonon frequencies for the relevant branch of the spectrum, and so a very small dispersion is required. This is most likely to occur in molecular crystals, where the mode frequencies for optical branches often lie close to the vibration frequencies for the individual molecules. Provided that enough polarons are produced than of course one should be able to test for the existence of localized modes directly by studying infrared absorption in the frequency range in which modes would be expected to lie.

VI. CONCLUSIONS

In Sec. II, by expanding electronic single-site and overlap-energy integrals as a function of lattice normal coordinates up to second order, an expression for the potential at and near a minimum-energy nuclear configuration in an adiabatic theory of polarons has been obtained under conditions when the polarons are "nearly small," that is when electronic wave functions associated with the minimum are concentrated mainly on one ion, but contain slight admixtures of functions for neighboring ions. It has been shown that, in the expansion of the potential energy about a particular minimum as given by Eqs. (2.44) and (2.45), the following three types of terms occur which tend to produce localized modes of vibration for motion about the minimum: (1) Terms arising from electronic overlap energies which can arise because (a) the amount of spreading of electronic wave functions to neighboring sites will depend on lattice coordinates and (b) since the electronic overlap integral depends on ionic position, even for a fixed amount of spreading, the overlap energy depends on these positions; (2) terms arising from second-order dependence of single ion electronic

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[30] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **26**, 29 (1961).

[31] R. P. Feynman, Phys. Rev. **97**, 660 (1955).

energies on ionic displacements; (3) anharmonic terms in the ordinary lattice potential energy. The second and third types of terms can also occur in small-polaron theory, but the first type cannot, since its occurrence depends on wave-function spreading.

By use of a generalized tight-binding method for obtaining wave functions, and by dividing transitions between neighboring minima into those diagonal and nondiagonal in oscillator occupation numbers as in small-polaron theory, bandwidths as a function of temperature for our adiabatic theory of nearly small polarons have been studied in Sec. III for a few special cases. If localized modes are not formed, results are similar to those of the usual type of small-polaron theory, that is, the bandwidth is decreased over that for a rigid lattice by a factor $\exp\{-\frac{1}{2}S(2\bar{n}+1)\}$, where S equals the sum of squares of differences of mode displacements between one minimum and the next. Thus the bandwidth decreases as the temperature rises, and presumably in due course a temperature will be reached at which the uncertainty in energy due to scattering becomes equal to the bandwidth, and then a band model will no longer be suitable. The actual value of the parameter S differs somewhat from that which occurs in small-polaron theory because of the slightly modified displacements.

If localized modes are formed, then calculations become more difficult, but for the special case of only one localized mode associated with each minimum, and negligible displacements for the nonlocalized modes, it has been shown that at nonzero temperatures a discrete distribution of bandwidths will occur, with a mean width which may increase with increasing temperature.

The effect of localized-mode formation on optical absorption due to transitions between a wide valence band, for which electron-phonon coupling is neglected, and an adiabatic nearly small-polaron conduction band, has been treated in Sec. IV in the same model with only one localized mode, by using the method of finding transition probabilities between approximate stationary states of the electron-phonon system by perturbation theory, with the electron-radiation interaction as a perturbation. In the model considered, the absorption coefficient K may be split up in parts $K_{p,r}$ involving emission of p-localized phonons and absorption of r-nonlocalized phonons, and the integral of the product of the refractive index n, and the phonon energy Ω, and K satisfies (4.32). At $T=0$ these results are identical in form with those obtained in Ref. 3 for absorption due to transitions between a wide band and an ordinary small-polaron band without localized modes, but the dependence of absorption on temperature for the two cases is somewhat different. For a given strength of electron-phonon coupling, the long-wavelength tail to the absorption increases more rapidly with increasing temperature if localized modes are present.

A continuum-polarization model of electron-phonon interactions has been used in Sec. V to obtain explicit expressions for the main parameters occurring in the theory of the previous sections, and numerical values have been found for a simplified model of a possible conduction band in $SrTiO_3$. The calculations indicate that electronic states may exist from which both adiabatic nearly small polarons and weak coupling, large polarons can be formed, and that the lowest energy polaron state may suddenly change from one type to the other as electronic overlap integrals or electron-phonon interactions are altered in magnitude.

APPENDIX A

In this Appendix we show that if all terms proportional to ϵ in Sec. II are neglected, and if a continuum-polarization model is used for electron-phonon interactions and dispersion of phonon frequencies is ignored, then (3.4) holds for large $|\mathbf{R}-\mathbf{R}'|$.

Under neglect of terms in ϵ, from (2.44), (2.45), and (2.36), we see that modes i for the minimum associated with $\mathbf{R}$ are just the normal modes for the perfect crystal displaced by an amount depending on $\mathbf{R}$. For a continuum-polarization model of electron-phonon interactions the quantity $E_\lambda^{(1)}(\mathbf{R})$ defined in (2.8) is zero except for modes λ in the longitudinal-polar-optical branch of the lattice vibration spectrum, and for these modes, classified according to wave vector $\mathbf{w}$, the function $E_{\mathbf{w}}^{(1)}(\mathbf{R})$ is given by (5.7) and (5.5). Thus, using (5.17), (5.6) and the corresponding equation for $q_{-\mathbf{w}}$, we find that the annihilation operators $b_i(\mathbf{R})$ can be chosen so that

$$b_i(\mathbf{R}) \propto \{b_{\mathbf{w}}+d_{\mathbf{w}}(\mathbf{R})\}\,, \qquad \text{(A1)}$$

where

$$d_{\mathbf{w}}(\mathbf{R})=(B/w)\exp(-i\mathbf{w}\cdot\mathbf{R})\,, \qquad \text{(A2)}$$

with B independent of $\mathbf{w}$ and $\mathbf{R}$.

Now, since $d_{\mathbf{w}}$ is small we may show, using Eq. (15) of Ref. 3 that

$$\begin{aligned}\langle\chi_{n\mathbf{R}}|\chi_{n\mathbf{R}'}\rangle=\textstyle\prod_{\mathbf{w}}\,(1-(n_{\mathbf{w}}+\frac{1}{2})\,|d_{\mathbf{w}}(\mathbf{R})-d_{\mathbf{w}}(\mathbf{R}')|^2\\ -\operatorname{Im}[d_{\mathbf{w}}(\mathbf{R})\{d_{\mathbf{w}}^*(\mathbf{R}')-d_{\mathbf{w}}^*(\mathbf{R})\}])\\ =\exp\{-\tfrac{1}{2}S_{\mathbf{R}-\mathbf{R}'}(2\bar{n}+1)\}\,, \qquad \text{(A3)}\end{aligned}$$

where Im denotes the imaginary part, and $S_{\mathbf{R}-\mathbf{R}'}$ is defined by

$$S_{\mathbf{R}-\mathbf{R}'}=\textstyle\sum_{\mathbf{w}}\,|d_{\mathbf{w}}(\mathbf{R})-d_{\mathbf{w}}(\mathbf{R}')|^2. \qquad \text{(A4)}$$

In obtaining the right-hand side of (A3) we make use of the fact that in summing over wave vectors the contributions from the imaginary part of products of mode displacements cancel in pairs.

Substituting for $d_{\mathbf{w}}(\mathbf{R})$ from (A2) and replacing summation by integration over a spherical Brillouin zone of radius w_0, we deduce that

$$S_{\mathbf{R}-\mathbf{R}'}=b\{1+[\operatorname{Si}(w_0r)/w_0r]\}=b\{1+O(1/w_0r)\}\,, \qquad \text{(A5)}$$

where we have written $r=|\mathbf{R}-\mathbf{R}'|$, the coefficient b is a constant independent of r, and Si is the function defined in (5.13). The right-hand equality in (A5) holds because $\mathrm{Si}(x)$ tends to a constant value as $x\to\infty$.

From (A3) and (A5) we deduce that

$$\langle\chi_{n\mathbf{R}}|\chi_{n\mathbf{R}'}\rangle=K+O(C/|\mathbf{R}-\mathbf{R}'|)\,, \tag{3.4}$$

where K and C are constants.

APPENDIX B

In this Appendix we discuss orthogonalization of the states $|\chi_{n\mathbf{R}}\rangle$ when the overlaps $\langle\chi_{n\mathbf{R}}|\chi_{n\mathbf{R}'}\rangle$ satisfy

$$\langle\chi_{n\mathbf{R}}|\chi_{n\mathbf{R}'}\rangle=K+L_r\,, \tag{B1}$$

where $r=|\mathbf{R}'-\mathbf{R}|$, K is a constant, L_r is nonzero only for small r, and

$$\begin{aligned} &K\ll 1\\ &L_r\ll 1,\quad \text{all}\quad r\,. \end{aligned} \tag{B2}$$

We show that under these conditions orthogonalization can be performed without drastically altering the state $|\chi_{n\mathbf{R}}\rangle$.

We carry out the orthogonalization in two stages. First, we define states $|\mathbf{R}\rangle$ by

$$|\mathbf{R}\rangle=F_1\{|\chi_{n\mathbf{R}}\rangle-N^{-1}\sum_{\mathbf{R}'}|\chi_{n\mathbf{R}'}\rangle\}\,, \tag{B3}$$

where F_1 is a normalization factor and N is the number of unit cells in the crystal. Using (B1) and the assumption that L_r is zero except for small r we may deduce that

$$F_1=(1-K)^{-1/2}+O(1/N)\,, \tag{B4}$$

and that for $\mathbf{R}'\neq\mathbf{R}$

$$\langle\mathbf{R}|\mathbf{R}'\rangle=L_r(1-K)^{-1}+O(1/N)\,. \tag{B5}$$

Further, using (B2), (B3), and (B4), we may show that

$$|\,|\mathbf{R}\rangle-|\chi_{n\mathbf{R}}\rangle|\ll 1\,. \tag{B6}$$

We have now completed the first step of our orthogonalization procedure, i.e., we have removed the constant term from the overlaps. In order to carry out the second stage we suppose that the final-orthogonalized functions $|\chi'_{n\mathbf{R}}\rangle$ may be written as

$$|\chi'_{n\mathbf{R}}\rangle=F_2\{|R\rangle-\sum_{\mathbf{R}''}b_{\mathbf{R}''-\mathbf{R}}|\mathbf{R}''\rangle\}\,, \tag{B7}$$

where F_2 is a normalization factor, and $b_{\mathbf{R}''-\mathbf{R}}$ are expansion coefficients to be determined. For simplicity we limit our considerations to states with real wave functions, and hence we assume that overlaps and the expansion coefficients $b_{\mathbf{R}''-\mathbf{R}}$ are real. Thus, from (B7) we find that

$$\begin{aligned}\langle\chi'_{n\mathbf{R}}|\chi'_{n\mathbf{R}'}\rangle=F_2{}^2\{\langle\mathbf{R}|\mathbf{R}'\rangle-\sum_{\mathbf{R}''\neq\mathbf{R}'}b_{\mathbf{R}''-\mathbf{R}}\langle\mathbf{R}''|\mathbf{R}'\rangle\\ -\sum_{\mathbf{R}'''\neq\mathbf{R}}b_{\mathbf{R}'''-\mathbf{R}'}\langle\mathbf{R}|\mathbf{R}'''\rangle+\sum_{\mathbf{R}'',\mathbf{R}'''}b_{\mathbf{R}''-\mathbf{R}}b_{\mathbf{R}'''-\mathbf{R}'}\\ \times\langle\mathbf{R}''|\mathbf{R}'''\rangle-b_{\mathbf{R}-\mathbf{R}'}-b_{\mathbf{R}'-\mathbf{R}}\}\,.\end{aligned} \tag{B8}$$

Now, since $\langle\mathbf{R}''|\mathbf{R}'\rangle=0$ except in a small region of the crystal, the second, third, and fourth terms in the bracket on the right-hand side of (B8) will be smaller than the last two by a factor of the order of an overlap integral, and so, ignoring these terms, setting the right-hand side of the equation equal to zero and choosing a symmetrical solution, we find that

$$b_{\mathbf{R}'-\mathbf{R}}\simeq\tfrac{1}{2}\langle\mathbf{R}|\mathbf{R}'\rangle=\tfrac{1}{2}L_r(1-K)^{-1}\,. \tag{B9}$$

Further, since the overlaps L_r are small and are confined to a limited region, we may deduce from (B7) and (B9) that

$$|\,|\chi_{n\mathbf{R}}{}'\rangle-|\mathbf{R}\rangle|\ll 1\,. \tag{B10}$$

Combining this with (B6) we see that

$$|\,|\chi_{n\mathbf{R}}{}'\rangle-|\chi_{n\mathbf{R}}\rangle|\ll 1\,. \tag{B11}$$

Thus, if L_r is confined to a limited region, we have shown that an orthogonalized set of states $|\chi_{n\mathbf{R}}{}'\rangle$ can be constructed from states satisfying (B1) and (B2) in such a way that the new set only differ slightly from the old set. However, according to (3.4) we expect that actually $L_r\sim(C/r)$ for large r, where C is a constant. We have not succeeded in proving that an orthogonalization procedure can be found such that (B11) is satisfied in this case, but as terms in the overlap which are constant or of short range have been dealt with satisfactorily, and $L_r\sim(C/r)$ is in some sense intermediate between the constant and short range cases, by interpolation we expect that such an orthogonalization is possible.