Acoustic deformation-potential polaron

Mehmet Rona and Serpil Ayasli
Department of Physics, The Middle East Technical University, Ankara, Turkey
(Received 3 August 1976)

We have found the energy-momentum relation of the acoustic deformation-potential polaron to be nearly parabolic. This means that the energy crossing arguments may be misleading as a tool to justify forms of the energy-momentum relations for polarons. We have studied the strong-coupling limit to develop a better understanding of the self-trapping state. We have concluded that in silicon and germanium self-trapping of electron due to the deformation-potential interaction is not expected. We further have given evidence suggesting that in the calculations of the energy levels of impurity atoms in materials where the acoustic deformation potential is dominant the inclusion of the polaron effects might be necessary.

I. INTRODUCTION

In the deformation-potential[1] model of the electron-phonon interaction, the electron interacts with the local strain accompanied by an acoustic wave. One equates the local electronic energy shift due to such a fluctuating strain with the observed shift under a homogeneous strain of the same magnitude. Hence this model is expected to be successful in the description of the interaction of an electron with long-wavelength phonons.

In addition to scattering electrons from one state to another, such an interaction would dress the electron, modifying its ground state and mass. In the present case, we refer to the composite system as the acoustic-deformation-potential (ADP) polaron.

The polaron problem has received considerable attention in recent years.[2-4] There is now a rather clear picture associated with many aspects of the problem such as the binding to impurities, behavior in a magnetic field, internal structure, and the energy-momentum relations of free polarons.

Among the various polaron problems, the deformation-potential polaron seems to have received relatively little attention. Toyozawa[5,6] has discussed the self-trapping of an electron due to its interaction with the acoustic-phonon field through deformation-potential coupling. Kittel[7] has discussed the ground state of the acoustic deformation-potential polaron using second-order perturbation theory and calculated the number of virtual phonons in the cloud accompanying the electron. Whitfield and Tomak[8] have discussed the possibility that the ADP polaron effect might contribute to the binding energy of shallow traps in homopolar semiconductors. Gray[9] has analyzed the optical deformation-potential polaron in a uniform magnetic field. While this paper was being written, we learned of the recent work of Whitfield and Shaw[10] on the deformation-potential polaron in one dimension. Their paper includes a derivation of the interaction Hamiltonian and analysis of the problem in one dimension contributing to a better understanding of the piezoelectric polaron. The strong-coupling limit is treated and exactly soluble models are given. This work also made us aware of a paper by Sumi and Toyozawa[11] which elaborates on the relationship of the self-trapping state to the small polaron along the lines of the previous work of Toyozawa.[5,6]

The primary purpose of the present paper is to study the dynamics of the ADP polaron. We are mainly interested in determining whether all polarons involving acoustic virtual phonons have an anomalous energy-momentum relation. This work is presented in Sec. II. In Sec. III, we study the structure of the ADP polaron. Self-trapping of electrons due to the ADP interaction and ADP polaron correction to the impurity binding energies are discussed in Sec. IV and V.

II. MOTION OF THE DEFORMATION-POTENTIAL POLARON AT ZERO TEMPERATURE

Schultz[12] has discussed the motion of the polaron using an argument based on the bending over of the free electron energy-momentum relation due to its crossing the dispersion relation of the free phonon field. This argument was used to guess the energy-momentum relation of the optical polaron. Whitfield *et al.*[13,14] applied this argument to the optical and piezoelectric polarons. Recently, Sheka *et al.*[15] have presented a variational theory giving the energy-momentum relation for the optical and the piezoelectric polarons of arbitrary coupling strengths. Based on functional integration, this theory seems to offer added theoretical support to the results of the energy-momentum relation calculations given for the optical[13] and piezoelectric[14,16] polarons.

The energy-crossing arguments refer to the existence of an interaction between an electron

and a particular branch of lattice vibrations but not to its form. Since much theoretical evidence has been amassed in the case of piezoelectric interaction leading to a polaron energy having an asymptotically linear dependence on momentum, our attention has been drawn to the acoustic-deformation-potential polaron. Even though this type of polaron effect has received relatively little attention, it would be relevant for silicon, a material which has been studied extensively. Therefore, it seems nearly impossible that evidence pointing to an anomalous energy-momentum relation would not appear among the observations. This is what motivated us to analyze the energy-momentum relation of the acoustic-deformation-potential polaron.

A. The Hamiltonian

Polarons have been discussed using a Hamiltonian of the form

$$H=\frac{p^2}{2m}+\sum_{\vec{q}}\hbar\omega_{\vec{q}}a_{\vec{q}}^{\dagger}a_{\vec{q}}+\sum_{\vec{q}}Q_{\vec{q}}(a_{\vec{q}}+a_{-\vec{q}}^{\dagger})e^{i\vec{q}\cdot\vec{r}}, \quad (1)$$

where $\vec{p}$ and $\vec{r}$ refer to the electron momentum and coordinate, $a_{\vec{q}}$ and $a_{\vec{q}}^{\dagger}$ destroy and create a phonon with wave vector $\vec{q}$, and $Q_{\vec{q}}$ is the amplitude of the interaction between the electron and the qth mode of lattice vibrations. The band mass of the electron is taken to be a constant and $\omega_{\vec{q}}$ is the dispersion relation for the field of relevant lattice vibrations. When these comprise the acoustic modes, one writes $\omega_{\vec{q}}=s|\vec{q}|$, taking s to be the spherical average of the velocity of sound in the medium. In this case if one expresses energies in terms of ms^2 and lengths in terms of $\hbar/ms$, one can write the ADP polaron Hamiltonian as

$$H=\frac{p^2}{2}+\sum_{\vec{q}}|\vec{q}|a_{\vec{q}}^{\dagger}a_{\vec{q}}+\sum_{\vec{q}}Q_{\vec{q}}(a_{\vec{q}}+a_{-\vec{q}}^{\dagger})e^{i\vec{q}\cdot\vec{r}}, \quad (2)$$

where the physical quantities and operators retain their previous meanings but are dimensionless. For the present problem the interaction amplitude is given by

$$Q_{\vec{q}}=E_1\left(\frac{|\vec{q}|}{2\rho V}\right)^{1/2}=\left(\frac{\alpha|\vec{q}|}{2V}\right)^{1/2}, \quad (3)$$

where E_1 is the band-edge shift per unit volume, ρ is the density of the medium, and V is the volume of the crystal. The second equality defines a convenient dimensionless coupling constant α in terms of previously defined parameters. In Appendix A, we observe that in silicon and germanium the deformation-potential coupling between the electron and the field of acoustic-lattice vibrations is weak. This was the motivation to apply the perturbation theory, the variational theory of Lee, Low, and Pines[17] and Gurari[18] and the Tamm-Dancoff approximation with one quantum cutoff to the present problem.

B. Perturbation theory

Starting with an uncoupled electron and the field of acoustic-lattice vibrations, we calculate the energy correction by the second-order perturbation theory where the correction is first order in α,

$$E^{(2)}(p)=\frac{p^2}{2}+\sum_{\vec{q}}\frac{Q_q^2}{p^2/2-(\vec{p}-\vec{q})^2/2-q} \quad (4)$$

$$=\frac{p^2}{2}+\frac{\alpha}{3\pi^2 p}\left\{\left[1+3p^2+\left(\frac{\kappa}{2}\right)^3\right]\ln\left(\frac{1+\frac{1}{2}\kappa-p}{1+\frac{1}{2}\kappa+p}\right)\right.$$
$$\left.-p(p^2+3)\ln\left(\frac{(1+\frac{1}{2}\kappa)^2-p^2}{1-p^2}\right)-(1+3p^2)\ln\left(\frac{1-p}{1+p}\right)-p\left(\frac{\kappa}{2}\right)\left(\frac{\kappa}{2}-4\right)\right\} \quad (p<1), \quad (5)$$

where κ is the cutoff on the magnitude of the phonon wave vectors.

In order to get an idea about how this result compares with a similar calculation in the case of the piezoelectric polaron,[14] we write

$$\lim_{p\to 0}E^{(2)}(p)=E(0)+p^2/2m^*, \quad (6)$$

and compare the self-energies $E(0)$ and the effective masses for the two polarons for small p Table I.

Figure 1 shows the energy-momentum relation given by Eq. (5). It should be noted that unlike the piezoelectric polaron, the derivative of energy with respect to momentum at $P=1$ is not singular. Even though for a sufficiently large α one observes anomalies such as a negative mass,[14] for a coupling constant that characterizes silicon such a problem does not arise.

C. Intermediate-coupling theory

This theory[17] is based on using a trial state:

$$|\psi_I\rangle=T_1T_2|0\rangle, \quad (7)$$

where T_1 represents the Bogoliubov canonical transformation

TABLE I. Energy-momentum relations of the acoustic-deformation-potential polaron (ADPP) and the piezoelectric polaron (PEP) for small momenta $[E(P)=E(0)+p^2/2m^*]$.

Type of polaron	Interaction amplitude Q_q	Self-energy $E(0)$	Inverse effective mass $1/m^*$
ADPP by the perturbation theory	$(\alpha q/2V)^{1/2}$	$-(\alpha/\pi^2)(\frac{1}{2}\kappa)^2$	$1-(2\alpha/\pi^2)[\frac{2}{3}\ln(\frac{1}{2}\kappa+1)-1]$
PEP by the perturbation theory	$(4\pi\alpha/qV)^{1/2}$	$-(4\alpha/\pi)[\ln(\frac{1}{2}\kappa+1)]$	$1-(4\alpha/3\pi)[1-(\frac{1}{2}\kappa+1)^{-2}]$
ADPP by the intermediate-coupling theory	$(\alpha q/2V)^{1/2}$	$-(\alpha/\pi^2)(\frac{1}{2}\kappa)^2$	$\{1+(2\alpha/\pi^2)[\frac{2}{3}\ln(\frac{1}{2}\kappa+1)-1]\}^{-1}$

$$T_1=\exp\left(-i\vec{r}\cdot\sum_{\vec{q}}\vec{q}a_{\vec{q}}^{\dagger}a_{\vec{q}}\right), \tag{8}$$

and T_2 transforms to the coherent states of the field of lattice vibrations

$$T_2=\exp\left(\sum_{\vec{q}}f_{\vec{q}}(a_{\vec{q}}^{\dagger}-a_{\vec{q}})\right). \tag{9}$$

The $f_{\vec{q}}$ are variational parameters chosen to minimize the expectation value of the ground-state at fixed polaron momentum p,

$$f_{\vec{q}}=Q_q/(\tfrac{1}{2}q^2+|\vec{q}|-\vec{q}\cdot\vec{v}). \tag{10}$$

The upper bound to the energy at fixed p is given by

$$E_I(p)=\frac{p^2}{2}-\frac{(\vec{p}-\vec{v})^2}{2}-\sum_q\frac{Q_q^2}{\frac{1}{2}q^2+|\vec{q}|-\vec{q}\cdot\vec{v}}, \tag{11}$$

with the

$$\vec{p}=\vec{v}+\sum_{\vec{q}}\frac{Q_q^2}{(\frac{1}{2}q^2+|\vec{q}|-\vec{q}\cdot\vec{v})^2}\vec{q}. \tag{12}$$

Here $\vec{v}$ is the polaron velocity.[14]

The last two expressions yield the following energy-momentum relation for the ADP polaron:

$$E_I(p)=\frac{p^2}{2}-\frac{(\vec{p}-\vec{v})^2}{2}+\frac{\alpha}{3\pi^2v}\left\{\left[1+3v^2+\left(\frac{\kappa}{2}\right)^3\right]\ln\frac{1+\frac{1}{2}\kappa-v}{1+\frac{1}{2}\kappa+v}-v(v^2+3)\ln\frac{(1+\frac{1}{2}\kappa)^2-v^2}{1-v^2}-(1+3v)^2\ln\frac{1-v}{1+v}-\kappa\left(\frac{\kappa}{2}-4\right)\right\}$$
$$(v<1), \tag{13}$$

$$|\vec{p}-\vec{v}|=\frac{\alpha}{3\pi^2v^2}\left\{\left[1-3v^2+\left(\frac{\kappa}{2}\right)^3\right]\ln\frac{1+\frac{1}{2}\kappa-v}{1+\frac{1}{2}\kappa+v}+(1-3v^2)\ln\frac{1+v}{1-v}+2v^3\ln\frac{(1+\frac{1}{2}\kappa)^2-v^2}{1-v^2}+\kappa v\left(\frac{\kappa}{2}-1\right)\right\}\quad(v<1). \tag{14}$$

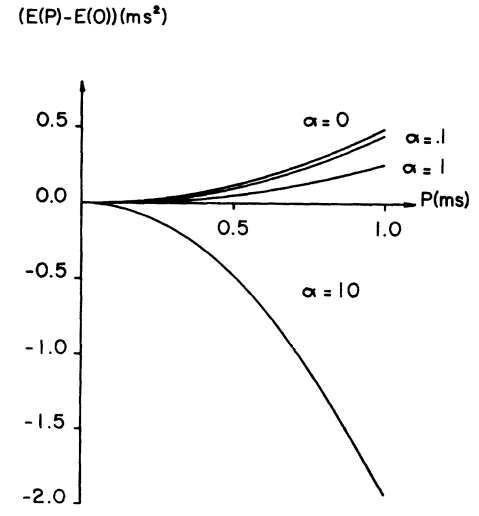

FIG. 1. Acoustic-deformation-potential polaron energy-momentum relation given by second-order perturbation theory ($\kappa=300$).

For small p, we can cast Eqs. (13) and (14) in the form of Eq. (6). The appropriate parameters for this representation is given in Table I.

To compare the intermediate coupling energy-momentum relation of the ADP polaron with that of the piezoelectric polaron both are plotted in Fig. 2.

D. Tamm-Dancoff approximation with one quantum cutoff

The last analysis of the weak coupled ADP polaron which we present involves utilizing the Tamm-Dancoff approximation with one phonon cutoff. This approximation involves a diagonalization of the interaction term using a truncated basis of zero phonon and one phonon states. It has been noted[13,14] that this approximation is particularly suited to cases where the optical modes are involved in the lattice distortion since it treats the energy (not the velocity) in a self-consistent manner.

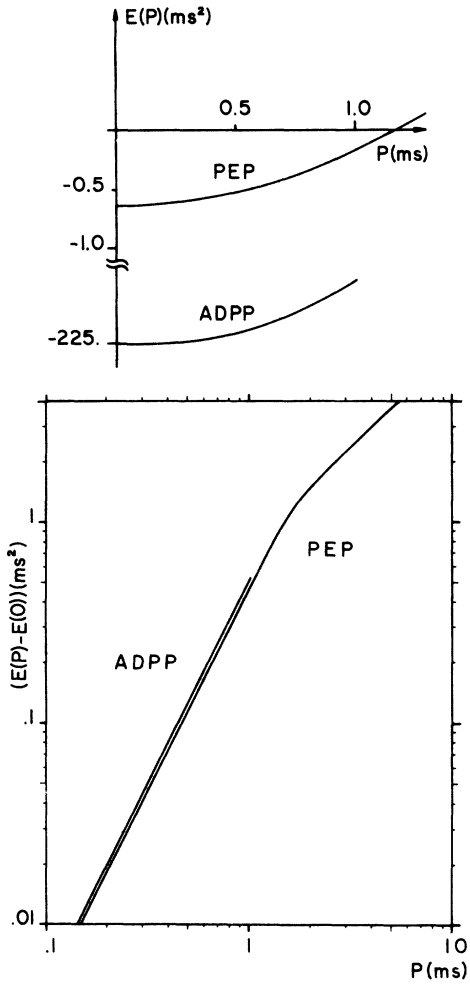

FIG. 2. Comparison of the energy-momentum relations of the piezoelectric polaron (PEP) and acoustic-deformation-potential polaron (ADPP) given by the intermediate-coupling theory of Lee, Low, and Pines ($\alpha = 0.1$ and $\kappa = 300$).

The Tamm-Dancoff approximation gives the polaron energy in terms of the integral equation

$$E_{\mathrm{TD}}(p) = \frac{p^2}{2} + \sum_{\vec{q}} \frac{Q_q^2}{E_{\mathrm{TD}}(p) - \frac{1}{2}(\vec{p}-\vec{q})^2 - |\vec{q}|} \,. \tag{15}$$

For the ADP polaron the energy is given by a complicated transcendental equation. The energy-momentum relation given by the Tamm-Dancoff approximation is plotted in Fig. 3.

E. Discussion of the weak-coupling theories of the ADP polaron motion

Energy-crossing arguments point to anomalous energy-momentum relations for polarons. For polarons involving the acoustic modes, the anomaly would be a linear dependence of energy on momentum for large p.[14]

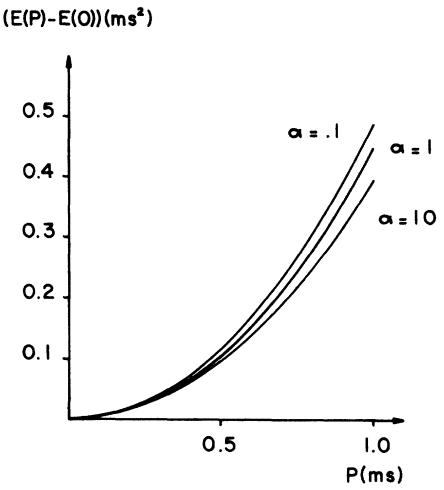

FIG. 3. Acoustic-deformation-potential polaron energy momentum relationship given by the Tamm-Dancoff approximation with one quantum cutoff ($\kappa = 300$).

For the piezoelectric polaron such an energy-momentum relation is given by the intermediate-coupling theory,[14] a strong-coupling theory,[16] and by a technique employing functional integration.[15] However, in the case of the ADP polarons none of the weak coupling theories yields an anomaly of the type described above.

An anomalous energy-momentum relation of an electron interacting with longitudinal-acoustic phonons has been pointed out to be related to the degeneracy of the unperturbed energies when the electron (polaron) reaches the velocity of sound.[14]

The success of the intermediate-coupling theory in yielding the predicted anomaly in the dynamics of the piezoelectric polaron has been ascribed to the fact that the former treats the polaron velocity (not energy) self-consistently. The anomaly has been shown to exist at nonzero temperatures,[19] when the anisotropy of the crystal is included,[20] and even if screening is taken into account.[21]

What seems to render the velocity of sound an upper bound to the piezoelectric polaron velocity is the divergence of the energy of the lattice distortion as $v \to 1$. One can show this by calculating the expected value of the phonon energy operator with the intermediate-coupling ground state in Eq. (7),

$$E_f = \langle \psi_I | \sum_{\vec{q}} |\vec{q}| a_{\vec{q}}^{\dagger} a_{\vec{q}} | \psi_I \rangle \tag{16}$$

$$= \frac{V}{2\pi^2} \int_0^{\kappa} dq \, \frac{q Q_q^2}{(\frac{1}{2}q+1)^2 - v^2} \,. \tag{17}$$

For the piezoelectric polaron $Q_q^2 \propto q^{-1}$ and the integral has a logarithmic infrared divergence when $v = 1$. On the other hand, for the ADP polaron

$Q_q^2 \propto q$ and, therefore, E_f is finite even when $v=1$.

We conclude that the anomalous energy-momentum relation given by the intermediate-coupling theory for the piezoelectric polaron is a result of the Coulombic nature of the interaction between the electron and the field. On the other hand, the local nature of the deformation-potential interaction precludes an important contribution of the long-wavelength phonons. Hence, the intermediate-coupling theory of the ADP polaron does not yield a linear energy-momentum relation as $v \to 1$.

The energy-momentum relation given by the perturbation theory [Eq. (5)] is not useful as $p \to 1$ even for small α, since the unperturbed energies become degenerate in that limit. Although the Tamm-Dancoff approximation [Eq. (15)] treats this degeneracy correctly, it is not useful either since the correct threshold is determined by the velocity and not the energy of the electron when the latter interacts with the longitudinal-acoustic phonons.

III. STRUCTURE OF THE DEFORMATION-POTENTIAL POLARON

A qualitative discussion of the structure of polarons has been given by Fröhlich.[22] Devreese has discussed the internal structure in connection with the optical absorption and cyclotron resonance of polarons.[23] A calculation of the structure of the displacement field of the piozoelectric polaron based on the intermediate coupling theory was given by Rona.[24] The most detailed analysis of the internal structure of the moving piezoelectric polaron was published by Thomchick and Whitfield.[25] They noted that the interaction Hamiltonian is the potential energy of the electron in the polarization field of the lattice. Following them, we calculate the internal structure of the ADP polaron by considering the lattice potential

$$V_I(r) = \langle \psi_I | \frac{1}{e} \sum_{\vec{q}} Q_{\vec{q}} (a_{\vec{q}} + a^{\dagger}_{-\vec{q}}) e^{i\vec{q}\cdot\vec{r}} | \psi_I \rangle , \tag{18}$$

where $|\psi_I\rangle$ is the intermediate-coupling ground state.

For the stationary ADP polaron ($v=0$), we find

$$V_I(r) = \frac{2\alpha}{e\pi^2} \left(\frac{1-\cos(\kappa r)}{2r^2} - \frac{1}{r} \left(\cos(2r)\{\mathrm{si}[2r(1+\tfrac{1}{2}\kappa)] - \mathrm{si}(2r)\} - \sin(2r)\{\mathrm{ci}[2r(1+\tfrac{1}{2}\kappa)] - \mathrm{ci}(2r)\} \right) \right) . \tag{19}$$

For large κ, we readily obtain

$$\lim_{r \to 0} V_I(r) = \frac{2\alpha}{e} \frac{1}{\pi^2} \left(\frac{\kappa}{2} \right)^2 . \tag{20}$$

To compare the structure of the piezoelectric and ADP polarons, we show Eqs. (19) and (25) of Ref. 25 in Fig. 4. Note that outside the piezoelectric polaron radius ($r=1$ in units of $\hbar/ms$), the potential is Coulombic. The size of the ADP polaron lattice distortion is almost an order of magnitude smaller. Within the latter, we have a Yukawa-type potential and outside a rapidly vanishing fluctuating component is observed. For silicon the size of the lattice distortion is of the order of a few tens of atomic spacing and the continuum approximation is marginally justified. The relatively small size of the potential well around the electron raises the possibility that the adiabatic theory of the polaron state might be appropriate for the ADP polaron.

IV. ADIABATIC THEORY OF THE ACOUSTIC-DEFORMATION-POTENTIAL POLARON

Although the adiabatic theory is appropriate for strong-coupled polarons, the size of the potential well we calculated in Sec. II suggests that self-trapping might occur even when the coupling constant α is small.

To investigate this possibility, we write a trial state

$$|\psi_A(\vec{r}-\vec{R})\rangle = \Phi(\vec{r}-\vec{R}) e^{S(\vec{R})} |0\rangle , \tag{21}$$

where the exponential operator describes a displacement field centered about the point $\vec{R}$, and $\Phi(\vec{r}-\vec{R})$ is a trial wave function for the electron. We choose

$$\phi(\rho) = \left(\frac{2}{\pi\beta^2} \right)^{3/4} e^{-(\rho/\beta)^2} \tag{22}$$

and

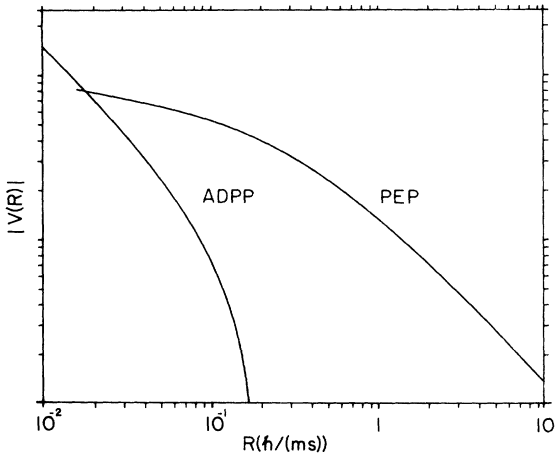

FIG. 4. Variation of the potential of the piezoelectric polaron (PEP) and the acoustic-deformation-potential polaron (ADPP) with distance.

$$S(R)=\sum_{\vec{q}} d_{\vec{q}}(a_{\vec{q}}e^{i\vec{q}\cdot\vec{R}}-a_{\vec{q}}^{\dagger}e^{-i\vec{q}\cdot\vec{R}}), \tag{23}$$

where β and $d_{\vec{q}}$ are variational parameters.

The expected value of the polaron Hamiltonian obtained by using the trial state $|\psi_A(r-R)\rangle$ is minimized with respect to the lattice-distortion parameters $d_{\vec{q}}$ if we choose

$$d_{\vec{q}}=-Q_q \mathrm{Re}c_q/|\vec{q}|\ , \tag{24}$$

where

$$c_q=\int d^3\rho\,|\phi(\rho)|^2 e^{i\vec{q}\cdot\vec{\rho}}\ . \tag{25}$$

At this point, the minimum value of the energy depends on β the spread of the Gaussian trial state

$$E_A(\beta)=\frac{3}{2}\frac{1}{\beta^2}-\sum_q \frac{Q_q^2}{\omega_q}e^{-(q\beta/2)^2}. \tag{26}$$

When the sum is evaluated, it is seen that the function $E_A(\beta)$ has a minimum if and only if $\alpha\kappa/12\pi^{3/2}$ is greater than approximately 1.58. For a finite value of the cutoff κ, as α increases from the minimum value that satisfies the above condition to infinity, the value which minimizes Eq. (26) varies between approximately $4/\kappa$ and zero. We recall that the quantity Q_q^2/ω_q essentially classifies the range of the interaction.[21] For both the acoustic- and optical-deformation-potential interactions, Q_q^2/ω_q is q independent and the corresponding strong-coupling theories are equivalent.

We conclude that the existence of a bound state of the narrow potential well set up by the electron depends on the phonon wave-vector cutoff κ in addition to the strength of the interaction. This sets the deformation-potential polaron apart from the corresponding piezoelectric and optical polarons which are insensitive to an upper cutoff on the phonon wave vector magnitudes. Another unique aspect of the narrow nature of the potential well due to the ADP interaction will be covered in Sec. V.

V. BINDING OF AN ADP POLARON TO AN IMPURITY

Consider an electron bound to a singly charged impurity in a medium where its interaction with the field of acoustic-lattice vibrations is described by the acoustic deformation potential.

We will start with the Hamiltonian[26]

$$H=\frac{p^2}{2}-\frac{\beta}{r}+\sum_{\vec{q}}\omega_{\vec{q}}a_{\vec{q}}^{\dagger}a_{\vec{q}}+\sum_{\vec{q}}Q_{\vec{q}}(a_{\vec{q}}+a_{-\vec{q}}^{\dagger})e^{i\vec{q}\cdot\vec{r}}-\sum_{\vec{q}}Q_{\vec{q}}(a_{\vec{q}}+a_{\vec{q}}^{\dagger})\ , \tag{27}$$

where $\beta=e^2/\epsilon_0\,\hbar s$ is the inverse Bohr radius expressed in units of $\hbar/ms$ with ϵ_0 representing the static dielectric constant. The last term describes the interaction between the positively charged impurity which is located at the origin of the coordinate system and the medium. This term is ostensibly eliminated by means of the unitary transformation

$$U=\exp\left(\sum_{\vec{q}} d_{\vec{q}}(a_{\vec{q}}-a_{\vec{q}}^{\dagger})\right), \tag{28}$$

with

$$d_{\vec{q}}=-Q_q/\omega_{\vec{q}}\ . \tag{29}$$

The transformed Hamiltonian is

$$H'=U^{\dagger}HU=\frac{p^2}{2}-\frac{\beta}{r}+\sum_{\vec{q}}\omega_{\vec{q}}a_{\vec{q}}^{\dagger}a_{\vec{q}}+\sum_{\vec{q}}Q_{\vec{q}}(a_{\vec{q}}+a_{-\vec{q}}^{\dagger})e^{i\vec{q}\cdot\vec{r}}+2\sum_{\vec{q}}\frac{Q_q^2}{\omega_{\vec{q}}}e^{i\vec{q}\cdot\vec{r}}-\sum_{\vec{q}}\frac{Q_q^2}{\omega_{\vec{q}}}\ . \tag{30}$$

The last two terms correspond to the modification of the impurity potential due to the concomitant lattice deformation and to the self-energy correction. The latter is a constant which does not play a role in the structure of the impurity states. The term which modifies the potential is more interesting. For both the polar and piezoelectric interactions $Q_q^2/\omega_q\propto q^{-2}$ and the modification renormalizes β, the strength of the Coulombic interaction. Thus in these cases, the unitary transformation in Eq. (28) eliminates the last term in Eq. (27). In the case of the ADP interaction, however, this term gives rise to a repulsive δ-function-type hard-core contribution

$$H''=H'+\sum_{\vec{q}}\frac{Q_q^2}{|\vec{q}|}=\frac{p^2}{2}-\frac{\beta}{r}+\sum_{\vec{q}}|\vec{q}|\,a_{\vec{q}}^{\dagger}a_{\vec{q}}+\alpha\delta(\vec{r})+\sum_{\vec{q}}Q_{\vec{q}}(a_{\vec{q}}+a_{\vec{q}}^{\dagger})e^{i\vec{q}\cdot\vec{r}}\ . \tag{31}$$

We will take

$$H^0=\frac{p^2}{2}-\frac{\beta}{r}+\sum_{\vec{q}}|\vec{q}|\,a_{\vec{q}}^{\dagger}a_{\vec{q}} \tag{32}$$

as the unperturbed Hamiltonian and study the eigenstates of Eq. (31) by the perturbation theory. Since we will confine ourselves to the absolute zero of temperature, the basis states as shown in

$$\left(\frac{p^2}{2}-\frac{\beta}{r}+\sum_{\vec{q}}|\vec{q}|\,a_{\vec{q}}^{\dagger}a_{\vec{q}}\right)\Psi_\eta|0\rangle=E_\eta\Psi_\eta|0\rangle \tag{33}$$

will be used. Here $\Psi_\eta=|n,l,m\rangle$ are the hydrogen-

ic eigenstates and $|0\rangle$ is the phonon vacuum.

The δ-function perturbation gives a positive first-order correction to s states and no correction to p states. The last term in Eq. (31) gives the polaron correction to the energy of the electron in the hydrogenic state Ψ_η. To first order α, we get

$$\Delta E_\eta = \alpha\langle\eta|\,\delta(\vec{r})\,|\eta\rangle - \sum_{\vec{q}\,\eta'} \frac{Q_q^2\,|\langle\eta'|\,e^{i\vec{q}\cdot\vec{r}}\,|\eta\rangle|^2}{E_{\eta'} - E_\eta + |\vec{q}|}\,. \tag{34}$$

For the piezoelectric and optical polarons the energy correction is given by only the second term in Eq. (34). Since its exact evaluation has not been possible, various approximation techniques have been employed for both optical[27] and piezoelectric[28] polarons. The simple model Hamiltonian in Eq. (27) is not realistic enough to deal with the problem of calculating the energy states of an impurity in an actual material. Therefore, instead of using a lengthy systematic approximation scheme, we will point out some of the salient features of the problem to motivate a rigorous analysis.

Consider a situation where the binding energy is such that for all η', $E_{\eta'} - E_\eta \gg \kappa$, the maximum wave-vector amplitude. In this case, we truncate the summation only to pick up the leading terms

$$\Delta E^T_{n,l,m} = \alpha\langle n, l, m|\,\delta(\vec{r})\,|n, l, m\rangle - \sum_{l',m'\,\vec{q}} Q_{\vec{q}}^2\,\frac{|\langle nl'm'|e^{i\vec{q}\cdot\vec{r}}|nlm\rangle|^2}{|\vec{q}|}\,. \tag{35}$$

For the ADP interaction the quantity $Q_q^2/|q| = \alpha/2V$ is wave-vector independent. Because of this one can at once perform the $\vec{q}$ integration and later obtain

$$\Delta E_{nlm} = \alpha\langle nlm|\,\delta(\vec{r})\,|nlm\rangle - \frac{\alpha}{2}\sum_{lm'}\int d^3r\,|\psi_{nl'm'}(r)|^2\,|\psi_{nlm}(r)|^2\,. \tag{36}$$

To demonstrate this result we calculate the truncated correction to the $2s$ and $2p$ states

$$\Delta E_{200} = -\frac{1}{8}\beta^2 + \frac{1}{8}\frac{\alpha}{\pi}\beta^3 - \frac{7}{2^9}\frac{\alpha}{\pi}\beta^3\,, \tag{37a}$$

$$\Delta E_{210} = -\frac{1}{8}\beta^2 + 0 - \frac{9}{2^9}\frac{\alpha}{\pi}\beta^3\,. \tag{37b}$$

We note that the positive correction to the energy of the s state dominates the decrease of the energy due to polaron effects related to the hydrogenically bound electron. It should be remembered, however, that the second term of Eq. (34) is an infinite sum such that the contribution of terms with $n' < n$ and $n' > n$ in $\eta = \{n, l, m\}$ has opposite signs.

It is interesting to recall that the Kohn-Luttinger effective-mass-approximation description of the energetically shallow impurities underestimates ionization energies without considering the polaron-effect modification of the potential of the impurity. For this reason the truncated polaron-effect correction given in Eq. (37a) seems to have the wrong sign. On the other hand, the truncation is not justifiable for a typical shallow impurity in silicon. Although a systematic approximate energy level evaluation based on a crude model is not too useful, we hope that the heuristic analysis presented above will motivate the inclusion of polaron effects in the calculations of energetically shallow and deep impurity levels in materials where the deformation-potential interaction is dominant.

VI. CONCLUSIONS

If an electron interacts with the longitudinal-acoustic mode of lattice vibrations, the phonon emission threshold is reached when the electron velocity is equal to the velocity of sound. This gives the upper bound theory of Lee, Low, and Pines a special significance in calculating the energy-momentum relation of the polaron involving the acoustic phonons. The reason for this is directly related to the fact that the Lee, Low, and Pines theory treats the polaron velocity self-consistently.

For the ADP polaron this theory gives a parabolic energy-momentum relation as $v \to 1$ and stops at $v = 1$, the threshold for phonon emission. Thus we showed that the energy-crossing arguments which are used to guess the qualitative structure of the energy-momentum relations of polarons might be misleading. In the particular case of the piezoelectric polarons, we identified the singularity which keeps polaron velocity below the velocity of sound with the long-wavelength phonons and therefore the long range of the Coulombic interaction. We further discussed the self-trapping of electrons due to the ADP interaction and obtained a condition involving the strength of the interaction and the upper cutoff on phonon wave-vector magnitudes in order for such a state to be possible. The appropriate parameters for silicon and germanium does not satisfy the condition for the existence of a self-trapped state.

When the ADP interaction is dominant, the localized static deformation accompanying a charged impurity increases the energy of the unperturbed hydrogenic s states but not the p states. There is also a perturbation which modifies the energy of all the states to account for the polaron effects related to the hydrogenic electron. The heuristic argument we have presented to substantiate these

corrections is hoped to motivate the inclusion of the ADP interaction in the calculation of the states of the energetically deep and shallow impurities in appropriate materials such as silicon.

ACKNOWLEDGMENTS

One of us (M.R.) gratefully acknowledges the support by the NATO Research Grant No. 727 which made a very fruitful and continuing collaboration with George Whitfield possible. His thanks are also due to John F. Rich for making private computational facilities available.

APPENDIX A

To estimate the strength of the coupling between an electron and the field of acoustic-lattice vibrations via the deformation-potential interaction in silicon and germanium, we write $\alpha = E_1^2/\rho$, where E_1 is the dimensionless quantity representing band-edge shift per unit volume, and ρ is the dimensionless mass density of the medium. E_1 is related to the deformation-potential constants Ξ_d and Ξ_u discussed by Herring and Vogt[29] as $E_1 = \Xi_d + \frac{1}{3}\Xi_u$. Referring to the data of Murase *et al.*,[30] we obtain the size of the coupling constants appropriate for both materials as $\alpha \approx 0.01$.

[1]J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).
[2]*Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum, New York, 1963).
[3]*Polarons in Ionic Crystals and Polar Semiconductors*, edited by J. T. Devreese (Elsevier, New York, 1972).
[4]Polarons, *Series of Selected Papers in Physics* (Physical Society of Japan, Tokyo, 1974).
[5]Y. Toyozawa, Prog. Theor. Phys. 26, 29 (1961).
[6]Y. Toyozawa, in Ref. 2.
[7]C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1964), p. 134.
[8]G. Whitfield and M. Tomak, Phys. Solidi B 64, K33 (1974).
[9]J. H. Gray, III, thesis (The Pennsylvania State University, 1975) (unpublished).
[10]G. Whitfield and P. Shaw, Phys. Rev. 14, 3346 (1976).
[11]H. Sumi and Y. Toyozawa, J. Phys. Soc. Jpn. 35, 137 (1973).
[12]T. D. Schultz, Solid State and Molecular Theory Group, MIT Technical Report No. 9, 1956 (unpublished).
[13]G. Whitfield and R. Puff, Phys. Rev. 139, A338 (1965).
[14]G. Whitfield, J. Gerstner, and K. Tharmalingam, Phys. Rev. 165, 993 (1968).
[15]V. I. Sheka, L. Khazan, and E. V. Mozdor, Phys. Status Solidi B 72, 833 (1975).
[16]R. Parker, G. Whitfield, and M. Rona, Phys. Rev. 10, 698 (1974).
[17]T. D. Lee, F. Low, and D. Pines, Phys. Rev. 90, 297 (1953).
[18]M. Gurari, Philos. Mag. 44, 329 (1953).
[19]M. Engineer and G. Whitfield, J. Phys. Soc. Jpn. 34, 564 (1973).
[20]J. J. Licari and G. Whitfield, Phys. Rev. B 9, 1432 (1974).
[21]M. Rona and G. Whitfield, Phys. Rev. B 7, 2727 (1973).
[22]H. Fröhlich, in Ref. 2.
[23]J. T. Devreese, in Ref. 3.
[24]M. Rona, *Proceedings of the Fourth Science Congress* (TBTAK, Ankara, 1973).
[25]J. Thomchick and G. Whitfield, Phys. Rev. B 10, 3458 (1974).
[26]K. K. Bajaj, in Ref. 3.
[27]P. M. Platzman, Phys. Rev. 125, 1961 (1962); D. M. Larsen, *ibid.* 187, 1147 (1969); K. K. Bajaj and T. D. Clark, Solid State Commun. 8, 825 (1970); 8, 1419 (1970); K. K. Bajaj, *ibid.* 8, 1665 (1970); J. Sak, Phys. Rev. B 3, 3365 (1971); M. H. Engineer and N. Tzoar, *ibid.* 5, 3029 (1972); D. M. Larsen, *ibid.* 9, 823 (1974).
[28]K. K. Bajaj, M. J. Goovaerts, and J. T. Devreese, Solid State Commun. 12, 1197 (1973); M. Engineer, *ibid.* 14, 123 (1974); M. Matsuura and S. Wang, *ibid.* 15, 613 (1974); M. M. Engineer and N. Tzoar, *ibid.* 17, 589 (1975).
[29]C. Herring and E. Vogt, Phys. Rev. 101, 944 (1955).
[30]K. Murase, K. Enjouji, and E. Otsuko, J. Phys. Soc. Jpn. 29, 1248 (1970).