Polarons in an Electric Field

DAVID M. LARSEN
National Bureau of Standards, Washington, D. C.
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Wave functions for a polaron in a uniform external electric field F/e are calculated in the weak coupling approximation to first order in the electron-phonon interaction at zero temperature. The electric field is treated exactly. It is shown that the wave function is not an analytic function of the applied field in the neighborhood of $F=0$, but can be expanded in an asymptotic power series in F valid near $F=0$. The distortion, due to F, of the distribution of polarization potential around the electron is calculated in the weak-field limit. It is shown that this distortion effect in typical crystals is small for reasonable values of the applied field.

INTRODUCTION

THE problem of the motion of electrons in the conduction band of a polar crystal has attracted considerable theoretical attention in recent years.[1–3] Generally, the Hamiltonian of Fröhlich is used to study the wave functions and energy eigenvalues of low-lying states of the crystal-electron system.[4] One finds for the lowest lying states that the effect of the electron-phonon coupling is to change the moving free electron into a more complicated kind of excitation corresponding to a moving electron which carries along with it a distortion of the crystal lattice induced by the Coulomb field of the electron. This excitation is called a "polaron." The important point is that the excitation moves freely through the crystal without change of momentum provided that: (1) The polaron momentum is too small for a phonon to be emitted by the polaron with conservation of energy and momentum, and (2) there do not exist free phonons initially, which could be absorbed or scattered.

It is expected that at low but nonzero temperature and low-polaron momentum the polaron wave function computed at zero temperature should serve well to describe the polaron between scattering events. By calculating the probability of the various processes leading to momentum change of the polaron, one can attempt to calculate, for example, the mobility of electrons in a polar crystal[5] in an applied electric field.

In previous calculations, however, the applied electric field was assumed only to accelerate the polaron; no attempt was made to assess the effects of the electric field on the structure of the polaron wave function. The purpose of the present paper is to calculate, by perturbation theory, the polaron wave function in the presence of a uniform external electric field.

In order to introduce the unperturbed states for our problem, we consider the Schrödinger equation describing an electron in a uniform time-independent electric field,

$$[(\hat{p}^2/2m)-Fz]\psi=i\hbar(\partial\psi/\partial t)\,, \tag{1}$$

where m is the electron mass, $\hat{p}$ is the electron momentum operator, $-i\hbar\nabla$, F is the force on the electron due to the external field, taken to lie in the z direction, and z is the z component of the displacement of the electron.

In one dimension, a set of solutions to (1) is given by

$$\psi_{k_{0z}}(z,t)=\exp[-i\hbar(6m\mathfrak{F})^{-1}\{(k_{0z}+\mathfrak{F}t)^3-k_{0z}^3\}]\times\exp[i(k_{0z}+\mathfrak{F}t)z]\,, \tag{2}$$

where $\mathfrak{F}=F/\hbar$.

The solutions (2) are convenient because of the properties

$$\int\psi^*_{l_{0z}}(z,t)\psi_{k_{0z}}(z,t)dz=\delta(l_{0z}-k_{0z})\,,$$

$$\hat{p}\psi_{k_{0z}}(z,t)=(\hbar k_{0z}+Ft)\psi_{k_{0z}}(z,t)\,.$$

We can thus regard the functions $\psi_{k_{0z}}$ as a natural generalization of the plane waves states $\exp[i(k_{0z}z-\hbar k_{0z}^2t/2m)]$, which are the solutions of (1) when $F=0$. It is useful to think of $\psi_{k_{0z}}$ as an eigenfunction of the momentum with instantaneous momentum eigenvalue $p(t)$ given, in our one-dimensional problem, by $p(t)=\hbar k_{0z}+Ft$.

When no external electric field is present, the starting point for a perturbation calculation of the polaron wave function[6] is the product wave function

$$e^{i\mathbf{k}_0\cdot\mathbf{r}}|0\rangle\,, \tag{3}$$

which describes a freely propagating electron and the crystal in its ground state. The crystal ground state, $|0\rangle$, is defined by $\sum_{\mathbf{l}}b_{\mathbf{l}}^\dagger b_{\mathbf{l}}|0\rangle=0$, where $b_{\mathbf{l}}^\dagger$ creates a longitudinal optical phonon of wave vector $\mathbf{l}$. We ignore all other modes of excitation of the crystal.

Because of the degeneracy of the unperturbed states which occurs when $k_0>1/r_0$, where

$$r_0=(\hbar/2m\omega)^{1/2}$$

[1] *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Ltd., Edinburgh, 1963).
[2] R. P. Feynman, P. W. Hellwarth, C. K. Iddings, and P. G. Platzman, Phys. Rev. **127**, 1004 (1962).
[3] T. D. Schultz, Phys. Rev. **116**, 526 (1959).
[4] T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. **90**, 297 (1953).
[5] F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1955).
[6] H. Fröhlich, Adv. Phys. **3**, 325 (1954).

and $\hbar\omega$ is the energy of an optical phonon, perturbation theory starting with the state (3), breaks down when $k_0 > 1/r_0$. This corresponds physically to the possibility of emission of a phonon by the moving electron, so that the state (3) is far different from a stationary state of the perturbed system.

In the presence of an electric field, we may hope to proceed by perturbation theory from a wave function analogous to (3); specifically, we take as unperturbed wave functions

$$|\mathbf{k}_0,0\rangle = \exp[i(\mathbf{k}_{0\perp}\cdot\mathbf{r} - \hbar^2 k_{0\perp}^2 t/2m)]\psi_{k_{0z}}(z,t)\,|0\rangle, \quad (4)$$

where $\mathbf{r}$ and $\mathbf{k}_0$ are the electron displacement and initial wave vector, respectively, with respective components $\mathbf{z}$ and $\mathbf{k}_{0z}$ in the direction of the force, and $\mathbf{k}_{0\perp} = \mathbf{k}_0 - \mathbf{k}_{0z}$. By analogy with the field-free case we might expect that the simple perturbation theory will fail for those values of t such that

$$p(t) \gtrsim \hbar/r_0, \quad (5)$$

where

$$\mathbf{p}(t) = \hbar\mathbf{k}_0 + Ft\mathbf{z}/z. \quad (6)$$

We expect that, if initially the total wave number of the system is sufficiently small compared to $1/r_0$ and no free phonons are present, the time-dependent wave function obtained by perturbation theory on $|\mathbf{k}_0,0\rangle$ will closely approximate the true wave function of the system until such time as (5) begins to hold.

In the next section we show how perturbation theory analogous to the usual Rayleigh-Schrödinger perturbation theory for the time-independent Schrödinger equation can be applied to the time-dependent Schrödinger equation when the unperturbed states are not stationary states but are of the form (4).

FORMULATION OF PERTURBATION THEORY

Our model of an electron inside a polar crystal and acted upon by a uniform external electric field is defined by the Schrödinger equation

$$(H_0 - Fz + \lambda H_1)\varphi_{\mathbf{k}_0} = i\hbar(\partial\varphi_{\mathbf{k}_0}/\partial t), \quad (7)$$

$$H_0 = \frac{\hat{p}^2}{2m} + \hbar\omega\sum b_{\mathbf{l}}^\dagger b_{\mathbf{l}}, \quad (8)$$

$$\lambda H_1 = \hbar\omega\left(\frac{4\pi\alpha}{\mathcal{S}}\right)^{1/2}\sum_{\mathbf{l}}\frac{1}{l}(e^{-i\mathbf{l}\cdot\mathbf{x}}b_{\mathbf{l}}^\dagger + e^{i\mathbf{l}\cdot\mathbf{x}}b_{\mathbf{l}}), \quad (9)$$

where[7,8]

$$\alpha = \frac{1}{2\hbar\omega}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right)\frac{e^2}{r_0},$$

$\mathcal{S} = Vr_0^{-3}$, V = volume of crystal, $\mathbf{l}$ is a wave vector in units of $1/r_0$, $\mathbf{x}$ is the electron displacement in units of r_0, and λ is a labeling parameter giving the order of smallness of the term in which it appears. We assume that the crystal is so large that the electron can assume continuous values of momentum.

We take solutions of (7) with $\lambda = 0$ as our set of unperturbed states, which can therefore be defined as

$$|\mathbf{k}_0 + \sum\mathbf{k}n_{\mathbf{k}}, \{n_{\mathbf{k}}\}\rangle = [\prod_{\mathbf{k}} n_{\mathbf{k}}!]^{-1/2}\prod_{\mathbf{k}}(b_{\mathbf{k}}^\dagger)^{n_{\mathbf{k}}}|\mathbf{k}_0,0\rangle. \quad (10)$$

The orthonormality relation is

$$\langle\mathbf{k},\{n_{\mathbf{k}}\}|\mathbf{l},\{n_{\mathbf{l}}\}\rangle = \delta(\mathbf{k}-\mathbf{l})\delta_{\{n\mathbf{k}\},\{n\mathbf{l}\}}, \quad (11)$$

where the quantity $\delta_{\{n\mathbf{k}\},\{n\mathbf{l}\}}$ equals one or zero depending upon whether the set of occupation numbers $\{n_{\mathbf{k}}\}$ is or is not identical to the set $\{n_{\mathbf{l}}\}$.

We assume that for the time interval of interest we can take

$$\varphi_{\mathbf{k}_0} = U\exp\left[-\frac{i}{\hbar\mathcal{F}}\int^{k_{0z}+\mathcal{F}t} G(\mathbf{k}_{0\perp},\xi)d\xi\right]|\mathbf{k}_0,0\rangle, \quad (12)$$

where $G(\mathbf{k}_{0\perp},\xi)$ is a c-number function and

$$U^\dagger U = 1, \quad [U,\partial/\partial t] = 0$$

so that U is a time-independent unitary operator. Inserting (12) into (7) and performing the time differentiation we obtain

$$\{(H_0+\lambda H_1)U + F[U,z]\}|\mathbf{k}_0,0\rangle = \left\{G(\mathbf{k}_{0\perp},k_{0z}+\mathcal{F}t) + \frac{\hbar^2(k_{0z}+\mathcal{F}t)^2 + \hbar^2 k_{0\perp}^2}{2m}\right\}U|\mathbf{k}_0,0\rangle. \quad (13)$$

We assume that for $\alpha \ll 1$ and for times in the interval of interest we can expand U and G in powers of $\alpha^{1/2}$, or equivalently, in powers of λ. Thus we write

$$G(\mathbf{k}_{0\perp},k_{0z}+\mathcal{F}t) = G^{(0)} + \lambda G^{(1)} + \lambda^2 G^{(2)} + \cdots. \quad (14)$$

$$U = 1 + \lambda S + \lambda^2(\tfrac{1}{2}S^2 + \sigma) + \cdots. \quad (15)$$

From the fact that U is unitary, the operators S and σ must obey

$$S^\dagger = -S, \quad \sigma^\dagger = -\sigma. \quad (16)$$

Inserting (14) and (15) into (13) we obtain to order λ^2:

$$H_0|\mathbf{k}_0,0\rangle = \left\{G^{(0)} + \frac{\hbar^2[(k_{0z}+\mathcal{F}t)^2 + k_{0\perp}^2]}{2m}\right\}|\mathbf{k}_0,0\rangle, \quad (17)$$

$$\{[H_0 - Fz, S] + H_1\}|\mathbf{k}_0,0\rangle = G^{(1)}|\mathbf{k}_0,0\rangle, \quad (18)$$

$$\{H_0(\tfrac{1}{2}S^2+\sigma) + H_1 S + F[\tfrac{1}{2}S^2+\sigma, z]\}|\mathbf{k}_0,0\rangle = \{(\tfrac{1}{2}S^2+\sigma)H_0 + G^{(1)}S + G^{(2)}\}|\mathbf{k}_0,0\rangle. \quad (19)$$

To obtain the lowest order perturbation correction

[7] The dielectric constants ϵ_∞ and ϵ are defined in Ref. 6.

[8] It is to be understood that in all summations the term corresponding to zero-wave number is omitted.

to the wave function $|\mathbf{k}_0,0\rangle$ we must solve (18) for S and $G^{(1)}$.

To solve (18) we try

$$S=\sum S_1, \quad S_1=e^{-i\mathbf{l}\cdot\mathbf{x}}f_1^*(\hat{p})b_1^\dagger-f_1(\hat{p})e^{i\mathbf{l}\cdot\mathbf{x}}b_1, \quad (20)$$

where $f_1(\hat{p})$ is to be determined by (18). We anticipate that it will be possible to write

$$f_1(\hat{p})=h_1(u(\hat{p}))+ig_1(u(\hat{p})), \quad (21)$$

where [9]

$$u(\hat{p})=\left(\hbar\omega-\frac{\hbar\sum_\alpha \hat{p}_\alpha l_\alpha}{mr_0}+\frac{\hbar^2l^2}{2mr_0^2}\right)^2, \quad (22)$$

and h_1 and g_1 are real valued functions. To show this, we insert (20) into (18) and use the general commutator identity

$$[z,A(\hat{p})]=i\hbar(\partial/\partial\hat{p}_z)A(\hat{p})$$

to obtain

$$\left(\omega-\frac{\mathbf{p}(t)\cdot\mathbf{l}}{mr_0}+\frac{\hbar l^2}{2mr_0^2}\right)f_1(\mathbf{p}(t))+iF\frac{\partial f_1(\mathbf{p}(t))}{\partial p_z}=-\omega\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{1}{l}, \quad (23)$$

which can be written

$$\begin{aligned}\pm u^{1/2}h_1(u)-\hbar F\frac{\partial}{\partial p_z}g_1(u)&=-\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{\hbar\omega}{l},\\ \pm u^{1/2}g_1(u)+\hbar F\frac{\partial}{\partial p_z}h_1(u)&=0,\end{aligned} \quad (24)$$

where the upper signs are used if

$$\omega-\mathbf{p}(t)\cdot\mathbf{l}/mr_0+\hbar l^2/2mr_0^2>0.$$

If we change the independent variable from p_z to u, define

$$\beta=mr_0/2\hbar^2l_zF \quad (25)$$

and decouple Eqs. (24), we get

$$\begin{aligned}\frac{d^2}{du^2}h_1(u)+\beta^2h_1(u)&=\mp\hbar\omega\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{\beta^2}{lu^{1/2}},\\ \beta g_1(u)-\frac{\partial h_1(u)}{\partial u}&=0.\end{aligned} \quad (26)$$

Solving (26) we obtain

$$\tilde{f}_1(u)\equiv h_1(u)+ig_1(u)=[I_2(\beta,u)+iI_1(\beta,u)]e^{-i\beta u}+\zeta(\mathbf{l})e^{-i\beta u}, \quad (27)$$

where for $\beta>0$, $p(t)<\hbar/r_0$,

$$I_1(\beta,u)=-\hbar\omega\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{\beta^{1/2}}{l}\left[\int_0^{\beta u}\frac{\cos u'}{u'^{1/2}}du'-\left(\frac{\pi}{2}\right)^{1/2}\right], \quad (28a)$$

$$I_2(\beta,u)=\hbar\omega\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{\beta^{1/2}}{l}\left[\int_0^{\beta u}\frac{\sin u'}{u'^{1/2}}du'-\left(\frac{\pi}{2}\right)^{1/2}\right],$$

and for $\beta<0$, $p(t)<\hbar/r_0$

$$I_1(\beta,u)=\hbar\omega\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{(-\beta)^{1/2}}{l}\left[\int_0^{-\beta u}\frac{\cos u'}{u'^{1/2}}du'-\left(\frac{\pi}{2}\right)^{1/2}\right], \quad (28b)$$

$$I_2(\beta,u)=\hbar\omega\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{(-\beta)^{1/2}}{l}\left[\int_0^{-\beta u}\frac{\sin u'}{u'^{1/2}}du'-\left(\frac{\pi}{2}\right)^{1/2}\right].$$

The integrals appearing in (28a,b) are the well-known Fresnel integrals. Of particular interest is the asymptotic expansion for $\tilde{f}_1(u)$ when $|\beta|u(p(t))\gg1$:

$$\tilde{f}_1(u)\sim-\hbar\omega\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{1}{lu^{1/2}}\left[1-\frac{i}{2\beta u}+3!!\left(\frac{-i}{2\beta u}\right)^2+5!!\left(\frac{-i}{2\beta u}\right)^3+\cdots\right]+\zeta(\mathbf{l})e^{-i\beta u}. \quad (29)$$

The expansion (29) can also be derived directly from (18), treating the external force in (18) as a perturbation.

In (27) and (29), $\zeta(\mathbf{l})$ defines a set of integration constants. To determine $\zeta(\mathbf{l})$ uniquely, we require that S be so chosen that the unperturbed state $|\mathbf{k}_0,0\rangle$ is transformed into the perturbed state $(1+\lambda S)|\mathbf{k}_0,0\rangle$ when the electron-phonon interaction is slowly (but not too slowly) turned on. The reader is referred to Appendix A, where it is shown that this requirement implies $\zeta(\mathbf{l})=0$.

In order to understand the physical meaning of setting $\zeta(\mathbf{l})=0$ we observe that if S is a solution of (18) obeying (16) and if $[S',H_0-Fz]=0$ with $S'^\dagger=-S'$, then $S+S'$ is a solution of (16) and (18) and the state $\varphi=S'|\mathbf{k}_0,0\rangle$ satisfies

$$(H_0-Fz)\varphi=i\hbar(\partial\varphi/\partial t). \quad (30)$$

Because the form of $S+S'$ is restricted by the ansatz of (20), the most general possible form for $\lambda S'$ is a superposition of one phonon unperturbed states of the form $\sum_1(\xi(\mathbf{l})e^{-i\mathbf{l}\cdot\mathbf{x}}e^{i\beta u}b_1^\dagger-\text{H.c.})$ where λS and the c-number function $\xi(\mathbf{l})$ are taken to be of order λ. Thus the state $[1+\lambda(S+S')]|\mathbf{k}_0,0\rangle$ where S is evalu-

[9] To simplify the notation we shall often use the symbol u or $u[p(t)]$ to denote the quantity $[\hbar\omega-(\hbar\mathbf{p}(t)\cdot\mathbf{l}/mr_0)+(\hbar^2l^2/2mr_0^2]^2$.

ated by setting $\zeta(\mathbf{l})=0$ in (27) before inserting (27) into (20), is, to order λ, the state that arises adiabatically from the initial state $[1+\lambda S']|\mathbf{k}_0,0\rangle$ upon turning on the electron-phonon interaction. The requirement $\zeta(\mathbf{l})=0$ is therefore equivalent to requiring that the initial state be simply $|\mathbf{k}_0,0\rangle$ with no admixture of one-phonon unperturbed states.

Setting $\zeta(\mathbf{l})=0$ for all $\mathbf{l}$ completes the specification of S. Since S has no diagonal elements in the unperturbed states, (18) implies $G^{(1)}=0$.

The solution of (19), giving the second-order correction to the wave function in λ can be carried out in a manner similar to that given above. [An outline of this calculation appears in Appendix B.]

The solution specified by (20), (27), and (28a,b) is not satisfactory for $p(t)\gtrsim\hbar/r_0$ because when $p(t)\gtrsim\hbar/r_0$ there exist values of $\mathbf{l}$ such that $u\approx 0$, and when $u\approx 0$ the solution for f in Appendix A does not approximate the solution of (23).

POLARIZATION POTENTIAL IN WEAK-FIELD LIMIT

We wish to find an expansion of $(1+\lambda S)|\mathbf{k}_0,0\rangle$ in the limit $F\to 0$ with Ft held constant. By taking the limit this way we focus attention on the explicit F dependence of the perturbed wave function as opposed to its implicit dependence on F due to the change of the instantaneous momentum, $p(t)$.

From the fact that (29) is a divergent asymptotic series, it is clear that $F=0$ is a singular point of $\tilde{f}(u)$, hence of the perturbed wave function.

If we introduce the dimensionless unperturbed electron momentum by

$$\mathbf{q}(t)=(r_0/\hbar)\mathbf{p}(t) \tag{33}$$

we can write (29) in the form

$$f_1\left(\frac{\hbar\mathbf{q}(t)}{r_0}\right)\sim-\left(\frac{4\pi\alpha}{8}\right)^{1/2}\frac{1}{l}[1-2\mathbf{q}(t)\cdot\mathbf{l}+l^2]^{-1}\times\left[1+\left(\frac{-2iFr_0}{\hbar\omega}\frac{l_z}{(1-2\mathbf{q}(t)\cdot\mathbf{l}+l^2)^2}\right)+3!!\left(\frac{-2iFr_0}{\hbar\omega}\frac{l_z}{(1-2\mathbf{q}(t)\cdot\mathbf{l}+l^2)^2}\right)^2+\cdots\right]. \tag{34}$$

The dimensionless parameter characterizing the expansion of (34) is the ratio of the change of potential energy of an electron in the external field over a distance of the order of the size of the polaron, to the phonon energy. If the external electric field is as strong as 1000 V/cm and we take r_0 and $\hbar\omega$ equal to 10^{-7} cm and 0.025 eV, respectively, we find that $2Fr_0/\hbar\omega=8\times10^{-3}$. This means that even in quite strong applied fields the distortion of the polaron wave function will be a small effect, at least for slow polarons.

To get some insight into how the electric field distorts the polaron wave function, it is useful to calculate the average polarization potential at position $\mathbf{r}_p$ when the electron is at the origin, denoted by $\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}$. This is given by

$$\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}=\frac{\hbar\omega}{e}\left(\frac{4\pi\alpha}{8}\right)^{1/2}\left\langle 0,\mathbf{k}_0\right|(1-\lambda S)\delta(\mathbf{r})\times\sum_\mathbf{l}\frac{1}{l}[e^{-i\mathbf{l}\cdot\mathbf{y}}b_\mathbf{l}^\dagger+\text{H.c.}](1+\lambda S)\left|\mathbf{k}_0,0\right\rangle, \tag{35}$$

where $+e$ is the electronic charge, $\mathbf{y}=\mathbf{r}_p/r_0$ and $\delta(\mathbf{r})$ is the Dirac delta function of the electron displacement, $\mathbf{r}$. Expanding the delta function in plane waves and evaluating the matrix element gives

$$\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}=\frac{2\hbar\omega}{e}\left(\frac{4\pi\alpha}{8}\right)^{1/2}\text{Re}\sum_\mathbf{l}\frac{1}{l}e^{-i\mathbf{l}\cdot\mathbf{y}}f_\mathbf{l}(\mathbf{p}(t)). \tag{36}$$

The expansion of f given by (34) gives an expansion of $\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}$ from (36). Inserting the lowest order term from (34) into (36) yields

$$\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}^{(0)}=-\frac{\hbar\omega\alpha}{\pi^2 e}\int d^3v\frac{\cos\mathbf{v}\cdot\mathbf{y}}{v^2(1-2\mathbf{q}(t)\cdot\mathbf{v}+v^2)}, \tag{37}$$

which is the familiar result for the weakly coupled polaron.[6] Considering the term linear in F in (34) as generating the first correction in $\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}$ due to the external electric field we obtain

$$\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}^{(1)}=-\frac{\hbar\omega\alpha}{\pi^2 e}\left(\frac{2Fr_0}{\hbar\omega}\right)\frac{\partial}{\partial z}\times\int d^3v\frac{\cos\mathbf{v}\cdot\mathbf{y}}{v^2(1-2\mathbf{q}(t)\cdot\mathbf{v}+v^2)^3}, \tag{38}$$

where z is the component of $\mathbf{y}$ in the direction of the external force. Both $\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}^{(0)}$ and $\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}^{(1)}$ are time-dependent because of the time dependence of $\mathbf{q}(t)$. It is most convenient to evaluate $\langle\phi(\mathbf{r}_p)\rangle_\mathbf{q}$ at that time at which $q(t)=0$; we denote this value by $\langle\phi(\mathbf{r}_p)\rangle_0$. Then

$$\langle\phi(\mathbf{r}_p)\rangle_0^{(0)}=-\frac{2\hbar\omega\alpha}{e}\frac{1}{y}(1-e^{-y}),$$

$$\langle\phi(\mathbf{r}_p)\rangle_0^{(1)}=-\left(\frac{2Fr_0}{\hbar\omega}\right)\frac{2\hbar\omega\alpha}{e}\times\left[-\frac{1}{y^2}+\frac{1}{8}\frac{e^{-y}}{y^2}(y^3+4y^2+8)\right]\cos\theta, \tag{39}$$

where θ is the angle between $\mathbf{y}$ and the direction of the force.

At large distances from the electron ($r_p \gg r_0$) we find

$$\langle\phi(\mathbf{r}_p)\rangle_0^{(0)} \sim -\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon}\right)\frac{e}{r_p}, \tag{40}$$

$$\langle\phi(\mathbf{r}_p)\rangle_0^{(1)} \sim \frac{2Fr_0}{\hbar\omega}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon}\right)\frac{er_0}{r_p^2}\cos\theta. \tag{41}$$

The expression given in (40) is the potential due to the spherically symmetric distribution of polarization charge induced by the electron. This term is the known result in the absence of an external electric field. Thus (41) shows that the effect of a weak field is to distort the spherical polarization charge distribution so that there is a decrease in positive charge in the direction of acceleration of the electron.

Successively higher order terms in f [in (34)] give rise to terms of successively higher multipolarity in the mean polarization at great distance from the electron.

DISCUSSION

We have based our calculation on perturbation theory, considering only the lowest term in an expansion of the wave function as a power series in $\alpha^{1/2}$. In the absence of an external electric field there is reason to believe that perturbation theory is appropriate even for values of $\alpha^{1/2}$ which are not small.[10] In the limit of zero field ($F \to 0$, $Ft \to 0$) the wave functions obtained in this paper approach continuously the weak-coupling wave functions in the absence of a field. These facts suggest that our procedure of studying the weakly coupled polaron in an electric field by expanding in powers of $\alpha^{1/2}$, is a reasonable one.

The question remains as to the conditions under which wave functions of the form $\varphi_{\mathbf{k}_0}$ can be used to describe the state of the electron between scattering events in a Boltzmann equation description of mobility at nonzero temperature.

We shall confine ourselves to a few qualitative remarks. First, we would expect that a necessary condition for being able to speak of isolated scattering events is that the mean time, τ, between collisions obey

$$(F\tau)^2/2m \ll \hbar\omega, \tag{42}$$

$$\tau \gg 1/\omega. \tag{43}$$

If (42) and (43) are not satisfied, then there exists the possibility of emission of real phonons between collisions.

In order to satisfy (42) and (43) simultaneously we must have

$$(Fr_0/\hbar\omega)^2 \ll 1. \tag{44}$$

Thus, the usefulness of the functions $\varphi_{\mathbf{k}_0}$ in discussing the mobility of electrons in crystals is confined to the low-field limit (in which limit, as mentioned earlier, it would have been permissible to have treated the external electric field as a perturbation, at least for low-average electron drift momentum).

The form of the expansion of f in (34) suggests that as the mean drift momentum of the electron approaches $\hbar/r_0$ the asymptotic expansion of given in (34) fails and the effects of the applied field on the wave function may become non-negligible. On the other hand, neglecting terms of order λ^2 and higher is probably a bad approximation in this case.

It is difficult to discuss quantitatively the question of the effects of the external field on the electron mobility. In general we expect that these effects will be very small when $Fr_0/\hbar\omega \ll 1$ and the drift momentum is much smaller than $\hbar/r_0$. The change in the polaron wave function due to the presence of the applied field will alter the phonon-polaron scattering cross section and also the rate of change of the average electron momentum between collisions.

To estimate the effect of a finite but weak electric field on the mobility μ, computed in the limit of zero field, we must first identify the quantities which play the role of effective masses in our treatment.

It is easy to show, using (B5), that the mean current carried by a slow polaron in the direction i is given by

$$j_i = ep_i(t)/m_i^*(F) \tag{45}$$

where $p_i(t)$ is the component of the polaron momentum $\mathbf{p}(t)$ in the i direction and

$$\frac{1}{2m_i^*(F)} = \frac{1}{2m} + \lim_{p_i(t)\to 0} p_i^{-2}(t)\left(\frac{4\pi\alpha}{8}\right)^{1/2}\hbar\omega \times \mathrm{Re}\sum_l \frac{(f_l(p_i(t)) - f_l(0))}{l}. \tag{46}$$

Expanding f_l from (34) we obtain

$$\frac{1}{m_z^*(F)} \approx \frac{1}{m^*(0)} + \frac{0.738\alpha}{m}\left(\frac{2Fr_0}{\hbar\omega}\right)^2,$$
$$\frac{1}{m_y^*(F)} \approx \frac{1}{m_x^*(F)} = \frac{1}{m^*(0)} + \frac{0.246\alpha}{m}\left(\frac{2Fr_0}{\hbar\omega}\right)^2, \tag{47}$$

where

$$\frac{1}{m^*(0)} = \frac{1}{m}\left(1 - \frac{\alpha}{6}\right)$$

as is well known.[6]

If we take the zero-field mobility μ to be proportional to $(m/m^*(0))^3$ as in Ref. 3, then it seems natural to expect an additive correction to μ of order $\alpha(2Fr_0/\hbar\omega)^2\mu$ arising from the field induced shift of the effective mass. But since $(2Fr_0/\hbar\omega)^2$ will typically not exceed 6×10^{-5}, this correction is completely negligible com-

[10] G. Höhler and A. Mullensiefen, Z. Physik **157**, 159 (1959).

pared to uncertainties in both polaron mobility theories[1] and experiments.[11]

SUMMARY

We have obtained solutions of the time-dependent Schrödinger equation for an electron interacting with an external electric field and the lattice vibrations of a polar crystal. The solutions are valid in the weak coupling limit for periods of time during which the electron momentum is sufficiently small so that the wave function can be described by a perturbation series in powers of $\alpha^{1/2}$, starting with unperturbed wave functions given by (4). An upper bound for the time interval during which our treatment holds is implicit in condition $p(t)<\hbar/r_0$.

We find that the electric field, although acting only on the electron, distorts the distribution of positive polarization charge surrounding the electron, inducing, to lowest order in $Fr_0/\hbar\omega$ a dipole moment in the direction opposite to the direction of the external force. One can visualize this situation by imagining that the positively charged polarization cloud has inertia and tends to lag the electron, which is pulling it along.

While no convergent expansion in powers of $Fr_0/\hbar\omega$ exists for the wave function, treating the external field in perturbation theory results in a correct asymptotic representation of the wave function when

$$Fr_0/\hbar\omega\ll 1, \quad p(t)\ll\hbar/r_0.$$

Under these conditions, corrections to the mobility are expected to be very small.

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APPENDIX A

To determine $\zeta(\mathbf{l})$ we shall solve (7) by assuming that at $t=0$, $\lambda H_1=0$ and that at $t=0$, λH_1 is turned on so that it achieves its final value given by (9) after a time t_0 which satisfies

$$|\mathbf{p}(t_0)-\mathbf{p}(0)|\ll\hbar/r_0 \quad \text{and} \quad \omega t_0\gg 1. \tag{A1}$$

For simplicity we take

$$\lambda H_1=t\sum_{\mathbf{l}}\gamma_{\mathbf{l}}(e^{-i\mathbf{l}\cdot\mathbf{x}}b_{\mathbf{l}}^{\dagger}+e^{i\mathbf{l}\cdot\mathbf{x}}b_{\mathbf{l}}) \tag{A2}$$

where

$$\gamma_{\mathbf{l}}=\frac{\hbar\omega}{t_0}\left(\frac{4\pi\alpha}{S}\right)^{1/2}\frac{1}{l}. \tag{A2}$$

In addition, if $\chi_{\mathbf{k}_0}(t)$ is the solution of (7) with interaction (A2) we require the initial condition

$$\chi_{\mathbf{k}_0}(0)=|\mathbf{k}_0,0\rangle \tag{A3}$$

be satisfied. We assume $k_0\ll\hbar/r_0$.

Since we wish to choose S in (15) in such a way that the perturbed state results from adiabatically turning on the electron-phonon interaction, we require that S (and therefore $\tilde{f}$) be so chosen that

$$\chi_{\mathbf{k}_0}(t_0)-(1+\lambda S)|\mathbf{k}_0,0\rangle=O(\lambda^2,\lambda/\omega t_0). \tag{A4}$$

[11] D. C. Burnham, F. C. Brown, and R. S. Knox, Phys. Rev. 119, 1560 (1960).

We use the same ansatz as before for solving (7) to first order in λ, except that we replace $f_1(\hat{p})$ [see (20)] and $\tilde{f}_1(u)$ by $f_1(\hat{p},t)$ and $\tilde{f}_1(u,t)$, respectively. The equation obtained for $f_1(\mathbf{p}(t),t)$, analogous to (18), is

$$\left(\omega-\frac{\mathbf{p}(t)\cdot\mathbf{l}}{mr_0}+\frac{\hbar l^2}{2m}\right)f_1(\mathbf{p}(t),t)+iF\frac{\partial f_1(\mathbf{p}(t),t)}{\partial p_z}=-\hbar^{-1}\gamma_{\mathbf{l}}t-i\frac{\partial f_1(\mathbf{p}(t),t)}{\partial t}.$$

Transforming from the independent variable p_z, to u given by (22) we obtain

$$-\frac{i}{\beta}\frac{\partial\tilde{f}_1(u,t)}{\partial u}+\tilde{f}_1(u,t)=-\gamma_{\mathbf{l}}tu^{-1/2}-i\hbar u^{-1/2}\frac{\partial\tilde{f}_1(u,t)}{\partial t},$$

which, for $\beta>0$, has the solution

$$\tilde{f}_1(u,t)=i\beta^{1/2}\gamma_{\mathbf{l}}e^{-i\beta u}\left[t\int_{\beta u(p(t))}^{\infty}\frac{e^{i\xi}}{\xi^{1/2}}d\xi+\hbar\beta^{1/2}\int_{\beta u(p(0))}^{\beta u(p(t))}\frac{d\eta}{\eta^{1/2}}\int_{\eta}^{\infty}d\xi\frac{e^{i\xi}}{\xi^{1/2}}\right] \tag{A5a}$$

and for $\beta<0$

$$\tilde{f}_1(u,t)=-i(-\beta)^{1/2}\gamma_{\mathbf{l}}e^{-i\beta u}\left[t\int_{-\beta u(p(t))}^{\infty}\frac{e^{-i\xi}}{\xi^{1/2}}d\xi+\hbar(-\beta)^{1/2}\int_{-\beta u(p(0))}^{-\beta u(p(t))}\frac{d\eta}{\eta^{1/2}}\int_{\eta}^{\infty}d\xi\frac{e^{-i\xi}}{\xi^{1/2}}\right]. \tag{A5b}$$

We note that $\tilde{f}_1(u,0)=0$, in accordance with (A3). From (A1) we have $Ft_0\ll\hbar/r_0$; hence, $(Fr_0\omega t_0)/\hbar\omega\ll 1$ but since $\omega t_0\gg 1$, we conclude $Fr_0/\hbar\omega\ll 1$ from which it follows that $|\beta|u(p(t_0))\gg 1$ and $|\beta|u(p(0))\gg 1$ for all $\mathbf{l}$. We can therefore replace the integrals in (A5) by their asymptotic forms for large $|\beta|u$. In this way we find that the first term in the bracket is of order $(|\beta|u)^{-1/2}t_0$ while the second term is of order $(|\beta|u^2)^{-1/2}\hbar$. But since u is of order $(\hbar\omega)^2$ the second term is negligible (of order $1/\omega t_0$) compared to the first.

Thus, by comparison of (28a,b) with (A5a,b) we conclude that (A4) is satisfied only when for all $\mathbf{l}$, $\zeta(\mathbf{l})=0$ to the order of our calculation.

APPENDIX B

In this section we solve (19) for $G^{(2)}$ and derive the differential equation whose solution specifies σ. We have from (19)

$$\{H_0(\tfrac{1}{2}S^2+\sigma)+H_1S+F[\tfrac{1}{2}S^2+\sigma,z]\}|\mathbf{k}_0,0\rangle=\{(\tfrac{1}{2}S^2+\sigma)H_0+G^{(2)}\}|\mathbf{k}_0,0\rangle. \tag{B1}$$

Using the relations

$$\tfrac{1}{2}H_0S^2-\tfrac{1}{2}S^2H_0+F[\tfrac{1}{2}S^2,z]=\tfrac{1}{2}[H_0-Fz,S^2]$$
$$=\tfrac{1}{2}\{S[H_0-Fz,S]+[H_0-Fz,S]S\}=\tfrac{1}{2}[H_1,S]-H_1S,$$

we obtain from (B1)

$$[H_0-Fz,\sigma]|\mathbf{k}_0,0\rangle=\{-\tfrac{1}{2}[H_1,S]+G^{(2)}\}|\mathbf{k}_0,0\rangle. \tag{B2}$$

If we make the ansatz

$$\sigma=\sum_{\mathbf{l},\mathbf{m}} e^{-i(\mathbf{l}+\mathbf{m})\cdot\mathbf{x}} X_{\mathbf{l},\mathbf{m}}^*(\hat{p}) b_{\mathbf{m}}^\dagger b_{\mathbf{l}}^\dagger - \text{H.c.} \quad \text{(B3)}$$

then σ satisfies (B2) if

$$\hbar\omega[2-2\mathbf{q}(t)\cdot(\mathbf{l}+\mathbf{m})+(\mathbf{l}+\mathbf{m})^2]X_{\mathbf{l},\mathbf{m}}(\mathbf{p}(t)) + iFr_0\frac{\partial}{\partial p_z}X_{\mathbf{l},\mathbf{m}}(\mathbf{p}(t)) = \frac{\hbar\omega}{4l}\left(\frac{4\pi\alpha}{S}\right)^{1/2}[f_{\mathbf{m}}(\mathbf{p}(t)-\hbar\mathbf{l})-f_{\mathbf{m}}(\mathbf{p}(t))] + \frac{\hbar\omega}{4m}\left(\frac{4\pi\alpha}{S}\right)^{1/2}[f_{\mathbf{l}}(\mathbf{p}(t)-\hbar\mathbf{m})-f_{\mathbf{l}}(\mathbf{p}(t))] \quad \text{(B4)}$$

and if

$$G^{(2)}=\tfrac{1}{2}\langle 0,\mathbf{k}_0|[H_1,S]|\mathbf{k}_0,0\rangle = \mathrm{Re}\left(\frac{4\pi\alpha}{S}\right)^{1/2}\hbar\omega\sum_{\mathbf{l}}\left(\frac{f_{\mathbf{l}}(\mathbf{p}(t))}{l}\right). \quad \text{(B5)}$$

This verifies that the ansatz (B3) is correct.

In solving (B4) we must choose the integration constant so that, in analogy to (A4), the adiabatic condition

$$\chi_{\mathbf{k}_0}(t_0)-[1+\lambda S+\lambda^2(\tfrac{1}{2}S^2+\sigma)]|\mathbf{k}_0,0\rangle=O\left(\lambda^3,\frac{\lambda}{\omega t_0}\right)$$

is satisfied.

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Infrared Transmission and Fluorescence of Doped Gallium Arsenide

DALE E. HILL
Central Research Department, Monsanto Chemical Company, St. Louis, Missouri
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Experimental measurements of the fundamental optical absorption edge show that with increased doping, *n*-type GaAs exhibits a shift of the optical absorption edge to higher energy at 77°K, while *p*-type GaAs at 300°K shows a shift to lower energy. For *n*-type GaAs at 300°K and *p*-type GaAs at 77°K, a combination of the two effects is observed. Fluorescence emission for the relatively low doped *n*-type GaAs occurs at nearly the energy of the band gap, while the highest doped materials emit at higher energies. The *p*-type fluorescence occurs through the acceptor state at 77°K, but not at 300°K. A deep level, presumably an acceptor level about 0.08 eV above the valence band, was found for Ge-doped GaAs.

I. INTRODUCTION

THE discovery of the efficient emission of infrared light by forward biased GaAs diodes[1] and the subsequent construction of GaAs lasers[2] has created considerable interest in the optical properties of this semiconductor. In order to determine some of the possible effects of material parameters on the performance of these devices, and because of general interest in the properties themselves, the following investigation of transmission and fluorescence of doped GaAs has been carried out.

First, the absorption edge of GaAs is measured for crystals with various types and levels of doping. The shifts in the absorption edge are interpreted as either a "Burstein" type shift,[3] an effect of the impurities themselves,[4,5] or a combination of the two. It is attempted to fit the first type of shift to the expression of Kaiser and Fan[6] and some difficulties are noted. The fluorescence results are then presented and discussed in relation to absorption data.

II. EXPERIMENTAL TECHNIQUE

The first figure shows the experimental arrangement for both the transmission and fluorescence experiments. A Bausch and Lomb grating monochromator with a grating blazed for 2 μ first order was used in the second order in which case it has a dispersion of 66 Å/mm. A type 7102 photomultiplier was used as a detector in conjunction with a Perkin-Elmer model 107 chopper amplifier.

Filters for the transmission measurements were necessary to minimize scattered light. These were either the RG-1 or RG-10 filter[7] (red and infrared trans-

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