except that the bands are two dimensional in nature and separated in space. The electron-band or surface states are perturbed out of the conduction band to form a surface-state band which overlaps the valence band in energy.

The filling of these surface states with electrons out of the valence band gives rise to the observed p-type surface conductivity. The states perturbed out of the conduction band are most likely associated with the unfilled orbitals of the germanium surface atoms. These same types of unfilled orbitals are found in the dislocations associated with grain boundaries, and the similarity in conduction properties between the clean surface and medium-angle grain boundaries is shown.

The data are still very crude and it is hoped that greater accuracy will be obtained in the future.

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Slow Electrons in Polar Crystals: Self-Energy, Mass, and Mobility*

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The parameters for the Feynman model of a polaron are evaluated numerically for various values of the electron lattice interaction α, in the usual idealization of the problem of a slow electron in a polar crystal. The self-energy and effective mass thus obtained are compared with earlier polaron theories, indicating the superiority of the Feynman model for a wide range of α. The polaron size and the effect of the continuum approximation are estimated, and it is concluded that the alkali halides, at least, may be in the border region for the validity of this approximation. The problem of calculating polaron mobility as determined by scattering with longitudinal optical mode phonons is analyzed and previous theories are critically reviewed. A new theory based on the Feynman model is developed in which the Boltzmann equation is used with resonance scattering considered as the fundamental scattering process. A comparison with previous theories shows some improvements and stresses still doubtful points. A comparison with various experiments suggests the possible inadequacy of the usual idealization.

I. INTRODUCTION

We consider the behavior of a slow electron in the conduction band of a polar crystal in which the interaction between the electron and the longitudinal optical modes of lattice vibration is too strong to be treated by perturbation theory, i.e., we consider the single entity of an electron and its associated cloud of virtual phonons, the polaron. We idealize the problem in the usual way by (1) neglecting all but the longitudinal modes, (2) treating the latter as a vibrating continuum, (3) assuming that the lattice frequencies all equal the same constant ω, (4) assuming that the electrons in all filled bands follow the electron in the conduction band inertialessly, and (5) by replacing the periodic potential by an effective mass m, which we call the *bare* electron mass (to be distinguished from m_e, the mass of an electron in free space). Thus, we assume the system to have the Hamiltonian

$$H=\mathbf{p}^2/2m+\sum_k \mathcal{V}_k(\tau_k e^{i\mathbf{k}\cdot\mathbf{r}}+\tau_k^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}})+\sum_k \hbar\omega\tau_k^\dagger\tau_k,$$

where

$$\begin{aligned}\mathcal{V}_k&=\hbar\omega(4\pi\alpha/V)^{\frac{1}{2}}(\hbar/2m\omega)^{\frac{1}{4}}k^{-1}\equiv\mathcal{V}/k,\\ \alpha&=(e^2/2\hbar\omega)(2m\omega/\hbar)^{\frac{1}{2}}(\epsilon_\infty^{-1}-\epsilon_0^{-1}).\end{aligned}\tag{1.1}$$

The problem of fundamental theoretical interest is to find a theory capable of giving the very low-lying states of this system (those of a slow polaron without free phonons) or at least capable of determining the properties of a free, slowly moving polaron characterized by these states: the polaron self-energy, effective mass, charge distribution, etc. A problem of more direct experimental interest is to apply such a theory to the behavior of the polaron in interaction with external fields and thermal phonons, e.g., to calculate the polaron mobility or the cyclotron resonance response.

Calculations of the second kind share all the difficulties found in self-energy and effective mass calculations, so that a theory which is incapable of reasonably accurate results for the properties of a slow, freely

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moving polaron should not be considered reliable in calculations of mobility and cyclotron resonance response. Calculations of the second kind also have their own characteristic difficulties, so that a satisfactory theory of the self-energy, for example, may still not yield a reliable value for the mobility. Even if both kinds of obstacles are overcome for an electron-lattice system idealized in the usual way, the predictions of the theory may be of dubious value to the experimentalist because of the questionable validity of the idealization.

It is our purpose first to see to what extent existing polaron theories solve the first problem, second to adapt the most successful of these theories to the calculation of polaron mobility, and third to analyze experiments in terms of this theory. In Sec. II, we present numerical results for the polaron self-energy, mass and size evaluated from the theory due to Feynman and compare these results with those of earlier theories. The comparison shows the inadequacy of the earlier theories for intermediate values of the interaction strength, of interest in several real crystals, and so demonstrates a need for a mobility theory based at least on Feynman's description or something better.

In Sec. III, we analyze the problems arising when one attempts to calculate electron mobility assuming the Boltzmann equation. This leads us to a discussion of resonance scattering, to be considered the fundamental scattering mechanism, and to the identification of resonance momentum, velocity, width, and coupling renormalization as the critical factors along with the polaron mass determining mobility.

In Sec. IV, we review previous theories and conclude that for an important range of intermediate values of the coupling strength they are not really satisfactory, not only because they are based on descriptions of a very slow electron that are not sufficiently accurate in this range, but also because in the scattering analysis they contain further assumptions that seem unjustified or lead to apparently inconsistent results.

In Sec. V, a theory of resonance scattering is developed based on Feynman's theory for the very slow polaron. The resonance scattering rate is then evaluated for the usual idealization making certain reasonable approximations.

In Sec. VI, the critical factors determining mobility are analyzed both for their behavior with increasing coupling strength and for their sensitivity to the approximations made in the usual idealization. It is concluded that the usual model may be inadequate for the calculation of mobility even though it is sufficient for calculating the polaron mass. We suggest that a breakdown of the usual model may complicate the temperature dependence of the optical mode mobility, but make no calculations.

In Sec. VII, some remarks are made concerning the experimental situation. In particular, it is observed that experiments are not yet sufficient either to confirm or reject any polaron theory, and that they may not even be sufficiently unambiguous to determine the parameters of any theory. Finally, it is emphasized that several assumptions which are fundamental to the usual idealization may not be satisfied.

II. SELF-ENERGY, MASS, AND SIZE OF A FEYNMAN POLARON

Of all the various published theories of self-energy and effective mass of a slow polaron[1] only that of Feynman[2] gives essentially the correct behavior in both weak- and strong-coupling limits and a smooth unambiguous interpolation between them.[3] Since calculations of the slow-polaron mobility have been based on various of these theories, it seems wise to find out precisely how good (or bad) they are in the intermediate-coupling region by comparing them with the self-energy and effective mass numerically evaluated from expressions given by Feynman. It is also interesting to see what the Feynman theory says about polaron size and the validity of the continuum approximation for the lattice vibrations.

Feynman found as an upper bound for the self-energy of a polaron

$$E_f \leqslant \tfrac{3}{2}(v-w)-A-B, \tag{2.1}$$

where

$$A=\alpha\pi^{-\frac{1}{2}}\omega(v/w)\int_0^\infty d\tau\, e^{-\tau}[\tau j(\tau)]^{-\frac{1}{2}},$$

$$B=3(v^2-w^2)/4v,$$

$$j(\tau)=1+(v\omega/w^2)(1-w^2v^{-2})\tau^{-1}(1-e^{-v\tau/\omega}),$$

and where w and v are variable parameters having the dimensions of (seconds)$^{-1}$. We set $\hbar=1$ throughout. As we shall discuss in more detail in Sec. V, Feynman's theory leads naturally to a zeroth-order effective mass

$$m_0=(v/w)^2m. \tag{2.2}$$

[1] For reviews of various aspects of polaron theory see **A**; S. I. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle* (Akademie-Verlag, Berlin, 1954), a translation of *Issledovania po Elektronnoi Teorii Kristallov* (Gostekhizdat, 1951); H. Fröhlich, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 325; H. Haken, in *Halbleiterprobleme*, edited by W. Schottky (F. Vieweg und Sohn, Braunschweig, 1955), Vol. 2, p. 5 ff.; G. R. Allcock, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 412.

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

[3] T. D. Lee and D. Pines, Phys. Rev. **92**, 883 (1953), developed a theory that is exact for weak coupling and gives the correct asymptotic behavior for strong coupling, but the latter only if a cutoff is introduced in the lattice field. It will be seen in Table I that it is not satisfactory for intermediate coupling. S. V. Tyablikov, Zhur. Eksptl. i Teoret. Fiz. **25**, 688 (1953); and G. Höhler, Z. Physik **140**, 192 (1955), have both formulated theories capable of yielding both the weak- and strong-coupling limits, but they seem to offer no straightforward way of finding the intermediate-coupling behavior. E. P. Gross (to be published) has formulated a theory capable of giving both limiting behaviors but there is still some question about the smoothness of approach to the weak-coupling limit and about the numerical values in the intermediate-coupling region.

TABLE I. Parameters of Feynman theory, and self-energies and effective masses of several theories for various coupling strengths; $\hbar=1$.

α	3	5	7	9	11
v/ω	3.44	4.02	5.81	9.85	15.5
w/ω	2.55	2.13	1.60	1.28	1.15
E_f/ω	−3.1333	−5.4401	−8.1127	−11.486	−15.710
E_{ulp}/ω	−3.0000	−5.0000	−7.0000	− 9.000	
E_{lp}/ω	−3.10	−5.30	−7.58	− 9.95	−12.41
E_g/ω	−3.09	−5.24	−7.43	− 9.65	−11.88
E_{pbt}/ω			−6.83	−10.31	−14.7
m_0/m	1.78	3.56	13.2	59.2	181
m_f/m	1.89	3.89	14.4	62.8	185
m_{ulp}/m	1.50	1.83	2.17	2.50	
m_{lp}/m	1.61	2.15	2.82	3.58	4.4
m_{pbt}/m		14.5	55.7	152	340

Feynman has given a somewhat *ad hoc* expression for an effective mass expected to be a little more accurate than m_0, *viz.*,

$$m_f=m\left[1+\tfrac{1}{3}\alpha\pi^{-\frac{1}{2}}(v/w)^3\int_0^\infty e^{-\tau}\tau^{\frac{1}{2}}[j(\tau)]^{\frac{1}{2}}d\tau\right]. \quad (2.3)$$

Using the Whirlwind Digital Computer, we have minimized the upper bound in (1.1) with respect to both v and w for $\alpha=3$, 5, 7, 9, and 11. The best values of v and w, the resulting self-energy, and the masses m_0 and m_f are tabulated in Table I. For comparison, we have also included tabulations of the self-energy and effective mass as computed according to the theories of Lee, Low, and Pines,[4] Lee and Pines,[3] and Gross,[5] which are exact in the weak coupling limit, and according to asymptotic formulas of Pekar,[6] Bogolubov,[7] and Tyablikov[8] valid in the strong-coupling limit.

The self-energies in Table I, with the exception of that of the strong-coupling theory E_{pbt}, are all derived from variational principles. The superiority of the Feynman theory is evident over the whole range of interest. Also evident is the smooth interpolation afforded by the Feynman theory for the effective mass and the fact that in the intermediate-coupling region the discrepancies with both groups of theories are not insignificant. We note that only small differences occur between m_f and m_0. In Appendix A we have computed first-order corrections to m_0 in a systematic way based on the formalism developed in Sec. V. It is shown there that the improved mass m_1 lies between m_0 and m_f for all α and that the percentage correction $(m_1-m_0)/m_0$ is only two percent for $\alpha=3$ and 5. The accuracy of m_0 is encouraging, since it is m_0 which it is most convenient to use in the mobility theory developed in Sec. V.

To see the validity of the continuum approximation it is useful to have an estimate of the polaron size. The Feynman approximation is essentially to replace the lattice by a second particle connected to the electron by a spring, as discussed in Sec. V. It is therefore possible to estimate the size of the Feynman polaron by calculating the root mean square distance between the electron and the second particle. The frequency of the harmonic oscillator composed of the electron and the second fictitious particle is v. The reduced mass of their relative motion is

$$\mu=m(m_0-m)/m_0=m(v^2-w^2)/v^2.$$

The ground harmonic oscillator wave function for the relative coordinate ϱ is therefore

$$\varphi_0(\rho)=(\mu v/\pi)^{\frac{3}{4}}\exp(-\mu v\rho^2/2),$$

which defines a Feynman polaron radius:

$$r_f\equiv(\langle\rho^2\rangle)^{\frac{1}{2}}=(3/2\mu v)^{\frac{1}{2}}. \quad (2.4)$$

Using the weak- and strong-coupling expansions given by Feynman for w and v, we find

$$r_f\underset{\alpha\to 0}{\sim}(3/0.44\alpha)^{\frac{1}{2}}(2m\omega)^{-\frac{1}{2}}, \quad (2.5a)$$

$$r_f\underset{\alpha\to\infty}{\sim}3(\pi/2)^{\frac{1}{2}}\alpha(2m\omega)^{-\frac{1}{2}}. \quad (2.5b)$$

We have computed r_f for various α and found the following:

α	3	5	7	9	11
$r_f(2m\omega)^{\frac{1}{2}}$	1.42	1.00	0.748	0.557	0.443

Although this definition of the polaron radius is somewhat arbitrary, it is still interesting to compare the values of r_f with the dimensions of a unit cell to get an idea about the validity of the continuum approximation. In Table II we have listed the lattice constant a and ratio r_f/a (assuming $m=m_e$) for some typical polar crystals. We have also tabulated the characteristic

TABLE II. Lattice constant, Feynman polaron radius, characteristic length, and cutoff $k_c=2\pi/a$ for various crystals, assuming $m=m_e$.

Crystal	a, A	r_f/a	$(\hbar/2m\omega)^{\frac{1}{2}}$, A	$k_c=(2\pi/a)(\hbar/2m\omega)^{\frac{1}{2}}$
LiF	4.02	1.57	6.84	10.6
NaF	4.62	1.57	8.68	11.8
NaCl	5.63	1.81	10.88	12.1
NaBr	5.96	2.08	12.15	12.8
NaI	6.46	2.12	13.18	12.8
KCl	6.28	1.72	12.09	12.1
KBr	6.58	1.88	13.76	13.1
KI	7.05	2.31	18.99	16.9
RbCl	6.54	1.65	13.02	12.5
RbBr	6.85	1.77	15.47	14.2
RbI	7.33	2.07	16.9	14.5
Cu_2O	2.46	5.93	8.83	22.5
AgCl	5.54	8.43	12.5	14.2

[4] Lee, Low, and Pines, Phys. Rev. **90**, 297 (1953). Also M. Gurari, Phil. Mag. **44**, 329 (1953).

[5] E. P. Gross, Phys. Rev. **100**, 1571 (1955). We have used Gross's principal axis transformation in combination with the special choice of the shift function f_k given by Lee, Low, and Pines. No effective-mass calculation has been performed.

[6] See Pekar, reference 1. We have used the asymptotic form $E_{pbt}=-(0.1088\alpha^2+\frac{3}{2})\omega$.

[7] S. I. Bogolubov, Ukrain. Mat. Zhur. **2**, 3 (1950).

[8] S. V. Tyablikov, Zhur. Eksptl. i Teoret. Fiz. **21**, 377 (1951).

length $(\hbar/2m\omega)^{\frac{1}{2}}$ and the cutoff $k_c=2\pi/a$, the latter in units of $(2m\omega/\hbar)^{\frac{1}{2}}$. Here, k_c is the cutoff in the (100) direction for the NaCl type lattice and is very near the Debye cutoff [$=(3/\pi)^{\frac{1}{3}}k_c$ for NaCl type]. k_c is usually assumed infinite.

Table II shows that even assuming $m=m_e$ the polaron may not be much larger than a unit cell. If $m>m_e$, the continuum approximation becomes rapidly worse. For example, we have computed r_f/a for NaCl assuming $m=2m_e$ and $m=\frac{1}{2}m_e$ and have found $r_f/a=0.856$ and 3.30, respectively, demonstrating that r_f is a sensitive function of m/m_e.

To get a more quantitative idea of the error made in the continuum approximation, we can introduce a Debye cutoff into the Feynman expressions for self-energy and effective mass. One readily verifies that (2.1) is replaced by

$$E_f(k_0)=\tfrac{3}{2}(v-w)-A_{k_0}-B, \tag{2.6}$$

where

$$A_{k_0}=\alpha\pi^{-\frac{1}{2}}\omega(v/w)\int_0^\infty d\tau\, e^{-\tau}[\tau j(\tau)]^{-\frac{1}{2}} \times\operatorname{erf}\{k_0(w/v)[\tau j(\tau)/2m\omega]^{\frac{1}{2}}\}.$$

For $k_0\to\infty$, the error function goes to unity and $A_{k_0}\to A$. If k_0 is finite but large, the error function goes rapidly to unity with increasing τ, so that the only change in A comes from the region of small τ during which we may replace $\exp(-\tau)$ by unity and $j(\tau)$ by v^2/w^2. The change in A is approximately

$$A_{k_0}-A\simeq\alpha\pi^{-\frac{1}{2}}\omega\int_0^\infty d\tau\,\tau^{-\frac{1}{2}}\{\operatorname{erf}[k_0(\tau/2m\omega)^{\frac{1}{2}}]-1\} =-\alpha(2\omega/\pi)(2m\omega)^{\frac{1}{2}}/k_0. \tag{2.7}$$

Thus for large but finite cutoff the ground-state energy of the polaron is higher by $\alpha(2\omega/\pi)(2m\omega)^{\frac{1}{2}}/k_0$, which is independent of v and w. This means that m_0 is unchanged to first order in $1/k_0$. The introduction of a finite k_0 can easily be shown to replace the Feynman mass expression (2.3) by

$$m_f(k_0)=m\Big\{1+\tfrac{1}{3}\alpha\pi^{-\frac{1}{2}}(v/w)^3\int_0^\infty d\tau\, e^{-\tau}\tau^{\frac{1}{2}}[j(\tau)]^{-\frac{3}{2}} \times[\operatorname{erf}(k_0(w/v)(\tau j/2m\omega)^{\frac{1}{2}}) -2\pi^{-\frac{1}{2}}\exp(-(k_0^2/2m\omega)(w/v)^2\tau j(\tau))]\Big\}. \tag{2.8}$$

For large k_0 similar approximations as for (2.7) give

$$m_f(k_0)\simeq m_f-(4\alpha/3\pi)(2m\omega/k_0^2)^{\frac{1}{2}}m. \tag{2.9}$$

To see quantitatively just what effect an intermediate cutoff has on the description of a slow polaron, we have considered the case $\alpha=5$ for several different values of k_0, the smallest being $k_0=\pi\sqrt{3}/r_f$ or $r_f\simeq 0.9a$, where r_f is defined by (2.4), the polaron radius *without* cutoff. The results are given in Table III. We see that the effective mass is changed by about 4% and the self-energy by about 11%. Also we observe that there is now a slightly greater discrepancy between m_0 and m_f suggesting that the Feynman approximation may not be quite so good as it is in the continuum.

TABLE III. Effect of cutoff, $\alpha=5$.

Cutoff k_c	v	w	m_0/m	$E/\hbar\omega$	m_f/m
∞	4.02	2.13	3.56	−5.44	3.89
$\pi\sqrt{3}/r_f\simeq\pi/a$	3.95	2.15	3.38	−4.83	3.73

We conclude that for $r_f>a$, the continuum approximation leads to only small errors in the simplest properties of a slow polaron. If $m>m_e$ in the alkali halides, however, r_f may be so small as to make the approximation bad. The alkali halides are thus near the doubtful region.

We may remark that the Feynman approximation gives the exact results in two classical limits, *viz.*, (1) when $k_0\to 0$ for fixed α so that the quantum fluctuations in the electron motion become unimportant and (2) when $\alpha\to\infty$ for fixed k_0 so that the quantum fluctuations in the lattice vibrations become unimportant. Expanding the error function in a power series in its argument, one can minimize (2.6) in these limits. In both cases, $E\sim-2\alpha\omega\pi^{-1}(k_0^2/2m\omega)^{\frac{1}{2}}$. In the first case $v\to w$, so that $m_0\to m$; in the second case, $v/w\sim(8\alpha/9\pi)^{\frac{1}{2}}(k_0^2/2m\omega)^{\frac{1}{4}}$ and $w/\omega\to 1$, so that $m_0\sim m(8\alpha/9\pi)\times(k_0^2/2m\omega)^{\frac{3}{2}}$. These are just the classical results, since $m_{\rm cl}=m[1+(8\alpha/9\pi)(k_0^2/2m\omega)^{\frac{3}{2}}]$.

III. NATURE OF THE MOBILITY PROBLEM

The mobility of the polaron will be limited by scatterings from imperfections and from acoustic and optical modes of vibrations. We shall assume sufficiently pure substances and sufficiently high temperatures so that imperfection scattering can be ignored. We shall also assume sufficiently high temperatures so that there are enough optical mode phonons with their much higher interaction to dominate as the principal scatterers over the more numerous but less strongly coupled acoustic phonons. One hopes that this minimum temperature is still below the maximum temperature permitted by subsequent approximations. Since polarons interact much more strongly with the longitudinal optical modes than with the transverse optical modes, we may neglect the latter in scattering processes just as is done in the virtual phonon cloud. We thus assume the validity of the Hamiltonian of (1.1) for the mobility problem as well as for the calculation of self-energy and effective mass. It should be emphasized that this is an additional assumption whose validity is not implied by the validity of the earlier assumption.

The fundamental difference between the calculation of polaron mobility and bare electron mobility is due to the much more complicated nature of the polaron, its energy-momentum relation, the way it reacts to incident

phonons and external forces, and the lack of a good theory for freely propagating polarons except for very slow ones at very low temperatures. Of course, all conduction electrons in polar crystals are really polarons. The distinction between polaron and electron is simply whether or not virtual as well as real phonon processes are considered, i.e., whether or not we go to higher than the lowest order in the coupling constant α. To approximate a polaron by a bare electron may or may not be a good approximation depending on the crystal and the process under investigation; for mobility in polar crystals such as the alkali halides, at least, it is a bad approximation.

In calculating polaron mobility we shall be forced to use the Boltzmann equation for want of a better approach.[9] Implicit in the derivation of the Boltzmann equation is a physical picture of charge carriers propagating as relatively simple well-defined particles undergoing a succession of scatterings which are also reasonably well defined. This picture requires,[10] for example, that the collision time between successive scatterings should be sufficiently long that the energy of the particle between scatterings be sharp compared with the characteristic energy of the problem, in our case kT:

$$\hbar/\tau \ll kT. \tag{3.1}$$

For sufficiently strong interactions,[11] this inequality may be satisfied only at quite low temperatures when τ is large but when other approximations made previously are not valid. We shall nevertheless assume that (3.1) is satisfied, realizing that this assumption seriously limits the applicability of this theory (and of all previous polaron mobility theories as well) to the actual experimental situation, as will be clear in Sec. VII.

One must also be careful that in computing τ the initial and final states actually used are well defined. Thus, although the state of a very slow polaron at $T=0°\mathrm{K}$ can be well defined through an adiabatic switching-on procedure leading to real particle states,[12] such a procedure may not be valid for a faster polaron that has sufficient energy to emit a phonon spontaneously (something which cannot occur in relativistic field theories where most of the concern with real particle states occurs).

Ideally, one would like to make a canonical transformation on the Hamiltonian to a new set of variables in terms of which the Hamiltonian would naturally separate into parts representing the polaron, the modified phonon field, and the residual interaction. Even in those polaron theories where this has been possible in some sense, it is certainly not clear that the same transformation which describes slow polarons will equally well describe faster ones, ones moving fast enough to emit real phonons spontaneously. It is not clear, for example, that the energy-momentum relation valid for polarons almost at rest can be extrapolated in any simple way to these faster polarons even if it does have meaning to speak of polarons with such energies as well-defined entities.

The difficulties attaching to the notion of the polaron as a well-defined entity, are related to difficulties in defining the fundamental scattering processes. Several authors[13] have taken them to be simple absorptions and emissions of phonons. Aside from the minor calculational difficulty due to the very inelastic nature of these collisions, which can be overcome,[14] there are a few more basic difficulties with this approach. (1) The lifetime of a fast polaron (one that has absorbed a phonon) before it emits a phonon almost certainly violates (3.1), assumed in the derivation of the Boltzmann equation. (2) The matrix elements of the transitions that must be calculated require knowledge of the polaron wave function for polarons moving fast enough to emit real phonons spontaneously. (3) Energy and momentum conservation laws must be satisfied and, in phonon absorption, the density of final states is needed (hence polaron velocity), both requiring knowledge of the dispersion law for faster polarons.

The first objection has been overcome by arguing that since the phonon emission probability ($\sim\bar{n}+1$) is much greater than the absorption probability ($\sim\bar{n}$), one may assume each absorption is immediately followed by an emission, that the transition probability for the two successive processes is insignificantly different from that for the absorption alone, and that for slow polarons the double process is isotropic. This has the additional advantage that the double process now considered as fundamental is elastic (since all phonons are assumed to have the same frequency).

If the possibility of two successive phonon absorptions, and hence of emissions, is neglected, which certainly seems reasonable at not too high temperatures, then a more rigorously correct procedure is to calculate the quantum mechanical transition probability of the double process directly[15] and not to rely on the intuitive

[9] In recent times some progress has been made with direct treatment of the density matrix and its equation of motion by D. A. Greenwood, Proc. Phys. Soc. **71**, 585 (1958); R. Kubo, Can. J. Phys. **34**, 1274 (1956); M. Lax, Phys. Rev. **109**, 1921 (1958); and others. In principle this would be a better way to compute polaron mobility as well, since one could by-pass several difficult questions. It has so far not been possible to adapt these methods to the problem of polaron mobility where virtual and real processes are equally important and where, as a result, the correlations between phonons are essential.

[10] See, for example, R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), Chap. 6, for a discussion of the validity of the Boltzmann equation.

[11] For *very* strong interactions there are theoretical reasons for believing that τ might begin to increase so that (3.1) might again be satisfied. See Sec. VI C.

[12] M. Gell-Mann and M. Goldberger, Phys. Rev. **91**, 398 (1953).

[13] Fröhlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950); Pekar, reference 1, especially Sec. 17–20; A. Morita, Science Repts. Research Inst. Tohoku Univ. **38**, 1 (1954); and **39**, 73 (1955); Morita, Horie, and Hasegawa, Science Repts. Research Inst. Tohoku Univ. **38**, 158 (1954).

[14] D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

[15] Such a calculation was first made by F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1955).

argument that this rate is essentially the same as the simple absorption rate. Such a calculation has the additional advantage that both the initial and final polaron states are now slow polaron states which can be reasonably well defined, in principle. The matrix element of the transition actually receives contributions from the two Compton scattering diagrams of Fig. 1. Because real phonon absorption is possible, (a) is actually a form of resonance scattering, analogous to resonance fluorescence when photons are incident on atoms. The sharpness of the intermediate states is high for very slow final (and hence initial) polarons, since then the volume of phase space into which the intermediate state can decay by phonon emission is very small.

A simple analysis of a model polaron-phonon Hamiltonian along the lines of the classical resonance fluorescence calculations[16] is instructive in showing the relationship between the simplest form of resonance scattering and the intuitive arguments advanced to make the simple absorption scattering tractable. It will also be of heuristic value when we analyze direct calculations of the second-order scattering process. and try to interpret the process as a simple resonance scattering process. Let us suppose it is possible to describe the polaron-phonon system by a Hamiltonian of the form

$$\begin{aligned}\mathcal{H}&=E(\mathbf{P})+\sum_k Z_k\mathcal{V}_k(\tau_k e^{i\mathbf{k}\cdot\mathbf{r}}+\tau_k^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}})+\sum_k \hbar\omega\tau_k^\dagger\tau_k\\&=\mathcal{H}_p+\mathcal{H}_{\rm int}+\mathcal{H}_f,\end{aligned}\tag{3.2}$$

in which the residual interaction can be treated by perturbation theory. Here $\mathbf{P}$ is the polaron momentum operator, τ_k and $\tau_k^\dagger$ are modified phonon annihilation and creation operators, and Z_k is an effective screening factor introduced because of the difference between bare electrons and polarons. For low temperatures when the rate of phonon absorption is very small, a resonance scattering calculation gives for the transition rate per unit time for a polaron from momentum P_0 to a final momentum in a solid angle $d\Omega_n$ about P_n

$$\begin{aligned}W(P_n,P_0)d\Omega_n=\frac{2\pi}{\hbar}\frac{V}{(2\pi\hbar)^3}d\Omega_n\rho_n\int d\Omega_i dP_i\,P_i^2\\\times\frac{|\langle n|\mathcal{H}_{\rm int}|i\rangle|^2|\langle i|\mathcal{H}_{\rm int}|0\rangle|^2}{(E_0-E_i)^2+\frac{1}{4}\beta_i^2},\end{aligned}\tag{3.3}$$

where

$$\rho_n=V(2\pi\hbar)^{-3}P_n^2/(dE/dP)_{P=P_n}.$$

Here $|i\rangle$ is the intermediate state in which the polaron has momentum $\mathbf{P}_i$ and a phonon of wave vector $(\mathbf{P}_i-\mathbf{P}_0)/\hbar$ has been absorbed, and $|n\rangle$ is the final state in which a phonon $(\mathbf{P}_i-\mathbf{P}_0)/\hbar$ has been absorbed and a phonon $(\mathbf{P}_i-\mathbf{P}_n)/\hbar$ has been emitted. $E_i+\frac{1}{2}i\beta_i$ is the complex energy of this intermediate state. β_i is just the transition rate per unit time for the decay of a polaron of momentum $\mathbf{P}_i$ through phonon emission, and is thus given by

$$\beta_i=2\pi\hbar^{-1}\int d\Omega_n\,\rho_n|\langle n|\mathcal{H}_{\rm int}|i\rangle|^2.\tag{3.4}$$

Implicit is the requirement that

$$E(\mathbf{P}_n)=E(\mathbf{P}_0).\tag{3.5}$$

For very slow initial and hence final polarons, $\beta_i\to 0$ and all quantities become isotropic, so (3.3) becomes

$$\begin{aligned}W(\mathbf{P}_n,\mathbf{P}_0)d\Omega_n=2\pi\hbar^{-1}|\langle r|\mathcal{H}_{\rm int}|0\rangle|^2\rho_r d\Omega_n\\\times 8\pi^2\hbar^{-1}\rho_n|\langle n|\mathcal{H}_{\rm int}|r\rangle|^2/\beta_r.\end{aligned}\tag{3.6}$$

Here $|r\rangle$ and P_r refer to the resonance state for which

$$E(P_r)=E(P_0)+\hbar\omega.\tag{3.7}$$

Because of (3.4), the fractional factor on the right of (3.6) is just unity and (3.6) reduces to the simple phonon absorption rate. The relevant physical quantities characterizing the transition rate are the resonance momentum P_r, defined by (3.7), the resonance velocity entering in ρ_r defined by $u_r=(dE/dP)_{P=P_r}$, and the coupling renormalization factor for the resonance phonon, Z_r. The mass m^* of a slow polaron does not itself appear in the scattering amplitude.

Actually, it is too much to expect that the original electron-lattice Hamiltonian can be transformed into a form such as (3.2) that would be valid throughout the scattering process. For this reason, the second-order scattering probability may not have the simple structure of (3.3), although if it should, one might then expect the width β_r to be related to the basic matrix elements occurring in the numerator of (3.3) according to the relation (3.4). The intuitive equivalence of the simple absorption and resonance scattering rates would then be justified.

The problem of determining the transition rate of the double process and, if it has the structure of (3.3) of determining the quantities P_r, u_r, and Z_r must still be solved. Let us consider what has been done in this direction.

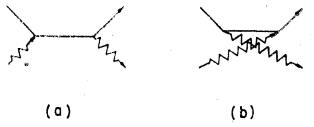

FIG. 1. Second-order diagrams contributing to polaron-phonon scattering. Solid lines represent polarons; wavy lines, phonons.

IV. REVIEW OF POLARON MOBILITY THEORIES

According to Sec. II, the polaron theories of Fröhlich, Pelzer, and Zienau,[17] of Lee, Low, and Pines[4] and of Pekar upon which calculations of polaron mobility

[16] V. Weisskopf, Ann. Physik **9**, 23 (1931).

[17] See Fröhlick, Pelzer, and Zienau, reference 13. This early self-energy calculation, the first attempt to go beyond second-order perturbation theory in the region of small α, is distinctly inferior to the later theory of reference 4.

have been based, are unsuitable for calculating even the self-energy and effective mass over an important range of values for α. These theories are, then, hardly reliable in describing the more complicated features affecting mobility. Even if they were, however, there would be additional reasons for doubting their validity, which we now discuss.

Both the weak coupling theory of Fröhlich, Pelzer, and Zienau and the strong coupling theory of Pekar are based on a calculation of the simple absorption rate. Both theories assume the polaron mass to be independent of P, i.e., they approximate $E(P)$ by a parabola, in determining P_r and u_r, which we believe to be unjustified. Furthermore, as we have seen, to justify a mobility calculation based on the simple absorption rate one wants to have a double scattering rate with the resonance structure of (4), which would follow from a Hamiltonian such as (3). Although a Hamiltonian of approximately this form is derived by Pekar in which $E(P)$ is parabolic, the validity of this Hamiltonian even for very strong coupling is doubtful except for polarons essentially at rest.[18]

Morita *et al.*[18] in three elaborate papers have attempted to calculate the simple absorption and emission rates by solving an integral equation for an R-matrix derived in a manner patterned after Gell-Mann and Goldberger.[12] They have then used the Howarth and Sondheimer[14] method to solve the Boltzmann equation. There are basic theoretical objections to the definitions of the initial and final states, however,[19] and several additional approximations must be made in solving the resulting equations, so that the procedure appears to be invalid.

Low and Pines[15] have made a direct calculation of the resonance scattering rate, using as initial and final states slow polaron states calculated by Lee, Low, and Pines, or equivalently working with the Lee, Low, and Pines transformed Hamiltonian. In principle, this is most advantageous because, as we have discussed, it avoids treating intermediate states, which are difficult to describe, and only assumed the Lee, Low, and Pines description to be valid for slow polaron states. To evaluate the resonance scattering matrix in practice, however, one is forced into a one-quantum approximation. This rests on the implicit assumption that the Lee, Low, and Pines description gives higher states in good approximation as well. Or equivalently, it implies definite assumptions about the nature of the phonon cloud around the polaron in the intermediate state,[20] thus partly canceling the advantage mentioned above. It is still interesting to compare the results of Low and Pines with the simple resonance picture sketched above, because the discrepancies, indicating a true breakdown in the simple resonance picture or reflecting the inadequacies of the Lee, Low, and Pines description in combination with the one-quantum approximation, will suggest criteria for interpreting the mobility theory developed in Sec. V.

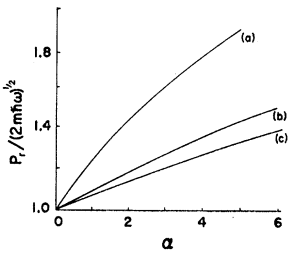

FIG. 2. Resonance momentum $P_r/(2m\hbar\omega)^{\frac{1}{2}}$ *vs* coupling constant α. (a) From Low and Pines scattering theory; (b) from Lee, Low, and Pines energy spectrum $E_{llp}(P)$; (c) from parabola approximation with Lee, Low, and Pines effective mass.

For $P_0 \to 0$ the structure of the transition rate calculated by Low and Pines is just that of (3.3) with

$$E(P)=E(P\to 0)+\hbar\omega x^2[1-\alpha F(x)][1+\alpha F(x)]^{-1}, \quad (4.1a)$$

$$u_r=f(\alpha)(2\hbar\omega/m)^{\frac{1}{2}}, \quad (4.1b)$$

$$|\langle n|\mathcal{H}_{\rm int}|r\rangle|^2=\mathcal{V}k_r^2, \quad (4.1c)$$

and

$$\beta=8\pi^2\hbar^{-1}(m/m^*)^2\rho_n|\langle n|\mathcal{H}_{\rm int}|r\rangle|^2. \quad (4.1d)$$

Here $F(x)$ and $f(\alpha)$ are functions given by Low and Pines, $x=P/(2m\hbar\omega)^{\frac{1}{2}}$, and x_r is the solution of

$$1=x_r^2[1-\alpha F(x_r)][1+\alpha F(x_r)]^{-1}. \quad (4.1e)$$

We wish to make four remarks:

(1) According to (4.1d), β is not given by (3.4) as would be expected in a simple resonance structure. This could be a fault of the one-quantum approximation or a result of a true breakdown of the simple resonance picture, suggested by (3.2), for the intermediate state, although in the latter event, one would expect β to be modified by a factor relating to the intermediate state rather than by $(m/m^*)^2$, which relates to the slow polaron state.

(2) According to (4.1a) there is no renormalization of the coupling constant. This is certainly *not* the case for intermediate or strong coupling,[21] so that one might expect corrections to first order in α just as for the other important physical quantities.

(3) The resonance momentum P_r has been computed for various values of α from (4.1e). In Fig. 2 it is compared with the resonance momentum obtained with the parabola approximation and the Lee-Low-Pines effective mass, i.e., $P_r=(2m_{llp}\hbar\omega)^{\frac{1}{2}}$, and with the resonance momentum obtained from $E_{llp}(P_r)=E_{llp}(0)$

[18] See, for example, Y. Yafet, *Technical Report* No. 2, University of Illinois, Urbana, 1954 (unpublished).

[19] Although taking account of the self-energy effects of the electron lattice interaction (albeit, within the parabola approximation), Morita *et al.* have not taken proper account of the change in polaron wave function due to the interaction [as has been discussed, for example, for the meson-nucleon case by G. C. Wick, Revs. Modern Phys. **27**, 339 (1955)]. This is particularly bad for the final state in phonon absorption where the real state, being capable of spontaneous emission, is entirely different from a fast bare electron state.

[20] A detailed discussion of this point is given in A, Chap. 5, Secs. E, F, and G.

[21] See, for example, Pekar, reference 1, Sec. 17.

$+\hbar\omega$, where $E_{llp}(P)$ is the slow polaron spectrum computed by Lee, Low, and Pines. It is remarkable that the resonance momentum from the scattering theory is significantly larger than the other two, suggesting either that the parabola approximation in this and other theories is bad, or that the residual interaction in the Lee-Low-Pines Hamiltonian has a much larger effect than permitted by the one-quantum approximation, or both.

(4) For small α the resonance velocity u_r is not changed to first order in α, as is the resonance momentum and as other quantities would be expected to be. More significant perhaps is that the resonance velocity is an increasing function of α, rather than a decreasing function as it would be with the parabola approximation where it is $(2\hbar\omega/m^*)^{\frac{1}{2}}$.

In conclusion we suggest that even if the Lee-Low-Pines theory gave the mass m^* accurately, certain features of the mobility calculation would still cast some doubts on its applicability to this calculation. It is not even clear that it gives the right first-order corrections to the Fröhlich-Mott mobility formula (obtained by perturbation theory). For intermediate values of α it, as other theories, seems inapplicable. For these reasons we proceed to a calculation of mobility based on Feynman's description.

V. RESONANCE SCATTERING OF A FEYNMAN POLARON

A. Formulation of Theory

A mobility calculation based on Feynman's polaron theory will have two advantages: the parameters of the free polaron as they affect the mobility will be given by the more accurate Feynman theory, and most of the objections previously encountered in making the parabola approximation or in using the Low scattering formalism[22] will be overcome. The curious behavior for the resonance velocity found by Low and Pines remains, however, and is even stronger, a difficulty still unresolved. There remain some necessary approximations mainly to do with transients, which have not been rigorously justified but which, it seems, should not seriously affect the quantitative results.

The essential features of Feynman's approach to the polaron are the replacement of the particle-field problem by a two-particle problem and the formulation of the two problems in such a way that they can be directly compared. The parameters of the two-particle problem are chosen by a variational principle to optimize the degree to which the second system approximates the first, insofar as the dynamics of the first particle are concerned. To use the two-particle approximation to the polaron ground state in calculating the polaron mobility, we must formally satisfy two requirements. First, we should like an exact formulation of polaron-phonon scattering in which the properties of a free polaron are in some way separated from the intricate details involved in the scattering process. Second, we should like, if possible, to replace the polaron as it appears in such a formulation by the two-particle approximating system introduced by Feynman.

The first requirement has been met in Feynman's formulation of quantum electrodynamics.[23] There it is shown that the transformation function from a state with an electron at $\mathbf{r}'$ and the field in the bare vacuum state at time t' to the state with the electron at $\mathbf{r}''$ and the field again in the bare vacuum state at time t'' is given by the path integral[24]

$$\langle \mathbf{r}''t'' \,|\, \mathbf{r}'t' \rangle = \int \mathfrak{D}\mathbf{r}(t) \exp\left[i \int_{t'}^{t''} L_p dt \right] G_{00}[\mathbf{r}(t)], \quad (5.1)$$

where $L_p = \frac{1}{2}m(d^2r/dt^2)^2$ is the particle Lagrangian and

$$G_{00}[\mathbf{r}(t)] = \prod_k \left\{ \int\int dX_k'' dX_k' \, \phi_0^*(X_k''t'')\phi_0(X_k't') \times \int \mathfrak{D}X_k(t) \exp\left[i \int_{t'}^{t''} (L_f^k + L_I^k) dt \right] \right\}. \quad (5.2)$$

Here $\Phi_0(X_k't')$ is the ground harmonic oscillator wave function with a phase factor $\exp(-\frac{1}{2}i\omega t)$; L_f^k and L_I^k are the Lagrangians of the $\mathbf{k}$th mode of the field and its interaction with the electron, respectively. Thus $G_{00}[\mathbf{r}(t)]$ is the vacuum-to-vacuum transformation function for the field, assuming the electron to move on a path $\mathbf{r}(t)$. For the electron-lattice Lagrangian one finds

$$G_{00}[\mathbf{r}(t)] = \exp\left[i \left(\tfrac{1}{2}i\alpha\omega^2(2m\omega)^{-\frac{1}{2}} \int\int_{t'}^{t''} |\mathbf{r}(t) - \mathbf{r}(s)|^{-1} e^{-i\omega|t-s|} dt ds \right) \right] \equiv \exp(iS). \quad (5.3)^2$$

Similarly, if initially a phonon $\mathbf{k}'$ is present and finally a phonon $\mathbf{k}''$ is present, Feynman obtained the transformation function

$$\langle \mathbf{r}''\mathbf{k}''t'' \,|\, \mathbf{r}'\mathbf{k}'t' \rangle = \int \mathfrak{D}\mathbf{r}(t) \exp\left[i \int_{t'}^{t''} L_p dt \right] G_{k''k'}[\mathbf{r}(t)]. \quad (5.4)$$

For the electron-lattice problem one finds

$$G_{k''k'}[\mathbf{r}(t)] = -\mathcal{V}_{k'}\mathcal{V}_{k''} \int\int_{t'}^{t''} dt_1 dt_2 e^{-i\omega(t_1-t_2)} \times \int \mathfrak{D}\mathbf{r}(t) \exp\left[-i \int_{t'}^{t''} \mathbf{f}(t)\cdot\mathbf{r}(t) dt \right] G_{00}[\mathbf{r}(t)], \quad (5.5)$$

[22] F. E. Low, Phys. Rev. **97**, 1392 (1955).

[23] R. P. Feynman, Phys. Rev. **76**, 769 (1949).

[24] For convenience we usually set $\hbar = 1$ here and in what follows.

where

$$\mathbf{f}(t)=-\mathbf{k}'\delta(t-t_1)+\mathbf{k}''\delta(t-t_2), \tag{5.6}$$

and the term $\mathbf{f}(t)\cdot\mathbf{r}(t)$ in the action represents the effect of the two phonon collisions on the path of the polaron.

Expression (5.5) has the two features we have required. First, as it stands it allows an exact formulation of the scattering problem. One has only to sum over all particle paths $\mathbf{r}(t)$ consistent with the constraints of the problem. Thus if one wishes the probability amplitude that a polaron be scattered from velocity $\mathbf{u}'$ to $\mathbf{u}''$ by a phonon going from $\mathbf{k}$ to $\mathbf{k}''$, one must use the kernel $G_{k''k'}[\mathbf{r}(t)]$ and sum over all paths that get through a pair of shuttered collimating slits set to select particles of velocity $\mathbf{u}'$ shortly after time t' and that also get through a similar filter selecting velocity $\mathbf{u}''$ shortly before t''. One must in addition make two corrections. One must correct for the decrease in particle flux effected by the initial filter by renormalizing the incident flux so that unit particle flux emerges from the first filter. Also one must realize that at the final time t'' the polaron may be almost anywhere in space depending on the times at which $\mathbf{k}'$ was emitted and $\mathbf{k}''$ absorbed. Thus the determination of final velocity must be done with a continuous set of velocity filters distributed over space and the path integral over paths through the filter at a particular point in space must be multiplied by a definite but somewhat *ad hoc* phase factor appropriate to that point, reflecting the correlation of velocity measurements at different points. Although the particle is initially and finally a bare electron rather than a polaron, this should not affect the final scattering probability, since when the velocity filters are introduced it is the average velocity of the particle over a period of time that is selected. During most of this time the interaction can be considered turned on and the particle will have its cloud of virtual phonons.[25]

The second advantage of Feynman's formulation is that the properties of the free polaron are contained explicitly in the propagation kernel $G_{00}[\mathbf{r}(t)]$, which refers only to the coordinate of the electron and can therefore be replaced approximately by the kernel describing the propagation of the electron in the two-particle problem, imposing some appropriate initial and final conditions on the second particle. Writing $G_{00}=\exp(iS)$, Feynman's approximation was to replace S by S_0, where

$$S_0=-\tfrac{1}{4}iC\int\int_{t'}^{t''}(\mathbf{r}(t)-\mathbf{r}(s))^2e^{-iw|t-s|}dtds + \int_{t'}^{t''}(A+B)dt, \tag{5.7}$$

w and C are certain parameters, and A and B are related constants.

It is useful to see the precise relation of S_0 to a system composed of an electron of mass m connected to a fictitious particle of mass M by a zero-length spring of spring constant k and with potential energy of the unextended spring defined to be U_0. If the electron m is fixed at the point $\mathbf{r}$, it is convenient to introduce time independent harmonic oscillator states $\varphi_n(\mathbf{x}-\mathbf{r})$ around $\mathbf{r}$ for the second particle corresponding to a frequency $(k/M)^{\frac{1}{2}}$. Then the transformation function from the state at t' in which the electron is at $\mathbf{r}'$ and the second particle is in $\varphi_0(\mathbf{x}-\mathbf{r}')$ to the state at t'' in which the electron is at $\mathbf{r}''$ and the second particle is in $\varphi_0(\mathbf{x}-\mathbf{r}'')$ can be shown to be[26]

$$\begin{aligned}\langle\mathbf{r}''\phi_0(\mathbf{x}''-\mathbf{r}'')t''\,|\,\mathbf{r}'\phi_0(\mathbf{x}'-\mathbf{r}')t'\rangle &= \int\mathfrak{D}\mathbf{r}(t)\exp\Big[i\int_{t'}^{t''}L_p dt+S_0\Big]\\ &\times\exp\Big[-iC\int_{t'}^{t''}\{(\mathbf{r}(t)-\mathbf{r}')^2e^{-iw(t-t')}\\ &\quad+(\mathbf{r}(t)-\mathbf{r}'')^2e^{-iw(t''-t)}\}\Big],\end{aligned} \tag{5.8}$$

if[27]

$$U_0=-(A+B+\tfrac{3}{2}w),\quad k=2Cw^{-1},\quad\text{and}\quad M=2Cw^{-3}. \tag{5.9}$$

A study of (5.8) indicates that the dynamical effects of the electron arising from the motion of the second particle are principally contained in S_0 and that the additional terms in the effective action represent the transient effects due to the specific choice of initial and final states of the second particle. Strictly speaking, the effects of a particular initial and final state are not

[25] Here we have implicitly assumed that the phonon-polaron collisions take place after the particle has gone through the initial velocity filter and before its final velocity is determined; i.e., we have assumed that the virtual phonon cloud has been acquired on turning on the field before the first phonon-polaron collision (absorption or emission) and that the second collision (emission or absorption) occurs before the interaction is turned off and the phonon cloud is lost. This assumption is rigorously valid in the limit of a very long time between the two filters; the probability of the collisions occurring in any particular finite time interval will become negligible in this limit, so that one can, with negligible error, neglect contributions to the transformation function arising from collision times near the end points. Somewhat simpler is the case of free propagation treated in Appendix A in which the vacuum-to-vacuum transition itself is of interest. There again one must look at the propagation only over long time intervals so that the times, in these intervals, during which the electron is acquiring and losing its virtual cloud constitute a very small part of the total interval. Then the behavior of the electron during these times has negligible effect on the average behavior over the whole interval.

[26] This is a straightforward calculation, since the action is quadratic in the coordinates. See reference 23; **A**, p. 155; or K. Yamazaki, Progr. Theoret. Phys. (Kyoto) **15**, 508 (1956).

[27] The extra term $\frac{3}{2}w$ is due to the fact that the state $\phi_0(\mathbf{x}-\mathbf{r})$ is taken to be time independent, whereas in (5.2) it was assumed to have the phase factor appropriate to the zero-point energy of the phonon field.

transients, since in the two-body system under consideration no possibility of decay has been introduced. This can be remedied in part if we ascribe to w, whenever it appears in S_0 or the transient terms of the action, a small negative imaginary part so that $w \to w - i\epsilon$ and $\exp[-iw(t-t')] \to 0$ as $t \to \infty$, etc. In calculating path integrals using the approximate action S_0 instead of the exact action S, the velocity filters then reduce the emergent flux both because only one velocity is selected and because of the enforced decay of higher internal states of the two-particle system resulting from the imaginary part of w.[28]

It would now seem that if S_0 is a good approximation to S, a good approximation to the scattering amplitude can be obtained from (5.4) by replacing S by S_0 and making the appropriate renormalizations described above. One real failure of this approximation is that the Feynman polaron's energy levels being the energies of the two-particle system are all real. The width of the intermediate state using S_0 in (5.4) would therefore be zero and the integration over all intermediate states (characterized for example by $\mathbf{k}'$ or $\mathbf{k}''$ for given $\mathbf{u}'$ and $\mathbf{u}''$) would not be finite. For this reason we must introduce corrections to the description of propagation in the intermediate state.

We may consider the replacement of S by S_0 as the zeroth-order approximation in the exact expansion

$$\exp(iS) = \exp(iS_0)\exp[i(S-S_0)] = \exp(iS_0)[1+i(S-S_0)+\cdots], \quad (5.10)$$

so that the scattering amplitude is

$$\langle \mathbf{u}''\mathbf{k}''t'' | \mathbf{u}'\mathbf{k}'t' \rangle = -\mathcal{U}_{k'}\mathcal{U}_{k''}\int\int_{t'}^{t''} dt_1 dt_2 \times \exp[-i\omega(t_1-t_2)]\int \mathfrak{D}\mathbf{r}(t)[1+i(S-S_0)+\cdots] \times \exp\left[i\int_{t'}^{t''}(\tfrac{1}{2}m(d\mathbf{r}/dt)^2-\mathbf{f}\cdot\mathbf{r})dt+iS_0\right]. \quad (5.11)$$

Any of the path integrations appearing in these expressions can now be reduced to the evaluation of ordinary Riemann integrals because of the quadratic structure of S_0. For example, since

$$|\mathbf{r}|^{-1} = \tfrac{1}{2}\pi^{-2}\int d^3k\, k^{-2}e^{i\mathbf{k}\cdot\mathbf{r}},$$

and

$$r^2 = [\nabla_k^2 e^{i\mathbf{k}\cdot\mathbf{r}}]_{k=0} = \int d^3k e^{i\mathbf{k}\cdot\mathbf{r}}\nabla_k^2\delta(\mathbf{k}),$$

then

$$\int \mathfrak{D}\mathbf{r}(t)(S-S_0)\exp\left[i\left(\int_{t'}^{t''}\tfrac{1}{2}m(d^2\mathbf{r}/dt^2)+S_0\right)\right]$$
$$= \tfrac{1}{2}iV(2\pi)^{-3}\int d^3k\,\mathcal{U}_k^2\int\int_{t'}^{t''}dt_1dt_2\,e^{-i\omega|t_1-t_2|}$$
$$\times\int\mathfrak{D}\mathbf{r}(t)\exp\left[i\int_{t'}^{t''}(\tfrac{1}{2}m(d^2\mathbf{r}/dt^2)-\mathbf{f}_k\cdot\mathbf{r})dt+iS_0\right]$$
$$-\tfrac{1}{4}iC\int d^3k\,\nabla_k^2\delta(\kappa)\int\int_{t'}^{t''}dt_1dt_2\,e^{-iw|t_1-t_2|}$$
$$\times\int\mathfrak{D}\mathbf{r}(t)\exp\left[i\int_{t'}^{t''}(\tfrac{1}{2}m(d^2\mathbf{r}/dt^2)-\mathbf{f}_k\cdot\mathbf{r})dt+iS_0\right]$$
$$-(A+B)T\int\mathfrak{D}\mathbf{r}(t)\times\exp\left[i\int_{t'}^{t''}\tfrac{1}{2}m(d^2\mathbf{r}/dt^2)dt+iS_0\right], \quad (5.12)$$

where

$$\mathbf{f}_k = -\mathbf{k}[\delta(t-t_1)-\delta(t-t_2)].$$

Similar expressions can be derived for higher powers of $(S-S_0)$. The structure of the correction terms as exhibited in (5.11) suggests that, as in quantum electrodynamics, they can be represented by higher-order Feynman diagrams in which the bubbles now stand for what we shall call "quasi-phonons." By a quasi-phonon bubble diagram we shall mean the diagram representing the three correction terms exhibited in (5.12) taken together.

We propose to include corrections in the form of virtual quasi-phonons only for the propagation of the Feynman polaron between the absorption of $\mathbf{k}'$ and the emission of $\mathbf{k}''$. Since, as in ordinary perturbation theory, no finite order corrections can yield a finite width for the intermediate state, we must sum over an infinite set of diagrams. To make calculations easier it is desirable to work in a Hamiltonian operator formalism rather than in the path integral formalism. We wish to set up an extended Hamiltonian K which, if treated by path integrals, would lead to an expansion such as (5.11). From our discussion of S_0 it is clear that a Hamiltonian leading to an action S_0 is

$$K_{\text{part}} = (\mathbf{P}^2/2m_0)+H_\rho+U_0 = (\mathbf{P}^2/2m_0)+(\boldsymbol{\pi}^2/2\mu)+\tfrac{1}{2}\mu v\boldsymbol{\varrho}^2 - (A+B+\tfrac{3}{2}w). \quad (5.13)$$

Here $\mathbf{P}$ is the momentum operator canonically conjugate to the center-of-mass coordinate $\mathbf{R}=(m\mathbf{r}+M\mathbf{x})/(m+M)$; $\boldsymbol{\pi}$ is canonically conjugate to the interparticle separation $\boldsymbol{\varrho}=\mathbf{r}-\mathbf{x}$; $m_0=m+M$ is the polaron mass m^* in zeroth approximation; $\mu=mM/m_0$; and $v=\sqrt{(k/\mu)}$

[28] For a more complete discussion, see A, p. 155 ff. and Appendix O.

is the frequency of the two-particle oscillator. In calculating all transformation functions, we must remember that the initial and final states should be the ground harmonic oscillator state in their dependence on ϱ.

Contributions to the virtual quasi-phonon diagrams like the first terms of (5.12) are exactly obtained by including the original Hamiltonian (setting the zero-point energy equal to zero) in the unperturbed part K_0 of K and the interaction part of the original Hamiltonian in the perturbed part K_1. Contributions to the virtual quasi-phonon diagrams like the second term of (5.12) have a similar structure except that the factor $\mathcal{U}_k V/2(2\pi)^3$ is replaced by the very singular factor $-\frac{1}{4}C\nabla_\kappa^2\delta(\boldsymbol{\kappa})$. To account for such a factor one must include in the interaction part K_1 a term with similar structure to the original electron-lattice interaction term but with the coupling constant $\mathcal{U}_k$ replaced by the constant $\pm i[4\pi^3 C\nabla_\kappa^2\delta(\boldsymbol{\kappa})/V]^{\frac{1}{2}}$, and one must include in the noninteracting part K_0 a field with all modes having the same frequency w and with zero-point energy equal to zero.

The third term in (5.12) is obtained simply by including the additive constant $A+B$ in K_1. Actually whether it is considered part of K_0 or K_1 should not make any difference, if we sum over all quasi-phonon diagrams. However, considering it part of K_1 will in general make first-order corrections to the self-energy vanish for a polaron at rest. This has the advantage that inclusion of K_1 in something like a one-quantum approximation will not change the polaron self-energy from what it would be if K_1 were neglected. The one-quasi-phonon terms will therefore relate solely to the scattering.

We are thus led to consider the extended Hamiltonian $K=K_0+K_1$ with

$$\begin{aligned} K_0&=(\mathbf{P}^2/2m_0)+(\boldsymbol{\pi}^2/2\mu)+\tfrac{1}{2}\mu v^2\varrho^2-(A+B+\tfrac{3}{2}w)\\ &\quad+\textstyle\sum_k \omega\tau_k^\dagger\tau_k+\sum_\kappa wb_\kappa^\dagger b_\kappa,\\ K_1&=\textstyle\sum_k \mathcal{U}_k(\tau_k e^{i\mathbf{k}\cdot\mathbf{r}}+\tau_k^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}})-i(4\pi^3C/V)^{\frac{1}{2}}\\ &\quad\times\textstyle\sum_\kappa(\nabla_\kappa^2\delta(\boldsymbol{\kappa}))^{\frac{1}{2}}[b_\kappa\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})+\text{c.c.}], \end{aligned} \tag{5.14}$$

and with the additional constraints that initially and finally in any transformation function, the relative coordinate ϱ and the b_κ, $b_\kappa^\dagger$ field shall be in their ground states and the τ_κ, $\tau_\kappa^\dagger$ field shall be in the appropriate states. The use of this Hamiltonian in a time-dependent formalism with these initial and final constraints gives the same results as the evaluation of the corresponding path integrals of (5.11) when the appropriate renormalizations due to transients are performed.[29]

B. Evaluation of Resonance Scattering Amplitude

We now use the extended Hamiltonian K to make an approximate calculation of the scattering amplitude.

[29] It is observed that the extended Hamiltonian K is not Hermitian. This should cause no real concern, since the constraints will require that the non-Hermitian part always occur multiplied by its Hermitian conjugate and this product is Hermitian.

Since we intend introducing quasi-phonon corrections only in the intermediate state, the velocity filters selecting paths with average velocities $\mathbf{u}'$ and $\mathbf{u}''$ are equivalent to the requirement that the initial and final states of the two-particle system have momenta $\mathbf{P}'$ and $\mathbf{P}''$ where $\mathbf{P}'=m_0\mathbf{u}'$ and $\mathbf{P}''=m_0\mathbf{u}''$. That we are justified in neglecting quasi-phonon corrections to the free propagation of a slow polaron is indicated in Sec. II and Appendix A where m_0 is shown to be a good approximation to the polaron mass. Thus we seek the transition amplitude $\langle\mathbf{P}''0;\mathbf{k}''0t''|\,\mathbf{P}'0;\mathbf{k}'0t'\rangle$, where the first zero in a state vector indicates the ground internal state of the two-particle system and the second zero indicates the vacuum state of the b_κ, $b_\kappa^\dagger$ field. Since

$$\begin{aligned} \lim_{\epsilon\to0+} i(2\pi)^{-1}\int_{-\infty}^{\infty} e^{-iE(t''-t')}(E-K+i\epsilon)^{-1}dE&\\ =e^{-iK(t''-t')},\quad t''>t',&\\ =0,\qquad\qquad t''<t',& \end{aligned}$$

we have

$$\begin{aligned} \langle\mathbf{P}''0;\mathbf{k}''0t''|\,\mathbf{P}'0;\mathbf{k}'0t'\rangle&=-i\int\int_{t'}^{t''}dt_1dt_2\\ &\times\Big\langle\mathbf{P}''0;\mathbf{k}''0\Big|e^{-iK_0(t''-t_2)}K_{k''}{}^\dagger\frac{i}{2\pi}\int_{-\infty}^{\infty}dE\,e^{-iE(t_2-t_1)}\\ &\times(E-K+i\epsilon)^{-1}K_{k'}e^{-iK_0(t_1-t')}\Big|\mathbf{P}'0;\mathbf{k}'0\Big\rangle. \end{aligned} \tag{5.15}$$

Here $K_{k''}{}^\dagger$ and $K_{k'}$ are respectively the parts of K_1 creating a phonon $\mathbf{k}''$ and annihilating a phonon $\mathbf{k}'$, and $\epsilon\to0+$ is understood.

In (5.15) we have explicitly neglected quasi-phonon corrections except to the propagation of the intermediate state. For large $t''-t'$, in the usual way,

$$\begin{aligned} &\langle\mathbf{P}''0;\mathbf{k}''0t''|\,\mathbf{P}'0;\mathbf{k}'0t'\rangle\\ &\qquad=2\pi i\delta(E''-E')R_{P''k'';P'k'}, \end{aligned} \tag{5.16}$$

where

$$\begin{aligned} R_{P''k'';P'k'}&=\langle\mathbf{P}''0;\mathbf{k}''0|\,K_{k''}{}^\dagger(E'-K+i\epsilon)^{-1}\\ &\quad\times K_{k'}|\,\mathbf{P}'0;\mathbf{k}'0\rangle. \end{aligned} \tag{5.17}$$

Substituting explicitly for $K_{k''}$ and $K_{k'}$,

$$\begin{aligned} R_{P''k'';\,P'k'}&=\mathcal{U}_{k''}\mathcal{U}_{k'}\langle\mathbf{P}''+\mathbf{k}''0;00|\exp(-i\mathbf{k}''\cdot\varrho M/m_0)\\ &\times(E'-K+i\epsilon)^{-1}\exp(i\mathbf{k}'\cdot\varrho M/m_0)|\,\mathbf{P}'+\mathbf{k}'0;00\rangle. \end{aligned} \tag{5.18}$$

We may introduce the formal expansion

$$(E'-K+i\epsilon)^{-1}=G_{E'}\sum_{\nu=0}^{\infty}(K_1G_{E'})^\nu, \tag{5.19}$$

where $G_{E'}=(E'-K_0+i\epsilon)^{-1}$. From (5.12) we see that nth-order corrections from $(A+B)$ always accompany $2n$th-order corrections from $\bar{K}_1\equiv K_1-(A+B)$. Also, only terms in (5.19) with an even power of K_1 can contribute to R. Hence we may regroup terms in (5.19):

$$R_{P''k'';P'k'}=\mathcal{U}_{k''}\mathcal{U}_{k'}\Big\langle \mathbf{P}''+\mathbf{k}''0;00\Big|\exp(-i\mathbf{k}''\cdot\varrho M/m_0)$$
$$\times G_{E'}\sum_{\nu=0}^{\infty}[(\bar{K}_1G_{E'}\bar{K}_1+A+B)G_{E'}]^{\nu}$$
$$\times\exp(i\mathbf{k}'\cdot\varrho M/m_0)\Big|\mathbf{P}'+\mathbf{k}'0;00\Big\rangle. \quad (5.20)$$

To make further calculation possible we now make two approximations:

(1) In a diagrammatic analysis of (5.20), we neglect all diagrams except those in which only one quasi-phonon is present at a time.

(2) Whenever there are no quasi-phonons present, we assume the two-particle oscillator is internally in its ground state. Thus we sum over graphs in Fig. 3.

The first of these approximations is analogous to (but slightly different from) a one-quantum approximation. It is made in the belief that in most ways the Feynman polaron is a good approximation to the intermediate state and that the decay of this resonance state can be calculated by summing over the diagrams of Fig. 3. We shall see that including these quasi-phonon corrections has little effect on the resonance momentum but a considerable effect on the resonance velocity.

The second approximation is felt to be reasonable on the following two grounds. First, the matrix element $\langle 0|\exp(i\mathbf{k}\cdot\varrho M/m_0)|0\rangle=\exp[-(k^2/4\mu v)(M/m_0)^2]$, and the element $\langle 0|\exp(i\mathbf{k}\cdot\varrho M/m_0)|n\rangle$ has an additional factor $(k^2/2\mu v)^{n/2}(iM/m_0)^n(n!)^{-\frac{1}{2}}$. Transitions to excited internal states will thus be *relatively* important only for $k\sim(2\mu v)^{\frac{1}{2}}(m_0/M)=(2mv)^{\frac{1}{2}}(1-w^2v^{-2})^{-\frac{1}{2}}$. This quantity tends to ∞ both for $\alpha\to 0$ and $\alpha\to\infty$, having a minimum of about $(11m\omega)^{\frac{1}{2}}$ at about $\alpha=5$. For such large k, all matrix elements are small through the factor $\exp[-(k^2/4\mu v)(M/m_0)^2]$. Secondly, for weak coupling the associated energy denominators will be large due to the recoil with such a large momentum of the light two-particle system, and for strong coupling the associated energy denominators will be large because of the high excitation energy v of the internal two-particle oscillator states. The increase in energy denominators due to internal excitation should be very strong when there are no virtual quasi-phonons present, since then the energy denominators would otherwise be close to zero.[30] Since it is possible to proceed without assuming the two-particle system to remain in its ground state while virtual quasi-phonons are present, we shall do so. It is then easy to see explicitly that to assume no internal excitation while quasi-phonons are present would introduce only small corrections.

Making the above-mentioned assumptions we replace the operators $\exp(-i\mathbf{k}''\cdot\varrho M/m_0)$, $\bar{K}_1G_{E'}\bar{K}_1+A+B$,

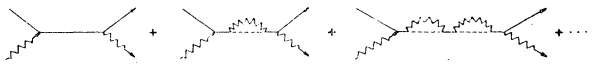

FIG. 3. Diagrams summed over in calculating phonon-polaron scattering with quasi-phonon (wavy lines) corrections. Solid lines represent the two-particle oscillator propagating in its ground internal state, and the dotted lines represent propagation in an arbitrary internal state.

and $\exp(i\mathbf{k}'\cdot\varrho M/m_0)$ by the appropriate diagonal matrix elements so that

$$R_{P''k'';P'k'}=\mathcal{U}_{k'}\mathcal{U}_{k''}\exp[-(k''^2+k'^2)(4v\mu)^{-1}(M/m_0)^2]$$
$$\times\delta(E'-E'')\delta(\mathbf{P}'+\mathbf{k}',\mathbf{P}''+\mathbf{k}'')[E'+\omega-\langle\mathbf{P}0;00|K_0$$
$$+K_1G_{E'}K_1+A+B|\mathbf{P}0;00\rangle]^{-1}, \quad (5.21)$$

where

$$\mathbf{P}=\mathbf{P}'+\mathbf{k}'=\mathbf{P}''+\mathbf{k}'',$$
$$E'=(\mathbf{P}'^2/2m_0)+\omega+\tfrac{3}{2}(v-w)-(A+B)=\text{total energy},$$

and

$$\langle\mathbf{P}0;00|K_0|\mathbf{P}0;00\rangle$$
$$=(\mathbf{P}^2/2m_0)+\tfrac{3}{2}(v-w)-(A+B). \quad (5.22)$$

This suggests that the coupling constant is modified with the factor

$$Z_k^{\frac{1}{2}}=\exp[-(k^2/4\mu v)(M/m_0)^2]. \quad (5.23)$$

The term $\langle\mathbf{P}0;00|K_1G_{E'}K_1+A+B|\mathbf{P}0;00\rangle=V_{00}(E',\mathbf{P})$ is a function of the initial energy E' and the total momentum $\mathbf{P}$. It is shown in Appendix B, that in the limit $\mathbf{P}'\to 0$ and $E'\to\omega$,

$$V_{00}(\omega,\mathbf{P})/\omega=\alpha\pi^{-\frac{1}{2}}(P^2/2m\omega)^{\frac{1}{2}}\int_0^{\infty}d\tau\, e^{-x\tau(1-1/j)}(x\tau)^{-1}$$
$$\times F((x\tau/j)^{\frac{1}{2}})+(1-w^2v^{-2})\{-(3v/4\omega)(1-w^2v^{-2})$$
$$\times[Y^{-1}-(Y+vw^{-1})^{-1}]-(3w/4\omega)Y^{-2}+xY^{-3}\}$$
$$+(A+B)-i\alpha x^{-1}P'\exp[-(P^2/2\mu v)(M/m_0)^2], \quad (5.24)$$

where[31]

$$x=P^2/2m_0\omega,$$
$$Y=(P^2/2m_0+w-\omega)/w,$$
$$j=j(\tau)=1+(v\omega/w^2)(1-w^2v^{-2})\tau^{-1}(1-e^{-v\tau/\omega}), \quad (5.25)$$

$$F(x)=\exp(-x^2)\int_0^x\exp(\xi^2)d\xi.$$

The resonance momentum is obtained by setting the real part of the denominator of R equal to zero:

$$\omega=P_r^2/2m_0+\mathrm{Re}V_{00}(\omega,P_r). \quad (5.26)$$

The resonance velocity is obtained by differentiating the right-hand side of (5.26) with respect to P_r and

[30] They would not be exactly zero, since the momentum of the phonon absorbed in resonance scattering of a very slow Feynman polaron will turn out to differ somewhat from $(2m_0\omega)^{\frac{1}{2}}$ for which the energy denominator would vanish.

[31] $F(x)$ is tabulated by W. L. Miller and A. R. Gordon, J. Phys. Chem. **35**, 2877 (1931).

using the relation $F'(x)=-2xF(x)+1$:

$$v_r=(P_r/m_0)-\alpha\pi^{-\frac{1}{2}}(\omega/2m)^{\frac{1}{2}}\int_0^\infty d\tau\, e^{-x\tau(1-1/j)}$$
$$\times[(2+(x\tau)^{-1})F((x\tau/j)^{\frac{1}{2}})+(x\tau j)^{-\frac{1}{2}}]$$
$$+(1-w^2v^{-2})(w/v)(P_r/m_0)\{(3v/4\omega)(1-w^2v^{-2})$$
$$\times[Y^{-2}-(Y+vw^{-1})^{-2}]+\tfrac{3}{2}(w/v)Y^{-3}-3xY^{-4}\}. \quad (5.27)$$

Finally, the resonance width is

$$\tfrac{1}{2}\beta=\alpha x_r^{-1}P'\exp(-2Mx_r^2/v)$$
$$=\alpha x_r^{-1}P'\exp[-(P_r^2/2\mu v)(M/m_0)^2], \quad (5.28)$$

which agrees exactly with the emission rate β of a polaron with a mass at rest of m_0 and with a coupling constant renormalization factor given by (5.23).

The resonance scattering rate for very slow polarons is finally obtained from (3.6) with the occupation numbers n_k replaced by their thermal average $\bar{n}$, $[\exp(\hbar\omega/kT)-1]^{-1}$:

$$1/\tau=\int W(P_n,P_0)d\Omega_n=2\omega\alpha\bar{n}Z_r(2\omega/m)^{\frac{1}{2}}v_r^{-\frac{1}{2}}. \quad (5.29)$$

VI. EVALUATION OF RESULTS AND COMPARISON WITH OTHER THEORIES

From the standard mobility expression $\mu=e\tau/m^*$ and (5.29), one obtains for the mobility of a slow polaron

$$\mu=\frac{e}{2m\omega}\frac{1}{\bar{n}\alpha Z_r}\frac{m}{m_0}\frac{v_r}{(2\hbar\omega/m)^{\frac{1}{2}}}\text{ esu.} \quad (6.1)$$

Here $m_0=(v/w)^2m$ is tabulated in Table I. Numerical evaluations of P_r, v_r and Z_r for $\alpha=3$, 5, and 7 are compared with their values in the limit of zero coupling in Table IV.

A. Resonance Momentum

Of particular interest is the value of P_r. If the corrections we have made to the zeroth-order Feynman description are to be meaningful, they must be small. In particular, we should compare P_r with the value obtained by making the parabola approximation, $P_r=(2m_0\omega)^{\frac{1}{2}}$. The corrections to the parabola value are seen to be never more than about 15%.

We observe also that the resonance momentum can easily be within a factor of three or four of the maximum phonon wave vector $k_c=2\pi/a$.[32] The large resonance momentum can invalidate the assumed forms of both the free field term and the electron-field interaction term of the original Hamiltonian, at least for short wavelengths. Although this may not seriously alter the value of the self-energy and effective mass, which may depend mainly on virtual phonons of longer wavelength, it can affect calculations of mobility in two important ways. First, the frequencies of the short-wavelength modes involved in resonance scattering may differ considerably from the constant ω assumed for all longitudinal modes, since the constant frequency assumption is reasonable only for long wavelengths. The short-wavelength modes probably have a lower frequency, nearer to the frequency of the transverse modes, since there is less polarization charge associated with the short wavelength modes.[33] This should first of all change the value of the resonance momentum, P_r (and hence u_r and Z_r) because a different phonon frequency will enter into the resonance condition (5.26). Secondly, the temperature-dependent factor $[\exp(\hbar\omega/kT)-1]^{-1}$ should show a difference from that involving the usual frequency $\omega=(\epsilon/\epsilon_\infty)^{\frac{1}{2}}\omega_{\text{rest}}$,[34] which may be observable and which would be a valuable check on the theory. For this check, it would be useful to have an independent determination of the longitudinal optical spectrum by a method such as neutron diffraction. Unfortunately at temperatures high enough to separate the optical mobility from the effects of acoustic modes and imperfections, the initial polaron momentum may not be so near zero. Then phonons of a range of wavelengths become important in the scattering, a range where the frequency is not constant. Consequently the density of phonons effective for scattering would not vary simply as $[\exp(\hbar\omega/kT)-1]^{-1}$.

A second important possible error in the original Hamiltonian derived from the continuum approximation is in the interaction term. The coupling strength between polaron and resonance phonon can be signifi-

TABLE IV. Resonance momentum, velocity, and coupling renormalization of a polaron for various α's.

α	0	3	5	7
$P_r/(2m\hbar\omega)^{\frac{1}{2}}$	1	1.54	2.13	3.83
$v_r/(2\hbar\omega/m)^{\frac{1}{2}}$	1	2.58	3.57	3.92
Z_r	1	0.736	0.444	0.096

[32] For an NaCl type lattice, a is the side of the basic cube, $\simeq$5 A. The maximum k in the [100], [110], and [111] directions are then respectively $2\pi/a$, $(2\pi/a)\sqrt{2}$, and $(2\pi/a)\sqrt{3}/2$, For the alkali halides $k_c\simeq 12(2m_e\omega/\hbar)^{\frac{1}{2}}$. The Debye cutoff is $k_0=(3/\pi)^{\frac{1}{3}}k_c$. This raises an additional objection against the mobility theory of Pekar. Consider NaCl for example. Supposing the electron mass due to the periodic potential to be $2.78m_e$ as Pekar deduces from his F-center theory, an unreliable estimate but one which favors the strong-coupling theory, Pekar finds α to be about 8.8 and the polaron mass $m_p=386m_e$. Even if the resonance momentum were as small as given by the parabola approximation, one would find $k_r=(2m_p/\hbar)^{\frac{1}{2}}\simeq 1.82\times10^8$ cm^{-1} compared with $2\pi/a=1.114\times10^8$ cm^{-1}, so that the scattering mechanism assumed to be responsible for mobility could not even occur, for want of any phonons of such short wavelength. Even assuming $m=m_e$ and making the parabola approximation, Pekar would find $\alpha=5.3$, $m_p\simeq 18.3m_e$, and $k_r=0.394\times10^8$ cm^{-1}, too close to the lattice cutoff to allow the constant-frequency approximation and the continuum approximation treatment of the resonance phonon mode's interaction. Corrections to the parabola approximation increase k_r and so worsen the approximation.

[33] See, for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Chap. 2, Sec. 6.

[34] Lyddane, Sachs, and Teller, Phys. Rev. **59**, 673 (1941); H. Callen, Phys. Rev. **76**, 1394 (1949); Pekar, reference 1, Sec. 30.

cantly incorrect even before it is renormalized through the factor Z_k. An accurate estimate of this would have to be made before mobility could be used for an experimental determination of the effective mass of the bare electron.

B. Resonance Velocity

We notice that the resonance velocity v_r is much greater than would be predicted by the parabola approximation (which gives a decrease rather than an increase of resonance velocity with increasing coupling constant). This behavior is similar to that found by Low and Pines in their analogous $f(\alpha)$ function and probably springs from the same source, the use of a one-quantum approximation in evaluating the R matrix. It is not surprising that the resonance velocity should differ considerably from the velocity that a polaron of momentum P_r would have if it were accelerated slowly to this value rather than scattered there suddenly in a phonon collision. In fact, it is the very nature of the decaying intermediate state that it should depend on the manner in which it is created. Whether the resonance velocity is so much higher, even higher at all, than would be obtained by slow acceleration of the polaron to P_r is still an open question. Neither the theory of Low and Pines, in which the effect is small, nor the theory presented here, in which it is correspondingly larger, suggest any reasonable way of internally checking the validity of this conclusion.

C. Coupling Renormalization

The third important quantity is the renormalization factor Z_r. The presence of this coupling constant renormalization is to be expected and appeared in the strong coupling theory of Pekar but not in Low and Pines's theory. Both Z_r and Pekar's similar factor go to zero for large coupling, although Pekar's goes to zero for small coupling rather than to unity as does Z_r and as one expects in terms of the physical picture suggested by Feynman's polaron.

For small coupling the polaron is a point electron moving slowly round a second fictitious particle over a large region of localization. The electron behaves as a free point charge during the short time the phonon is being absorbed, so there is no renormalization of the interaction. In this respect the description is better than that of Pekar (which is not expected to hold in the weak-coupling region, although applied by Pekar to the relatively weak coupling cases of PbO and Cu_2O), since in the various adiabatic approximations, the electron moves rapidly round a point in the lattice, which moves with uniform velocity but which does not vibrate instantaneously against the motions of the electron. Thus in the various adiabatic theories, the polaron simply behaves as a more and more diffuse charge cloud as the coupling becomes smaller, and the effective coupling constant to phonons of a given wavelength tends to zero when the radius of the polaron exceeds this wavelength.

For large coupling two things happen. First, the polaron's mass increases, and in consequence so does the resonance momentum P_r. The wavelength of the absorbed phonon decreases as $1/m^*$ or $1/\alpha^4$. At the same time, the electron is becoming more localized and is moving faster in its region of localization. For strong coupling, the incident phonon sees the smeared out electron charge distribution, whose radius decreases, at least until it gets down to the order of magnitude of a lattice spacing, but only as $1/\alpha^2$. Thus for strong coupling, the phonon wavelength is smaller than the polaron size and the resonance phonon goes right through the polaron with very little scattering. For this reason Z_r goes to zero with large α. Thus, if we could neglect the natural cutoff introduced by the lattice and assume the resonance to be arbitrarily sharp, then for this idealized case, we would conclude that the mobility has a minimum as a function of α and then begins to increase for large α.[35]

These considerations of Z_r raise another important point. If the coupling is sufficiently strong, the detailed structure of the charge distribution in the polaron becomes important. It is just this structure which is most in doubt in any theory in which the periodic potential is treated in the effective-mass approximation and the lattice vibrations of short wavelength are treated in the continuum approximation, and even more so in the Feynman theory where, in addition, the charge distribution is assumed Gaussian.

The rapid decrease of Z_k with increasing k can also have its effect on the temperature dependence of the mobility. For higher temperatures the resonance scattering becomes unsharp in a temperature dependent way depending on the energy distribution of slow polarons. Phonons of nonresonance wavelengths with significantly different renormalized interactions with the polaron become important so that the effective interaction that limits mobility becomes temperature dependent.

VII. EXPERIMENTAL SITUATION

The most important aspect of the experimental situation is that as yet there has been no independent attempt to verify polaron theories other than mobility measurements. Thus, both the weak- and strong-coupling theories, in which the mobility is a rapidly changing essentially monotonic function of one variable

[35] Yafet[19] has considered this unphysical behavior an objection to the strong-coupling theories, emphasizing the need to include both the lattice structure and nonresonance scattering. He concludes for the strong-coupling theories that in the limit of extremely slow polarons the nonresonance scattering contribution goes to zero but that even at low temperatures the resonance is sufficiently broad as to make nonresonance scattering important. Actually calculations of the nonresonance contribution proved very formidable in Yafet's formulation of mobility in the strong-coupling theory and they seem equally formidable for our formulation in the Feynman theory.

parameter, m (decreasing for weak coupling theories, increasing for strong coupling theories), have "explained" the results.

In actual experiments on polaron mobility the assumptions made in the various theories have not always been fulfilled. One difficulty has been to isolate the effect of the optical modes from those of the acoustic modes, imperfection scattering and trapping by shallow traps. Another difficulty has been the relatively limited range of temperatures over which both the Boltzmann equation and the inequality $kT \gg \hbar/\tau$ have been satisfied. In spite of very careful experiments, there have been almost none in which the microscopic mobility due to optical-mode scattering has been unambiguously identified over a reasonable range of temperatures in which the present theory (including the Boltzmann equation) is valid and in which the coupling constant is large enough to distinguish the results from the simple perturbation theory of Fröhlich and Mott.[36]

The most detailed direct measurements of *drift* mobility are those of Brown[37] and Brown and Dart[38] in AgCl. AgCl has the advantage that the time before trapping of photoelectrons can be made of the order of several microseconds, so that the actual drift velocity of electrons excited at one face of a thin crystal by strongly absorbed optical excitation or by single β particles can be measured by measuring the transit time across the crystal. Unfortunately, it is not possible to isolate the optical-mode scattering to a sufficiently low temperature because of apparent multiple trapping in shallow traps.[39]

More recent measurements of *Hall* mobility by Kobayashi and Brown[40] in AgCl avoid the shallow trapping difficulty and give data down to 10°K. Although unknown imperfection scattering mechanisms make the interpretation uncertain below about 25°K, a reasonable fit of the data above this temperature can be achieved by combining an optical mobility $\mu_0 \propto [\exp(\Theta/T)-1]$ with an acoustic mobility $\mu_a \propto T^{-\frac{3}{2}}$ according to $\mu^{-1}=\mu_0^{-1}+\mu_a^{-1}$. For AgCl, using $\omega=(\epsilon/\epsilon_\infty)^{\frac{1}{2}}\omega_{\text{rest}}$, $\epsilon=12.3$ and $\epsilon_\infty=4.04$, one obtains $\Theta=280$°K, which is within the limits of experimental error. Unfortunately, the experimental data are not sufficient to determine Θ directly from the temperature dependence (which, according to Sec. VI A, should give a different value) or to distinguish deviations from a fixed Θ with varying T mentioned in Sec. VI. Furthermore, this low value of Θ limits the applicability of any of the polaron mobility theories to a rather narrow range of low temperatures, because of the restriction to slow polarons. Even more restrictive, possibly, is the temperature range over which the Boltzmann equation itself is valid. Specifically, if we accept Kobayashi and Brown's experimental estimate of the optical mode mobility and their use of Low and Pines's mobility formula, then $\alpha=2.2$ with $m=0.29m_e$, so that at $T=100$°K the collision time of optical phonons with polarons is $m^*\mu_0/e=5.74\times10^{-14}$ sec compared with the characteristic time for this temperature, $\hbar/kT=7.62\times10^{-14}$ sec. Even at $T=70$°K the inequality (3.1) assumed in deriving the Boltzmann equation is only weakly fulfilled since $\tau=2\hbar/kT$ at this temperature.[41] The situation is somewhat different if we choose the mass m to fit the data of Kobayashi and Brown with our mobility formula (6.1). We must then choose $m/m_e=0.85$ for which $\alpha=3.64$, $m_0=2.15$, $m=1.83m_e$, $v_r=2.95(2\hbar\omega/m)^{\frac{1}{2}}$ and $Z_r=0.65$. This value of m/m_e is obtained by trial and error in which m_0/m is interpolated from Table I, and v_r and Z_r are interpolated from Table IV. For this value of m/m_e we can also find, interpolating from Table IV, that $P_r=1.7(2m\hbar\omega)^{\frac{1}{2}}$, which is to be compared with $k_c=19.18(2m\omega/\hbar)^{\frac{1}{2}}$ for AgCl. Thus the continuum approximation is valid.

These results suggest three observations. First, even though the coupling is not strong in AgCl, still the differences between the theory of Low and Pines and the present theory are already marked. Second, the great sensitivity of mobility to the assumed bare electron mass m allows almost any theory to fit the data with a not unreasonable assumption for the value of m. Finally, for the present theory, AgCl is already in a region where the theory is becoming quantitatively unreliable, not only because of the curiously large values of v_r but also because of a renormalization factor Z_r based on a Gaussian charge distribution in the polaron which is at best a rough approximation.

An attractive crystal in one respect is MgO which has a Debye temperature for the longitudinal optical modes of 1710°K for which $\alpha=2.3(m/m_e)^{\frac{1}{2}}$. The high Debye temperature insures a fairly wide temperature range in which the polaron can be considered very slow and the resonance can be considered reasonably sharp. Assuming $m=m_e$, our theory gives $P_r=1.4(2m\hbar\omega)^{\frac{1}{2}}$ compared with $k_c=7.63(2m\omega/\hbar)^{\frac{1}{2}}$, so that the resonance momentum is not too large either. Measurements of the drift mobility of the charge carriers has been made in MgO between 200°K and 600°K by Marshall, Pomerantz, and Shatas[42] by bombarding a thin crystal of MgO with 1-μsec pulses of 1.3-Mev electrons and measuring the current of the electrons and holes excited thereby. A rough fit to the data can be obtained by

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[39] F. C. Brown and K. Kobayashi, J. Phys. Chem. Solids **8**, 300 (1959).
[40] K. Kobayashi and F. C. Brown, Phys. Rev. **113**, 507 (1959).
[41] It is possible, however, that this criterion for the validity of the Boltzmann equation is too severe, and that it should be replaced by one of the form $\hbar/\tau \ll \Delta E$ in which ΔE is a measure of the energy change of the polaron in a collision. [See F. J. Blatt, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 4, p. 311 ff.] Since the double scattering process is essentially elastic for moderate T, the Boltzmann equation would then be valid to much higher temperatures. This modified criterion has not been rigorously proved, however.
[42] Marshall, Pomerantz, and Shatas, Phys. Rev. **106**, 432 (1957).

combining reciprocals of an acoustic mobility μ_a and an optical mobility μ_o. This fit suggests that above about 260°K the optical modes dominate. Unfortunately the experiments do not give the mobility unambiguously because of two uncertainties. First, the mobility due to holes is not distinguished from the mobility due to electrons. Second, the mobility itself is not measurable, only the secondary current. This depends on the number of charge carriers excited by each bombarding electron and the average distance they move before being trapped, neither of which has been directly determined experimentally.

VIII. SUMMARY

We have started with a comparison of the Feynman polaron theory with earlier theories of polaron self-energy and mass and have concluded that except in the truly weak and strong coupling situations it is the only satisfactory theory. Turning to the problem of mobility, we have rejected previous mobility calculations based on earlier polaron theories on additional grounds arising from a study of the Boltzmann equation and the theory of resonance scattering. We have then developed a theory of resonance scattering based on Feynman's polaron formulation and used it to evaluate the polaron mobility approximately. It was found that the resonance momentum, velocity, and coupling constant renormalization played critical roles. Even at very low temperatures when the resonance is sharp, both the assumption of constant lattice frequency and the continuum approximation have been shown to be important and questionable in determining those features of the polaron, the free lattice, and their effective interaction that are important for mobility. We have furthermore indicated that the resonance scattering may be very sensitive to departures from a sharp resonance, which are associated with rising temperatures. This could lead to temperature-dependent effects if the coupling were strong enough, although they would be very difficult to calculate and probably also to observe. Finally in analyzing three sets of experiments we have seen that the range of T may be relatively small in which both the Boltzmann equation and the slow-polaron approximations are valid, and that imperfection scattering, acoustic mode scattering, and trapping make an unambiguous determination of optical mode scattering difficult. The sensitivity of mobility to the unknown effective electron mass m and the monotonicity of weak and strong coupling theories with m diminish the value of having "explained" experiments, particularly in view of a lack of another experimental approach to the polaron.

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APPENDIX A

It is possible to estimate the accuracy of m_f or m_0 by using the extended Hamiltonian formalism developed in Sec. V to calculate corrections to m_0 due to quasi-phonon processes. The ground energy of the polaron should be the lowest eigenvalue of the extended Hamiltonian K or equivalently, the lowest pole of the Green function $(E-K+i\epsilon)^{-1}$ when $\epsilon \to 0+$. To evaluate the self-energy and effective mass approximately, consider the matrix element $\langle \mathbf{P}0;00|(E-K+i\epsilon)^{-1}|\mathbf{P}0;00\rangle$. Using approximations similar to those made in obtaining (5.21), we have

$$\langle \mathbf{P}0;00|(E-K+i\epsilon)^{-1}|\mathbf{P}0;00\rangle \simeq [E-E_0(P)+i\epsilon-V_{00}(E,P)]^{-1}, \quad \text{(A-1)}$$

where $E_0(P)=E_f+(P^2/2m_0)$ and where $V_{00}(E,P) \equiv \langle \mathbf{P}0;00|\bar{K}_1 G_E \bar{K}_1 + A + B|\mathbf{P}0;00\rangle$ as in Sec. V. A first-order value for the self-energy, $E_1(P)$, of a polaron of momentum $\mathbf{P}$ is obtained from the pole of (A-1) when $\epsilon \to 0$:

$$E_1(P)=E_0(P)+V_{00}(E_1,P). \quad \text{(A-2)}$$

A calculation analogous to that given in Appendix B shows that

$$V_{00}(E,P)=A+B-\mathfrak{A}(\Delta E,P)-\mathfrak{B}(\Delta E,P), \quad \text{(A-3)}$$

where

$$\mathfrak{A}(\Delta E,P)=2\pi^{-\frac{1}{2}}\alpha\omega\int_0^\infty d\tau \times \exp\{-(1-\omega^{-1}\Delta E)\tau+[P^2\tau/2m_0 j(\tau)]\} \times (P\tau/m_0)^{-1}F((P^2\tau/2m_0\omega j(\tau))^{\frac{1}{2}}), \quad \text{(A-4)}$$

and

$$\mathfrak{B}(\Delta E,P)=\tfrac{3}{4}(v^2-w^2)v^{-1}\{1-[v\Delta E/w(v+w)]\} \times [1-(\Delta E/w)]^{-2}[1-(\Delta E)(v+w)^{-1}]^{-1} -(P^2/2m_0)(v^2-w^2)v^{-2}[1-(\Delta E/w)]^{-3}. \quad \text{(A-5)}$$

Here $F(x)$ and $j(\tau)$ are given by (5.25). From these definitions we see that

$$\mathfrak{A}(0,0)=A \quad \text{and} \quad \mathfrak{B}(0,0)=B. \quad \text{(A-6)}$$

The transcendental equation (A-2) for ΔE then becomes

$$\Delta E(P)=[\mathfrak{A}(0,0)-\mathfrak{A}(\Delta E,P)] +[\mathfrak{B}(0,0)-\mathfrak{B}(\Delta E,P)]. \quad \text{(A-7)}$$

For $P=0$ the solution to (A-7) is obviously $\Delta E=0$, or $V_{00}(E_0,0)=0$. There is no correction to the Feynman

energy at $P=0$, since the term $A+B$ was included in K_1 to produce just this result.

To compute the first-order effective mass m_1 we must expand (A-7) in powers of P^2. Differentiating with respect to P^2 at $P=0$, $\Delta E=0$, we find that

$$(\partial(\Delta E)/\partial P^2)_{P=0}=-(\partial(\mathfrak{A}+\mathfrak{B})/\partial(\Delta E))_{0,0}\times(\partial(\Delta E)/\partial P^2)_{P=0}-(\partial(\mathfrak{A}+\mathfrak{B})/\partial P^2)_{0,0},$$

so that

$$(\partial(\Delta E)/\partial P^2)_{P=0}=-(\partial(\mathfrak{A}+\mathfrak{B})/\partial P^2)_{0,0}\times[1+(\partial(\mathfrak{A}+\mathfrak{B})/\partial(\Delta E))_{0,0}]^{-1}. \quad \text{(A-8)}$$

Now

$$1/m_1=2(\partial E_1/\partial P^2)=(1/m_0)+2(\partial(\Delta E)/\partial P^2)_{P=0}. \quad \text{(A-9)}$$

It is interesting to compare this with Feynman's expression for the effective mass. It is easily seen from (2.3) that

$$m_f=m_0[1+2m_0(\partial(\mathfrak{A}+\mathfrak{B})/\partial P^2)_{0,0}]. \quad \text{(A-10)}$$

Combining (A-8), (A-9), and (A-10) we obtain

$$m_1=m_0\{1-[(m_f/m_0)-1]\times[1+(\partial(\mathfrak{A}+\mathfrak{B})/\partial(\Delta E))]^{-1}\}. \quad \text{(A-11)}$$

For very small α, $[\partial(A+B)/\partial(\Delta E)]_{0,0}=O(\alpha)$ and $(m_f/m_0)-1=O(\alpha)$, so that $m_1=m_f[1+O(\alpha^2)]$. This is an improvement over m_0, which, though never differing from m_f by more than about 10%, does not agree with m_f to first order in α for small α. For increasing α, $[\partial(B+A)/\partial(\Delta E)]_{0,0}$ increase from zero rapidly, and since $(m_f/m_0)>1$ for all α, we have for large enough α the inequalities

$$m_0\leqslant m_1\simeq m_0\{1+[(m_f/m_0)-1]\times[1+(\partial(\mathfrak{A}+\mathfrak{B})/\partial(\Delta E))_{0,0}]^{-1}\}<m_0\{1+[(m_f/m_0)-1]\}=m_f. \quad \text{(A-12)}$$

Thus the correction made by m_1 to m_0 is less than the correction made by m_f and in the same direction. In particular, for $\alpha=3$ and 5 we have computed m_1. The results are as follows:

α	m_f/m	m_0/m	m_1/m
3	1.89	1.78	1.82
5	3.89	3.56	3.63

The smallness of the difference between zeroth- and first-order effective masses is another justification for the procedure employed in Sec. V.

We have also computed ΔE as a function of P for $\alpha=5$ up to $P=1.76(2m\omega)^{\frac{1}{2}}$. ΔE is negative and increases in absolute value with increasing P. For $P=1.76(2m\omega)^{\frac{1}{2}}$ it is still only -0.084ω, compared with a self-energy for this P of the order of -5ω, so that insofar as this is a good first-order correction procedure, the zeroth-order Feynman approximation is a good one and the corrections can be treated as small.

APPENDIX B

We wish to evaluate

$$V_{00}(E',\mathbf{P})=\langle\mathbf{P}0;00|\bar{K}_1G_{E'}\bar{K}_1+A+B|\mathbf{P}0;00\rangle=V\mathcal{U}^2(2\pi)^{-3}\int d^3k\,k^{-2}\langle0|e^{i\mathbf{k}\cdot\mathbf{r}}[E'-K_0(\mathbf{P})-\omega+i\epsilon]^{-1}e^{-i\mathbf{k}\cdot\mathbf{r}}|0\rangle-\tfrac{1}{2}C\int d^3\kappa\,\delta(\boldsymbol{\kappa})\nabla_\kappa^2\times\langle0|\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})[E'-K_0(P)-w+i\epsilon]^{-1}\times\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})|0\rangle+(A+B) \quad \text{(B-1)}$$

in the limit that the initial momentum $\mathbf{P}'\to0$. It is sufficient here to evaluate only the first term on the right, since the second term is similar and elementary. For simplicity, we take $\omega=1$.

Since $\mathbf{r}=\mathbf{R}-(M/m_0)\boldsymbol{\varrho}$, we have

$$\langle0|e^{i\mathbf{k}\cdot\mathbf{r}}[E'-K_0(P)-1+i\epsilon]^{-1}e^{-i\mathbf{k}\cdot\mathbf{r}}|0\rangle=\langle0|\exp[i\mathbf{k}\cdot\boldsymbol{\varrho}(M/m_0)][E'-K_0(\mathbf{P}-\mathbf{k})-1+i\epsilon]^{-1}\exp[-i\mathbf{k}\cdot\boldsymbol{\varrho}(M/m_0)]|0\rangle. \quad \text{(B-2)}$$

Furthermore, since $E'=(P'^2/2m_0)+1$ for $P'\to0$ and since $(x+i\epsilon)^{-1}=-i\int_0^\infty dt\exp[(-\epsilon+ix)t]$, we obtain

$$\int d^3k\,k^{-2}\langle0|e^{i\mathbf{k}\cdot\mathbf{r}}[E'-K_0(P)-1+i\epsilon]^{-1}e^{-i\mathbf{k}\cdot\mathbf{r}}|0\rangle=-i\int_0^\infty dt\,e^{-\epsilon t}\int d^3k\,k^{-2}\exp\left[i\frac{\mathbf{P}^2-(\mathbf{P}-\mathbf{k})^2}{2m_0}t\right]\times\langle0|\exp[i\mathbf{k}\cdot\boldsymbol{\varrho}(M/m_0)]\exp(-iv\boldsymbol{\gamma}^\dagger\cdot\boldsymbol{\gamma}t)\times\exp[-i\mathbf{k}\cdot\boldsymbol{\varrho}(M/m_0)]|0\rangle\equiv-iI, \quad \text{(B-3)}$$

where

$$\boldsymbol{\gamma}=\boldsymbol{\varrho}(\mu v/2)^{\frac{1}{2}}+i\boldsymbol{\pi}(2\mu v)^{-\frac{1}{2}}$$

and

$$\boldsymbol{\gamma}^\dagger=\boldsymbol{\varrho}(\mu v/2)^{\frac{1}{2}}-i\boldsymbol{\pi}(2\mu v)^{-\frac{1}{2}}. \quad \text{(B-4)}$$

Simple operational manipulations with harmonic oscillator variables give

$$\langle0|\exp[i\mathbf{k}\cdot\boldsymbol{\varrho}(M/m_0)]\exp(-iv\boldsymbol{\gamma}^\dagger\cdot\boldsymbol{\gamma}t)\times\exp[-i\mathbf{k}\cdot\boldsymbol{\varrho}(M/m_0)]|0\rangle=\exp[-(M/m_0)^2(k^2/2\mu v)(1-e^{-ivt})]. \quad \text{(B-5)}$$

Using (B-5), choosing the polar axis along $\mathbf{P}$ and calling $\cos(\mathbf{P},\mathbf{k})=\xi$, and performing two of the $\mathbf{k}$-space integrations, we obtain

$$I=2\pi\int_0^1 d\xi\int_0^\infty dt\,e^{-\epsilon t}\exp\left[i\frac{P'^2-P^2(1-\xi^2/j(it))}{2m_0}t\right]\times[2\pi m_0/itj(it)]^{\frac{1}{2}}, \quad \text{(B-6)}$$

where $j(\tau)$ is as given in (5.25) with $\omega=1$.

We now write

$$I=I_1+I_2, \tag{B-7}$$

where I_1 and I_2 are the contributions to I for $\xi<\xi_c$ and $\xi>\xi_c$, respectively, and where

$$\xi_c^2=1-(P'/P)^2. \tag{B-8}$$

To evaluate I_1, we observe that for $|t|\to\infty$ and $\mathrm{Im}t\leq 0$, $j(it)\to 1$ and $P^2[1-(\xi^2/j(it))]-P'^2>0$. Hence in I_1 we may integrate from 0 to $-i\infty$ rather than from 0 to ∞. Using the function $F(x)$ defined in (5.25) and letting $\xi_c\to 1$, we can also perform the ξ-integration, obtaining finally

$$I_1=-i2\pi^{\frac{3}{2}}P\int_0^\infty d\tau\, e^{i\epsilon\tau} \times\exp\{-(P^2\tau/2m_0)[1-(1/j(\tau))]\} \times F((P^2\tau/2m_0 j)^{\frac{1}{2}})(P^2\tau/2m_0)^{-1}, \tag{B-9}$$

a convergent integral to be evaluated numerically.

To evaluate I_2, pick a fixed T so large that

$$(v^2-w^2)(vw^2)^{-1}/T\ll 1. \tag{B-10}$$

Now decompose I_2:

$$I_2=I_{21}+I_{22}, \tag{B-11}$$

where I_{21} and I_{22} are the contributions to I_2 from $t<T$ and $t>T$, respectively. I_{21} is of the order $(1-\xi_c)T$ and may be neglected when $\xi_c\to 1$. In I_{22} we may expand:

$$1/j(it)=1-(v^2-w^2)(vw^2)^{-1}[1-\exp(-ivt)](it)^{-1}+O(1/t^2), \tag{B-12}$$

so that

$$I_{22}=2\pi\exp[-(P^2/2\mu v)]\int_{\xi_c}^1 d\xi\int_T^\infty dt\, e^{-\epsilon t} \times\exp[it(P^2/2m_0)(x^2-x_0^2)] \times\left[\sum_{n=0}^\infty\frac{1}{n!}\left(\frac{P^2}{2m_0}\frac{v^2-w^2}{vw^2}\right)^n e^{-i\hbar vt}\right]\left(\frac{2\pi m_0}{it}\right)^{\frac{1}{2}} \times[1+O(1/T)]. \tag{B-13}$$

As $\xi_c\to 0$ all but the $n=0$ term in the sum give contributions to the double integral of the order $(1-\xi_c)$, since when $\xi=\xi_c$, the integral on t converges for $n\neq 0$ neglecting $O(1/T)$; and writing $\int_T^\infty dt$ as $\int_0^\infty dt-\int_0^T dt$, the second double integral of the $n=0$ term is also of order $1-\xi_c$. Thus

$$I_{22}=2\pi\exp[-(P^2/2\mu v)]\int_{\xi_c}^1 d\xi\int_0^\infty dt\, e^{-\epsilon t} \times\exp[it(P^2/2m_0)(\xi^2-\xi_c^2)](2\pi m_0/it)^{\frac{1}{2}} +O(1-\xi_c). \tag{B-14}$$

Letting $t=is^2$, the remaining double integral can be performed:

$$I_{22}=4\pi^2 m_0 P^{-1}\exp(-P^2/2\mu v)\ln\left[\frac{1+(1-\xi_c^2)^{\frac{1}{2}}}{\xi_c}\right] +O(1-\xi_c). \tag{B-15}$$

As $\xi_c\to 1$, $I_{22}=O((1-\xi_c)^{\frac{1}{2}})$ justifying the neglect of $O(1-\xi_c)$. Hence finally

$$I_{22}\to 2\pi^2 P'(P^2/2m_0)^{-1}\exp(-P^2/2\mu v). \tag{B-16}$$

The first term on the right in (B-1) is now obtainable from (B-7), (B-9), and (B-16). The second term on the right in (B-1) is readily obtained using (B-5). In the appropriate units (B-1) reduces to (5.24).