

A discussion is given in the reference cited showing that in the almost-free-electron case, the APW method leads to energies, and wave functions outside the spheres, almost exactly characteristic of free electrons. Graphs are also given showing that for an alkali metal like sodium, the quantities like  $F_{nij}$  of Eq. (7), or the summation over  $l$  in Eq. (14), can be very small over considerable ranges of energies, leading to the free-electron behavior of the energy bands in such a case, whereas for such an element as copper, this situation does not hold at all. Of course, the wave functions inside the spheres are entirely different from plane waves. In the reference cited, the similarity of this problem to the Ramsauer effect in the scattering of electrons by atoms is stressed, in which in certain cases

a single plane wave outside an atomic sphere matches almost perfectly to the solution inside, without the requirement of scattered waves. This is the same case in which a single plane wave outside the spheres, or a single augmented plane wave, forms very nearly an exact solution of the energy-band problem.

I am much obliged to Professor Ziman for correspondence and conversation relating to this problem, and to my colleague Dr. Keith Johnson for valuable discussions. Dr. Johnson is investigating further the relation between the APW and Green's-function methods.<sup>5</sup>

<sup>5</sup> Note added in proof. Since sending in this paper, Professor Ziman has pointed out to the author the very recent paper by P. Lloyd, Proc. Phys. Soc. (London) **86**, 825 (1965), who arrives at conclusions similar to those of the present paper.

## Phonon-Broadened Optical Spectra: Urbach's Rule

G. D. MAHAN

*General Electric Research and Development Center, Schenectady, New York*

(Received 28 December 1965)

Starting from Frölich's Hamiltonian for conduction-electron-optical-phonon interactions, an approximate Green's function  $G(p, t)$  is derived. The spectral density derived from this Green's function is shown to possess an exponential tail at low energies,  $E/\omega_0 \ll 0$ . This demonstrates that Urbach's rule can be derived from Frölich's Hamiltonian. The approximate Green's function  $G(p, t)$  is shown to be related to the intermediate-coupling models for polarons.

### I. INTRODUCTION

THE low-energy tail of the direct absorption edge of polar materials decreases exponentially in energy. This phenomenon, known as Urbach's<sup>1</sup> rule, has been observed in many materials.<sup>2</sup>

The major result of this calculation is showing that Urbach's rule can be theoretically derived from Frölich's Hamiltonian<sup>3</sup>

$$H = \epsilon_p + \omega_0 \sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \sum_{\mathbf{q}} iQ(\mathbf{q})(a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} - a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}),$$

$$Q(\mathbf{q})^2 = 4\pi\alpha\omega_0^{3/2} / q^2 (2m)^{1/2},$$

$$\epsilon_p = p^2 / 2m,$$

for electrons in a parabolic conduction band having a linear interaction with optical phonons in a polar crystal. Starting from this Hamiltonian, the spectral function<sup>4</sup>  $A(p, E)$  is evaluated using a modification of second-order perturbation theory. This spectral density has an exponential tail for  $E/\hbar\omega_0 < 0$ . The exponential tail in the spectral density leads to an Urbach's rule in

optical absorption. This represents the first derivation of an exponential tail caused by a linear interaction between conduction-band electrons and optical phonons.

Previous theoretical discussions<sup>2, 5-12</sup> of Urbach's rule were either based upon impurity effects or conventional perturbation theory. Toyozawa's<sup>5</sup> model of quadratic coupling between localized exciton and optical phonons, which is similar to an impurity model in form, has received much attention.<sup>2, 10</sup> The semiclassical derivation of quadratic exciton-phonon interactions, which neglects the exciton recoil, predicts an exponential tail. However, Keil<sup>13</sup> has recently shown that a quantum-mechanical derivation of quadratic coupling does not generally predict an Urbach's rule, and the usefulness of Toyozawa's model is now in doubt. Some other impurity models<sup>11, 12</sup> are based on the low-energy band

<sup>5</sup> Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **22**, 455 (1959); Technical Report of the Institute for Solid State Physics, Ser. A, No. 119, 1964 (unpublished).

<sup>6</sup> W. P. Dumke, Phys. Rev. **108**, 1419 (1957).

<sup>7</sup> D. G. Thomas, J. J. Hopfield, and M. Power, Phys. Rev. **119**, 570 (1960).

<sup>8</sup> R. E. Dietz, J. J. Hopfield, and D. G. Thomas, J. Appl. Phys. **32**, 2282 (1961).

<sup>9</sup> B. Segall (to be published).

<sup>10</sup> H. Mahr, Phys. Rev. **132**, 1880 (1963).

<sup>11</sup> D. Redfield, Phys. Rev. **130**, 916 (1963).

<sup>12</sup> B. I. Halperin, Phys. Rev. **139**, A104 (1965).

<sup>13</sup> T. H. Keil, Phys. Rev. **140**, A601 (1965).

<sup>1</sup> F. Urbach, Phys. Rev. **92**, 1324 (1953).

<sup>2</sup> R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5.

<sup>3</sup> H. Frölich, Advan. Phys. **3**, 325 (1954).

<sup>4</sup> A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1963).

tail caused by the electric fields of impurities. Also, recent calculations<sup>14</sup> on acoustical phonon broadening of impurity levels show that a low-energy exponential tail is always predicted. Impurity states can have a low-energy exponential tail for a variety of reasons.

In contrast to these extrinsic explanations of Urbach's rule, there remains the view that it is an intrinsic effect.<sup>6-9</sup> Experiments<sup>7,8,15</sup> on the low-energy absorption edge of exciton states in type II-IV semiconductors show structure which is clearly identifiable as caused by optical-phonon-induced absorption. Thomas *et al.*<sup>7</sup> and Dietz *et al.*<sup>8</sup> showed that the edge in CdS and ZnO could be explained by considering the exciton-optical-phonon polar interactions. Recent calculations by Segall<sup>9</sup> on Marple's<sup>15</sup> CdTe absorption edge data include processes involving the absorption of two optical phonons. The excellent agreement between theory and experiment in these areas verifies that the correct explanation for the absorption edge has been found. However, a generalized Urbach's rule cannot be derived by this conventional perturbation theory approach because of the calculational difficulties of including processes involving many phonons.

By starting with Fröhlich's Hamiltonian, the present derivation calculates an intrinsic property. Processes involving many phonons are included by doing perturbation theory in an unconventional way. The physical basis for the approximate Green's function used in the derivation is discussed in Sec. II. It is related to the intermediate coupling polaron models.<sup>16-19</sup> Section III discusses some of the ordinary properties of this Green's function, while the exponential low-energy tail of the spectral density  $A(p, E)$  is derived in Sec. IV. The relation between  $A(p, E)$  and the optical absorption is discussed in Sec. V.

## II. DERIVATIONS OF $G(p, t)$

The physical property of interest is the spectral density  $A(p, E)$  of an electron in a parabolic conduction band. This is obtained from the electron Green's function<sup>4</sup>

$$G(p, t) = -i \langle TC_p(t) C_p^\dagger(0) \rangle. \quad (2.1)$$

After Fourier-transforming this function to find  $G(p, E)$  the spectral density is defined by

$$A(p, E) = -2 \operatorname{Im} G(p, E). \quad (2.2)$$

The spectral density describes the properties of the electron, including its density of states

$$\rho(E) = \int \frac{d^3 p}{(2\pi)^3} A(p, E). \quad (2.3)$$

A necessary condition for deriving Urbach's rule is that  $G(p, t)$  must accurately describe the electron's coupling to many phonons, at least in the limit  $\alpha \ll 1$ . In this section, a simple Green's function is derived which does predict an exponential edge in  $A(p, E)$  for  $E/\omega_0 \ll 1$ , where  $E$  is measured relative to the conduction-band minimum. Since all of the approximations of the result are contained in the starting formula for  $G(p, t)$ , several different derivations of the same  $G(p, t)$  are presented, each of which adds some insight into the validity of the approximate form.

The most intuitive derivation is by analogy with the Green's function for a localized, nondegenerate, impurity state. The exact Green's function for this model impurity state is<sup>14,20</sup>

$$G(t) = -i\theta(t) \exp\{-i(E_0 + \Sigma_0)t - I_0(t)\},$$

where

$$\begin{aligned} \theta(t) &= 1 & t > 0 \\ &= 0 & t < 0, \end{aligned} \quad (2.4)$$

$E_0$  is the resonant energy,  $\Sigma_0$  is the polaron shift, and

$$I_0(t) = \sum_q \{ \operatorname{Num}^-(q) (1 - e^{-i\omega_0 t}) + \operatorname{Num}^+(q) (1 - e^{i\omega_0 t}) \}. \quad (2.5)$$

The two functions  $\operatorname{Num}^\pm(q)$  are the numbers of phonons<sup>21</sup> of frequency  $\pm\omega_0$  surrounding the impurity levels

$$\begin{aligned} \operatorname{Num}^-(q) &= Q(q)^2 (N+1) / \omega_0^2, \\ \operatorname{Num}^+(q) &= Q(q)^2 N / \omega_0^2, \end{aligned} \quad (2.6)$$

where  $N$  is the thermal occupation number of the phonons. The time-dependent parts of (2.5) are those for a phonon cloud, assuming no excitation at  $t=0$ .

An approximate Green's function for an electron of momentum  $p$  in a conduction band can be deduced by the same arguments. Now the number of phonons is

$$\begin{aligned} \operatorname{Num}^-(q) &= Q(q)^2 (N+1) / (\Omega^-)^2, \\ \operatorname{Num}^+(q) &= Q(q)^2 N / (\Omega^+)^2, \\ \Omega^\pm &= \epsilon_p - \epsilon_{p-q} \pm \omega_0, \end{aligned} \quad (2.7)$$

and the time development is

$$(1 - e^{i\Omega^\pm t}).$$

This leads to the Green's function

$$\begin{aligned} G(p, t) &= -i\theta(t) \exp\{-i(\epsilon_p + \Sigma_p) - I(p, t)\} \\ I(p, t) &= \sum_q Q(q)^2 \left\{ \frac{N+1}{(\Omega^-)^2} (1 - e^{i\Omega^- t}) + \frac{N}{(\Omega^+)^2} (1 - e^{i\Omega^+ t}) \right\}, \\ \Sigma_p &= \sum_q Q(q)^2 \{ (N+1) / \Omega^- + N / \Omega^+ \}. \end{aligned} \quad (2.8)$$

This will be used in deriving Urbach's rule.

<sup>14</sup> C. B. Duke and G. D. Mahan, Phys. Rev. **139**, A1965 (1965).

<sup>15</sup> D. T. F. Marple (to be published).

<sup>16</sup> S. Tomonaga, Progr. Theoret. Phys. (Kyoto) **2**, 6 (1947).

<sup>17</sup> M. Gurari, Phil. Mag. **44**, 329 (1953).

<sup>18</sup> T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. **90**, 297 (1953).

<sup>19</sup> W. Van Haeringen, Phys. Rev. **137**, A1902 (1965).

<sup>20</sup> K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950); M. Lax, J. Chem. Phys. **20**, 1752 (1952).

<sup>21</sup> For a discussion of the number of phonons in a polaron cloud see C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 134 ff.

The Green's function (2.8) can also be derived by an unusual truncation of the equations of motion for  $G(p, t)$ . This equation is<sup>22</sup>

$$(i\partial/\partial t - p^2/2m)G(p, t-t') = \delta(t-t') - i \sum_q Q(q)^2 \int_0^{-i\beta} dt_2 [\mathfrak{D}^{(0)}(q, t_2-t) + \mathfrak{D}^{(0)}(q, t-t_2)] \times \langle TC_{p-q}(t) \sum_{p'} C_{p'-q}^+(t_2) C_{p'}(t_2) C_{p'}^+(t') \rangle. \quad (2.9)$$

The  $\mathfrak{D}^{(0)}$  are the phonon Green's functions. Since we are just considering one electron in the conduction band, the time ordering on the four-fermion product may be dropped, with the requirement that  $t > t_2 > t'$ .

The usual way of evaluating this equation is to Fourier-transform it. The resulting equation for  $G(p, E)$  is solved by expressing the last term as a product of the self-energy  $\Sigma(p, E)$  and  $G(p, E)$ . The procedure to obtain  $G(p, t)$  in (2.8) is quite different. The last term will be factored into a  $G(p, t)$  and a coefficient. This factoring is achieved by inserting

$$1 \equiv \sum_{p''} C_{p''}^+(t) C_{p''}(t)$$

into the four-fermion expression between  $C_{p'}(t_2)$  and  $C_{p'}^+(t')$ . This last term can be then approximated by

$$iG(p, t-t') \exp[i(t-t_2)(\epsilon_p - \epsilon_{p-q})]. \quad (2.10)$$

The total last term in (2.9) becomes

$$G(p, t-t') \left\{ \Sigma_p - \sum_q Q(q)^2 \left[ \frac{N+1}{\Omega^-} e^{i\Omega^-(t-t')} + \frac{N}{\Omega^+} e^{i\Omega^+(t-t')} \right] \right\}. \quad (2.11)$$

This gives a linear differential equation in (2.9) for  $G(p, t-t')$  which is easily solved. The solution is just (2.8).

The truncation of the time equations is an unusual approach which deserves comment. As will become clear, the  $G(p, E)$  obtained from (2.8) describes the electron propagation for  $E \sim 0$  in a similar way as does the Green's function obtained through truncation of the energy equations. However, the present  $G(p, E)$  describes processes involving many phonons, and therefore gives a reasonable  $A(p, E)$  over a large range of energy. Thus the truncation of the time equations seems more useful than the usual truncation of the energy equation. The difficulty is that the analytical derivation of  $G(p, E)$  from  $G(p, t)$  is difficult, although it is possible when  $E/\hbar\omega_0 \ll 0$ . It is also possible to truncate the equations for  $G(p, t)$  at a higher order, although this has not been investigated.

<sup>22</sup> R. Puff and G. D. Whitfield, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum Press, Inc., New York, 1963), p. 177.

Van Haeringen<sup>19</sup> recently described an exactly solvable, zero-temperature, polaron model which included some recoil effects. This model, which was related to the intermediate-coupling schemes, neglected correlations between the momenta of the phonons in the polaron cloud. When  $T \rightarrow 0$  ( $N \rightarrow 0$ ) the approximate Green's function (2.8) appears equivalent to Van Haeringen's model. Both models are based on the same principle of neglecting correlation in the phonon momenta, and they have the same self-energies. Thus (2.8) also seems to be the finite-temperature Green's function for Van Haeringen's model.

Correlations between phonon momenta in the polaron cloud should not be important for  $\epsilon_p \ll \hbar\omega_0$ . This is the basis of most intermediate-coupling polaron schemes.<sup>16-19, 23</sup> The Green's function (2.8) should accurately describe the electrons properties for  $\epsilon_p \ll \hbar\omega_0$ ; it is shown in Sec. IV that it does give an Urbachian edge to  $A(p, E)$ . But correlations in the phonon momenta are important for  $\epsilon_p > \hbar\omega_0$ , and intermediate-coupling schemes are not valid in this region. The present method cannot be applied to finding  $A(p, E)$  for  $\epsilon_p > \hbar\omega_0$ . Attempts at evaluating  $A(p, E)$  in this region encounter difficulties which are discussed in Sec. IV. This also means that the density-of-states integral (2.3) cannot be done at the present time.

### III. EVALUATION OF $G(p, E)$

Some of the properties of the Green's function (2.8) are discussed in this section. The self-energy and renormalization function are given, which is a necessary preliminary to deriving the low-energy tail in the next section. Only the leading terms are presented, and the actual asymptotic forms are given in Appendix A.

The first step is to find the Fourier transform

$$G(p, E) = \int_{-\infty}^{\infty} dt e^{iEt} G(p, t). \quad (3.1a)$$

It is convenient to use dimensionless units, where energy is measured relative to  $\hbar\omega_0$ , and  $S = t\omega_0$ . Then (3.1) becomes

$$G(p, E) = -i \int_0^{\infty} dS \exp\{-iS(E - \epsilon_p) - J(p, S)\}, \quad (3.1b)$$

where

$$J(p, S) = iS\Sigma_p + \frac{\alpha}{2\pi} \int_{-\infty}^{\infty} dZ \int_{-1}^1 d\mu \times \left\{ \frac{N+1}{\omega_-^2} (1 - e^{iS\omega_-}) + \frac{N}{\omega_+^2} (1 - e^{iS\omega_+}) \right\}, \quad (3.2)$$

$$\omega_{\pm} = \Omega_{\pm}/\omega_0 = -Z^2 \pm 1 + \epsilon_p \mu^2.$$

<sup>23</sup> The intermediate-coupling results are based on variational calculations. The Green's function (2.8) can be made to appear closer to these methods by using  $\Omega_{\pm} = -\epsilon_q \pm \hbar\omega_q - qp/m(1-\eta)$ , where  $\eta$  is the Lee, Low, and Pines (Ref. 18) variational parameter.

The central peak of the spectral density is governed by the behavior of  $J(p, S)$  as  $S \rightarrow \infty$ . Except at  $\epsilon_p = 0$  and  $\epsilon_p = 1$ , these limits are

$$J(p, S) \xrightarrow{S \rightarrow \infty} iS \Sigma_p + \Delta_p + O(e^{iS}/S), \quad (3.3)$$

where the self-energy  $\Sigma_p$  and renormalization function  $\Delta_p$  are

$$\begin{aligned} \epsilon_p < 1: \quad \Sigma_p &= -(\alpha/\sqrt{\epsilon_p})[(N+1) \sin^{-1} \sqrt{\epsilon_p} \\ &\quad + iN \sinh^{-1} \sqrt{\epsilon_p}], \\ \Delta_p &= \frac{1}{2} \alpha \left[ \frac{N+1}{(1-\epsilon_p)^{1/2}} - i \frac{N}{(1+\epsilon_p)^{1/2}} \right]; \end{aligned} \quad (3.4)$$

$$\begin{aligned} \epsilon_p > 1: \quad \Sigma_p &= -(\alpha/\sqrt{\epsilon_p})[(N+1) \frac{1}{2} \pi \\ &\quad + i(N+1) \cosh^{-1} \sqrt{\epsilon_p} + iN \sinh^{-1} \sqrt{\epsilon_p}], \\ \Delta_p &= \frac{1}{2} \alpha i \left[ \frac{(N+1)}{(\epsilon_p-1)^{1/2}} - \frac{N}{(1+\epsilon_p)^{1/2}} \right]. \end{aligned}$$

At  $\epsilon_p = 1$ , the asymptotic form is

$$\begin{aligned} J(\epsilon_p = 1, S) &\xrightarrow{S \rightarrow \infty} iS \Sigma(\epsilon_p = 1) - i\alpha N / 2\sqrt{2} \\ &\quad + 2\alpha(N+1)(iS)^{1/2} / \sqrt{\pi} + O(S^{-1/2}). \end{aligned} \quad (3.5)$$

For  $\epsilon_p = 0$ , the integral (3.2) can be done analytically in terms of the Fresnel integrals<sup>24</sup>

$$C_2(x) - iS_2(x) = \int_0^x \frac{dt e^{-it}}{(2\pi t)^{1/2}}. \quad (3.6)$$

For  $p = 0$

$$\begin{aligned} J(0, S) &= \left[ \alpha / (i\pi)^{1/2} \right] \{ (N+1) [ -iS^{1/2} e^{-iS} \\ &\quad + (2S+i) (\frac{1}{2}\pi)^{1/2} (C_2(S) - iS_2(S)) ] \\ &\quad + N [ iS^{1/2} e^{iS} + (2S-i) (\frac{1}{2}\pi)^{1/2} \\ &\quad \times (C_2(S) + iS_2(S)) ] \}. \end{aligned} \quad (3.7)$$

For  $\epsilon_p \ll 1$ , the main peak of the spectral density is an asymmetric Lorentzian

$$A(p, E) \approx -2 \operatorname{Im} \left\{ \frac{\exp(-\Delta_p)}{E - \epsilon_p - \Sigma_p} \right\}; \quad (E \approx \epsilon_p + \Sigma_p). \quad (3.8)$$

The asymmetry is caused by the imaginary parts of the renormalization function. Similar asymmetries are found in spectral densities of phonon broadened impurity states.<sup>14</sup> As  $\epsilon_p \rightarrow 1$ , the main peak ceases to be Lorentzian, as is evident from the  $(iS)^{1/2}$  term in (3.5). Of course, for  $\epsilon_p > 1$  the Green's function does not accurately describe the many-phonon processes.

The fact that the  $p = 0$  cases possesses an analytical

<sup>24</sup> *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964), Appl. Math. Ser. 55.

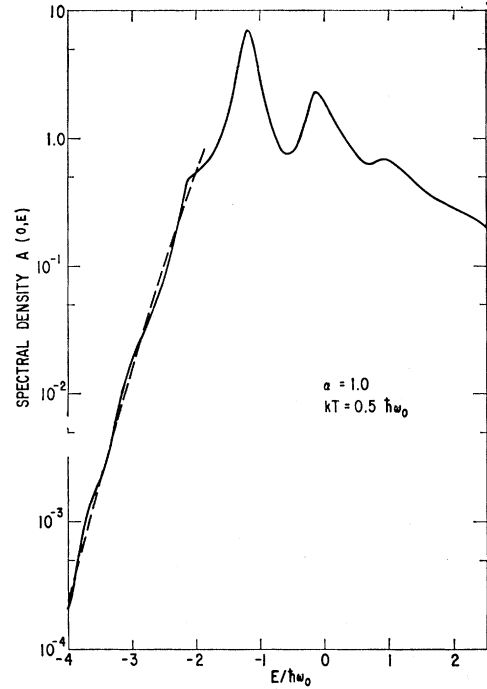


FIG. 1. The spectral density  $A(0, E)$  for a  $p = 0$  conduction electron interacting with optical phonons:  $\alpha = 1$  and  $kT = 0.5 \hbar \omega_0$ . The solid line is a numerical calculation using (2.2), (3.1b), and (3.7). The dashed line is the asymptotic result using (4.8) and (4.10). The low-energy exponential tail is quite evident.

result (3.7) allows the spectral density  $A(0, E)$  to be investigated in more detail. Figures 1 and 2 show the results of numerical calculations of  $A(0, E)$  using (3.7) in (3.1b). The central asymmetric Lorentzian peak at  $E = \operatorname{Re} \Sigma_0 = -\alpha(N+1)$  is quite evident, and there are also peaks at  $\Sigma_0 + 1$  and  $\Sigma_0 + 2$ . The Green's function (2.8) clearly describes processes involving many phonons. The low-energy ( $E \ll 0$ ) tail is exponential. The

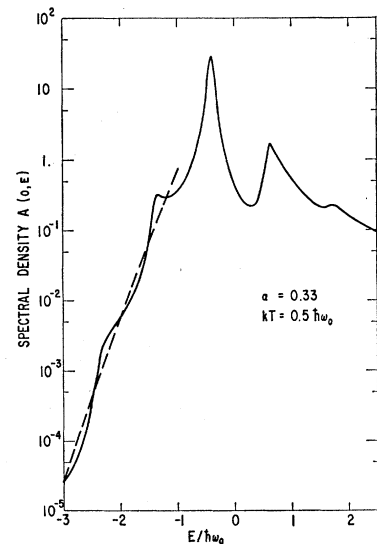


FIG. 2. The spectral density  $A(0, E)$  for a  $p = 0$  conduction electron interacting with optical phonons:  $\alpha = 0.33$  and  $kT = 0.5 \hbar \omega_0$ . The solid line is a numerical calculation using (2.2), (3.1b), and (3.7). The dashed line is the asymptotic result using (4.8) and (4.10).

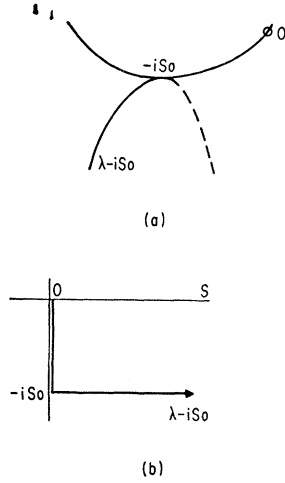


FIG. 3. The contour of integration for deriving Urbach's rule when  $E/\omega_0 < 0$ . The contour descends the imaginary axis to  $-iS_0$  ( $S_0$  is real and positive) which is the saddle point. The integrand is constantly decreasing from 0 to  $-iS_0$ , as shown schematically in Fig. 1(a). The contour then changes direction and drops down the saddle along the line of steepest descent,  $-iS_0$  to  $\lambda - iS_0$ . The integral from 0 to  $-iS_0$  contributes just to the real part of  $G(p, E)$ , while the contour  $-iS_0$  to  $\lambda - iS_0$  gives the imaginary part of  $G(p, E)$  and the spectral density.

dotted line is the asymptotic form of  $A(0, E)$  whose derivation is given in the next section.

#### IV. URBACH'S RULE

For Urbach's rule we need  $G(p, E)$  for negative energies. The Green's function for  $E < 0$  is obtained by a saddle-point integration. For  $E < 0$  the saddle point of the integrand of (3.1) occurs along the negative imaginary axis at  $-iS_0$  ( $S_0$  is real and positive). As indicated in Fig. 3(a), this point is a minimum for integration along the imaginary axis, and a maximum for integration perpendicular to the imaginary axis. Thus the integration of steepest descent is that shown in Fig. 3(b).

To find the saddle point, we analytically extend  $J(p, S)$  in (3.5) to the negative imaginary axis,  $iS \rightarrow y$ . This makes  $J(p, -iy)$  a real function. Define  $K(p, y)$  by

$$-(\partial^2/\partial y^2)J(p, -iy) = +K(p, y) \\ = [\alpha/(\pi y)^{1/2}][(N+1)e^{-y} + Ne^y] \int_0^1 d\mu e^{\epsilon p \mu^2 y} \quad (4.1)$$

and

$$J(p, 0) = 0, \\ \left. \frac{J(p, y)}{dy} \right|_{y=0} = 0.$$

Then define  $U(p, y)$  and  $V(p, y)$  by

$$J(p, -iy) = - \int_0^y dy' (y-y') K(p, y') \quad (4.2) \\ = -yU(p, y) + V(p, y),$$

where

$$U(p, y) = \int_0^y dy' K(p, y'), \quad (4.3) \\ V(p, y) = \int_0^y dy' y' K(p, y').$$

The evaluation of  $U$  and  $V$  is discussed in Appendix B, where it is shown that the integral for  $V$  can be done analytically. Both  $U$  and  $V$  are positive functions.

The position of the saddle point is determined by finding the maximum of

$$f(p, y) = y(-E + \epsilon_p) - yU + V, \quad (4.4)$$

which occurs at  $y = S_0$

$$\partial f/\partial S_0 = 0 = -E + \epsilon_p - U(p, S_0) \quad (4.5)$$

and at the saddle point

$$f(p, S_0) = V(p, S_0). \quad (4.6)$$

The path of steepest descent, Fig. 3(b), has two segments. Since the integrand of (3.1b) is entirely real on the imaginary axis, the integration segment from  $0 \rightarrow -iS_0$  contributes just to the real part of the Green's function. The main contribution is near the origin,

$$\text{Re}G(p, E) \simeq - \int_0^{S_0} dy e^{y(E - \epsilon_p)} = \frac{1}{E - \epsilon_p}, \quad (4.7)$$

which is the correct form of the real part of the Green's function as  $E \rightarrow -\infty$ .

The integration segment, from  $-iS_0 \rightarrow \lambda - iS_0$  as  $\lambda \rightarrow \infty$ , gives the imaginary part of the Green's function, or  $A(p, E)$ . Using standard saddle-point techniques<sup>25</sup> gives

$$A(p, E) = \left( \frac{2\pi}{K(p, S_0)} \right)^{1/2} \exp[-V(p, S_0)], \quad (4.8)$$

where  $S_0$  depends upon  $E$ ,  $\epsilon_p$ ,  $\alpha$ , and temperature in (4.5). The implied equation (4.5) for  $S_0$  is complicated by the fact that  $V(p, S_0)$  does not possess a simple analytical form except at  $p=0$ .

The case  $p=0$  simplifies since the integral in (4.1) for  $K(0, y)$  is eliminated. The results can be expressed in terms of error functions and Dawson's integral<sup>26</sup>  $F(x)$

$$K(0, y) = [\alpha/(y\pi)^{1/2}][(N+1)e^{-y} + Ne^y], \quad (4.9a)$$

$$U(0, y) = (\alpha/\sqrt{\pi})[(N+1)\sqrt{\pi} \text{erf}(\sqrt{y}) \\ + 2Ne^{y/2} F(\sqrt{y})], \quad (4.9b)$$

$$V(0, y) = \alpha \frac{1}{2} (N+1) [\text{erf}(\sqrt{y}) - 2(y/\pi)^{1/2} e^{-y} \\ + (\alpha N/\sqrt{\pi}) e^{y/2} [\sqrt{y} - F(\sqrt{y})]]. \quad (4.9c)$$

For low temperatures ( $N \ll 1$ ), the saddle point  $S_0$  becomes large enough that (4.5) can be solved by using the asymptotic expansions for  $U$ . For  $p=0$ , and neg-

<sup>25</sup> P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

<sup>26</sup> Dawson's Integral is defined in Appendix B, and tabulated in Ref. 24.

lecting  $e^{-S_0}$ , (4.5) becomes

$$E' = -E + \text{Re}\Sigma_0 \\ = \frac{\alpha N e^{S_0}}{(\pi S_0)^{1/2}} \left( 1 + \frac{1}{2S_0} + \frac{3}{4S_0^2} + \dots \right), \quad (4.10a)$$

where  $E'$  is the negative energy as measured from the polaron edge. Similar asymptotic expansions for  $V$  and  $K$  can be used to relate them to  $U$ , and hence to  $E'$

$$V = E' \left( S_0 - 1 - \frac{1}{2S_0} - \frac{5}{4S_0^2} \dots \right), \quad (4.10b)$$

$$K = E' \left( 1 + \frac{1}{2S_0} + \frac{3}{4S_0^2} + \dots \right)^{-1}. \quad (4.10c)$$

In the limit  $kT/k\omega_0 \ll 1$ , then ( $\beta = 1/kT$ ),

$$S_0 \xrightarrow[kT \ll \hbar\omega_0]{} \beta + \ln[E'(\pi\beta)^{1/2}/\alpha],$$

and the spectral function (4.8) becomes

$$A(0, E) = \left( \frac{2\pi}{E'} \right)^{1/2} \left( \frac{\alpha e}{(\pi\beta)^{1/2} E'} \right)^{E'} e^{-E'\beta}, \quad (E' < 0) \\ (kT \ll \hbar\omega_0) \quad (4.11)$$

which is clearly exponential.

Figures 1 and 2 show calculations of  $A(0, E)$  for  $kT = 0.5\hbar\omega_0$ , with  $\alpha = 1.0$  and  $0.33$ . The dotted line shows the low-energy exponential tail which was calculated using (4.8) and (4.10). It was necessary to include the first correction terms in the asymptotic expansions in order to obtain the desired accuracy.

The spectral density for  $p \neq 0$  can also be found by employing the asymptotic expansions for  $U(p, S_0)$ ,  $V(p, S_0)$ , and  $K(p, S_0)$  derived in Appendix B. This has been done and gives an exponential tail in  $A(p, E)$  for all  $p$ . However, the results for  $\epsilon_p > 1$  are not meaningful, since the Green's function (2.8) is not accurate in this region. One symptom of this difficulty is that numerical work indicates the integral over  $\epsilon_p$  for the density of states in (2.3) apparently does not converge for some values of  $E$ . Nevertheless, the fact that an asymptotic low-energy exponential edge is obtained for  $A(0, E)$  shows that Urbach's rule can be derived from Fröhlich's Hamiltonian.

## V. DISCUSSION

Starting from Fröhlich's Hamiltonian, the spectral density  $A(p, E)$  is derived for an electron in a polar

crystal. For energies below the conduction band, the spectral density has an exponential form. Since our approximate Green's function is related to the intermediate-coupling schemes, particularly that of Van Haeringen,<sup>19</sup> the results are limited to  $\epsilon_p/\omega_0 \ll 1$ .

Urbach's rule states an effect observed in optical absorption experiments. The relation between the absorption constant and the spectral density  $A(p, E)$  is that the absorption constant is related to an integral over the spectral densities of the conduction and valence band. This integral also contains corrections for electron-hole Coulomb interactions. However, these exciton effects are not important far below the conduction band for optical absorption in a strong electric field.<sup>27</sup> Thus it is probably also true that exciton effects are not important in our polaron induced absorption edge, except perhaps to lower the upper limit of this edge to the exciton energy. Our main result, then, is that Urbach's rule can be derived from Fröhlich's Hamiltonian.

One feature of the result, best exemplified in (4.11), is that the strength of this exponential tail depends only weakly upon the coupling parameter  $\alpha$ . In (4.11),  $\alpha$  enters the exponent as  $E' \ln \alpha$ . This agrees with experiment, since a large number of different materials, representing a wide range of values of  $\alpha$ , have similar strengths in their asymptotic tail.<sup>2,5</sup>

Another observation of great importance is that other types of electron-optical-phonon interactions<sup>28</sup> will also produce an exponential tail. The polar interaction was used here because the nature of the polar interaction is understood, and this is certainly the relevant interaction for many materials.

## ACKNOWLEDGMENTS

Helpful conversations with Dr. C. B. Duke, Dr. B. Segall, and Dr. D. T. F. Marple are gratefully acknowledged.

## APPENDIX A

The asymptotic form of  $J(p, S)$ , defined by (3.2), can be expressed in terms of the functions<sup>24</sup>

$$E_2(x) = C_2(x) + iS_2(x) = \int_0^x \frac{dt}{(2\pi t)^{1/2}} e^{it}, \\ E_i(x) = \int_x^\infty \frac{dt e^{it}}{it^2}.$$

<sup>27</sup> C. B. Duke, Phys. Rev. Letters **15**, 625 (1965); M. Alferieff and C. B. Duke (to be published).

<sup>28</sup> H. Ehrenreich and A. W. Overhauser, Phys. Rev. **104**, 331 (1956).

For large  $S$ ,

$$J(p, S) = iS\Sigma_p - \frac{\alpha}{(2i\epsilon_p)^{1/2}} E_2(S\epsilon_p) [(N+1)E_i^*(S) + NE_i(S)] + \frac{\alpha i(N+1)}{(2i(1-\epsilon_p))^{1/2}} E_2^*(S(1-\epsilon_p))$$

$$- \frac{i\alpha N}{(2i(1+\epsilon_p))^{1/2}} E_2(S(1+\epsilon_p)) + \frac{\alpha N e^{iS(1+\epsilon_p)}}{2(1+\epsilon_p)(iS\pi)^{1/2}} \sum_{k=0}^{\infty} \frac{\Gamma(k+\frac{3}{2})}{[iS(\epsilon_p+1)]^k} \sum_{l=0}^k \frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})} (1+\epsilon_p)^l$$

$$+ \frac{\alpha(N+1)e^{-iS(1-\epsilon_p)}}{2(1-\epsilon_p)(iS\pi)^{1/2}} \sum_{k=0}^{\infty} \frac{\Gamma(k+\frac{3}{2})}{[iS(\epsilon_p-1)]^k} \sum_{l=0}^k \frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})} (1-\epsilon_p)^l.$$

For  $\epsilon_p > 1$ , the third term is replaced by

$$[\alpha i(N+1)/(2i(\epsilon_p-1))^{1/2}] E_2(S(\epsilon_p-1)),$$

and for  $\epsilon_p = 1$ , the last term is replaced by

$$\alpha(N+1) \left(\frac{iS}{\pi}\right)^{1/2} \sum_{l=0}^{\infty} \frac{l!}{(-iS)^l (2l+1)}.$$

**APPENDIX B**

The saddle point of  $J(p, S)$  for  $S = -iS_0$  ( $S_0$  is real and positive) can be found from the asymptotic expansions. The asymptotic expansions can be derived from the result for  $J(p, S)$  in Appendix A, by letting  $iS \rightarrow S_0$ . But for the saddle-point method it is more convenient to express  $U$  and  $V$  separately. The results can be expressed in terms of error functions and Dawson's integral

$$\operatorname{erf}(x) = 2/(\pi)^{1/2} \int_0^x dt e^{-t^2} \rightarrow 1 - \frac{e^{-x^2}}{x\sqrt{\pi}} \left[ 1 + \sum_{m=1}^{\infty} \frac{1 \times 3 \times 5 \times \dots \times (2m-1)}{(-2x^2)^m} \right],$$

$$F(x) = e^{-x^2} \int_0^x dt e^{t^2} \rightarrow \frac{1}{2x} \left[ 1 + \sum_{m=1}^{\infty} \frac{1 \times 3 \times 5 \times \dots \times (2m-1)}{(2x^2)^m} \right].$$

The terms are

$$K(p, y) = \frac{\alpha}{y(\pi\epsilon_p)^{1/2}} e^{\epsilon_p y} F((\epsilon_p y)^{1/2}) [(N+1)e^{-y} + Ne^y],$$

and for  $\epsilon_p < 1$ :

$$V(p, y) = \alpha(N+1) \left[ \frac{1}{2(1-\epsilon_p)^{1/2}} \operatorname{erf}(y(1-\epsilon_p))^{1/2} - \frac{1}{(\pi\epsilon_p)^{1/2}} e^{-y(1-\epsilon_p)} F((y\epsilon_p)^{1/2}) \right]$$

$$+ \frac{\alpha N}{\sqrt{\pi}} e^{y(1+\epsilon_p)} \left[ \frac{1}{\sqrt{\epsilon_p}} F((y\epsilon_p)^{1/2}) - \frac{1}{(1+\epsilon_p)^{1/2}} F\{(y(1+\epsilon_p))^{1/2}\} \right];$$

for  $\epsilon_p > 1$ , the first term is changed to

$$\frac{\alpha(N+1)}{(\pi(\epsilon_p-1))^{1/2}} e^{y(\epsilon_p-1)} F\{(y(\epsilon_p-1))^{1/2}\}.$$

The asymptotic expansion of  $U(p, y)$  is

$$U(p, y) \xrightarrow{y\epsilon_p \gg 1} \operatorname{Re}\Sigma_p - \frac{\alpha F((y\epsilon_p)^{1/2}) e^{y\epsilon_p}}{y(\pi\epsilon_p)^{1/2}} \left[ Ne^y \sum_{l=0}^{\infty} \frac{l!}{y^l} - (N+1)e^{-y} \sum_{l=0}^{\infty} \frac{l!}{(-y)^l} \right]$$

$$+ \frac{\alpha N e^{y(1+\epsilon_p)}}{(2\sqrt{\pi})y^{3/2}(1+\epsilon_p)} \sum_{k=0}^{\infty} \frac{\Gamma(k+\frac{3}{2})}{[y(\epsilon_p+1)]^k} \sum_{l=0}^k \frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})} (1+\epsilon_p)^l + \frac{\alpha(N+1)e^{y(\epsilon_p-1)}}{(2\sqrt{\pi})y^{3/2}(1-\epsilon_p)} \sum_{k=0}^{\infty} \frac{\Gamma(k+\frac{3}{2})}{[y(\epsilon_p-1)]^k} \sum_{l=0}^k \frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})} (1-\epsilon_p)^l.$$

For  $\epsilon_p = 1$ , the last term is replaced by

$$\alpha(N+1) \left(\frac{y}{\pi}\right)^{1/2} \sum_{l=0}^{\infty} \frac{l!}{(-y)^l (2l+1)}.$$