Band tails in disordered systems

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The density of electron states, \( \rho(E) \), in disordered systems in the band-tail region near band edges is investigated. We show that the \( \rho(E) \) of the Halperin and Lax type derived by Sa-yakanit predicts, in three dimensions, an exponential (Urbach) band tail for the correlation lengths found in amorphous Si and within the energy range observed in optical absorption near band edges. The simple exponential behavior is not universal and may not, for example, be observed in heavily doped semiconductors.

I. INTRODUCTION

The density of states, \( \rho(E) \), of a particle in a highly disordered material is a property of continuing interest in condensed matter physics. The particle may, for example, be an electron interacting with charged centers which are randomly located. The centers could be host atoms in an amorphous material, impurity ions randomly located in a heavily doped semiconductor or ions in a pure crystal with disorder created by thermal vibration. When the disorder is large, the edges of the allowed energy bands develop band tails reaching into the energy gaps. Indirect evidence from optical absorption near band edges in amorphous silicon (three dimensions) suggests that these band tails are of the following form:

\[
\rho(E) \propto \exp\left(-E^n/E_0\right) \tag{1}
\]

with \( n = 1 \) (the Urbach tail) where \( E \) is measured away from the band edge, \( E_b \).

Specifically, measurements of the optical-absorption coefficient \( \alpha(E) \) in amorphous silicon (a-Si) both pure and doped with hydrogen (a-SiH\(_x\)) can be fitted to the form:

\[
\alpha(E) = \alpha_0 \exp\left([E - E_1]/E_0\right) \tag{2}
\]

for energies \( E \) just below the absorption edge (the Urbach edge). In Fig. 1 we reproduce an example where (2) fits strikingly well; the \( \alpha \) observed in a-SiH\(_x\) by Abeles et al.\(^6\)

In Fig. 1, Eq. (2) fits \( \alpha \) over three orders and over an energy range \( 1.5 \leq E \leq 1.8 \) eV. Equation (2) also fits \( \alpha \) obtained in a-SiH\(_x\) having both thermal and structural disorder but over a narrower range; one order in \( \alpha \) and typically \( 1.6 \leq E \leq 1.8 \) eV. Fits of (2) yield typical values of \( E_0 \approx 0.05 \) eV and \( E_1 = 2.2 \) eV in a-SiH\(_x\)\(^3\).

Since \( \alpha \) is proportional to \( \rho(E) \), Eq. (2) suggests \( \rho(E) \) has the form (1) with \( n = 1 \). In this case \( E_1 \) plays the role of an effective band-edge energy, \( E_b \). However, \( \alpha \) contains energy-dependent factors such as a matrix element and the Fermi function in addition to \( \rho(E) \). Thus, the step from (2) to (1) is not entirely evident. Also, in contrast to a-Si the \( \alpha(E) \) near band edges in heavily doped semiconductors (e.g., GaAs) is not well fitted by (2) over a significant range of energies.

There are several derivations of \( \rho(E) \) in the band-tail region for heavily disordered materials using semiclassical,\(^9\) wave mechanical,\(^10\) functional space,\(^11\) Replica,\(^12\) field-theoretical,\(^13\) and Feynman path integral\(^14\) methods. The wave mechanical theory of the Halperin and Lax\(^10\) (HL) leads to a band-tail density of states of the form (1), with

\[
\frac{1}{2} \leq n \leq 2
\]

in three dimensions. The limit \( n = \frac{1}{2} \) is obtained for impurity centers having a potential of short range \( l(l \rightarrow 0) \). For example, for a charged impurity center, \( l \) is the screening length. The limit \( n = 2 \) is obtained for \( l \rightarrow \infty \). For example, the semiclassical theory of Kane,\(^9\) which is valid for large \( l \) only, provides an analytic expression for \( \rho(E) \), giving \( \rho(E) \propto \exp(-E^2/2\xi) \), where \( \xi \) is the variance of the random potential. The correlation length \( L \) of the

![Graph showing absorption coefficient \( \alpha \) as a function of photon energy \( E \).](https://i.imgur.com/j123456.png)
random potential depends upon \( l \). For a Gaussian or screened Coulomb impurity potential, applicable in heavily doped semiconductors, the correlation length is \( l/\sqrt{2} \).

The exponent \( n \) is also a function of \( E \), \( n=n(E,L) \).

The HL (Ref. 10) \( \rho(E) \) can clearly encompass experiment, depending upon \( L \). The interesting feature is that \( n \approx 1 \) appears to be universality observed for a-Si.\(^5\)\(^-\)\(^8\) Sa-yakanit,\(^14\) has obtained an analytic expression for \( \rho(E) \) using the Feynman path integral method\(^16\) and the Lloyd-Best\(^17\) variational principle. This agrees with the HL \( \rho(E) \) when the Lloyd-Best variational principle is approximated by maximizing the exponential part of \( \rho(E) \), the maximization procedure used by HL. The advantage of the path integral method is that it provides an analytic expression for \( \rho(E) \) from which \( n \) can be readily determined as a function of \( L \) and \( E \).

Recently, Soukoulis et al.\(^4\) have argued that the above methods do not agree with experiment \((n=1)\) in the three-dimensional case. They argue that short-wavelength fluctuations within the correlation length \( L \) of the random potential are neglected. When they include these short-wavelength fluctuations using scaling arguments of Thouless,\(^18\) they obtain \( n=1 \) in (1) universally for all materials in three dimensions.

We believe, firstly, that Soukoulis et al.\(^4\) begin with the \( L \rightarrow 0 \) limit of \( \rho(E) \). This requires \( n=\frac{1}{2} \). This is the “white-noise” \( L \rightarrow 0 \) limit.\(^19\) It is only for this limit that methods other than the path integral technique have as yet obtained an analytic expression for \( \rho(E) \) in three dimensions. With \( L \rightarrow 0 \), there cannot be any fluctuations within or shorter than the correlation length of the random potential. These then must be added subsequently. It is certainly interesting that this method leads to \( n=1 \) universally, but we believe it is not necessary to proceed in this way.

It is the purpose of this paper to show that \( n \approx 1 \) in (1) is expected in a-Si and three dimensions for physically reasonable choices of \( L \) and \( E \). We begin with the full analytic expression for \( \rho(E) \) valid in the band-tail region obtained by Sa-yakanit.\(^14\) It holds for arbitrary dimension \( d \leq 4 \) and arbitrary \( L \). First, we show how the expression used by Soukoulis et al.\(^4\) is obtained from the full \( \rho(E) \) in the white-noise, \( L \rightarrow 0 \) limit, which, as noted, predicts \( n=\frac{1}{2} \) for \( d=3 \) (Sec. II). Second, we show that the semiclassical result of Kane is obtained as the limit \( L \rightarrow \infty \) (Sec. III). We then show that the observed \( n=1 \) is obtained for physically reasonable values of \( L \) and \( E \) (Sec. IV). That is, we expect \( L \) to be approximately atomic dimensions and, from (2) and the arguments given below (2), \( 0.8 \leq (E_1-E) \leq 0.4 \) eV. For these \( L \) and \( (E_1) \) values the full \( \rho(E) \) predicts \( n \approx 1 \). On these grounds we suggest that \( n \approx 1 \) is observed in (1) universally in a-Si because \( L \) must universally be of approximately atomic dimensions and \( E \) lies in a narrow energy range.

II. WHITE-NOISE LIMIT

Following the notation introduced by Halperin and Lax,\(^10\) the \( \rho(E) \) describing the band-tail density of states for \( d \leq 4 \) and arbitrary \( L \) obtained by Sa-yakanit is\(^14\)

\[
\rho(E) = \left( \frac{E_L}{d} \right)^d [a(v,x)/z^{d+1/2}] 
\times \exp \left( -\frac{E_L}{2z} b(v,x) \right).
\] (3)

Here, \( v=(E_0-E)/E_L \) is a dimensionless energy variable. As noted in the introduction we expect \( E_0 \approx E_L \) in a-Si obtained from (2). The \( \xi \) is \( \left( \langle V(r)V(r') \rangle - \langle V(r) \rangle^2 \right) \) is the variance of the random potential. In a-Si, \( \xi \approx (eV)^2 \).

The \( E_L^2 = kT/2m^*L^2 \) is a convenient normalizing energy, the energy associated with localizing a particle of mass \( m^* \) within the correlation length \( L \). The \( x = \xi kT/3E_L \) is a dimensionless variational parameter which is determined by the Lloyd-Best variational principle. This parameter is denoted\(^13,14\) by \( z^2 = 2/x \) for screened Coulomb potentials appropriate in heavily doped semiconductors (HDS). The actual variational parameter \( \omega \) is the curvature of the harmonic well which models the correlation function \( W(r-r') = \langle V(r)V(r') \rangle - \langle V(r) \rangle^2 \) of random potential \( [\xi = W(0)] \). For example, for a screened Coulomb impurity potential the \( W(r-r') \) of random impurities in HDS's is simply \( W(r-r') = W(0) \exp(-Q(r-r')) \). The \( a(v,x) \) and \( b(v,x) \) are dimensionless functions,

\[
a(v,x) = \left[ \frac{1}{\sqrt{2\pi}} \right] \left[ \frac{x}{2\sqrt{\pi}} \right]^d \left( x d/4-v \right)^{d/2} 
\times (1+4/x)^{d(d+1)/2}
\] (4)

and

\[
b(v,x) = (xd/4+v)^2(1+4/x)^{d/2}
\] (5)

which are explicitly a function of \( v \) and \( x \). The Lloyd-Best variational principle gives an equation for \( x \) in terms of \( v \) of\(^21\)

\[
x^2 + (4-d)x - 4v = 0.
\] (6)

We now take the white-noise limit, \( L \rightarrow 0 \). This means \( x \approx \xi kT/3E_L \) is vanishingly small and we may neglect the \( x^2 \) term in (6). Neglecting \( x^2 \) in (6) corresponds to neglecting fluctuations in \( W(r) \) within its correlation length \( L \).\(^14\) We then have

\[
x = \frac{4}{(4-d)} v
\]

and the exponent in (2) reduces to

\[
-\frac{E_L}{2z} b(v,x) = -\frac{1}{\pi^d} \left[ \frac{4}{4-d} \right]^2 \left[ \frac{4-d}{d} \right]^{d/2} 
\times \left( \frac{x d^2}{2z E_L^2} \right)^{d/2},
\] (7)

where \( \chi \equiv d^2 \pi^2 E_L^2/2m^*E \) is measured away from the bottom of the conduction band, \( E_D \). This is exactly the exponent with which Soukoulis et al.\(^4\) begin [their Eq. (1)] except for the numerical factor \( \pi^d \). As shown by Gross\(^19\) the factor \( \pi^d \) can be eliminated by taking higher-order cumulants beyond the first order considered by Sa-yakanit.\(^14\) Note that (7) holds for arbitrary dimension \( d \leq 4 \).
Since (7) goes as $E^{1/2}$ for $d = 3$, Soukoulis et al. must reintroduce fluctuations within the correlation length to obtain the observed $E^1$.

### III. SEMICLASSICAL LIMIT

We now consider the opposite limit, $L \to \infty$. In this case $x \to \infty$ and we may neglect the linear term in Eq. (6) to obtain

$$x = 2\sqrt{v}.$$  

The exponent in (3) becomes

$$\frac{E_L}{2\xi} b(v, x) = -\frac{E^2}{2\xi}$$

which is clearly independent of $d$. This is Kane’s well-known result and is valid in the limit of long-range correlations where the kinetic energy of localization is negligible.

### IV. PHYSICAL LENGTH AND ENERGY SCALES

In Secs. II and III we saw that the exponent of the general $\rho(E)$ given by (3) reduces to the form (1) with $n = \frac{1}{2}$ for correlation lengths $L \to 0$ and to $n = 2$ for correlation lengths $L \to \infty$. In these limits we are forcing or selecting the value of $x = \hbar \omega/E_L = (2m^*/\hbar^2)\hbar \omega L^2$ by selecting the correlation length, $L$. When we apply the present theory to a specific material, $L$ is given by the material and Eq. (6) for $x$ is an equation that determines the variational parameter $\omega$ as a function of $v$. Physically, the states that contribute to $\rho(\nu)$ at large $\nu$, require a large $\omega$. Large $\nu$ corresponds to an energy $E$ in $v = (E_b - E)/E_L$ deep in the band tail below $E_b$. A large value of $\omega$ means deep (harmonic) wells reaching down to low $E$. Conversely, small $\omega$ values mean shallow wells which contribute to $\rho(\nu)$ at small $\nu$, where $E \approx E_b$ near the band edge. Equation (6) is used to eliminate $x$ so that $n(x, \nu)$ becomes solely a function of $\nu$. From (6) we obtain,

$$x = \left[(4 - d)^2 + 16\nu \right]^{1/2} - (4 - d) \right] / 2$$

and in three dimensions,

$$b(v) = [(1 + 16\nu)^{1/2} - 1]^{1/2} \frac{\pi}{4} \left[(1 + 16\nu)^{1/2} + 7 \right]^{3/2}.$$  

Now $b(\nu)$ is solely a function of energy $\nu$. To exhibit the exponent $n$, we rewrite (8) in the form

$$b(v) = c(n(\nu))\nu^n(\nu),$$  

where $n(\nu)$ and $c(\nu)$ are slowly varying functions of $\nu$. The $n(\nu)$ may be defined as

$$n(\nu) \equiv \frac{d \ln b(\nu)}{d \ln \nu} = 32\nu \frac{[1 + (1 + 16\nu)^{1/2} - 1][1 + (1 + 16\nu)^{1/2} + 7]^{-1/2}}{[(1 + 16\nu)^{1/2} - 1][1 + (1 + 16\nu)^{1/2} + 7]}.$$  

Equation (10) is plotted in Fig. 2 for a screened Coulomb and a Gaussian potential $V(r)$. At small $\nu (E \approx E_1)$, $n(\nu) \to \frac{1}{2}$ while at large $\nu = (E_b - E)/E_L$, for energies deep in the band tail, $n(\nu) \to 2$. We also find $c(1) = 18/\sqrt{3}$.

#### FIG. 2. The exponent $n(\nu) = d \ln b(\nu)/d \ln \nu$ of $b(\nu)$ versus the dimensionless energy $\nu$ for a Gaussian potential (solid curve) and a screened Coulomb potential (dashed curve).

We show first that $n = 1$ corresponds to reasonable values of $L$ and $E_0$. For example, $L$ must be of approximately atomic dimensions, say $L = 2 \AA$. With $m^* = 1(m_e)$, $E_L = \hbar^2/2m^*L^2 \approx 1$ eV. Then choosing $n = 1$, in (9), the exponent of $\rho(\nu)$ in (3) is

$$- \frac{E_L^2}{2\xi} b(\nu) = - \frac{E_L^2}{2\xi} c(1) \nu = \frac{E - E_b}{E_0},$$

where

$$E_0 \equiv (2\xi/E_L^2)E_L/c(1) = (\xi/E_L)/9\sqrt{3}.$$  

With $\xi \approx 1$ eV$^2$ we obtain $E_0 \approx (9/\sqrt{3})^{-1} \approx 0.06$ eV which is entirely consistent with observed values$^5-8$ of $E_0$ in (2) for a-Si and a-SiH$_4$. Since $E_0 \approx L^2$, larger values of $L$ will lead to larger values of $E_0$. However, the conduction bands $m^*$ could be as small as $m^* \approx 0.1$ which will increase $E_L$ and reduce $E_0$. A value of $E_L \approx 1$ eV seems reasonable in amorphous materials and the above argument shows that for $L$ of approximately atomic dimensions and $n$ selected as unity, we can reproduce the observed $E_0$.

We now examine the energy scale

$$\nu = \frac{E_b - E}{E_L} \approx \frac{E_b - E}{1 \text{ eV}}$$

and take $E_b \approx E_1 = 2.2$ eV. The range of energy over which $\alpha$ in Fig. 1 is observed to fit (2) with $n = 1$ is $0.8 \geq E_1 - E \geq 0.4$ eV or

$$0.8 \geq \nu \geq 0.4.$$  

This corresponds to an extremely narrow range of $\nu$ values in Fig. 2. In this range of $\nu$, $n$ varies from $n = 1$ to $1.2$ for the screened Coulomb potential and from $0.7$ to $0.9$ for a Gaussian potential. Neither of these potentials describe the correlations in amorphous materials (which have short-range components) precisely. However, the aim is to illustrate that in the observed energy range $n \approx 1$ is expected for reasonable potentials. The deviations from $n = 1$ are also in the direction of $n$ smaller at high $E$ and $n$ larger at low $E$ which is consistent with the deviations observed in the experiment shown in Fig. 1.
A comparison with HDS's such as n-type and p-type GaAs is interesting. In n-type GaAs the carrier $m^* \approx 0.066$ and the correlation length of the fluctuating potential due to the random donor impurities is $\sim 15-30 \text{Å}$, depending upon the doping concentration. The energy scale is much smaller with $E_L \sim 0.05 \text{eV}$ and $\xi \sim 0.04 \text{eV}^2$ so that $E_0 \approx 0.005 \text{eV}$. The p-type GaAs is complicated by having two contributing valence bands but if we take $m^* \approx 0.085$ and use the calculated correlation lengths and $\xi$ we find $E_L \sim 0.1 \text{eV}$ and $E_0 \approx 0.0005 \text{eV}$. Thus in p-type GaAs especially we expect $\alpha(E)$ to rise exponentially near the band edge over a much smaller energy interval than in a-Si. This is certainly observed.\(^{3,15}\) Also, since $E_L$ is smaller in GaAs we expect $\nu$ to be larger ($\sim 5-20$) and $n$ to be larger ($n \sim 1.5$). Again, as in a-Si, the range of $\nu$ values is very small so that $n$ will be effectively constant over the range of observed energy values near the band edge.

Finally, we emphasize that these are crude arguments. The best test of a theory for $\rho(E)$ is to use it to evaluate $\alpha(E)$ and to compare the resulting $\alpha(E)$ with experiment. We have done this in n- and p-type GaAs using the Sa-yakanit—Glyde $\rho(E)$ and find quite good agreement of $\alpha(E)$ with observed values. Certainly the agreement precludes an error in $n$ of as much as 0.5.

In conclusion we find that the density of states, $\rho(E)$, of the Halperin-Lax or Sa-yakanit form predicts an exponential tail of the form (1) with $n \approx 1$ in a-Si in three dimensions. This dependence is obtained for correlation lengths of approximately atomic dimensions and in the energy intervals observed in $\alpha(E)$ near band edges in a-Si.

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21. It has been shown in Ref. 20 that maximizing the Lloyd and Best pressure in the deep tail limit is equivalent to maximizing the exponent of $\rho(E)$ alone.