Theory of Electron Band Tails and the Urbach Optical-Absorption Edge

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The density of states $\rho(E)$ in the tail for an electron in a correlated Gaussian random potential in three dimensions is constructed from first principles by means of a simple physical argument. This yields a linear exponential dependence of ρ on E which, for reasonable values of the rms potential fluctuation and correlation length, spans many decades, and occupies most of the experimentally observable energy range. This is suggested as the origin of the fundamental Urbach optical-absorption edge.

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In 1953, Urbach[1] proposed an empirical rule for the optical-absorption coefficient $\alpha(\omega)$ associated with electronic transitions from the valence to conduction band tail in disordered solids. As originally applied to silver and alkali halides, this rule states that $\alpha(\omega)\propto \exp[(\hbar\omega-\hbar\omega_0)/E_0]$, where $h\omega$ is the photon energy and E_0 and $\hbar\omega_0$ are fitting parameters, E_0 being proportional to kT in Urbach's original work. Subsequent experimental studies[2-6] on a variety of disordered semiconductors and glasses exhibiting this Urbach exponential spectral behavior which persists in some cases for up to five decades have strongly suggested that the Urbach absorption edge is a nearly universal property of disordered solids and that the underlying physics is both simple and general.

In contrast, theoretical efforts have considered a variety of fundamentally different physical origins of the Urbach edge. The simplest of these is in the electron-band-tail density of states (DOS). For heavily doped semiconductors with screened Coulomb impurities, Kane,[7] Bonch-Bruevich,[8] and others developed semiclassical treatments for the density of states which focused primarily on the probability distribution of the potential fluctuations. Taking advantage of the long-range nature of the impurity potential, it was shown that for a Gaussian probability distribution the deep tail forms a Gaussian density of states. Halperin and Lax[9] (H-L) recognized that the underlying physics changed completely for tail states near the band edge where the kinetic energy of localization plays a dominant role in determination of the scale of the most probable potential fluctuation. This leads to a density of states which scales exponentially with the square root of energy in three dimensions. These results have also been verified formally. In d spatial dimensions, Cardy[10] has shown for a Gaussian white-noise potential that

$$\rho(E)\sim |E|^{d(5-d)/4}\exp(-\text{const}\times|E|^{2-d/2}).$$

This result remains true in the limit that the de Broglie wavelength $\lambda\equiv\hbar/(2m|E|)^{1/2}$ is long compared to any finite correlation length L of the disorder. We will refer to this as the H-L limit. In the opposite limit of $L\gg\lambda$, it has been shown[11] that $\rho(E)\sim|E|^d\exp(-|E|^2/2V_{\rm rms}^2)$, recapturing the earlier, semiclassical results. Despite the firm mathematical foundation of these results, neither of these energy dependences can account for the universally observed Urbach tail. This discrepancy has led to extensive studies of alternative mechanisms including both Frenkel[12] and Wannier[13] excitons and their associated oscillator strengths.[14] Although important in certain molecular crystals and polar semiconductors, respectively, these effects cannot account for the universal nature of Urbach edges. For instance, in a-Si in which the exciton binding energy is small compared to the width of the band tail, these models are inapplicable[15]; nevertheless, Urbach's rule is accurately obeyed. Also, transient photoconductivity measurements in the glassy semiconductor As_2Se_3 have given direct evidence for linear exponential behavior in the conduction-electron DOS over five decades.[6]

The universal nature of Urbach's rule in both optical absorption and the one-electron DOS suggests a careful reexamination of the one-electron DOS in a random potential.[16-18] Accordingly, in this Letter we derive from first principles the density of states in the tail, obtaining asymptotically exact expressions for the

(H-L) tail and the Gaussian tail. We find that both of these regimes are experimentally inaccessible for reasonable choices of the rms potential fluctuation and spatial correlation length L, whereas the crossover regime ($\lambda \sim L$) is observable and exhibits essentially linear exponential behavior over many decades.

The disorder giving rise to exponential band tails is produced by lattice vibrations, impurities, and other deviations from perfect periodicity of the lattice. Since on the time scale of an optical-absorption event, the displacements arising from a finite temperature distribution of phonons may be considered essentially frozen, we are led to consider the density of states for an electron in a static random potential[9]:

$$[-\hbar^2\nabla^2/2m + V(x)]\psi(x) = E\psi(x). \tag{1}$$

With use of the central-limit theorem, the various forms of disorder contribute to an essentially Gaussian probability distribution for the Fourier components $V(k)$ of the following potential:

$$P\{V(k)\} \propto \exp[-S\{V\}],$$
$$S = \tfrac{1}{2}\int \frac{d^dk}{(2\pi)^d} V(k)B^{-1}(k)V(-k). \tag{2a}$$

For convenience the autocorrelation function

$$B(k) = V_{\text{rms}}^2(\pi L^2)^{d/2}\exp(-k^2L^2/4) \tag{2b}$$

is characterized by a correlation length L measuring the spatial extent of short-range order, typically of the order of the interatomic spacing. Band-tail states arise in such a model from potential fluctuations of depth V_0 large compared to the typical fluctuation V_{rms}, and the corresponding probability of occurrence is exponentially small. For instance, if we consider a potential fluctuation of the form $V(x) = -V_0\exp(-x^2/a^2)$ the probability of occurrence is determined by

$$S = (V_0^2/2V_{\text{rms}}^2)(a/L)^d[2-(L/a)^2]^{-d/2}. \tag{3}$$

This defines a variational problem[9,19] for the class of Gaussian potentials parametrized by a depth V_0 and a range a. As discussed previously,[11] the requirement that such a potential fluctuation contribute to the electronic density of states at an energy $-|E|$ places a constraint on the variational parameters V_0 and a. For $|E| \gg V_{\text{rms}}$ this becomes the requirement that the potential fluctuation possess a ground state at precisely an energy $-|E|$ since higher-order bound states at that energy would require a considerably less-probable potential.[9] In three dimensions this is the condition that the dimensionless radial Schrödinger equation

$$[-d^2/dr^2 - w\exp(-r^2)]u(r) = -f(w)u(r) \tag{4}$$

have an eigenfunction $u(r) \equiv \psi(r)/r$ with a single node at $r=0$. Here $w \equiv 2ma^2V_0/\hbar^2$ and the required constraint is that $f(w) = 2ma^2|E|/\hbar^2$. We have numerically evaluated the function $f(w)$. For $d=3$, there is a critical strength $w_c = 2.95$ at which a bound state first appears. For $w > w_c$, $f(w)$ is nonzero and is a smooth monotonically increasing function. For $f > 0.4$, the inverse function may be accurately described by the formula $w(f) \simeq 2.7 + 3\sqrt{f} + f$. However, there are limiting cases in which analytical results may be derived. For example, for localized states in the very deep tail ($\lambda \ll L$) the asymptotic behavior may be obtained by expansion of the potential fluctuation in a Taylor series about $r=0$, so that we^{-r^2} is replaced by $w(1-r^2)$. The eigenvalue of the associated harmonic-oscillator equation corresponding to the lowest wave function which vanishes at $r=0$ is $f(w) \simeq w - d\sqrt{w}$ ($w \to \infty$). Since the dimensionless localization length is of order $w^{-1/2}$ as $w \to \infty$, this is short compared to the range of accuracy of the Taylor expansion and the harmonic-oscillator approximation is self-consistent in this limit. If we define $z \equiv (L/a)^2$ and $y \equiv |E|/\epsilon_L$, where $\epsilon_L \equiv \hbar^2/2mL^2$, then (3) becomes

$$\tilde{S} \equiv 2V_{\text{rms}}^2/\epsilon_L^2 S = [w(y/z)]^2 z^2[z(2-z)]^{-d/2}, \tag{5}$$

where z is the single variational parameter and the function w is the inverse of the function f and has an argument $f \equiv y/z = 2ma^2|E|/\hbar^2$. In the harmonic-oscillator limit $w \sim f + d\sqrt{f}$, and sufficiently deep in the tail the kinetic-energy term $d\sqrt{f}$ is negligible in comparison with the binding energy f. It follows that $\tilde{S}$ has a local minimum at $z=1$ and that at this minimum $S = |E|^2/2V_{\text{rms}}^2$. Since the averaged density of states at $-|E|$ is simply the sum of the number of potential fluctuations having a ground state at precisely $-|E|$, weighted by their probability of occurrence, this yields the exponential part of the deep-tail Gaussian density of states. The energy-dependent prefactor is determined by consideration of fluctuations about the most probable potential well and requires a formal analysis as discussed previously.[10,11]

Using the numerical solution of the function $f(w)$ for the Gaussian potential, we have obtained the exponential part of the density of states in the tail throughout the energy spectrum. This is illustrated in Fig. 1. The Gaussian potential *Ansatz* is asymptotically exact for the deep tail (see below), whereas there are small deviations of the most probable potential fluctuation from a Gaussian shape in the shallow tail. The density of states exhibits a relatively linear exponential behavior,

$$\rho(E) \sim \exp(-14.4|E|\epsilon_L/V_{\text{rms}}^2) \quad (d=3), \tag{6}$$

over a range $0.1 < |E|/\epsilon_L < 2$. For instance, with $V_{\text{rms}} \sim \epsilon_L \sim 0.5$ eV the accurate linear exponential observable over the range $0.1 < |E|/\epsilon_L < 1$ easily spans five decades of the DOS. For $|E|/\epsilon_L \gg 2$, this crosses over to the Gaussian density of states, whereas

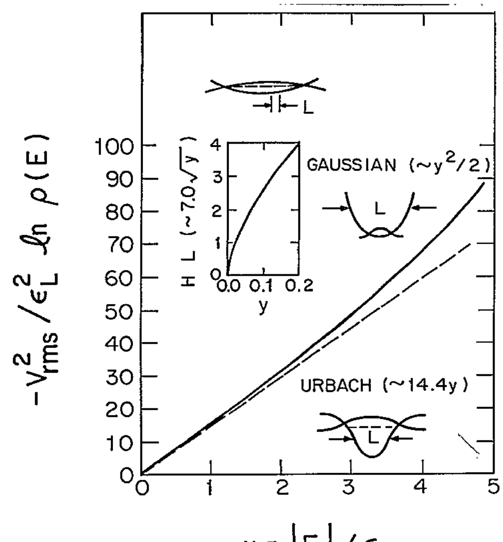

FIG. 1. Exponential part of density of states as a function of $y \equiv |E|/\epsilon_L$ exhibiting the Gaussian tail ($y >> 2$), the Urbach tail ($0.1 < y < 2$), and the H-L tail ($0 < y < 0.1$, see inset). The nature of the most probable potential fluctuation and wave function in each regime is illustrated schematically.

for $|E|/\epsilon_L << 0.1$ there is a Halperin-Lax density of states for which $\ln\rho(E) \sim -7.0|E|^{1/2}\epsilon_L^{3/2}/V_{\rm rms}^2$.

Considerable physical insight may be obtained by generalization of this physical argument to d spatial dimensions. An elementary argument[11] reveals that the essentially linear exponential behavior in $d=3$ arises from the increasing importance of the correlation L of the random potential in higher and higher spatial dimensions for $d<4$ and the consequent pinching of the Halperin-Lax behavior into a narrower and narrower enery regime near the continuum band edge. The self-consistency of the Gaussian–white-noise approximation $B(x)=\gamma^2\delta^d(x)$ relies on the constraint that the scale of the potential fluctuation be long compared to the actual spatial correlation length L. For the white-noise model, the action (3) becomes $S \sim V_0^2 a^d/\gamma^2$ for a potential fluctuation of any shape characterized by a single depth parameter V_0 and range a. For instance, in the case of a square well the constraint between V_0 and a to produce a bound state at energy $-|E|$ takes the form $|E|+1/a^2=V_0$. For $d<4$, S has a local minimum when the ratio of the range of the potential fluctuation to the electron de Broglie wavelength is $(a/\lambda)^2=(4-d)/d$. Since this ratio vanishes as $d\to 4$ for any fixed E, it is evident that the influence of the correlation length L is felt even for relatively shallow band-tail states in high dimensions. In three dimensions it is the consequent broad crossover regime between the Halperin-Lax tail and the Gaussian tail which manifests itself in the Urbach edge. The screened–Coulomb-impurity model of Halperin and Lax[9] involves longer-range correlations than our model, and the corresponding crossover regime does not exhibit such precise linearity.

In obtaining the variational function (5) we have restricted our attention to potentials which have a Gaussian form. A more general formulation follows from a replica-field-theory representation of the averaged one-electron Green's function.[10,11] An asymptotically exact density of states may be obtained by saddle-point (instanton) evaluation of the relevant functional integral. We have performed a detailed comparison of the instanton method to the above simple physical argument and find complete agreement apart from a 3% error of the numerical coefficient in the Halperin-Lax region. A one-loop renormalization of this instanton also reveals the existence of a shifted continuum band edge of order $V_{\rm rms}^2/4\epsilon_L$ relative to which the energy E is measured.[20]

An approximate analytical expression for the density of states in d dimensions may be obtained from this field theory by the assumption that the localized electron wave function takes the form

$$\psi(x)=(\pi a^2)^{-d/4}\exp(-x^2/2a^2)$$

where a is a variational parameter. This leads to an approximate density of states

$$-\ln\rho(E)\sim S'(a_{\min})=(\tfrac{1}{2}d\epsilon_a+|E|)^2(1+2\epsilon_L/\epsilon_a)^{d/2}/2V_{\rm rms}^2, \tag{7a}$$

where

$$\epsilon_a\equiv\hbar^2/2ma^2=4|E|/(4-d)\left(1+\{1+[4/(4-d)]^2|E|/\epsilon_L\}\right)^{-1}. \tag{7b}$$

Setting $d=3$ and substituting (7a) into (7b) leads to an extremely accurate analytical approximation which is virtually indistinguishable to the naked eye from the density of states in Fig. 1 throughout the deeper Urbach and Gaussian regimes. In the shallower Halperin-Lax region this Gaussian wave function *Ansatz* yields

$$\ln\rho(E)\sim -8.0|E/(4-d)|^{2-d/2}\epsilon_L^{d/2}/V_{\rm rms}^2.$$

The numerical coefficient here differs from the exact result of 6.8 for $d=3$ by 18%, leading to a corresponding underestimate of the density of states. The formulas (7a) and (7b) have also been obtained by a Feynman–path-integral representation of the averaged one-electron Green's function.[17] It is evident from these equations that the crossover between the Gaussian tail and the H-L tail occupies an energy regime

$(1-d/4)^2 < |E|/\epsilon_L < 4$ which broadens as $d \rightarrow 4$.

In summary, we have derived by means of a simple physical argument a quantitative theory of the electronic density of states in a correlated Gaussian random potential exhibiting linear Urbach exponential behavior over many decades. This arises from the influence of the correlation length of the disorder even in the shallow-energy, $|E|/\epsilon_L \sim (1-d/4)^2$, part of the tail. The Gaussian potential *Ansatz* yields a numerically accurate theory by allowing the wave function to tunnel exponentially into the classically forbidden region for the shallow tail states in which the kinetic energy of localization becomes a significant fraction of the potential depth. The Gaussian wave function *Ansatz* underestimates this tunneling effect and accordingly underestimates the density of states. We mention finally that the precise slope and range of the Urbach tail in a real material may be sensitive to the detailed nature of the correlations of the disorder and the presence of the valence (conduction) band. The model we have presented provides insight into the universality of Urbach tails and hopefully will provide a valuable starting point for the systematic incorporation of band structure, polaronic, and excitonic effects which may be important in particular materials.[20]

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