Simple derivation of exponential tails in the density of states

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The observed exponential tails in the density of states are shown to arise from a Gaussian distribution of local potential wells and an approximately linear relation between the binding energy and the square of the depth of the potential well.

The optical-absorption coefficient α in crystalline and amorphous semiconductors and in crystalline insulators often exhibits (over a limited range of frequencies) an exponential behavior of the form

$$\alpha=\alpha_0\exp[(\hbar\omega-E_f)/E_0] \tag{1}$$

known as the Urbach tail.[1] E_f is the so-called Urbach focus and E_0 determines the slope of the curve $\ln\alpha$ vs $\hbar\omega$; ω is the photon frequency and α_0, the preexponential factor, depends weakly on frequency. The quantity E_0 is of the order of 50 meV or less, the higher values appearing in amorphous materials.

Many theories have been proposed[2-7] to explain the rather general exponential behavior shown in Eq. (1). Most of them attribute the frequency dependence of α to an exponential tail in the density of states (DOS) in the top of the valence band and/or the bottom of the conduction band. Various physical mechanisms have been assumed and different formalisms have been employed in order to obtain the exponential tail in the DOS. This proliferation of formalisms and detailed physical mechanisms tend to obscure the common feature of a fluctuating potential being the source of the exponential tails in the DOS.

Recently Monroe and Kastner[8] have demonstrated through transient photocurrent measurements in glassy As_2Se_3 that the DOS appears to exhibit exponential tails over a rather extended energy range from 0.3 to 0.86 eV above the valence band.

The rather general character of the exponential tails in the DOS suggests a quasiuniversal mechanism that bypasses the complexity of real materials. It has been shown before[2,7] through the use of the coherent-potential approximation (CPA) that the assumption of independent local (i.e., of atomic scale) potential wells[9] whose depth follows a Gaussian distribution leads to an exponential DOS. It has also been pointed out[7] that the energy range over which the exponential behavior is exhibited is quite extended. In the present paper, we offer a simple physical explanation of why a Gaussian distribution of the depth of the potential wells leads to an exponential tail in the DOS. We also comment on the physical origin of a Gaussian distribution. Finally, we point out that our results are consistent with the recent observations of Monroe and Kastner.[8]

We considered the elementary problem of a bound state ($|E|$ is the binding energy) in a potential well of depth ε and three-dimensional (3D) volume a^3. Five types of potential wells (PW) were examined: A steplike PW in free space given by $V(\mathbf{r})=-\varepsilon$ for $r<r_0$ and $V(\mathbf{r})=0$ for $r>r_0$ (obviously $a^3=4\pi r_0^3/3$ in this case); a single site PW of depth $-\varepsilon$ in a tight-binding (TB) model[10] for a simple-cubic lattice (lattice constant a); a single site PW of depth $-\varepsilon$ in a TB model with a semicircular unperturbed DOS (lattice constant a); a PW of depth $-\varepsilon$ (or a potential bump of height ε) for the bottom of the conduction band (or the top of the valence band) in a TB model for hydrogenated silicon.[11] In all cases, we found[12] that over a range of energies the binding energy $|E|$ is a linear function of the square of the depth ε of the PW

$$|E|\simeq A\varepsilon^2-B \quad \text{for } E_1<|E|<E_2\ . \tag{2}$$

The zero of energy is chosen at the average value of the random potential $\langle\varepsilon\rangle$.

Combining Eq. (2) with a Gaussian distribution

$$p(\varepsilon)\sim\exp(-\varepsilon^2/2w^2) \tag{3}$$

for the depth ε, we obtain immediately an exponential DOS of the form

$$\rho(E)\sim\exp\left[-\frac{|E|}{E_0}\right] \tag{4}$$

with

$$E_0=2Aw^2 \tag{5}$$

Equation (4) gives the exponential DOS with a focus at zero, i.e., at the average value of the fluctuating potential; this focus is independent of the variance w^2.

In Table I we summarize our findings for the quantities A, E_1, E_2 in the five cases considered here. The case of a PW of Gaussian shape[14] of the form $\varepsilon(\mathbf{r})=-\varepsilon\exp(-\pi r^2/a^2)$ is also included in Table I. Note the extended range of validity of Eq. (2). The TB models are very important because they demonstrate that the validity of Eq. (2) by no means depends on the validity of the effective mass theory, in agreement with our previous findings.[7] For α-Si:H the range of the validity of Eq. (2) is more limited due to the nearby presence of another band of similar atomic character (p-type in this case).

TABLE I. Values of the constant A and range of validity of Eq. (2) for the various cases examined here (the Gaussian shape was studied by Soukoulis, Ref. 14). TB denotes tight-binding model with a bandwidth equal to 12 V.

Case	Effective-mass description	A	E_1	E_2	Energy Unit
Step potential well of 3D volume a^3	yes	0.023	0.5	6	$\hbar^2/2m^*a^2$
Gaussian potential well of 3D volume a^3	yes	0.010	0.3	6	$\hbar^2/2m^*a^2$
TB, semicircular DOS	no	0.064	0.2	3	V
TB, simple cubic	no	0.065	0.2	3	V
α-Si:H, valence band	no	0.007	0.1	0.3	eV
α-Si:H, conduction band	no	0.003	0.1	0.3	eV

In Fig. 1 we plot the binding energy $|E|$ and the decay length of the ground state versus ε^2 for a steplike spherical potential well of depth ε and 3-d volume a^3. $V=\hbar^2/2m^*a^2$. For $\varepsilon<\varepsilon_c=6.4116V$, there is no bound state. As ε just exceeds ε_c, a bound state appears with a huge decay length $\lambda\sim(\varepsilon-\varepsilon_c)^{-1}$; in this weakly bound regime the binding energy $|E|$ behaves as $(\varepsilon-\varepsilon_c)^2$. With increasing ε, λ drops very fast (e.g., for $\varepsilon\simeq 8.83V$, $\lambda\simeq 1.41a$) and we enter a regime where λ/a is of the order of 1 ($0.4\lesssim\lambda/a\lesssim 1.4$). It is in this regime ($\lambda/a\sim 1$) that the linear $|E|$-vs-ε^2 relation holds, as can be seen from Fig. 1. As ε increases beyond a value corresponding to $\lambda/a\simeq 0.4$, the $|E|$-vs-ε curve starts bending over and a very broad transition region follows until finally the asymptotic behavior $|E|=\varepsilon-4\varepsilon_c$ is reached for ε larger than $100V$ when λ/a is less than 0.1. For the semicircular TB model the asymptotic behavior $|E|=\varepsilon-6V$ is approached for values of $|E|$ larger or about equal to the total bandwidth. When $|E|$ reaches the asymptotic behavior of linear dependence on ε, then the DOS will exhibit a Gaussian distribution, as can be seen from Eq. (3).

In Fig. 2 we plot the binding energy $|E|$ versus the square of the depth of the potential well ε^2 for the five cases we examine here. We see that the $|E|\sim(\varepsilon-\varepsilon_c)^2$ regime [which would produce an $\exp(-c\sqrt{|E|})$ dependence for the DOS] is so narrow that it may be very difficult to observe. The large $|E|$ regime, where substantial departures from the linear $|E|$-vs-ε^2 relation appear, corresponds usually to so low a DOS that it may not be observable. Thus, in most cases the linear part producing an exponential DOS is left to dominate the tail. Possible exceptions may appear in narrow gap materials with the top of the valence band and the bottom of the conduction band having a similar atomic character and in cases where the extent of the local potential well is substantially larger than atomic scale. In these exceptional cases the energy scale is compressed and the asymptotic behavior $|E|\sim\varepsilon$ may be observable.

We comment now on the question of how common a Gaussian distribution may be. Lattice vibrations produce ionic displacements u which exhibit Gaussian tails [since the eigenfunctions of harmonic oscillators decay as $\exp(-u^2m\omega/2\hbar)$]. Due to the smallness of the displacement u, the induced time-dependent electronic potential depends linearly on u and hence must exhibit a Gaussian

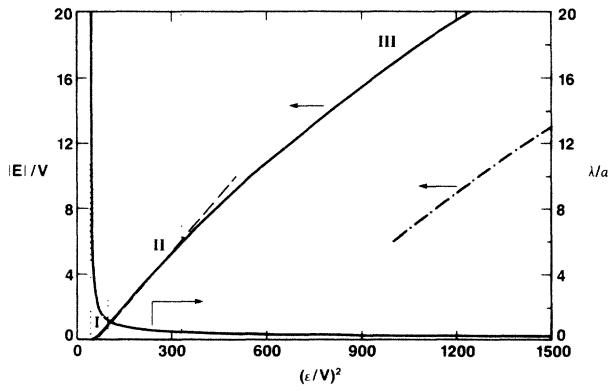

FIG. 1. Binding energy $|E|$ and decay length λ of the ground state in a steplike spherical potential well of depth ε and 3D volume a^3. $V=\hbar^2/2m^*a^2$, where m^* is the effective mass. Region I corresponds to $\lambda/a\gg 1$ and $|E|\sim(E-\varepsilon_c)^2$, where ε_c is the critical value for the appearance of a bound state. Region II corresponds to $1.4>\lambda/a>0.4$ and exhibits a linear $|E|$-vs-ε^2 relation. The asymptotic region III, where $|E|=\varepsilon-4\varepsilon_c$ (dash-dot curve) is approached when $\lambda/a<0.1$ and $\varepsilon\gtrsim 100$ V.

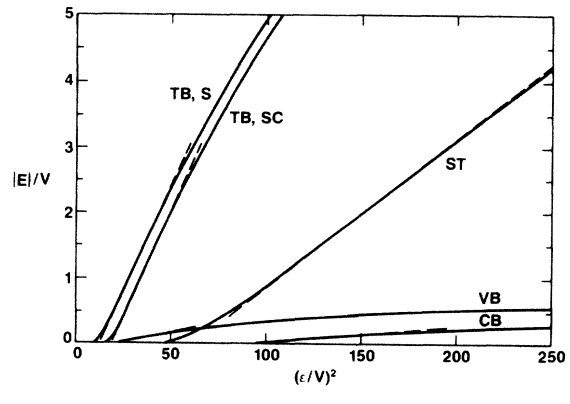

FIG. 2. Binding energy $|E|$ vs ε^2 in the five potential-well cases examined here. TB,S denotes the TB model with a semicircular unperturbed DOS; TB,SC denotes the simple-cubic TB model; ST denotes the steplike potential well; and VB and CB denote the VB and CB cases of our model for α-Si:H (see Ref. 11). The straight broken lines indicated the regions of an approximate linear $|E|$-vs-ε^2 relation. $V=\hbar^2/2m^*a^2$ for the ST case; $V=$bandwidth/12 for the TB models; and $V=1$ eV for the α-Si:H case.

distribution. For fast processes, such as optical absorption, the time dependence can be omitted and the phonon-induced fluctuations in the electronic potential will behave like local, static, random potential wells of Gaussian distribution. However, note that at zero temperature the phonon-induced electronic potential produces no tails in the DOS unless the strength of the electron-phonon coupling exceeds the value needed for small-polaron formation;[15] this results from energy conservation. (The gain from the electron-phonon coupling must exceed the loss from the local lattice deformation; at finite temperature the excited phonons may supply the missing energy and thus the tail in the DOS appears even for weak electron-phonon couplings.) Note also that for acoustic phonons and for low temperatures the extent of the phonon-induced potential wells is of the order of $a_0\Theta_D/T$, where a_0^3 is the volume per atom and Θ_D is the Debye temperature. If a deformation potential is assumed for the electron-phonon interaction, i.e., if

$$\varepsilon = E_s \nabla \cdot \mathbf{u} \ , \tag{6}$$

then one can easily show[10] that the variance w^2 of the phonon-induced random potential ε is given by

$$w_T^2 = \frac{E_s^2}{K} U_L \ , \tag{7}$$

where K is the bulk modulus and U_L is the lattice vibration energy per unit volume due to longitudinal phonons only. The quantity $a_0^3 U_L$ behaves as $(\hbar\omega_0/2)\coth(\hbar\omega_0/2kT)$ for optical phonons of frequency ω_0 or as the Debye function for acoustic phonons. Both expressions are almost identical (except at very low temperatures) and approach kT at high temperatures.

Combining Eqs. (5) and (7) with the value $A=0.065$ (appropriate for a single band) we find that

$$E_0 \simeq 3\lambda a_0^3 U_L \ , \tag{8}$$

where $\lambda = E_s^2 \bar{\rho}/2K$ and $\bar{\rho} = \frac{1}{12} V a_0^3$ is the band-averaged DOS per unit volume. The dimensionless quantity λ is similar to what appears in the theory of superconductivity; very rough estimates give λ of the order of 0.1. As Toyozawa pointed out,[2] exciton formation decreases substantially the value of V and hence increases λ so that 3λ may become close to 1.5 for excitons. A value of 1.5 for 3λ produces results for E_0 which are in excellent agreement with experimental observations in ionic crystals.[2]

In disordered materials, such as α-Si:H, where there are many independent sources of disorder (substitutional, topological, due to reconstruction, etc.) one expects that at least the tails of the probability distribution of the local potential fluctuations will exhibit Gaussian behavior. To the variance of this static disorder one must add the variance of the thermal disorder

$$w^2 = w_s^2 + w_T^2 \ . \tag{9}$$

As was pointed out by Cody,[16] Eq. (9) coupled with Eq. (7) is in good agreement with experimental data concerning the temperature dependence of the Urbach tail. For $w \simeq 1.6$ eV (which is consistent with several experimental data[17]) one finds that (using A from Table I) that $E_0 \simeq 16$ meV for the conduction band and $E_0 \simeq 36$ meV for the valence band. These values seem to be in fair agreement with the experimental estimates.[16]

For glasses, such as As_2Se_3, the upper part of the valence band is a subband of approximate total width $12V \simeq 4$–5 eV consisting of nonbonding (i.e., lone pair) p orbitals which are almost orthogonal to the antibonding orbitals of the bottom of the conduction band. Because of this near orthogonality the top subband of the valence band can be considered as an isolated single band for the present purposes and consequently (see Table I) $A \simeq 0.065$ and $E_2 \simeq 3V \simeq 1$ eV. This last number is consistent with the recent observation[8] of an exponential tail extending 0.85 eV above the top of the valence band.

Regarding the magnitude of the variance w_G^2 for glasses[18] of complex internal structure one may assume that there are complicated modes which freeze out at the glass-transition temperature T_g producing a static disorder below T_g. For $T > T_g$, the excitation of such modes costs elastic energy given by $a'^3 K\Delta^2/2$, where a' is the correlation length of the dilation Δ. At $T > T_g$ we have thermodynamic equilibrium; thus, the probability of occurrence of such modes is proportional to $\exp(-a'^3 K\Delta^2/2kT)$. For $T < T_g$ these modes are frozen out of thermodynamic equilibrium so that T is replaced by T_g in the Boltzmann factor. The electron will couple with such modes in a complicated way involving both a deformation potential interaction $E_s\Delta$ plus other terms which for simplicity could be assumed to be proportional to Δ. Thus, the effective coupling is expected to be of the form $\varepsilon = E_s'\Delta$. If the static disorder dominates over the thermal disorder all the way up to T_g one has to assume that the coupling E_s' is appreciably larger than the deformation coupling to phonons E_s. Substituting in the Boltzmann factor, we find again a Gaussian distribution for ε with a variance w_G^2 being equal to $w_G^2 = (E_s'^2/Ka'^3)kT_g$. Combining this expression with Eq. (5) and taking into account the thermal disorder as well we obtain

$$E_0 = 3\lambda' kT_g + 3\lambda a_0^3 U_L(T) \ , \tag{10}$$

where the dimensionless quantity $\lambda' \equiv E_s'^2 \bar{\rho}'/2K$ is expected to to be appreciably larger than λ. If one chooses λ' to be 0.4 and $\lambda = 0.1$, one finds that

$$E_0 = 1.2kT_g + 0.3kT \tag{11}$$

for T not so small but smaller than T_g. For As_2Se_3, $T_g \simeq 450$ K so at room temperature $E_0/k \simeq 630$ K; the value determined in Ref. 8 is $E_0/k = 550$ K. This 15% discrepancy may be due to a slight overestimation of the quantity A, and/or an overestimation of λ. The latter possibility can be checked by repeating the experiments of Ref. 8 at different temperatures.

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